Publications

Comprehensive Catalog
1982 – 2006

A Reference Book of the Bibliographies and Abstracts of the Separations Research Program Publications

Updated Spring 2006
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Authors and their Codes</td>
<td>3</td>
</tr>
<tr>
<td>Adsorption</td>
<td>4</td>
</tr>
<tr>
<td>Bioseparations</td>
<td>22</td>
</tr>
<tr>
<td>Dielectrically Enhanced Drying</td>
<td>24</td>
</tr>
<tr>
<td>Distillation</td>
<td>25</td>
</tr>
<tr>
<td>Electrochemical Separations</td>
<td>61</td>
</tr>
<tr>
<td>Extraction</td>
<td>62</td>
</tr>
<tr>
<td>Flue Gas Desulfurization/Acid Gas Treatment</td>
<td>84</td>
</tr>
<tr>
<td>General</td>
<td>136</td>
</tr>
<tr>
<td>Mass-Transfer Studies in Liquid-Liquid and Supercritical Extraction Devices</td>
<td>62</td>
</tr>
<tr>
<td>Membrane Technology</td>
<td>141</td>
</tr>
<tr>
<td>Supercritical Fluid Technology</td>
<td>283</td>
</tr>
<tr>
<td>Water/Wastewater Treatment</td>
<td>325</td>
</tr>
<tr>
<td>Index</td>
<td>35</td>
</tr>
<tr>
<td>Last Name</td>
<td>First Name</td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Bravo</td>
<td>Jose</td>
</tr>
<tr>
<td>Eldridge</td>
<td>Bruce</td>
</tr>
<tr>
<td>Fair</td>
<td>James</td>
</tr>
<tr>
<td>Freeman</td>
<td>Benny</td>
</tr>
<tr>
<td>General</td>
<td></td>
</tr>
<tr>
<td>Gloyna</td>
<td>E.F.</td>
</tr>
<tr>
<td>Humphrey</td>
<td>J.L.</td>
</tr>
<tr>
<td>Johnston</td>
<td>Keith</td>
</tr>
<tr>
<td>Kitto</td>
<td>G.B.</td>
</tr>
<tr>
<td>Koros</td>
<td>W.J.</td>
</tr>
<tr>
<td>Lloyd</td>
<td>Doug</td>
</tr>
<tr>
<td>Martin</td>
<td>C.L.</td>
</tr>
<tr>
<td>Paul</td>
<td>Don</td>
</tr>
<tr>
<td>Ritter</td>
<td>James</td>
</tr>
<tr>
<td>Rochelle</td>
<td>Gary</td>
</tr>
<tr>
<td>Schmidt</td>
<td>P.S.</td>
</tr>
<tr>
<td>Seibert</td>
<td>Frank</td>
</tr>
</tbody>
</table>
Adsorption

F-84-7
Adsorptive Separation Systems-An Overview
Fair, J. R. and J. M. Schork
Manuscript on file, Separations Research Program
This state-of-the-art review was made as part of a preliminary study by PhD candidate Joan Schork; it has not been submitted for publication. Some aspects of the design of adsorption units are reviewed. A comprehensive analysis of past work on adsorption kinetics (breakthrough) is included. Suggestions for future research needs are given.

F-85-10
Thermal Regeneration of Fixed Adsorption Beds
Schork, J. M.
Manuscript on file, Separations Research Program
This is a progress report on the PhD research described in F-84-7.

F-86-2 $15.00
Thermal Regeneration of Fixed Adsorption Beds
Schork, J. M.
PhD dissertation
In this work, thermal regeneration was studied through laboratory experimentation and nonequilibrium mathematical modeling. Temperature and effluent concentration data were collected during several adsorption-regeneration runs using laboratory-scale apparatus and a propane/N2/activated carbon system. A nonequilibrium, nonadiabatic computer model was used to simulate the experimental adsorption and regeneration data. Experimental and modeling results were used to study the effects of nonadiabatic operation, contact time, gas velocity, regeneration temperature, adsorbent particle size, and bed loading on regeneration efficiency.

F-87-1 PUBLISHED
Parametric Analysis of Thermal Regeneration of Adsorption Beds
Schork, J. M.; J. R. Fair
This study analyzes hot purge regeneration through laboratory experimentation and computer modeling. The model employed is nonisothermal and nonequilibrium. All gas-solid heat transfer resistance is assumed to be in the fluid film. Gas-solid mass transfer is represented by a linear driving force model with a variable, lumped-resistances coefficient. Experimental and modeling results are used to study the effects of the following parameters on regeneration efficiency: contact time, gas velocity, regeneration temperature, adsorbent particle size, nonadiabatic operation, level of initial bed loading, and uniformity of bedloading. This paper is based on dissertation work by Schork.

F-87-2
Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Joshi and Huang for the Adsorption Study Group Meeting.

F-87-8 $20.00
Adsorptive Drying of Organic Liquids
Joshi, S. R.
PhD dissertation
For this work, toluene was chosen as a representative hydrocarbon with limited water solubility, and its drying over solid desiccants was studied. The specific desiccants used were 1/8-inch H-152 activated alumina spheres, 1/16-inch and 1/8-inch 3A molecular sieve extrudates, and 1/16-inch
and 1/8-inch 4A molecular sieve extrudates. Isotherm and batch kinetic mass-transfer measurements were made, and breakthrough and regeneration data were taken in 1-inch- and 3-inch-diameter adsorbent beds. A linear driving force breakthrough model was developed and shown to represent the data taken here as well as the rather limited data available from the literature. Measurements on the regeneration step led to a mechanistic explanation of the concentration "roll-up" effect, and equilibrium modeling confirmed the explanation.

Some of the conclusions from the study were that the drying rate is controlled by intraparticle diffusion with surface diffusion being the dominant mechanism; bed efficiency improved with longer contact times and greater bed lengths. The alumina was more efficient than the sieves when water concentration was high, suggesting that compound beds of aluminas and sieves would represent an optimum combination for industrial purposes. Removal of adsorbed water with hot N2 was found to be a satisfactory method for regeneration.

F-87-9
Handouts for SRP Adsorption Study Group Meeting, October 1987
Includes copies of transparencies used by Joshi, Moosberg, Kitto, Munkvold, and De Sonier.

F-87-10  PUBLISHED
Parametric Analysis of Thermal Swing Cycle for Multicomponent Adsorption
Huang, C.C.; J. R. Fair

The purpose of the paper is to provide a parametric analysis of thermal swing adsorption when two adsorbates are involved. It provides a rational study of the variables that when properly manipulated can lead to significant reductions in energy consumption, at least when compared with empirical approaches that have been used in the past.

F-87-11  PUBLISHED
Study of the Adsorption and of Multiple Adsorbates in a Fixed Bed
Huang, C.C.; J. R. Fair

An experimental and theoretical study was made of the adsorption of ethane/propane mixtures from N2 or He. The study also covered the desorption of the mixtures using a purge of hot N2 or He. The adsorbent was Witco JXC activated carbon. A nonequilibrium, mechanistic model was developed and was shown to represent both adsorption and desorption processes. The model utilized mixture isotherm data predicted by the Flory Huggins form of the vacancy solution model. Both adsorption and hot purge regeneration were found to be intraparticle rate controlled processes with surface diffusion dominating the intraparticle mass-transfer mechanism. The dynamic model can be used for the simulation of a variety of commercial adsorption and desorption conditions.

F-87-12  $20.00
Thermal Regeneration of Fixed Multicomponent Adsorption Beds
Huang, C.C.
PhD dissertation

A 3-inch column packed with one foot of activated carbon was used as a fixed-bed adsorber. A dilute adsorbate mixture of ethane and propane was carried by an inert gas, either He or N2. In the regeneration step, the purge gas was either hot He or hot N2. Temperature and effluent concentration data were collected during several adsorption and regeneration runs. Parametric analyses were made for both adsorption and regeneration steps based on experimental and modeling results. The parameters included nonadiabatic operation, carrier or purge gas, inlet composition, flow rate, pressure, adsorbent particle size, initial bed temperature, regeneration temperature, and bed loading.
F-87-13  PUBLISHED
Steaming of Activated Carbon Beds
Schork, J. M.; J. R. Fair
The present communication reports results of an experimental investigation of heat transfer within an adsorbate-free bed of activated carbon. Temperature profiles within the bed were recorded as the bed was purged with low pressure steam. This work, undertaken as part of a continuing program on carbon bed adsorption and regeneration, is intended as a preliminary step in the investigation of steam regeneration.

F-88-1  PUBLISHED
Adsorptive Drying of Toluene
Joshi, S. R.; J. R. Fair
Adsorptive drying of liquids with limited water solubility is an important industrial operation. Adsorption isotherms were developed for a water-toluene system on several commercially important desiccants. The Langmuir-type equations predicted the isotherms on molecular sieves well. The isotherms on activated alumina were well predicted by a Freundlich equation. The intraparticle transport of water was found to be dominated by the surface diffusion. The intraparticle mass-transfer resistance was found to offer the controlling resistance to transport of water. The data show that almost 75% of the total resistance resided in the particle. A linear driving force mass-transfer model with a constant lumped-resistance coefficient was found to provide an acceptable fit to the experimental breakthrough data. In absence of available intraparticle diffusivities for water, except for 3A molecular sieves where the water transport is slow, a conservative estimate of the breakthrough could be obtained by the use of bulk diffusivity of water through toluene.

F-88-2
Handout for the Separations Research Program Spring Conference, April 1988
Includes transparencies used by Fair, Moosberg, Joshi, and Kim for the Adsorption Study Group Meeting.

F-89-2
Handouts for the Separation Research Program Fall Conference, September 1988
Includes copies of transparencies used by Wooten, Joshi, Chu, Alvarez, Munkvold, and De Sonier for the Adsorption Study Group Meeting.

F-89-9
Steam Regeneration of Activated Carbon Adsorbents
Alvarez-Trevit, J. A.
Manuscript on file, Separations Research Program
This is a proposal for PhD research that includes a detailed review of previous work on steam regeneration of activated carbon beds. It also contains the description of a breakthrough model that will be tested experimentally. Some emphasis is given to the unique nature of equilibrium adsorption of water on carbon. Finally, the report describes proposed experiments and methods for treating the experimental data.

F-89-12
Handouts from the Separations Research Program Fall Conference, September 1989
Includes copies of handouts used by Järvelin, Chu, Menon, DeSonier, and Munkvold for the Adsorption Study Group Meeting.

F-90-1
Handouts from the Separations Research Program Spring Conference, April 1990
Includes copies of transparencies used by Järvelin, Chu, Menon, and De Sonier for the Adsorption Study Group Meeting.
F-90-3
Handouts from the Separation Research Program Fall Conference, September 1990
Includes copies of transparencies used by Py, Menon, and De Sonier for the Adsorption Study Group Meeting.

F-90-4
Adsorption of Propane and Propylene
Järvelin, H.
Manuscript on file, Separations Research Program
The work reported here was carried out by Harri Järvelin, an SRP visiting scholar from Neste Oy, Finland, during 1989-1990. It represents the first reported work using the Xytel adsorption test system at the SRP laboratories. The adsorption of propane and propylene on various adsorbents was studied. The adsorbents were zeolite molecular sieves typed 4A, 5A, and 13X; silica gel, activated alumina, and activated carbon were also tested. Test data included breakthrough curves and depletion curves done on a pilot-scale adsorption test system. There is a remarkable difference between propane and propylene adsorption when molecular sieves are used. The adsorption capacity of silica gel was much lower than that of molecular sieves. With activated carbon and activated alumina it is impossible to separate propane and propylene. In the case of carbon, the difficulty was with selectivity. Adsorption on alumina was so small that it was impossible to detect.

F-91-2 PUBLISHED
Adsorptive Drying of Hydrocarbon Liquids
Joshi, S. R.; J. R. Fair
On the basis of experimental work coupled with mathematical modeling, a parametric analysis was made of the adsorptive drying of hydrocarbon liquids. The experimental work involved toluene and xylene dehydration over several dessicants. Equilibrium relationships and intraparticle diffusion coefficients were determined experimentally. The parameters required by the model are equilibrium constants, liquid film mass-transfer coefficients, intraparticle diffusion coefficients, and axial diffusivities. The model that was fitted to the experimental data was compared also with breakthrough data from the general literature; the model fit was quite good. It was found that in general the percentage bed utilization was substantially higher for the smaller particle sizes. Compound beds of aluminas and molecular sieves were simulated to take advantage of the higher water holding capacities of aluminas near saturation. Background information on distillative drying is included in the paper to enable comparisons between the distillative and adsorptive methods.

F-91-3
Handouts for the Separations Research Spring Conference, April 1991
Copies of transparencies used by Barnicki, Fair, and Menon for the Adsorption Study Group Meeting.

F-91-4 $20.00
Modeling and Simulation of Multicomponent, Nonisothermal Adsorption Cycles for Gas Separations
Chu, C.-S.
PhD dissertation
A comprehensive mathematical model has been developed to describe the mechanisms involved in the multicomponent, nonisothermal, nonequilibrium adsorption/ regeneration processes for the separation of gas mixtures. For the mass balance equations, four transfer mechanisms are considered: film transfer, pore diffusion, surface diffusion, and adsorption onto the surface. Thermal effects of adsorption/desorption are taken into account. The Ergun equation is used for the momentum balance. Variables calculated by the model are concentration and temperature of the gas and adsorbed phases, gas superficial velocity, adsorber wall temperature, and bed pressure. Single component isotherms may be represented by linear, Langmuir, and Redlich-Peterson relationships. For multicomponent equilibria, ideal adsorption solutions and vacancy solution
models may be used. The dynamic behavior of fixed-bed adsorbers subject to step changes in
concentration and temperature was studied. Parametric analyses were made for both temperature
swing and pressure swing processes. The general model can be implemented in either mainframe
or workstation computers. A simplified model, based on the general model, has been developed
and is available on a diskette for IBM PCs. This model retains most of the sign of the general
model, and test runs show close agreement between the models.

F-91-6 $10.00
Liquid-Phase Adsorption of Aromatic Compounds by Macrotreticular PS/DVB Resins: Equilibrium
and Dynamics
De Sonier, R. L.
PhD dissertation

The equilibrium and dynamics of the adsorption of a series of monosubstituted benzene
derivatives by highly crosslinked polystyrene/divinylbenzene (PS/DVB) copolymers were studied.
Alkylbenzenes, compounds having a polar substituent, and compounds having a H2-bonding
substituent were the three classes of adsorbates used. The effect of the solvent polarity and solute
(adsorbate) structure on equilibrium adsorption was investigated and aqueous solution isotherms
were measured. The extent of adsorption of all the solutes from aqueous solution could be
 correlated with the solute's aqueous solubility limit. A general isotherm expression for all the data
was developed. Capacity factors measured by liquid chromatography were used to quantify the
equilibrium adsorption from nonaqueous solvents. The decrease in adsorption as the solvent was
changed from methanol, ethanol, 1-propanol, 1-butanol to acetone could be quantified with a
solute's solvent-benzene partition coefficient. Within a family, trends were evident with molecular
descriptors for the methanol and ethanol capacity factors. The capacity factors of alkylbenzene
adsorbates increased as the van der Waals volume and molecular weight increased. The capacity
factors of the more polar adsorbates decreased with a solute's dipole moment. These trends
diminished as the solvent became more nonpolar. The capacity factors for the H2 bonding
adsorbates were not affected by a change in the solvent; none of the compounds adsorbed from
acetone. The dynamics of the removal of the solutes from aqueous solution were studied in a batch
adsorber. The intraparticle transport was characterized by an effective diffusivity based on a solid-
phase concentration driving force. These experimental investigations and their subsequent analysis
should aid the designer of a potential wastewater treatment process. The aqueous isotherm
information can be used to predict the extent of adsorption of the compounds to be removed from
the waste stream. The capacity factor data should provide a guide to the selection of the
appropriate solvent to remove the compounds from the resins and regenerate the adsorber. The
effective diffusivity values are required to predict breakthrough from fixed-bed adsorbers.

F-91-11
Energy Considerations in the Sorptive Removal of Contaminants from Discharge Gases
Fair, J. R.
Presented at the Thirteenth National Industrial Energy Technology Conference, Houston, Texas, June 1991
Adsorption and absorption are often competitive methods for the removal of pollutants from room
vents and other discharge gases. Characteristically, volumetric flow rates are high and contaminant
concentrations low. The principal energy inputs are for moving the gas through the sorption device
and for removing the sorbate from the sorbent. For a base-case application, the two sorption
processes are compared, and for each a discussion of the design parameters is provided. Finally,
some heuristics are presented that can enable engineers to make more rational analyses of sorption
applications to the correction of air pollution problems.

F-92-2 $10.00
Compound Adsorption Equilibria on Activated Carbon
Radushkevich method of characteristic curves to predict the isotherm for adsorption of a gas on
microporous materials, such as activated carbon. The method assumes the characteristic curves to
be independent of temperature and applies to multilayer adsorption on energetically nonuniform
surfaces. The original program has been modified to be interactive and user-friendly, and is
executable on an IBM personal computer running DOS. The program now allows the user to choose a preferred reference compound. If no reference data are known, the program uses a default reference data for toluene adsorption on Calgon-BPL(r) activated carbon.

**F-92-13**

*Adsorption of Aromatics from Water by Macroreticular Resins*

De Sonier, R. L.; J. R. Fair

Manuscript on file, Separations Research Program

The research described here is structured by an envisioned industrial process that uses a polymeric resin for removing an aromatic solute from an aqueous waste stream, with subsequent regeneration of the resin with a polar solvent. The recovered solute is then separated from the regenerant stream. Careful selection of the regeneration solvent can provide for effective recovery of the adsorbed compound. Thus, a normally unproductive pollution control step can be transformed into a closed-loop, materials recovery process.

**F-94-2**

*Equilibrium Adsorption of Gaseous Volatile Organic Compounds on Activated Carbon*

Simmons, M. A.

Manuscript on file, Separations Research Program

The presence of volatile organic compounds (VOCs) in both air and water streams is a major health and environmental concern. Emissions of VOCs to the atmosphere are limited by government regulation; therefore, the recovery of these compounds is necessary. Currently several techniques for recovering VOCs are regularly employed. This paper focuses on the removal of gaseous-phase VOCs by means of activated carbon adsorption. Numerous research efforts have examined the adsorption of VOCs by different adsorbents at different temperatures and concentration ranges. The objective of this paper is to consolidate the available equilibrium data for a limited number of specified compounds on activated carbon. This will result in the beginnings of a uniform database that encompasses a much broader range of temperatures, concentrations, and different types of activated carbons than any of the individual research efforts. This more extensive database will provide a larger pool of experimental data and better estimates of the coefficients of the Langmuir isotherm.

**F-94-6 PUBLISHED**

*Adsorptive Separation of Propylene-Propane Mixtures*

Järvelin, H.; J. R. Fair


The separation of propylene-propane mixtures is of great commercial importance and is carried out by fractional distillation. It is claimed to be the most energy-intensive distillation process practiced in the United States. The purpose of this paper is to describe experimental work that suggests a practical alternative to distillation for separating the C3 hydrocarbons: adsorption. As studied, the process involves three adsorptive steps: initial separation with molecular sieves with heavy dilution with an inert gas; separation of propylene and propane separately from the inert gas using activated carbon; and drying of the product streams with any of several available desiccants. The research information presented here deals with the initial step and includes both equilibrium and kinetic data. Isotherms are provided for propylene and propane adsorbed on three zeolites: activated alumina, silica gel, and coconut-based activated carbon. Breakthrough data are provided for both adsorption and regeneration steps for the zeolites, which are found to be superior to the other adsorbents for breakthrough separations. A flow diagram for the complete proposed process is included.

**F-94-7**

*Modeling of Tray-Type Steam Stripping Columns*

Fair, J. R.; R. L. Harvey

Presented at the AIChE Meeting, Atlanta, Georgia, Spring 1994

The steam stripping of organics from water is practiced extensively as a means for purifying process waste waters as well as for recovering the organics for possible re-use. The design of the
stripper has normally been carried out semi-empirically. In this paper, recently published Fractionation Research, Inc. (FRI) data are compared with data generated through the use of available models for the prediction of cross-flow sieve tray performance. The comparison is reasonably good, and only one adjustment was required in a model that heretofore has been validated only against distillation data. While the FRI tests cover only one solute (toluene) and one sieve tray design, it appears that the model is a reasonable one for designs of other systems and tray geometries. This is because the model is mechanistically based and takes into account flow rates and physical properties of the contacting phases as well as the geometric variables of the tray.

F-94-8
Rocha, J. A.; J. L. Bravo; J. R. Fair
Manuscript on file, Separations Research Program
In the first part of this paper (Rocha et al. 1993 [F-92-11]), models were developed for predicting liquid holdup, pressure drop, and flooding in distillation columns containing structured packings. The various commercially available packings were described, and the design correlations developed were based on rational, mechanistic models that provide a very good representation of experimental observations in larger-diameter columns. In Part II attention will be given to methods for predicting the mass-transfer performance of the same types of packings. In the present work the two-resistance approach will be used with the assumption of thermodynamic equilibrium at the phase interface. This should make the model useful for either rate-based or equilibrium stage-based computational routines; its basic ingredients are the gas- (or vapor-) phase mass-transfer coefficient, the liquid-phase coefficient, and the effective interfacial area. Concepts and methods developed in Part I will be retained since the interconnected relationships between film thickness, liquid spreading, and liquid holdup are important considerations for interphase mass transfer. Also, the model will be developed along modular lines so that as new packing materials and geometries are introduced they can be accommodated without major changes in the basic approach.

F-95-4 PUBLISHED $15.00
Separation of Propane and Propylene
Järvelin, H.
PhD dissertation
The separation of propylene-propane mixtures is of great commercial importance and is carried out by fractional distillation. It is claimed to be the most energy-intensive distillation practiced in the United States. The purpose of this paper is to describe experimental work that suggests a practical alternative to distillation for separating the C3 hydrocarbons: adsorption. The research information presented here deals with the initial step of an adsorptive separation process and includes both equilibrium and kinetic data. Isotherms are provided for propylene and propane adsorbed on three molecular sieves zeolites, two pentasil zeolites, silica gel, and coconut-based activated carbon. Breakthrough data are provided for both adsorption and regeneration steps for activated carbon, silica gel, activated alumina, and the molecular sieves, which were found to be superior to the other adsorbents for breakthrough separations. A flow diagram for the complete proposed process is included. Single-step adsorption cannot be utilized in propane/propylene separation. A three-step adsorption process based on heavy dilution with an inert gas is an interesting option. Adsorption can also be combined with other separation methods in order to reduce the high energy consumption of distillation. A hybrid process of adsorption and distillation is introduced. As a final part, a propane/propylene membrane separation is discussed, and a novel membrane structure is introduced and analyzed.
Modeling and Simulation of Co-Adsorption of Water Vapor and Organic Compounds in Fixed Activated Carbon Beds
Pacheco, M. A.
Master's thesis
A nonequilibrium mathematical model has been developed for describing the dynamics of fixed-bed adiabatic coadsorption of water vapor and organic compounds on activated carbon. The model is based on the equations that govern the mass and energy balance in the bulk phase and around the adsorbent particle. Three mass transfer mechanisms were considered: fluid-film mass transfer, particle pore diffusion, and surface diffusion. Adsorbent-fluid heat transfer resistance was considered while intraparticle heat transfer resistance was neglected. Thermal effects caused by the heats of adsorption were included. The micropore volume filling theory and the concept of maximum available pore volume were used to describe equilibrium coadsorption loading of water vapor and organics. Both the favorable and unfavorable sections of the water isotherm were considered for equilibrium loading calculations. The model was implemented in a computer program and the Numerical Method of Lines was used to solve the partial differential equations that describe the dynamics of the system. The model was validated using experimental data obtained from the literature for adsorption of toluene, ethyl acetate, and methylene chloride. Both the model and experimental data showed that water breaks through much earlier than the organic does in all the systems studied. It was also shown that when the feed relative humidity is above 50% there is a significant reduction in the capacity of the bed for adsorption of the organic, while a negligible effect is observed for lower values of relative humidity. As a consequence of the early water breakthrough and the thermal effects caused by the adsorption of water vapor, the model predicts an early temperature increase through the bed and a leading thermal front that is propelled by the gas flow rate. Significant differences between the dynamics of the organic concentration front and those of water vapor are predicted by the model. Good agreement between experimental data and model calculations regarding water and organic breakthrough and overall dynamics of the systems, was generally observed.

Steam Regeneration of Activated Carbon Adsorbents
Alvarez-Trevit, J. A.
Steam regeneration has been widely used for years in adsorption operations because it is cheap, easy-to-use and available. In addition, it allows the adsorbates to be recovered in subsequent separations through distillation and extraction. Despite its common practice very little is known about the mechanisms by which steam displaces the adsorbates from the adsorbent pores. The effect of condensing water and organic material on the pores, and the S-shaped water isotherm (type V of the Brunauer classification), makes it difficult to understand the mechanisms by which water displaces the adsorbate from the carbon pores. This project applies experimental and mechanistic work to explain such phenomena. An extensive literature survey of the highly specialized updated literature is given. Prior to experimentation, carbon characterization was made and a comparison with other carbon adsorbents from previous works was made. Sorption isotherms on carbon from water and organics used as adsorbates was then developed. During the experimentation, adsorption and steaming runs were conducted in a 3 inches diameter, 4 feet long Pilot-Scale Test System available at Balcones Research Center facility in north Austin. Extensive temperature and effluent concentration data were collected during these adsorption-steaming runs performed using volatile organic chemicals (voc's)/steam/nitrogen/activated carbon system. Regeneration was performed with saturated and superheated steam at various velocities and bed initial conditions. The effect on the bed adsorption capacities for various initial conditions following subsequent cycles with variance of several operating conditions was extensively observed. A primary focus of the study was the effect of the residual moisture left on the bed before being returned into adsorption operation. Also, the operating conditions used during the steaming runs explored this desorption process in the region of high steaming flow rates and very long steam regeneration times, allowing to observe the phenomena in conditions not explored before. A non-linear, shock-wave type, equilibrium-stage model was used to compare some of the
experimental steam regeneration data. Also, the simplified version of the Chu model was used for simulation of the adsorption runs and some of the propane regeneration runs using steam. Breakthrough and regeneration data were used to show the relative effect of steaming, drying and/or cooling in subsequent cycles. The three adsorbates used were (1) propane, which vaporizes and has a very little solubility with water; (2) acetone, which is water miscible; and (3) toluene, which is water immiscible. This presented the opportunity to view the relative impact of the organic/water/carbon systems on the cycle efficiencies. Equilibrium data for these three species was obtained by a gravimetric approach. Carbon characterization was also made. Coconut-shell type (Sorb-Tech) highly microporous activated carbon was used in all runs. Experimental data were gathered directly on a pilotscale basis. On the other hand, some heating runs of a dry, clean bed were made to allow the evaluation of heat transfer resistances of the adsorber. The main focus of this research was the study of the effects of non-adiabatic operation, steam contact times and superficial velocities, degree of superheat, bed initial conditions, and bed loading on regeneration efficiency.

**F-96-1 Steam Regeneration of Activated Carbon Beds**
Huggahalli, M.; J. R. Fair
Presented at the AIChE Annual Meeting, Chicago, Illinois, November 14, 1996

Thermal Swing Adsorption (TSA) processes using activated carbon adsorbents and incorporating steam as the regeneration fluid are common throughout the chemical process industries. Steam has the advantage of being a conveniently available plant utility and steam regeneration is considered a form of purge regeneration since it also sweeps out the desorbed compounds. As a result of condensation and adsorption, a significantly greater amount of energy can be supplied to the bed than a hot gas is capable of providing. The effectiveness of steam regeneration is further enhanced by the ability of water to displace adsorbed organics from the active sites on the carbon surface. Most organics are easily separated from the effluent steam which can be immediately condensed.

**F-96-10 $10.00**
The Effects of Humidity on the Activated-Carbon Adsorption of Organics
Menon, R. P.
Ph.D. Dissertation

Fixed-bed activated carbon adsorption systems are commonly used for organics removal in industrial gas purification and solvent recovery processes. Humidity is an important factor that determines the successful operation of these systems. The primary objective of this research was to develop an understanding of the role of water in the adsorption of organics onto activated carbon, through experimental breakthrough studies.

**F-97-1**
Sorptive Removal / recovery of organics from Air
James R. Fair; A. Frank Seibert
Manuscript on file, Separations Research Program

The class of chemicals popularly known as volatile organic compounds (VOCs) represent for the most part contaminating materials often found in discharge water and air from manufacturing operations. In many cases these organics are used in the operations as solvents, the volatility of which gives rise to their presence in emissions from the manufacturing facility. In this paper we are concerned with the removal of such VOCs from discharge air and the economics of selecting a separation method for removal as well as possible recovery for recycle to the manufacturing operations. Two frequently-practiced methods for removing VOCs are scrubbing and adsorption, and they embody the potential for recovering the VOCs for re-use. In this study we made process and economic comparisons of these methods, and chose the following candidate VOCs: acetone (completely miscible with water), ethyl acetate (partially miscible with water), and toluene (immiscible with water). All three of these chemicals are well-known contaminants of air streams. Further, their equilibrium and kinetic (breakthrough) characteristics have been studied in our adsorption laboratories. Flow diagrams for the methods are given. Two air feed rates were used:
10,000 cfm and 50,000 cfm. Loadings of the VOC's were taken as 1.0 and 0.1 mole-% (10,000 and 1,000 ppmv). The VOC's were recovered at 98+ wt-% purity. Complete details of the designs and economic evaluations are included in the paper. The results show the following: At both flow rates and at low concentrations, and for all three organics, adsorption requires 40 to 80% of the capital investment needed for scrubbing. The equivalent direct and indirect operating costs for adsorption were 15 to 67% of those for scrubbing. At the higher concentrations, the value of the recovered organics was more than the direct and indirect operating costs, and thus providing an economic advantage. At higher concentrations, adsorption is usually the winner, but this depends on the scrubbing solvent used, and whether water is introduced to the system. For example, toluene scrubbing with an organic solvent is cheaper than toluene adsorption on activated carbon, if steam is to be used for the carbon regeneration step.

F-02-1
The Effects of Humidity on the Adsorption of Organics on Activated Carbon
Menon, R.P.and Fair, J.R.

F-04-2
Absorption and Stripping
Fair, J.R.

H-86-1
Adsorptive Drying of Organic Liquids-An Update
Joshi, S. R.; J. L. Humphrey; J. R. Fair
Presented at the Industrial Energy Technology Conference, Houston, Texas, June 1986
The purpose is to review the state-of-the-art on adsorptive drying of liquid organics having limited water solubility and to make appropriate comparisons with the distillation method. Information on the determination of adsorption isotherms, the analysis for small amounts of water in mixtures, the modeling of adsorption kinetics, and the optimization of the regeneration step are included.

RT-00-1 PUBLISHED
A Statistical Mechanic Perspective on the Temperature Dependence of the Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity
Al-Muhtaseb, S.A.; Ritter, J.A.
J. Phys. chem. B., 103, 8104-8115 1999

RT-00-2 PUBLISHED
A New Model That Describes Adsorption of Laterally Interacting Gas Mixture on Random Heterogeneous Surfaces. 2. Correlation of Complex Binary and Prediction of Multicomponent Adsorption Equilibria
Al-Muhtaseb, S.A.; Ritter. J.A.
Langmuir, 15, 7732-7744 1999

RT-00-3 PUBLISHED
Roles of Surface Heterogeneity and Lateral Interactions on the Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity
Al-Muhtaseb, S.A.; Ritter, J.A.

RT-00-4 PUBLISHED
New Approximate Model for Nonlinear Adsorption and Concentration Dependent Surface Diffusion in a Single Particle
Botte, G.G.; Zhang, R.; Ritter, J.A.
Adsorption, 5, 373-380 1999
RT-00-5 PUBLISHED
High Gradient Magnetic Separation for the Treatment of High Level Radioactive Wastes
Ebner, A.D.; Ritter, J.A.; Nunez, L.

RT-00-6 PUBLISHED
New Magnetic Field Enhanced Process for the Treatment of Aqueous Wastes
Ebner, A.D.; Ritter, J.A., Ploehn, H.J.; Kochen, R.L.; Navratil, J.D.

RT-00-7 PUBLISHED
Correlation of the Double-Layer Capacitance with the Pore Structure of Sol-Gel Derived Carbon Xerogels
Lin, C.; Ritter, J.A.; Popov, B.N.
J. Electrochemical Society, 146, 3639-3643 1999

RT-00-8 PUBLISHED
A Mathematical Model of an Electrochemical Capacitor with Double Layer and Faradaic Processes
Lin, C.; Ritter, J.A.; Popov, B.N.; White, R.E.
J. Electrochemical Society, 146, 3168-3175 1999

RT-00-9 PUBLISHED
Development of Carbon-Metal Oxide Supercapacitors from Sol-Gel Derived Carbon-Ruthenium Xerogels
Lin, C.; Ritter, J.A.; Popov, B.N.; White, R.E.
J. Electrochemical Society, 146, 3155-3160 1999

RT-00-10 PUBLISHED
Pressure Swing Adsorption-Solvent Vapor Recovery-III: Comparison of Simulation with Experiment for the Butane-Activated Carbon System
Liu, Y.; Holland, C.E.; Ritter, J.A.
Sep. Sci. Tech., 34, 1545-1576 1999

RT-00-11 PUBLISHED
Pressure Swing Adsorption Cycles for Improved Solvent Vapor Enrichment
Liu, Y.; Ritter, J.A.; Kaul, B.K.
AIChE Journal, 46, 540-551, 2000

RT-00-12 PUBLISHED
Binary Isosteric Heats of Adsorption in Carbon Predicted from Density Functional Theory
Pan, H.; Ritter, J.A.; Balbuena, P.A.
Langmuir, 15, 4570-4578 1999

RT-00-13 PUBLISHED
Points of Zero Charge and Intrinsic Equilibrium Constants of Silica-Magnetite Composite Oxides
Shen, J.; Ebner, A.D.; Ritter, J.A.
J. Colloid and Interface Science, 214, 333-343 1999

RT-00-14 PUBLISHED
Equilibrium Theory for Solvent Vapor Recovery by Pressure Swing Adsorption: Analytic solution with Velocity Variation and Gas Phase Capacity
Subramanian, D.; Ritter, J.A.; Liu, Y.
Chemical Engineering Science, 54, 475-481 1999
RT-00-15  PUBLISHED
Determination of the Lithium Ion Diffusion Coefficient in Graphite
Yu, P.; Popov, B.N.; Ritter, J.A.; White, R.E.
J. Electrochemical Society, 146, 8-14 1999

RT-01-02
New Theoretical Correlation for the Capture Cross Section in High Gradient Magnetic Separation
Ebner, A.D.; Ritter, J.A.
AIChE Journal, in press 2001

RT-01-03  PUBLISHED
Ni-Composite Microencapsulated Graphite as the Negative Electrode in Lithium-Ion Batteries I. Initial Irreversible Capacity Study
Yu, P., Ritter, J.A.; White, R.E.; Popov, B.N.
J. Electrochemical Society, 147, 1280-1285 2000

RT-01-05  PUBLISHED
Carbonization and Activation of Sol-Gel Derived Carbon Xerogels
Lin, C.; Ritter, J.A.
Carbon, 38, 849-861 2000

RT-01-06  PUBLISHED
Ni-Composite Microencapsulated Graphite as the Negative Electrode in Lithium-Ion Batteries II. Electrochemical Impedance and Self-Discharge Studies
Yu, P.; Ritter, J.A.; White, R.E.; Popov, B.N.
J. Electrochemical Society, 147, 2081-2085

RT-01-07  PUBLISHED
Magnetic Hetero-Flocculation of Paramagnetic Colloidal Particles
Ebner, A.D.; Ritter, J.A.; Ploehn, H.J.
J. Colloid and Interface Science, 225, 39-46 2000

RT-01-08  PUBLISHED
Simulation of Gasoline Vapor Recovery by Pressure Swing Adsorption
Liu, Y.; Ritter, J.A.; Kaul, B.K.
Separation and Purification Technology, 20, 111-127 2000

RT-01-09  PUBLISHED
Palladium Microencapsulated Graphite as the Negative Electrode in Li-Ion Cells
Yu, P.; Haran, B.S.; Ritter, J.A.; White, R.E.; Popov, B.N.
J. Power Sources, 91, 107-117 2000

RT-01-10  PUBLISHED
Comparison of Finite Difference and Control Volume Methods for Solving Differential Equations
Botte, G.G.; Ritter, J.A.; White, R.E.
Computers and Chemical Engineering, 24, 2633-2654, 2000

RT-01-11  PUBLISHED
On the Correlation of Modified Antoine's Adsorption Isotherm Models with Experimental Data
Al-Muhtaseb, S.A.; LeVan, M.D.; Ritter, J.A.
Langmuir, 16, 8536-8538 2000
A new stepwise (SW) statistically optimized model and also a virial-type (VT) model were correlated successfully with adsorption equilibria for the \( n \)-alkane series \( C_1-C_7 \) on Westvaco BAX-1100 activated carbon over a wide range of temperatures and pressures. Both models predicted reasonable temperature-dependent isosteric heats of adsorption, and from these slight dependencies, sensible deviations between the adsorbed- and gas-phase heat capacities were indicated. However, the SW model was more reliable under extreme conditions. The SW model also showed that the observed linear dependence of \( \ln(P) \) on \( 1/T \) at constant loading, according to the Clausius-Clapeyron equation, only occasionally contributed to the overall description; statistically, more complicated temperature dependencies of \( \ln(P) \) were revealed, indicating that the temperature dependence on the isosteric heat of adsorption can be easily overlooked. The ideal-gas assumption, inherent in the Clausius-Clapeyron equation, was also relaxed. The resulting real-gas isosteric heats of adsorption were reduced compared to the ideal-gas values, especially at high loadings and high temperatures. Finally, the temperature-independent isosteric heats of adsorption predicted from the potential theory correlation developed in Part 1 of this series fell almost in the exact middle of the range predicted by the temperature-dependent SW and VT models for the lightly to moderately adsorbed alkanes, but severely under predicted those for the heavily adsorbed alkanes (i.e., heavier than \( n \)-propane).
**RT-01-17  PUBLISHED**  
**Elucidation of the Ion Binding Mechanism in Heterogeneous Carbon Composite Adsorbents**  
Puziy, A.M.; Poddubnaya, O.I.; Ritter, J.A.; Ebner, A.D.; Holland, C.E.  
Carbon, in press 2001

**RT-01-18  PUBLISHED**  
**Approximate Solutions for Galvanostatic Discharge of Spherical Particles- 1. Constant Diffusion Coefficient**  
Subramanian, V.R.; Ritter, J.A.; White, R.E.  
J. Electrochemical Society, in press 2001

**RT-02-1  PUBLISHED**  
**Equilibrium Theory Analysis of a Pressure Swing Adsorption Cycle Utilizing an Unfavorable Langmuir Isotherm. 1. Periodic Behavior**  
Daniel, K.D; Ritter, J.A.  
An isothermal equilibrium theory analysis of a simple two-step PSA process utilizing an adsorbate-adsorbent system that exhibits an unfavorable Langmuir isotherm has been carried out. Analytic expressions that directly describe the periodic state have been obtained and used to derive expressions for all of the important process performance indicators, with and without breakthrough of the heavy component into the light product. A design study with a H_{2}-metal hydride system revealed that the enrichment of this kind of PSA system ideally is always equal to the pressure ratio, regardless of whether breakthrough occurs. The breakthrough case compared to the no-breakthrough case caused the recovery of the light product to increase, but at the expense of the heavy-product recovery and light-product purity both decreasing below 100%. A parametric study revealed the effects of the most important process parameters on the process performance indicators and some subtle features that appear to be unique to this PSA process-isotherm combination. The design expressions developed here should be very useful for rapid feasibility studies, as the results represent the best possible separation that can be achieved with this kind of PSA process; they should also be insightful for training and educational purposes.

**RT-02-2  PUBLISHED**  
**New Analytical Solution for Nonlinear Adsorption and Diffusion in a Single Particle**  
Gadre, S.A.; Ritter, J.A.  

**RT-02-3  PUBLISHED**  
**Sol-Gel Derived Carbon Aerogels and Xerogels  Design of Experimental Approach to Materials Synthesis**  
Zanto, E.J.; Al-Muhtaseb, S.A.; Ritter, J.A.  

**RT-02-4  PUBLISHED**  
**High Enrichment and Recovery of Dilute Hydrocarbons by Dual Reflux Pressure Swing Adsorption**  
McIntyre, J.A.; Holland, C.E.; Ritter, J.A.  

**RT-02-5  PUBLISHED**  
**Equilibrium Theory Analysis of a Pressure Swing Adsorption Cycle Utilizing an Unfavorable Langmuir Isotherm 1. Periodic Behavior**  
Ebner, A.D.; Ritter, J.A.  
AIChE Journal, 48, 1679-1691, 2002
RT-02-6  PUBLISHED
New Model for Nonlinear Adsorption and Diffusion Based on a Quartic Concentration Profile Approximation
Gadre, S.A.; Ritter, J.A.

RT-02-7  PUBLISHED
Concentrating Dilute Sludge Wastes with High Gradient Magnetic Separation: Breakthrough Experiments and Performance
Ebner, A.D.; Ritter, J.A.

RT-02-8  PUBLISHED
Magnetic Field Orientation and Spatial Effects on the Retention of Paramagnetic Nanoparticles with Magnetite
Ebner, A.D.; Ritter, J.A.; Ploehn, H.J.

RT-02-9
Thermal Treatment of Sol-Gel Derived Nickel Oxide Xerogels
Lin, C.; Al-Muhtaseb, S.A.; Ritter, J.A.
J. Sol-Gel Science & Technology, submitted 2002

RT-03-1  PUBLISHED
Enriching Reflux and Parallel Equalization PSA process for Concentrating Trace Components in Air

The enrichment of useful trace components in air was carried out using a new two-bed pressure swing adsorption (PSA) process that utilized an enriching reflux (ER) cycle designed specifically for enriching the heavy component. Another new feature of this PSA process was the use of parallel equalization (PEQ), which not only saved recompression energy, but also favorably exchanged the axial concentration distribution between the two columns. These new PSA concepts were demonstrated by experimentally enriching Xe and CO2 in air using 13X MS zeolite. ER PSA substantially enriched both gases to values as high as 80 times the feed concentration with 90% recovery using a pressure ratio of only 12.5. This enrichment was far superior to that achieved with a conventional stripping reflux (SR) PSA cycle, which was limited thermodynamically to the pressure ratio, half-cycle time, feed flow rate, flow rate ratio (enriched gas/feed), and several different PEQ schemes on the enrichment of each gas. Increases in the flow rate and pressure ratios resulted in increases in the enrichments of both gases, whereas increases in the feed flow rate and half-cycle time revealed maxima in the enrichments. Partial PEQ through the upper half of the column nearer to the feed (lean) end was also determined to be superior to other PEQ schemes.

RT-03-2  PUBLISHED
Equilibrium Theory Analysis of a Pressure-Swing Adsorption Cycle Utilizing an Unfavorable Langmuir Isotherm. 2. Approach to Periodic Behavior
Daniel, K.D.; Ritter, J.A.

An isothermal equilibrium theory analysis of a simple two-step pressure-swing adsorption (PSA) process utilizing an adsorbate-adsorbent system that exhibits an unfavorable Langmuir isotherm was carried out. Analytical expressions that directly describe the approach to periodicity as a function of the cycle number were obtained and used to derive expressions for all of the important process performance indicators that change with the cycle number for the case with breakthrough of the heavy component into the light product (i.e., γ<1). This PSA process goes through four unique stages on the approach to the periodic behavior that are marked by different shock and simple waves and a shock wave that manifests and disappears before the periodic state is reached.
A case study with a H2-metal hydride system that exhibits an unfavorable Langmuir isotherm was used to reveal this unique behavior. This system was also used to show which process performance indicators are a function of the cycle number and how they change as process performance indicators are a function of the cycle number and how they change as periodicity is approached.

RT-03-3  PUBLISHED
Practical Modeling of Metal Hydride Hydrogen Storage Systems
Gadre, S.A.; Ebner, A.D.; Al-Muhtaseb, S.A.; Ritter, J.A.

A new approach is introduced to model the discharge behavior of a metal hydride hydrogen storage bed. The reversible reaction kinetics and the empirical van’t Hoff relationship used in a typical reactor model are replaced by a solid-phase diffusion equation and a semiempirical equilibrium \( P-C-T \) relationship. Two new semiempirical \( P-C-T \) models are also introduced based on modified virial and composite Langmuir expressions. By varying the heat- and masstransfer coefficients, the model was calibrated to experimental pressure and temperature histories obtained from a commercially viable metal hydride bed containing \( \text{Lm}_{1.06}\text{Ni}_{4.96}\text{Al}_{0.04} \). Overall, the results of this study showed that a fairly simple numerical model can do a reasonable job in predicting the discharge behavior of a fairly complicated metal hydride hydrogen storage bed over a wide range of hydrogen flow-rate demands. The extreme theoretical limits of isothermal equilibrium (analytical model), adiabatic equilibrium, nonadiabatic equilibrium, isothermal nonequilibrium, and adiabatic nonequilibrium conditions were also studied and compared to the actual behavior under nonadiabatic nonequilibrium conditions. These limiting cases revealed that the metal hydride hydrogen storage vessel was definitely heat-transfer-limited and only minimally mass-transfer-limited over a wide range of hydrogen discharge flow rates.

RT-03-4
Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels
Al-Muhtaseb, S.A.; Ritter, J.A.
Advanced Materials, in press, 2003

RT-04-1
Application of High Gradient Magnetic Separation Principles to Magnetic Drug Targeting
J. Magnetism and Magnetic Materials, 280, 184-201, 2004

RT-04-2
Retention of Paramagnetic Particles by Magnetite Particle Clusters with Multifunctional Character
Ebner, A.D. and Ritter, J.A.

RT-04-3
Retention of Iron Oxide Particles by Stainless Steel and Magnetite Magnetic Matrix Elements in High Gradient Magnetic Separation
Ebner, A.D. and Ritter, J.A.

RT-04-4
Equilibrium Theory Analysis of Dual Reflux PSA for Separation of a Binary Mixture
Ebner, A.D. and Ritter, J.A.
AIChE Journal, 50, 2418-2429, 2004
RT-04-5
New Methodology for the Measurement and Analysis of Adsorption Dynamics. Butane on Activated Carbon
Al-Muhtaseb, A. and Ritter, J.A.

RT-04-6
Analysis of Magnetic Drug Carrier Particle Capture by a Magnetizable Intravascular Stent. Part I Parametric Study with Single Wire Correlation
J. Magnetism and Magnetic Materials, in press on-line, 2004

RT-04-7
New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration
Reynolds, S.P., Ebner, A.D., and Ritter, J.A.
Adsorption, accepted, 2004

RT-04-8
On the Reversibility of Hydrogen Storage in Novel Complex Hydrides
Wang, J., Ebner, A.D., and Ritter, J.A.
Adsorption, accepted, 2004

RT-04-9
Two Dimensional Model for the Design of Metal Hydride Hydrogen Storage Systems
Gadre, S.A., Ebner, A.D., and Ritter, J.A.
Adsorption, accepted, 2004

RT-04-10
Synergistic Effects of Co-Dopants on the Dehydrogenation Kinetics of Sodium Aluminum Hydride
J. Alloys and Compounds, in press on-line, 2004

RT-04-11
Simulation of a Thermally-Coupled Metal Hydride Hydrogen Storage and Fuel Cell System
J. Power Sources, accepted, 2004

RT-04-12
Theoretical Analysis of a Transdermal Ferromagnetic Implant for Retention of Magnetic Drug Carrier Particles
Aviles, M.O., Ebner, A.D., Chen, H., Rosengart, A.J., Kaminski, M.D., and Ritter, J.A.
J. Magnetism and Magnetic Materials, accepted, 2004

RT-04-13
Magnetizable Intraluminal Stent and Functionalized Magnetic Carriers. A Novel Approach for Non-Invasive yet Targeted Drug Delivery
J. Magnetism and Magnetic Materials, accepted, 2004

RT-05-1
New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration
Reynolds, S.P., Ebner, A.D., and Ritter, J.A.
Adsorption, 11, pp. 531-536 (2005)
RT-05-2
On the Reversibility of Hydrogen Storage in Novel Complex Hydrides
Wang, J., Ebner, A.D., and Ritter, J.A.

RT-05-3
Two Dimensional Model for the Design of Metal Hydride Hydrogen Storage Systems
Gadre, S.A., Ebner, A.D., and Ritter, J.A.

RT-05-4
Synergistic Effects of Co-Dopants on the Dehydrogenation Kinetics of Sodium Aluminum Hydride

RT-05-5
Simulation of a Thermally-Coupled Metal Hydride Hydrogen Storage and Fuel Cell System

RT-05-6
Effect of Graphite on the Dehydrogenation and Hydrogenation Kinetics of Ti-Doped Sodium Aluminum Hydride
Wang, J., Ebner, A.D., Prozorov, T., Zidan, R., and Ritter, J.A.

RT-05-7
Theoretical Analysis of a Transdermal Ferromagnetic Implant for Retention of Magnetic Drug Carrier Particles
Aviles, M.O., Ebner, A.D., Chen, H., Rosengart, A.J., Kaminski, M.D., and Ritter, J.A.

RT-05-8
Magnetizable Intraluminal Stent and Functionalized Magnetic Carriers. A Novel Approach for Non-Invasive yet Targeted Drug Delivery

RT-05-9
Analysis of Magnetic Drug Carrier Particle Capture by a Magnetizable Intravascular Stent. Part 2. Parametric Study with Multi-Wire Two-Dimensional Model

RT-05-10
Sonochemical Doping of Ti-Catalyzed Sodium Aluminum Hydride
Prozorov, T., Wang, J., Ebner, A.D., and Ritter, J.A.
Journal of Alloys and Compounds, accepted (2005)

RT-05-11
Further Validation of the Quartic Concentration Profile Approximation for Describing Intraparticle Transport in Cyclic Adsorption
Gadre, A., Ebner, A.D., and Ritter, J.A.
Adsorption, accepted (2005)
Bioseparations

F-89-10 PUBLISHED
Commercially Attractive Bioseparation Technology
Fair, J. R.
Chemical Engineering Progress 85(12):38-44 (1989)
   The technologies that appear to play key roles in the commercial separation of biomixtures are discussed in this paper. Flow diagrams are provided for typical separations of fermentation broths. Fortunately, much of the equipment needed for such separations is not new to the chemical engineer, but special characteristics of biomixtures will require modifications to older designs. Considerable effort will be expended in making bioseparation systems (F-89-10) reliable and effective.

G-85-1 ($12.00)
Bioseparations: An Assessment of Current Technologies and Future Applications
Kitto, G. B.
Manuscript on file, Separations Research Program
   A review of various bioseparation methods and suggestions for future research needs.

G-86-1
Bioseparations -An Assessment of Current Technologies and Future Applications
Kitto, G. B. and J. L. Humphrey
Presented at the Industrial Energy Technology Conference, Houston, Texas, June 1986
   Given the characteristics and sensitivities of biomolecules, this paper reviews the chromatographic, electrophoresis, ultrafiltration, and extraction processes. These are the processes that appear to be the best methods for the final concentration and purification steps for a broad class of biomolecules. This is a summary of G-85-1.

G-86-2
Development of Scale-Up Procedures for a Microbial Enzyme
Kitto, G. B.
Manuscript on file, Separations Research Program
   Progress report on the Bioseparations Pilot Project from January through August 1986.
Now that the first products of biotechnology, including both those from recombinant DNA technologies and those relating to monoclonal antibodies, are assuming major importance in the marketplace, the problems and economics of protein and peptide purification are gaining increased importance. Scaleup means not just making things bigger but very often doing them in an entirely different way. A major thrust of the bioseparations project of the Separations Research Program at The University of Texas at Austin is the development of effective generic scaleup methods for taking protein products of biotechnology from the laboratory to pilot and industrial scale. Particular emphasis is being placed on the use of high performance liquid chromatography (HPLC) in downstream processing.

This paper describes the development of scaleup processing for the bacterial enzyme uracil-DNA glycosylase. Particular emphasis is placed on the development of effective means for scaling-up HPLC and the application of these techniques in a generic sense.

Vapor phase bioreactors have been used extensively to control odorous gases and are receiving increased attention as an efficient and cost-effective treatment method for volatile organic compound (VOC) emissions. However, an important issue related to bioreactors is their high sensitivity to shock loads and periods of process shutdown, which can significantly reduce treatment efficiency. The focus of this paper is the use of a novel closed absorption and humidification system to dampen dynamic load so toluene, methyl tert butyl ether (MTBE), and acetone, and to reduce their detrimental effect on a downstream bioreactor. A model based on the
mass transfer characteristics of target pollutants was developed and takes into account the closed water recirculation loop that minimizes fugitive emissions and simultaneously humidifies the influent gas stream. When water is used as the scrubbing liquid, model and experimental results indicate that the system effectively dampens hydrophilic compounds and segregates them from the hydrophobic compounds in the waste gas stream. The response of a vapor phase bioreactor to the pretreated stream has also been assessed and shows that the system works effectively with hydrophilic, but not hydrophobic, VOCs.

Dielectrically Enhanced Drying

**D-87-1**  
**Experimental Studies of Dielectric/Convective Drying in Non-Hygroscopic Porous Beds**  
Bergman, T. L.; T. A. Evans and P. S. Schmidt  
Presented at the Second Joint ASME/JSME Heat Transfer Conference, Honolulu, Hawaii, March 1987  
The use of microwave heating in the drying of industrial solids is a technology based mainly on empiricism. To optimize the efficiency of drying processes, it is necessary to understand the relevant drying phenomena. Experiments were carried out in a commercial microwave oven modified to accommodate a heated forced air flow over test samples to investigate microwave drying phenomena. To study the effects of variable permeability, test beds were constructed of uniform-sized borosilicate glass beads with diameters varying from 10 mm to 6 mm. Preliminary tests were also conducted with polymer pellets of comparable size but with different surface characteristics and physical properties. Water was evaporated from the beds with various combinations of microwave power density, air flow rate, and air temperature. The test sample mass was measured and air stream conditions were also monitored. The experimental results show that higher drying rates occur in beds of smaller beads (and, hence, smaller pore size and permeability) with and without dielectric heating. Dielectric heating (D-87-1), however, tended to decrease the influence of particle size and desensitize the drying rate to changes in convective conditions at the open surface. These effects were observed at low microwave power densities where the sample temperature was well below the saturation temperature. At power densities high enough to promote boiling, the drying rate becomes independent of convective conditions but is still sensitive to the permeability of the porous bed.

**D-87-2**  
**Microcomputer Spreadsheet Models for Evaluation of Industrial Microwave Heating Application**  
McNelis, B. J.; P. S. Schmidt and M. M. Crawford  
Microcomputer models have been developed using a well-known spreadsheet language (Lotus 1-2-3) to permit comparative evaluation of microwave and conventional heating methods (D-87-2); in two major industrial applications drying of pasta products and curing of rubber extrusions. Detailed capital and operating cost relationships were established to permit estimation of various production cost elements directly from plant equipment and operating data. First-pass production cost estimates and sensitivity studies can thus be carried out with a minimum of initial input using internally generated default parameters. The spreadsheet formulation allows the user to conveniently replace these default values for more detailed and accurate calculations. An approach is also described for evaluating intrinsic factors such as product quality and equipment flexibility which, while difficult to quantify in direct economic terms, may be important decision variables.

**D-87-3**  
**Model Studies of Evaporation under Combined Microwave and Convective Heating**  
Accad, J. M. and P. S. Schmidt  
Presented at the Eighth International Heat Transfer Conference, San Francisco, California, August 1986
A simple analytical model has been formulated to investigate the relative influence of various operating variables in evaporation under the influence of combined microwave and convective heating. A discussion of the physical mechanisms driving the system is presented and two regimes of microwave-assisted drying are defined: saturated (or boiling-point) drying and sub cooled drying. The model described here concentrates on the sub cooled regime. Parametric studies were carried out to explore the effects of changes in microwave power density, and air temperature, velocity, and RH on temperature-time history and evaporation rate of moisture from a free surface representative of the laboratory environment. Effects of temperature dependence of the dielectric loss factor and nonconstant input power density are also investigated.

D-87-4  $10.00
Modeling of Microwave/Convective Evaporation and Drying
Accad, J. M.
Master's thesis

Heating materials with microwaves is a relatively new technology. The volumetric deposition of power results in a radically different heating pattern, especially when applied to drying. Since the heat is generated volumetrically, the material's resistance to thermal diffusion is greatly reduced, and drying rates are substantially increased. Polar molecules, such as water, are particularly well suited to microwave absorption. In many drying situations, the solid matrix is transparent to microwaves and is, therefore, left unheated. As a result, microwave heating can be thought of as a selective process which has an interesting side-effect: by depositing more heat where there is more water (thereby helping remove the excess moisture), the liquid distribution eventually becomes uniform inside the porous solid. Although the potential advantages of microwave drying systems are promising, there remain a large number of technical problems to be solved. Furthermore, the large initial capital cost of such a system tends to deter the large industrial users from investing in an as yet untested operation. One of the problems is the lack of a complete economic analysis of the benefits achieved, and information on pay back and capital recovery. It is also believed that a better fundamental understanding of the microwave drying process is required before the economics can be evaluated. This thesis reviews the existing literature, presents the available drying theories, and proposes a new approach to microwave drying simulation.

Distillation

B-82-1  PUBLISHED
Generalized Correlation for Mass Transfer in Packed Distillation Columns
Bravo, J. L.; J. R. Fair
An improved correlation of mass-transfer rates for commercial-scale packed distillation columns has been developed. Packings represented are of the randomly arranged ring and saddle types. Basic data are from 231 evaluated runs covering eleven distillation systems. The correlation is shown to be more reliable and more general than previously published models, with 96% of the calculated data falling within ±20% of the observed values. For 95% confidence in design, a 1.6 safety factor is required.

B-85-1  PUBLISHED
Pressure Drop in Structured Packings
Bravo, J. L.; J. A. Rocha; J. R. Fair
Hydrocarbon Processing 65:45-49 (1986)
A model for calculating pressure drop in counter-current gas/liquid contacting columns packed with structured packing is presented and validated.
B-86-1

Modern Plastic Packing for More Efficient Separation Processes
Billet, R.
Presented at the SRP Fall Conference, October 1985
This paper presents the characteristics and process advantages of modern plastic random packings for absorption/stripping and low-temperature distillation. Substantial amounts of efficiency and hydraulic data are presented in a comparative format. Column scale-up is also discussed and a general comparison method using the pressure drop of each transfer unit is presented.

B-86-3

Prediction of Vapor and Liquid Equilibria for Sparingly Soluble VOCs in Water
Guinn, R. M.; J. L. Bravo
Manuscript on file, Separations Research Program
This paper shows how the nonrandom two-liquid (NRTL) model used to predict activity coefficients can be adapted to volatile organic compound (VOC) removal applications involving air or steam stripping.

B-86-4 $20.00

Design Manual-Packed Columns for Distillation, Absorption, and Stripping
Fair, J. R.; J. L. Bravo
A comprehensive manual for designing or retrofitting distillation columns that are to be used with various random and structured packings. Includes a computer diskette (for IBM PCs) containing the program for making design calculations.

B-86-5 PUBLISHED

Modern Plastic Packings for More Efficient Separation Processes
Billet, R.; J. L. Bravo
Mass-transfer performance and hydraulic studies were performed at Ruhr University in West Germany to assess the advantages and characteristics of some of the newer high-efficiency plastic packings for absorption, stripping, and low-temperature distillation. This paper presents the experimental results of such studies as well as the development of models to describe the performance of these packings.

B-87-1 $10.00

A Generalized Correlation for Mass Transfer in Packed Distillation Columns
Bravo, J. L.
Master's thesis
This thesis, completed in 1981 with most of it previously published, includes a very extensive data bank on mass-transfer efficiency and pressure drop for random packings. The data cover a wide range of systems and geometries, and include the necessary physical properties and equilibrium information.

B-87-2

Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Bravo, Martin, Stichlmair, and Hufton for the Distillation Study Group Meeting.

B-87-5 PUBLISHED

Separation of Azeotropic Mixtures via Enhanced Distillation
Stichlmair, J.; J. R. Fair; J. L. Bravo
By definition, an azeotropic mixture cannot be separated by direct distillation. However, it is often possible and practical to make the separation by distillation if an extraneous material (an "entrainer") is added to the system or if another unit operation is used in conjunction with the distillation. One key consideration, if classical azeotropic distillation is to be used, is the selection
of the entrainer material. And if distillation is to be coupled with another method, then the limits posed by the azeotrope must be taken into account. This paper covers these two considerations: entrainer selection and appropriate coupling of distillation with another separation technique. For either case, the approach may be called "enhanced distillation." Coverage will be limited to the separation of a given binary mixture that forms an azeotrope. General criteria for entrainer selection are given and several examples are included. Also the use of combinations of distillation with decantation, solvent extraction, stripping, and adsorption to separate azeotropic mixtures is illustrated.

B-87-6
Correlation of Flooding in Packed Columns and the Generalized Pressure-Drop Relation
Buchanan, J. E.; D. C. Dixon
In the design of a packed column for a vapor-liquid mass-transfer operation, prediction of the limiting flows of the two fluids is of central importance. But the methods currently in use are seriously unreliable and not well understood. The design method most generally recommended to use is a graphical correlation developed by Sherwood, Shapely, and Holloway (1938) or one of its many modifications or developments. The purpose of this report is to establish the proper form of that correlation, to demonstrate a theoretical justification for it and, following that theory, to explain its limitations and suggest how it might be improved.

B-87-7
Handouts for SRP Distillation Study Group Meeting, October 1987
Includes copies of transparencies used by Martin, McGlamery, Bravo, Hufton, Wooten, and Handler.

B-87-8
Analysis of VOCs at Low (parts per billion) Concentration Levels
Wooten, C.; N. E. Handler; R. L. De Sonier; J. L. Bravo
Manuscript on file, Separations Research Program
This paper describes the task of developing the analytical techniques to detect and quantify very low concentrations (less than 10 ppb) of VOCs in water. The technique described uses static headspace analysis to concentrate the VOCs from aqueous solutions; a gas chromatograph and electron capture detector were used for detection and quantification.

B-88-1
Performance of Structured Packings in Distillation Service-Experimental and Modeling Results.; J. L. Bravo; J. R. Fair
Presented at AIChE Spring National Meeting, New Orleans, Louisiana, March 1988
Experimental distillation data on several structured packings are presented. The variation of height equivalent to a theoretical plate (HETP) with bed depth is discussed and the mechanisms that we believe cause it are presented. Packings with very similar geometries but drastically different surface characteristics appear to exhibit different efficiencies because of differences in wetted area as well as in their ability to maintain flow distribution. Data on FlexipacTM, SulzerTM, and GempakTM structured packings are presented. The modeling of these data as to effective interfacial area for mass transfer is not complete and only preliminary information is shown. As before, the distillation system used for our studies was the cyclohexane/n-heptane mixture at 4.83 psia, 15 psia, 24 psia, and 60 psia. The test column is 16-7/8 inches in diameter, and tests were conducted with approximately 10 feet of packing.

B-88-2 REPLACED BY F-87-7-DISTILLATION
Steam Stripping of VOCs from Water
Wooten, C.; J. L. Bravo
Manuscript on file, Separations Research Program

The purpose of this project was to evaluate steam stripping as a means for removing VOCs from water. The evaluation of this technology focused on two primary goals. The first goal was to examine the feasibility of condensing the overhead vapor phase for recovery of the organic. Recovery of the organic in concentrated form would reduce the volume of contaminated material for disposal. The second goal was to collect mass-transfer data using a stainless-steel gauze structured packing for correlation studies using the models previously developed by the SRP. Much of the previous work done in the SRP with stainless-steel gauze structured packings in vapor-liquid service has been with systems in which the controlling resistance to mass transfer is in the vapor phase. The VOCs have very large Henry's constants and limited water solubility, so the resistance to mass transfer is liquid-side controlled. The compound used in the described experiments was trichloroethylene. The experimental apparatus and the analytical techniques used are described along with some of the problems encountered when working with systems with high volatilities and low solubility’s. The impact of adequate analytical capabilities and the resulting limitations are also discussed. Experimental mass-transfer data for stainless-steel gauze structured packing are presented along with comparisons to predicted values using both a model for mass transfer in structured packings and a model found to be applicable in other stripping operations. The degree of wetting or the effective interfacial area available for mass transfer appears to dictate the performance of the packing. Steam stripping is shown to be an effective method for removing VOCs from contaminated waters, and it offers environmental advantages over traditional methods of removal such as air stripping.

General Model for Prediction of Pressure Drop and Capacity of Countercurrent Gas/Liquid Packed Columns
Stichlmair, J.; J. L. Bravo; J. R. Fair

A new theoretical model that describes the hydraulic behavior of packed columns operating in countercurrent gas-liquid service is presented. The model applies both to random and structured packings. Some of the most important characteristics of the model are:

* A new general porosity term on the pressure-drop equation that was developed from data of single fluid flow through fluidized beds.
* The general pressure-drop equation presented is valid for dry as well as irrigated packings if the changes in bed porosity and particle diameter caused by liquid holdup are incorporated.
* The derivative of the pressure-drop equation yields a mathematical expression for the determination of the flooding point.

The model requires knowledge of the friction factor of a single particle, the porosity, and the surface area of the bed. It has been validated for several kinds of random and ordered packings without additional correlation parameters. The knowledge of liquid holdup is required, and a new predictive correlation based on a large collection of published data is also presented. The validity of the new approach is demonstrated by comparison with an extensive data bank that includes published data of several different researchers. This model represents an improvement over previous ones in that a single pressure-drop equation describes both the regions below and above the loading point and can be used to accurately predict the flood point. It represents a very useful tool for the design and analysis of packed columns for distillation, absorption, stripping, and direct contact heat transfer.
Mass-Transfer Performance of Structured Packings in Distillation Service
Bravo, J. L.; J. R. Fair; C. Fischer
Presented at AIChE Spring National Meeting, New Orleans, Louisiana, March 1988
Mass-transfer efficiency performance of several packings was evaluated on the basis of HETP. The results presented here show that surface characteristics of corrugated sheet-metal and gauze packings can have a distinct effect on mass-transfer efficiency. The surface can influence the degree of liquid spreading and thus affect the interfacial area for transfer. It can also influence the distribution of the flowing liquid with the bottom of the packed bed showing better or worse distribution depending on the packing itself and the quality of initial distribution. The results show the importance of the "intrinsic distribution characteristic" of a given packing. The present work demonstrates that structured packings of the gauze and sheet-metal types can be highly efficient, giving low values of the HETP. Includes a collection of experimental data.

Handout for the Separations Research Program Spring Conference, April 1988
Includes transparencies used by Bravo, Barnicki, and Chu for the Distillation Study Group Meeting.

A New SRP Program for Packed and Tray-Column Design
Macias, R. and J. L. Bravo
A comprehensive and interactive microcomputer program for the design of packed and trayed distillation columns has been assembled. It uses estimation methods available in the literature as well as SRP correlations for mass-transfer efficiency and hydraulic performance of packing and sieve trays.

Handouts for the Separations Research Program Fall Conference, September 1988
Includes copies of transparencies used by Bravo, Fischer, and Patwardhan for the Distillation Study Group Meeting.

Handouts for the Separations Research Program Spring Conference, April 1989
Includes copies of transparencies used by Bravo and Patwardhan for the Distillation/Extraction Study Group Meeting.

The T-By Tray: A Plug-Flow, Low-Pressure Drop Contacting Device for Cross-Flow Columns
Bravo, J. L.; B. M. Parker; T. J. Parker
This paper describes a new tray design developed for crossflow distillation, and stripping columns. This design promotes plug flow of liquid across the device and appears to reduce gas pressure drop as well.

A New Cocurrent Gas/Liquid Contacting Device for High Gas Rate Applications
Trutna, W. R.; J. L. Bravo
The objective of this study was to reduce distillation-absorption or stripping column sizes to less than half that of present equipment and, correspondingly, achieve a major reduction in capital costs. Experimental studies reported good progress toward achieving these goals. A new device for countercurrent contacting of liquid and gas, which involves cocurrent flow in each stage, is described. Both hydraulic and mass-transfer tests were conducted in the SRP's 16-7/8-inch-diameter column. Rates approximately double those of sieve trays were obtained in the hydraulic tests at low liquid rates in the mass-transfer tests. Although the test stage efficiencies for the
Trutna tray were slightly lower than for sieve trays, the HETP was less because of the reduced stage height. Analyses of both the above data and laboratory data indicate that prospects are good for mass-transfer demonstration of the high rates at high liquid flows together with higher stage efficiencies. Application areas and economic comparisons with other distillation systems are described briefly.

**B-89-7**
**Handouts from the Separations Research Program Fall Conference, September 1989**
Includes copies of handouts used by Bravo, Rocha, Parker, and Patwardhan for the Distillation Study Group Meeting.

**B-89-8 PUBLISHED**
**Influence of Effective Interfacial Areas in the Operation and Control of Packed Distillation Columns**
Bravo, J. L.; A. A. Patwardhan; T. F. Edgar
This paper explores the effect of the interfacial area behavior of different packings on the way the distillation column responds to varying loads. Implications for the design of control strategies are discussed as well. Experimental data obtained previously were used to establish the basis for the analysis. The data clearly show that different geometries and surface treatment characteristics have a strong influence on the amount and rate of change of interfacial area with column loading.

**B-90-1**
**Mass-Transfer Efficiency Modeling of Packed Absorbers and Strippers**
Bravo, J. L. and J. R. Fair
Correlations developed to describe mass-transfer efficiency of packed columns in distillation applications do not appear to fit absorption and stripping columns well in many cases. Previous work by the authors dealing with the characterization of effective interfacial areas in random packings indicated a marked difference in the availability of transfer area between distillation and absorption experimental data. A large data bank that included distillation as well as absorption data was studied in detail, and a correlation for the effective transfer area for distillation was developed. The present paper follows on that work and analyzes the absorption data from the same data bank together with experimental data obtained at the SRP for air and steam stripping. A new correlation for effective mass-transfer area is presented. The values predicted by this correlation are generally lower than the ones predicted by the distillation model for equivalent conditions. The reasons for this are discussed, as are applications to structured packings.

**B-90-2**
**SRP Experimental Data on Structured Packings in Distillation Service**
Rocha, J. A.; B. E. Reeves; J. L. Bravo; J. R. Fair
Manuscript on file, Separations Research Program
Mass-transfer, pressure-drop, and capacity characteristics of several commercially available structured packings have been measured in the SRP's pilot-plant. Both proprietary and nonproprietary data are presented in a rational and consistent form that allows an easier comparison between the different packings. Most of the data have been available to SRP sponsors before, but this document groups all available data together.

**B-90-3 PUBLISHED**
**Point Efficiencies on Sieve Trays**
Biddulph, M. W.; J. A. Rocha; J. L. Bravo; J. R. Fair
This report describes a study of the efficiency of sieve trays operating at various pressures on the system cyclohexane/n-heptane. Point efficiencies have been calculated from data on two sizes of column and have been found to be similar. This provides encouragement that scale-up using point efficiencies is possible, and provides the first values to be calculated rigorously from medium-scale sieve trays operating on a hydrocarbon system.
B-90-4
Handouts from the Separations Research Program Spring Conference, April 1990
Includes copies of transparencies used by Rocha, Biddulph, Bravo, Macias, and Barnicki for the Distillation Study Group Meeting.

B-90-5 REPLACED BY F-92-11-DISTILLATION

B-90-6 REPLACED BY F-92-11-DISTILLATION

B-90-7
Handouts from the Separations Research Program Fall Conference, September 1990
Includes copies of transparencies used by Bravo, Rocha, Thongpakdi, and Macías for the Distillation Study Group Meeting.

B-90-8
Bravo, J. L.; B. M. Parker; T. J. Parker
Tests in Pilot-Scale Equipment: Final Report to DOE
This report describes the development and preliminary testing of a tray design for cross-flow contacting of gas and liquid in absorption, stripping, and distillation applications. The device, called the T-By tray, was designed to promote liquid plug-flow conditions and to eliminate the negative effects of tray stagnant side zones. As liquid flows across the tray, the T-By tray has a unique baffle arrangement that reduces gas pressure drop by directing the flow of liquid in a special pattern on the tray. The tray has been characterized experimentally for capacity, mass-transfer efficiency, and pressure drop. Results of the evaluation tests are presented along with a comparison of data available in the literature.

B-91-1
Liquid Distribution and Mixing in Spray Towers
Bravo, J. L.
Manuscript on file, Separations Research Program
A technique to measure local mass-transfer rates within a spray column has been developed to obtain mass-transfer rate profiles that can be used to describe liquid distribution and the degree of mixing in the spray. Results from experiments conducted in a 0.39-m-diameter spray column are presented.

E-91-3
Retrofitting Distillation Columns for Maximum Energy Efficiency
Humphrey, J. L.; A. F. Seibert
Copies of transparencies used at the AIChE Spring Meeting, Houston, Texas, April 1991.

E-92-2 PUBLISHED
Separation Technologies: An Opportunity for Energy Savings
Humphrey, J. L., and A. F. Seibert
Chemical Engineering Progress, pp. 31-42 (1992)
Distillation operations by the US chemical and petrochemical industries consume the equivalent of over one million barrels of oil per day which represents 27% of industrial energy consumption. This paper addresses methods of improving distillation operations by making distillation more energy efficient or augmenting distillation with advanced processes to form energy-efficient hybrid systems. The effects of implementing advanced process control, high-efficiency packings, and distillation-adsorption hybrid and distillation-pervaporation hybrid systems on energy savings and the economics are reported.
**F-84-1 PUBLISHED**

**Historical Development of Distillation Equipment**

Fair, J. R.


This paper traces the evolution of modern devices for vapor-liquid contacting in distillation service.

**F-84-2 PUBLISHED**

**Prediction of Point Efficiencies on Sieve Trays. 1. Binary Systems**

Chan, H. and J. R. Fair


A correlation is presented that represents a distinct improvement over the currently used AIChE method. This correlation has been validated against a large data bank of commercial-scale distillation efficiencies.

**F-84-3 PUBLISHED**

**Prediction of Point Efficiencies on Sieve Trays. 2. Multicomponent Systems**

Chan, H. and J. R. Fair


A predictive model is developed on the basis of multicomponent diffusion theory and supported by laboratory measurements. A pseudo-binary model is then shown to give reasonable checks with the rigorous multicomponent model.

**F-84-4 PUBLISHED**

**Distillation Research Needs**

Fair, J. R.; J. L. Humphrey


A state-of-the-art report on the current situation and the corresponding needs for further research.

**F-84-5A PUBLISHED**

**Solvent Removal from Ethylene-Propylene Elastomers. 1. Determination of Diffusion Mechanism**

Matthews, F. J.; J. R. Fair.; J. W. Barlow; D. R. Paul; C. Cozewith


Removal of hexane from elastomers was studied experimentally and then modeled on a mechanistic basis. Part B includes data from plant-scale verification work (Exxon Chemical Co.).

**F-84-5B PUBLISHED**

**Solvent Removal from Ethylene-Propylene Elastomers. 2. Modeling of Continuous-Flow Stripping Vessels**

Matthews, F. J.; J. R. Fair; J. W. Barlow; D. R. Paul; C. Cozewith


Removal of hexane from elastomers was studied experimentally and then modeled on a mechanistic basis. Part B includes data from plant-scale verification work (Exxon Chemical Co.).

**F-84-6 $10.00**

**Mass-Transfer Characterization of a Counter-Current Spray Column**

Wang, T. R.

Master's thesis

Gas-phase mass-transfer measurements were made for two different solid-cone nozzles at varying elevations with respect to the air inlet. Wall effects were evaluated.
F-85-1  PUBLISHED
Mass Transfer in Gauze Packings
Bravo, J. L.; J. A. Rocha; J. R. Fair
Hydrocarbon Processing 64:91-95 (1985)
A model to predict mass-transfer performance of gauze structured packings is presented. A
specific method for defining the flow-channel geometry allows for the use of correlations very
similar to those applicable to wetted-wall columns. The model is verified using data available in
the literature.

F-85-2  PUBLISHED
Distillation: Energy Savings and Other Benefits from the Use of High-Efficiency Packings
Bravo, J. L.; J. R. Fair; J. L. Humphrey
In Proceedings of the Seventh Annual Industrial Energy Technology Conference, Public Utility
Commission of Texas, 1985
This paper covers the advantages derived from the use of high-efficiency packings in vacuum
distillation. In particular it focuses on retrofit applications where more throughput and lower
energy use are the objectives.

F-85-3  $10.00
Stripping Efficiency in a Stirred and Sparged Vessel
Talton, J. E.
Master's thesis
A study to determine the relative importance of gas- and liquid-phase mass transfer resistances in
sparged contactors. Results show that gas-phase resistance cannot be considered negligible.

F-85-4  $10.00
Actual Stage Requirements for Distillation Separations
Martin, C. L.
Master's thesis
A binary tray-efficiency model developed by Chan and Fair (F-84-2 and F-84-3) was used to
predict Murphree tray efficiency. This model was used in conjunction with the Naphtal-Sandholm
algorithm in a computer model to test for convergence in six systems. The result was that
convergence was achieved in all six systems.

F-85-5  $10.00
Entrainment from DistillationSieve Trays
Ruchirote, N.
Master's thesis
Entrainment of liquid from a crossflow sieve tray was measured for air-water and air-oil systems.
The measurements were compared with data from the literature and from special outside studies.
effects of operating and geometric parameters were evaluated and general relationships were
developed.

F-85-8  PUBLISHED
Stagewise Mass-Transfer Processes
Fair, J. R.
Treatment of scale-up and design principles for tray-type distillation columns, absorbers, strippers,
and extractors.

F-85-9  PUBLISHED
Continuous Mass-Transfer Processes
Fair, J. R.
Treatment of scale-up and design principles for packed distillation columns, absorbers, strippers,
and extractors.
The transition from the bubble to spray regimes on a perforated (sieve) tray was studied with regard to hydraulics and mass-transfer efficiency. Special experimental equipment was used to simultaneously monitor jetting characteristics of several individual holes on a sieve tray. A computer-based data acquisition circuitry was designed and built to digitally monitor eight electroresistivity probes independently located in separate holes of a sieve tray in a small air-water simulator. The average fraction of time that a given hole was inactive (liquid cover), issuing small bubbles, issuing large bubbles, or jetting was measured by the probes as a function of phase-flow rates and tray geometry. Additionally, a flotation device was used to measure three-point density profiles of the aerated mass on the tray. Gas- and liquid-phase mass-transfer efficiencies measured under the same conditions enabled correlation between the inversion and diffusional mechanisms. The final result is a mechanistic model that appears to offer better understanding of the processes that occur during the bubble-to-spray transition on distillation sieve trays.

This paper summarizes experimental techniques and preliminary findings described in F-86-11.

The objective of this work was to develop a model for mass transfer that would span the transition from simple bubbling to spray predominance and take into account the mechanisms imposed by the two-phase fluid mechanics. Gas- and liquid-phase mass-transfer efficiencies measured under the same conditions enabled correlation between the inversion and diffusional mechanisms. The final result is a mechanistic model that appears to offer better understanding of the processes that occur during the bubble-to-spray transition on distillation sieve trays.

Increased use of the so called "high-efficiency" packings in distillation, absorption, and stripping services represents one of the important developments in the field of fluid-mixture separations over the last few years. This paper describes the mass-transfer efficiency and the pressure-drop characteristics of structured packing and how they can be represented by mathematical models. The models can in turn be applied to the analysis and design of commercial columns containing the packings. New data on interfacial area behavior are included.
F-87-6 PUBLISHED
Bubble-to-Spray Transition on Sieve Trays
Prado, M.; K. L. Johnson; J. R. Fair
Chemical Engineering Progress March 1987, pp. 32-38
This paper is an abridgement of publication F-86-12 and in particular contains fewer details on the experimental techniques.

F-87-7 PUBLISHED
Distillation: Whither, Not Whether
Fair, J. R.
Chemical Engineering Research and Design 66:363-70 (1988)
Because of its pre-eminent position as a separating method, the future of distillation is not in doubt. How it might move in the future to better satisfy its key role in separations is the question to be addressed. This presentation provides a review of the state of the art, as well as some suggestions for further studies that might be in order for distillation.

F-87-14 $15.00
Performance and Scale-up of Laboratory-Scale Distillation Columns Containing Structured Packing
Hufton, J. R.
Master's thesis
Mass-transfer efficiency and column pressure drop were measured in a 25-mm-diameter column containing 0.58 m of SulzerTM laboratory-scale structured packing. Experiments were performed at total reflux with the chlorobenzene/ethylbenzene system at top pressures of 40, 78, 300, and 750 mm Hg. At about 70% of capacity, this packing produced heights equivalent to a theoretical plate (HETP) of 2 to 6 cm and pressure drops per unit packing height of 4.2 to 5.5 mbar/m. The laboratory-scale column exhibited efficiencies and pressure drops that were higher than those found in commercial-scale columns. Results predicted by a performance model derived from industrial-scale data were compared with the experimental data, and moderate agreement was noted. The model was then modified by regressing its parameters from the experimental data. Comparison of the results obtained from the revised model with the experimental data showed good agreement with at least 80% of the calculated data within ±20% of the experimental values. Equations for predicting the effect of the equivalent diameter of the packing on the efficiency and pressure drop in similar columns at equivalent conditions were determined from the performance model. The validity of this model, however, could not be determined conclusively. Methods for the scale-up of the laboratory results were investigated, but they could only be considered to be in a preliminary stage of development because performance data for the corresponding industrial-scale packing were not available for the test system studied in the present work.

F-87-16 PUBLISHED
Distillation
Fair, J. R.
This section includes comprehensive treatment of the subject in a 111-page chapter. The 1000-page book contains 22 chapters covering all important commercial separation processes.

F-88-3 PUBLISHED
Study of the Adsorption and Desorption of Multiple Adsorbates in a Fixed Bed
Huang, C.-C.; J. R. Fair
An experimental and theoretical study was made of the adsorption of ethane/propane mixtures from N2 or He. The study also covered the desorption of the mixtures using a purge of hot N2 or He. The adsorbent was Witco JXC activated carbon. A nonequilibrium, mechanistic model was developed and was shown to represent both adsorption and desorption processes. The model used mixture isotherm data predicted by the Flory Huggins form of the vacancy solution model. Both
adsorption and hot purge regeneration were found to be intraparticle rate controlled processes with surface diffusion dominating the intraparticle mass-transfer mechanism. The dynamic model can be used for the simulation of a variety of commercial adsorption and desorption conditions.

**F-88-4** PUBLISHED

**Hydrodynamics and Mass Transfer on Three-Phase Distillation Trays**
Herron, C. C.; B. K. Krueskie; J. R. Fair

Several oil-water mixtures were contacted by air in a sieve-tray distillation column simulator. The oil was mineral spirits with a 183°C-206°C boiling range and 51.8°API gravity. Two sieve-tray designs were used, and both hydraulic and mass-transfer measurements were made, the latter using acetone as the transferring solute. It was found that gas agitation caused the mixtures to behave as a homogeneous liquid that followed general correlations for pressure drop, liquid holdup, froth height, downcomer liquid level, and fractional entrainment. No unusual problems with foaming or entrainment were observed. Mass-transfer efficiency was influenced by oil-water ratio, with mild minima occurring at about 50 volume percent mixtures. It was concluded that when the immiscible liquids are both present in significant proportions, designers need not avoid formation of a second liquid phase for fear of unusual hydraulic or mass-transfer behavior.

**F-88-7** PUBLISHED

**Scale-Up of Laboratory Data for Distillation Columns Containing Corrugated Metal-Type Structured Packing**
Hufton, J. R.; J. L. Bravo; J. R. Fair

Laboratory-scale measurements were made of the mass-transfer efficiency of a gauze-type distillation column packing. The test mixture chlorobenzene/ethylbenzene was used, and several operating pressures in the range of 40- to 750-mm Hg were studied. It was found that the HETP data were correlated well by available models developed for commercial-scale structured packings. The final result of the work is a procedure that enables tests at 25-mm column diameter size to be used for predicting performance of a large-scale system using structured packing, gauze, or sheet metal.

**F-88-8** $20.00

**Liquid Film Transport Characteristics of Textured Metal Surfaces**
McGlamery, G. G.
PhD dissertation

The increasing popularity of corrugated structured packings for distillation and absorption columns has indicated the need for improved design procedures for their implementation. As a step toward answering this need, the transport characteristics of textured metal surfaces have been investigated. Eight stainless-steel textured surfaces were tested in a wetted-wall apparatus using five gas-liquid combinations under absorption conditions. The liquid-side mass-transfer efficiency kL, the wetted area, and the liquid-side mass-transfer coefficient kL were measured in these tests. The data from these experiments indicate that the greatest contribution to improved mass-transfer efficiency in structured packings results from roughness-induced turbulence in the liquid film. In the case of spreading liquids such as hydrocarbons, surface texture can also increase the wetted area of the packing surface. An additional factor, perforations in the textured surface, also increases the mass-transfer efficiency; however, the reason for this behavior is unclear.

A model developed from the experimental data provides reasonable estimates of the mass-transfer efficiency. The model uses an empirical correlation to predict the rivulet width and consequently the wetted area. Three separate correlations were developed to estimate the mass-transfer coefficient for varying degrees of roughness. The important physical properties used in the model are density, viscosity, interfacial tension, diffusion coefficient, and contact angle.
Air Stripping of Volatile Organics in Packed Columns: Experiments and Mathematical Modeling
Handler, N. E.

Master's thesis
The research described in this thesis focuses on the verification of mass-transfer correlations for air stripping in drinking water applications (i.e., the stripping of dilute solutions of volatile organic compounds (VOCs) using newly developed polypropylene packings). A pilot-scale packed column having a diameter of 167/8 inches and a packing height of 10 feet was operated over a wide range of superficial liquid and gas velocities (7.1-42.7 gpm/ft² and 53.3-1070 scfm/ft², respectively) using four polypropylene packings: 2-inch Pall™ Rings, Snowflake™, Cascade™ Mini-Rings 2A, and Nor-Pac™ 2. Trichloroethylene, tetrachloroethylene, and chloroform were studied individually and as a mixture at influent concentrations ranging from a few hundred mg/L to a few thousand mg/L. Influent and effluent water samples were obtained from the stripping column during experimentation and were analyzed using headspace analysis and gas chromatography. The data obtained were used to calculate experimental removal efficiencies and mass-transfer coefficients for the three compounds. The experimental values were then compared with values calculated using the Onda correlations. As secondary objectives, the effects of concentration and cosolutes on removal efficiency were also investigated and are described.

Distillation Columns Containing Structured Packing
Fair, J. R.; J. L. Bravo
Chemical Engineering Progress 86(1):19-29 (1990)
This paper provides a summary of the different capacity, pressure-drop, and mass-transfer efficiency estimation methods in use for structured packings in distillation service. A review of such methods and their limitations is provided with emphasis on methods developed by SRP researchers during the last few years.

Pressure Drop in High-Efficiency Structured Packings
Bravo, J. L.; J. R. Fair
Presented at the AIChE Spring National Meeting, Houston, Texas, April 1989
A detailed comparison of the Bravo-Rocha-Fair and the Stichlmair-Bravo-Fair models for pressure drop is presented in this paper. The Bravo model was developed specifically for structured packings of the corrugated-metal type whereas the Stichlmair model was developed for random and structured packings, and is more general. The latter also applies to the loading region. The models are compared against each other as well as the experimental data obtained in the SRP distillation test system for several structured packings. The Stichlmair model is also evaluated for its ability to predict the flood point for structured packings in distillation.

New Developments in Modeling Distillation and Other Separation Processes
Fair, J. R.
Presented at ASPENWORLD '88, Amsterdam, November 1988
This paper includes a progress report on modeling of distillation systems. The growing interest in alternate separation techniques and in systems where distillation is coupled with one or more of such alternatives is also discussed.

DISTILL: A KEE-Based Distillation Column Sequencing System
Barnicki, S. D.
Manuscript on file, Separations Research Program
DISTILL is a prototype version of a KEE-based distillation column sequencing system. DISTILL employs a set of five ordered heuristics to determine the optimum or near-optimum distillation train for a multicomponent mixture. There is no limit on the number of components in a mixture.
In its current implementation, DISTILL works only for sharp separations (i.e., complete separations) and for mixtures in which each component is a pure product. In relation to the SSAD, DISTILL represents a simplified version of the Liquid Split Manager.

F-90-2
Advanced Model-Based Control for Distillation
Riggs, J. B.; J. Watts; M. Beauford
Presented at the NPRA Computer Conference, Seattle, Washington, October 1990
Distillation-column composition control has long been recognized to be of major economic importance to the refining industry due to utility usage requirements, process throughput limitations, and the importance of product quality. The performance of conventional, proportional, integral, derivative, single-loop controllers suffers coupling between the ends of the column and is quite sensitive to controller tuning. As a result, distillation columns are operated with greater "give-away," resulting in high utility usage, low product recovery, reduced throughput, or greater variability in product. Nonlinear process model-based control uses a nonlinear approximate process model directly for control decisions and has been shown to provide substantial performance improvement over conventional control schemes by both column simulation and from industrial implementation experience. This paper outlines this advanced control approach and discusses the implementation procedure used and the results obtained for several industrial nonlinear process model-based control applications.

F-91-1 PUBLISHED
Distillation: King in Separations
Fair, J. R.
Several reasons for the popularity of distillation are discussed in some detail. Newer developments in distillation technology are also discussed.

F-91-7
Handouts for the Separations Research Program Spring Conference, April 1991
Copies of transparencies used by Martin, Patwardhan, Thongpakdi, and Bosley for the Distillation Study Group Meeting.

F-91-8 $10.00
Transfer of Gases to Liquid Films Flowing Over Enhanced Surfaces
Thongpakdi, D.
Master's thesis
This research is a continuation of work undertaken by G. McGlamery. The range of experimental conditions was extended and the enlarged data base was represented by a new correlation. The research encompassed a study of the effect of various metal surface enhancements on mass-transfer performance of a gaseous solute diffusing across a gas-liquid interface. The enhanced surfaces studied were those which can be applied to structured packings used in commercial gas-liquid contacting service. Combinations of eight textured surfaces made of stainless steel and five gas-liquid systems were tested in a special adsorption cell in which the liquid flowed vertically downward across the surface being tested. Volumetric liquid-film mass-transfer coefficients were measured in the tests. A general mass-transfer model for predicting volumetric liquid-film mass-transfer coefficient was developed for each individual textured surface. The model permits reasonable estimates of these coefficients, mostly within ±50% accuracy. The important parameters in the model are liquid mass flow rate, flow path length, liquid viscosity, liquid density, and diffusion coefficient.
A rigorous dynamic model based on fundamental material and energy balances, thermodynamic relationships, and mass-transfer expressions was formulated for a packed distillation test system separating cyclohexane and n-heptane at atmospheric pressure. The model contains six nonlinear partial differential equations and five nonlinear algebraic equations for the packing in addition to equations modeling the overhead accumulator, sump, total reboiler, and feed section. Dynamic model predictions compared well with experimental data obtained from step-tests conducted on the SRP large-scale packed distillation test system. An investigation into the influence of effective interfacial area on the operation and control of packed columns revealed that aggressive surface treatment of structured packings gives rise to input multiplicity and gain-sign changes. Packed columns were also found to exhibit output multiplicity and bifurcations. Steady-state stability conditions were developed, and model characteristics which led to output multiplicity and bifurcations were identified. An examination of the dependence of the dominant column time constant on operating conditions revealed that the holdup that undergoes the greatest composition change in response to a change in input governs the speed of response of the column. Nonlinear Model-Predictive Control (NMPC), a strategy for feedback control of constrained nonlinear processes, was developed. The algorithm can be used to control open-loop stable and unstable processes described by a wide variety of model equations, and addresses input, state, and output constraints in an explicit manner. The advantages of the algorithm were demonstrated by simulating the start-up of a continuously stirred tank reactor (CSTR) and control of a packed distillation column with infeasible set points. In each case, NMPC proved to be superior to traditional controllers and, in conjunction with a nonlinear model-based state/parameter estimation scheme, was used to control the packed column. When an infeasible set-point was specified as the control objective, NMPC took the process as close to the set-point as possible, in a least-squares sense, thus proving superior to linear control.
F-91-14
Metal Pall Rings in Distillation Service
Garcia, J. A.; C. L. Martin; J. R. Fair
Manuscript on file, Separations Research Program
The SRP has made studies of three nominal sizes of Pall Rings in the 16.88-inch distillation column. These packings were tested at three different pressures: 4.83, 24, and 60 psia. The standard SRP test system, cyclohexane/n-heptane, was used. Tests were performed at total reflux using an average packing height of 124.5 inches. The mass-transfer and pressure-drop experimental results were compared with results obtained earlier with a structured packing (FlexipacTM 2), and also with results predicted by available models.

F-91-15
How Surface Treatment and Geometry Affect the Performance of Structured Packings
Bravo, J. L.; J. A. Rocha; J. R. Fair
Presented at the AIChE Annual Meeting, Los Angeles, California, November 1991
The present work addresses one very important concerning the applications of structured packings. How is performance affected by surface enhancement and geometry? This is of interest especially because all structured-packing vendors offer essentially the same packing geometry (corrugated sheet) but vastly different surface treatments. The authors attempt to ascertain the importance of these treatments and how they influence performance.

F-91-16
Pressure-Drop Tests for 1.25-in. Jaeger Plastic Packing
Macias, Ricardo; J.R. Fair
Research Report
This report presents experimental pressure-drop data for a new high-efficiency plastic packing (nominal diameter = 1.25in) developed and manufactured by Jaeger Products, Inc. of Houston, Texas. Pressure-drop measurements were carried out in an 18.875-in. I.D. column made of fiberglass and packed to a depth of 6 ft. The test system was air-water flowing countercurrent through the packed section at ambient conditions.

F-92-1 PUBLISHED
Design of Baffle Tray Columns
Fair, J. R.
Hydrocarbon Processing 72(5):75-78, 80 (1993)
Baffle tray columns have about the same flooding capacity as crossflow trays, and according to dimensioning, can have lower pressure drops. Reasonable estimates of flood capacity and pressure drop can be made from correlations given in this paper. A lack of entrainment data for baffle tray columns suggests using a conservative design approach to flood. For estimating mass-transfer efficiency, an approach using heat transfer relationships is proposed. The approach has not been tested at the commercial scale but appears to give reasonable estimates of efficiency. For the approach to be refined, a considerable amount of plant testing will be required. This is particularly the case for conditions under which baffle tray contacting may be preferred.

F-92-3
Catalytic Distillation
Mejias, L.
Manuscript on file, Separations Research Program
This report is directed primarily to the application of catalytic distillation to the manufacture of methyl tert-butyl ether and related oxygenated compounds. It is based on a literature survey and represents an initial undertaking by the SRP in the more general area of reactive distillation.
F-92-4
Pressure Drop in an Operating High-Gravity Distillation Contactor
Dwivedi, V.
Manuscript on file, Separations Research Program
This study (completed by a University of Texas at Austin undergraduate) provides experimental pressure-drop and hydrodynamic findings on the SRP/Glitsch high-gravity distillation unit.

F-92-6
Distillation Contacting Devices: I. IMTP #40 Packing
Snyder, J.; J. A. García; A. F. Seibert; J. R. Fair
Manuscript on file, Separations Research Program
First in a series issued by the SRP, this paper reports mass-transfer, pressure-drop, and capacity characteristics of IMTP No. 40 random packing, which have been measured in the pilot-plant-scale distillation column of the SRP. The test system was cyclohexane/n-heptane at pressures of 4.83, 24, and 60 psia. The mass-transfer results are presented as HETP. The pressure-drop results are reported in inches of water per foot of packed height. Flooding conditions may be deduced from the pressure-drop and mass-transfer data.

F-92-7
Distillation Contacting Devices: II. CMR #2 Metal Packing
Martin, C. L.; J. A. García; A. F. Seibert; J. R. Fair
Manuscript on file, Separations Research Program
Second in the series, this paper reports mass-transfer, pressure-drop, and capacity characteristics of CMR No. 2 metal random packing.

F-92-8
Distillation Contacting Devices: III. Structured Packing-90° Corrugation
Martin, C. L.; J. A. García; A. F. Seibert; J. R. Fair
Manuscript on file, Separations Research Program
Third in the series, this paper reports mass-transfer, pressure-drop, and capacity characteristics of a special structured packing fabricated by Jaeger Products, Inc. This packing has the MAXPAK surface characteristics and arrangement plus the nominal 0.5-inch crimp height. However, the corrugation angle was 90° as contrasted with the usual 45° or 60°. Previous test data with the conventional 45°, 0.5-inch crimp height MAXPAK, presented earlier in an SRP report, were available for comparison.

F-92-9
Distillation Contacting Devices: IV. Metal Pall Rings -1, 1.5 and 2-inch Size
Martin, C. L.; J. A. García; A. F. Seibert; J. R. Fair
Manuscript on file, Separations Research Program
Fourth in the series, this paper reports mass-transfer, pressure-drop, and capacity characteristics of slotted Raschig rings.

F-92-10 PUBLISHED
Distillation
Fair, J. R.
This comprehensive article on distillation technology runs forty-five double-spaced pages plus thirty figures and two tables. All general aspects of distillation are covered.
Fair, J. R.; J. A. Rocha; J. L. Bravo
This paper replaces two earlier versions (B-90-5 and B-90-6). The first part of this paper deals with general equations that lead to improved methods for predicting liquid holdup, pressure drop, and flooding in columns containing structured packings. The second part provides an improved model for mass transfer that is consistent with the hydraulic parameters introduced in part one.

Improving Hydraulics and Efficiencies with the T-By Sieve Tray
Tedder, D. W.; J. L. Bravo; B. M. Parker; T. J. Parker
A modified sieve tray uses a system of weirs and risers to approximate liquid plug flow over a cross-flow, circular-section tray. Vapor-liquid contact is improved using a system of curtain-pattern vapor holes and intermediate weirs to form cells across the tray that promote liquid mixing into discrete, well-mixed pools, and stabilize froth. A theoretical model is used to analyze experimental data, guide tray design, and suggest new strategies for improving performance. These results indicate that tray efficiencies and stabilities can be increased without capacity losses. Pressure drop can also be manipulated to enhance performance.

Analysis of SRP Pressure-Drop Measurements
Rodriguez, J. N.; J. A. García
Manuscript on file, Separations Research Program
The SRP tests the performance of different contacting devices such as: trays, random and structured packings, and proprietary devices under distillation conditions. This report focuses on a suspected experimental pressure-drop error during evaluation of several structured packings.

RATE Program for Tray or Packed Column Rating or Design
Harvey, R. L.; R. Macías
Manuscript on file, Separations Research Program
RATE is a computer program that can be used to rate or design columns used in distillation, absorption, or stripping service. It can be used for sieve tray or packed columns, and for the latter the user has a choice of a large number of packing types and sizes. The program is available to SRP sponsors as a 5-1/4 inch diskette usable on IBM-type operating systems. While the program does not have a direct optimizing capability, it has a convenient scheme for changing dimensional or flow input variables, and alternate designs can be accommodated quickly. A user's guide accompanies the diskette. The program was written by Ricardo Macías and the guide was written by Roger Harvey.

Distillation Contacting Devices: V. Subcooled Reflux Studies on Structured Packing
García, J. A.; A. F. Seibert; J. R. Fair
Manuscript on file, Separations Research Program
Subcooled reflux studies were performed in the pilot-plant scale distillation of the SRP. These tests were carried out on a No. 2 structured packing; mass transfer, pressure-drop, and capacity data were taken with the degree of subcooling being controlled. The test system was cyclohexane/n-heptane at a pressure of 60 psia. At this pressure the extent of subcooling was the maximum achievable. The mass-transfer results are presented as HETP, but tabulated data are included on height of a transfer unit (HTU). The pressure-drop results are reported in inches of
water per foot of packed height. Flooding conditions may be deduced from the pressure-drop and mass-transfer data.

**F-93-6**

*Distillation Contacting Devices: VI. Sulzer-BXTM Structured Gauze Packing*

Garcia, J. A.; A. F. Seibert; J. R. Fair

Manuscript on file, Separations Research Program

Mass-transfer, pressure-drop, and capacity characteristics of Sulzer-BXTM structured gauze packing were performed in the pilot-plant scale distillation system of the SRP. The test system was cyclohexane/n-heptane at pressures of 4.83, 24, and 60 psia. The mass-transfer results are presented as HETP, but tabulated data are included on HTU. The pressure-drop results are reported in inches of water per foot of packed height. Flooding conditions may be deduced from the pressure-drop and mass-transfer data.

**F-93-7**

*Mass-Transfer and Hydraulic Operating Characteristics of a Pilot-Plant Scale High-Gravity Contacting Unit*

Kelleher, T. C.

Master's thesis

The high-gravity contacting unit, termed Higee for "high gravity," was used to obtain mass-transfer characteristics for distillation service, the first such data to be reported. Flooding characteristics were examined using the Sherwood correlation, which appears to hold for the Sumitomo CelmetTM packing (specific surface area = 2500 m2/m3) in this Higee unit. Volumetric mass-transfer coefficients were determined for cyclohexane/n-heptane at 24 and 60 psia by varying the reboiler duty and rotational speed at total reflux. Three rotational speeds up to 1200 rpm (326g) were used. Modeling of mass transfer in the Higee allowed determination of the ATU (area of a transfer unit). A correlation for gas-phase mass-transfer coefficients in the Higee is presented which predicted the ATU data within 30% when used in conjunction with the liquid-phase model of Singh.

**F-93-8**  **PUBLISHED**

*Reboilers*

Fair, J. R.


In this article, the methodology for analyzing or designing distillation column reboilers has been presented; in connection with material in the cited literature, one should have sufficient material for confident design or troubleshooting of reboilers with in-tube vertical boiling. As might be inferred from the article, emphasis by researchers and mathematical modelers has been on the vertical thermosiphon; in which there is an interesting integration of flow, geometry, and physical property variables. Related reboiler types embody once-through natural circulation and vertical forced convection arrangements. Research in recent years has improved the modeling status of the kettle reboiler, which has been found to function internally as a thermosiphon unit. Of the three most common reboiler types, the horizontal thermosiphon appears to be lagging in design technology; for this type few performance data have been published. Methods for the analysis and design of distillation column reboilers have been emphasized here but the reader must be reminded that the same methods can be used for other process vaporization tasks. This is particularly the case for refrigerant evaporators.

Replaces F-93-1

**F-93-9**

*Distillation Contacting Devices: VI. Sulzer BX Structure Gauze Packing*

Fair, J.R.; J.A. Garcia; A.F. Seibert

Mass transfer, pressure drop and capacity characteristics of Sulzer-BX structured gauze packing were performed in the pilot-plant scale distillation system of the Separations Research Program (SRP) at the University of Texas at Austin. The test system was cyclohexane/n-heptane at...
pressures of 4.83, 24 and 60 psia. The mass transfer results are presented as height equivalent to a theoretical plate (HETP), but tabulated data are included on height of a transfer unit (HTU). The pressure drop results are reported in inches of water per foot of packed height. Flooding conditions may be deduced from the pressure drop and mass transfer data.

Direct-Contact Heat Transfer in Structured Packings
Ayala, L. B.
Master's thesis

Direct-contact heat transfer for air-water systems was studied in a 16.8-inch-diameter column containing packing elements. Two modes of operation were used: humidification (cooling tower system) and dehumidification (cooler condenser system) of the air. The packings used were Sulzer-BX™, a gauze-type structured material; Intalox™ 1T, a sheet metal type structured material; Flexipac™ 2, another sheet metal packing; and 1.0-inch and 1.5-inch metal Pall rings, two random packings. These materials were chosen for their variations in surface area, surface treatment, expected type of interfacial area generation, and capacity. A primary objective of the work was to ascertain whether heat-transfer/mass-transfer analogies might apply for this method of contacting. Experimental values of the gas-phase mass-transfer coefficients were determined from the rate of evaporation. Mass-transfer coefficients for the liquid and gas phases were then predicted by a simulation program which uses previously tested predictive models for structured and random packings. It was found that the model predicted higher values of the gas-phase coefficient for both the random and structured packings. The Chilton-Colburn heat-transfer analogy was used to determine the individual-phase heat-transfer coefficients. Values of these coefficients were then combined to provide the overall volumetric heat-transfer coefficients. Comparing the values of $U_a$ from the analogy with those based on the sensible heating duty, it was found that the latter were within the same range or larger than the $U_a$ based on the Chilton-Colburn analogy. The effects of gas and liquid flow rate on the transfer coefficient were also studied. A comparison of the coefficients for the packings used indicated that at a given gas and liquid flow rate, the efficiency of the packing for mass transfer is a function of the specific surface area. In general, the packings with greater surface area generated larger values of mass-and heat-transfer coefficients. The coefficients were also found to be more sensitive to the gas flow rate than to the liquid flow rate; the dependency on the flow rates is presented in correlation form.

Modeling of a Reactive Distillation Column to Produce Tert-Amyl Methyl Ether
Mejias, L. J.
Master's thesis

A reactive distillation column for the synthesis of tert-amyl methyl ether (TAME) has been modeled using a steady-state equilibrium-stage model, RADFRAC, from the flowsheet simulator, ASPEN PLUS, the first such simulation to be reported in the open literature. The column was studied under the equilibrium operation mode. An equation to determine the equilibrium composition of the liquid phase was developed. Activity coefficients for this significantly nonideal system were represented by the UNIQUAC equation; the vapor phase fugacity coefficients were calculated using the Redlich-Kwong Equation State. Adjustable parameters for the UNIQUAC equation, binary interaction parameters, were fitted on published binary system vapor liquid equilibrium data for some of the binary pairs forming azeotropes. The data regression system of ASPEN PLUS™, based upon the maximum likelihood principle was used to estimate adjustable parameters. A parametric study with the main variables involved in this process was performed. Those variables were: amount of methanol, reflux ratio, methanol feed point, boil-up-ratio, feed rate, feed concentration, and pressure. Two different options were studied, one including a prereactor and the other one without a prereactor. The amount of methanol has been found to be the most critical variable for this process, and determines the level of conversion and separation of the reactants and products. The larger conversion and TAME composition were obtained with the option including a prereactor. High vapor rates in the bottom of the column were found as a necessary condition to keep the optimum methanol profile along the column. Such a profile is
necessary to assure a TAME product free of methanol as well as a high level of methanol in the reaction zone.

**F-94-4**

**Distillation Contacting Devices: VII. Mass-Transfer and Capacity Tests on Single and Double Beds; of No. 2 Structured Packing in Distillation Service**

Garcia, J. A.; A. F. Seibert; J. R. Fair

Manuscript on file, Separations Research Program

The Separations Research Program's distillation column was operated with bed heights of approximately 20 feet in two configurations: a single bed without any discontinuities and a double bed with intermediate collection and redistribution of the downflowing liquid. For both top and intermediate liquid distribution, the same device (Type 3C, perforated pipe) was used. The inside column wall contained special inserts at the openings to ensure that no unusual wall effects were created. The packing was a No. 2 structured packing. The system was cyclohexane/n-heptane, and the operation was at total reflux. The results are shown on the accompanying graphs. At 4.83 psia, the height equivalent to a theoretical plate (HETP) values for the single bed were 3 to 5 inches higher than those for the two beds. At 24 psia the difference was as high as 6 inches at low loadings, converging to essentially no difference at the highest practicable loading. At 60 psia the difference in HETP values declined as loading increased. As expected, there was a little difference in pressure drop between the two configurations, although at 60 psia the high vapor rate indicated an effect of pressure drop through the collector/distributor for the two-bed system. The distributors have been shown in the past to provide an excellent coverage of the column cross section. These devices provide about 40 pour points per square foot of area. It would appear that this initial distribution deteriorates as bed depth increases, perhaps converging on an "intrinsic" or "natural" distribution that depends on the packing type and size, and on the vapor-liquid traffic conditions. For most commercial installations, a height of 20 to 30 feet is the allowable maximum between redistributions. On the other hand, the height of packing for most SRP tests is in the 10 to 12 foot range; if data are to be used for deeper beds it would appear prudent to allow for some maldistribution.

**F-94-5**

**FleximaxTM 300 Metal Random Packing**

Garcia, J. A.; A. F. Seibert; J. R. Fair

Manuscript on file, Separations Research Program

Mass-transfer, pressure-drop, and capacity characteristics of the FleximaxTM random packing were performed in the SRP pilot-plant scale distillation system. The test system was cyclohexane/n-heptane at pressures of 4.83, 24, and 60 psia. The mass-transfer results are presented as HETP. The pressure-drop results are reported in inches of water per foot of packed height. Flooding conditions may be deduced from the pressure-drop and mass-transfer data.

**F-94-9**

**SRP Six-Inch Distillation Column**

Rocha, J. A.

Manuscript on file, Separations Research Program

When the distillation-extraction facility was installed at the Balcones Research Center, a small-scale distillation system was included. This system was designed to be corrosion resistant and was considered useful for specialty distillations requiring the stainless-steel material as well as for scale-up studies of various contacting devices. The system was equipped with three interchangeable columns of 2-inch, 4-inch, and 6-inch internal diameters. The system included integral condenser and reboiler, and was designed to operate at total reflux only. Its controls were connected with the Fischer-Porter System so that it could be operated from panels in the control room. A flow diagram of the system is shown in Figure 1. This distillation system has seldom been used for Separations Research Program (SRP) needs. In one case it was used with ceramic packing to study the acetic acid-water system. In another case it was used with structured packing to study steam stripping of organics. Despite its attractiveness for specialty testing, it had not been calibrated against the standard SRP test mixture, cyclohexane/n-heptane. The objective of this
study was to put the equipment in running order and to make a series of experiments on the standard test mixture, operating at a pressure of 24 psia. The 6.0-inch i.d. column would be filled with a gauze-type structured packing (Sulzer TM BX) which was on hand. Direct comparisons could be made with test data for the same packing, and same system, taken in the 16.875-inch column.

**F-94-10**

**A New Model for Predicting Mass Transfer in Distillation Columns Containing Random Packings**

Wagner, I.; J. R. Fair

Manuscript on file, Separations Research Program

A new model has been developed for the prediction and correlation of mass transfer rates in distillation columns containing random packings. The large bank of experimental data is drawn from SRP studies as well as those at Fractionation Research and other laboratories. Of importance is the inclusion of some of the newer "high efficiency" random packings: IMTP, CMR, Fleximax, and Nutter. The model is built upon the earlier SRP study of liquid holdup and gas pressure drop in beds of random or structured packing [Stichlmair et al., Gas Sep. Purif. 3(19) (1989)]. The only packing parameter needed is a "packing characteristic" which has a value of about 0.030 for 2-inch metal Pall and Raschig rings, and about 0.050 for the newer packings of 2-inch normal size. The model was found to fit 95% of the 326 data bank HETP values to within +/-25%, and all values within +/-30%.

**F-95-1**

**Mechanistic Modeling of Sieve Tray Efficiency**

Garcia, J. A.; J. R. Fair

Presented at the AIChE Spring National Meeting, Houston, Texas, March 1995

The mass transfer model of Prado (Prado, 1986; Prado and Fair, 1990) represented a first attempt to interpret distillation sieve tray efficiency in terms of realistic vapor-liquid contacting mechanisms and transfer coefficients. It was validated only for the oxygen/air/water and water vapor/air/water systems. That effort has now been extended to cover non-aqueous distillation systems, utilizing new efficiency measurements made at the Separations Research Program as well as at other laboratories. This paper represents a detailed progress report on this continuing search for a reliable means for predicting the mass transfer efficiency of sieve tray distillation columns. Point efficiency measurements were obtained in a semi-industrial scale distillation column with sieve trays using the cyclohexane/n-hexane test mixture at operating pressures of 33.3, 165.5, and 413.7 kPa (4.83, 24, and 60 psia). The column inside-diameter was 0.4286 m (16.875 in.) and sieve trays with 10% free area and 4.7625 mm (3/16 in.) diameter holes were used. A special splash baffle was used on each tray to ensure complete mixing of the liquid as well as to prevent liquid short-circuiting by direct throw over the outlet weir. Other tray details are given in the main text of the paper.

**F-95-2**

**Mass Transfer in Beds of Modern, High-Efficiency Random Packings**

Wagner, I.; J. R. Fair

Presented at the AIChE Spring National Meeting, Houston, Texas, March 1995

Prediction of the mass transfer efficiency of distillation columns containing random packings has long been considered a risky endeavor, primarily because of a lack of understanding of the complex two-phase flow that prevails in such packings. While reasonable mass transfer models have evolved for the older, bluff-body packings, such as Raschig rings and Berl saddles, the advent of newer, through-flow type metal random packings has left the existing models wanting. For one thing, there has been an insufficient amount of commercial-scale efficiency data published for these newer packings, at least enough data for preparing generalized models. For another, there is the problem of a different kind of surface generation in the newer packings, certainly a departure from the traditionally assumed liquid-film-flow and vapor-channel-flow approaches. The work described here has resulted from further investigations of the character of flow through the newer packings, particularly the work reported by Stichlmair et al. in 1989. In addition, a large amount of commercially important experimental data has become available in recent years,
especially from the Separations Research Program at The University of Texas at Austin and from Fractionation Research, Inc. These sources coupled with pertinent previously published information, provide a data bank of 326 experimental efficiency points. This bank comprises the basis for evaluating the model to be described below. The objective of the work was to develop a theoretical model taking into account the effect of irrigated pressure drop and liquid holdup on mass transfer.

**F-95-3 REPLACED BY E-95-2**

**F-95-6 PUBLISHED**

**Distillation**
Fair, J. R.

Distillation is the most widely used industrial method of separating liquid mixtures and is at the heart of the separation processes in many chemical and petroleum plants. This article presents an overview of the method; it is a reprinted chapter from a four volume set.

**F-95-7 $20.00**

**RATESTRIP Program for Designing Tray or Packed Columns for Stripping & Absorption**
Macías-Salinas, R.; R. L. Harvey
Manuscript on file, Separations Research Program

RATESTRIP is a computer program developed at the Separations Research Program (SRP), the function of which is to allow engineers to evaluate designs quickly and efficiently for absorption and stripping columns. The program is able to perform all necessary calculations for column design using sieve trays or packing.

**F-95-8**

**An Evaluation of the Onda Correlations for Mass Transfer with Large Random Packings**
Dvorak, B. I.; D. F. Lawler; J. R. Fair; N. E. Handle
Submitted to Environmental Science and Technology

Although large (>5 cm) polypropylene packings are frequently used in air stripping towers for environmental applications, few fundamental studies of the mass transfer on these large packing designs have been performed. For small packings, previous research has verified that the Onda correlations are valid for environmental applications. In this research, experimental data for air stripping were obtained using a pilot-scale stripping tower, three test compounds, and four polypropylene packings. Results showed that, in general, Onda is a good predictor of mass transfer for large random packings. However, Onda tended to underpredict mass transfer, with 90% of the data falling between a 16.5% over-prediction and 34.0% under-production of the observed mass transfer. The underpredictions tended to occur at high gas flow rates, and when the gas-film resistance predicted by Onda is large. Further analysis revealed that the functionality of the volumetric gas loading rate is incorrect in the Onda correlations.

**F-95-9 $15.00**

**Gas- and Liquid-Phase Axial Dispersion through Random and Structured Packings**
Macías-Salinas, R.

An experimental study of the extent of axial dispersion in both gas and liquid phases was conducted in a 0.43-m I.D. column packed with 25.4-mm ceramic Raschig rings, 25.4-mm metal Palls(r) rings, Sulzer(r) BX and Flexipac(r) 2. The column was operated at atmospheric pressure with air and water flowing counter-currently through the packing under trickle-flow conditions. The gas and liquid flowrates were varied from 0.25 to 4.312 kg/m2-s and from 3.25 to 8.5 kg/m2-s, respectively. The amount of axial dispersion was experimentally evaluated by means of residence time distribution (RTD) experiments using helium in the gas phase and an aqueous solution of NaCl in the liquid phase as inert tracers. An imperfect pulse of tracer was first injected into the inlet stream. The response of the tracer was then monitored at two different points along
the bed by means of thermal conductivity in the gas phase and electrical conductance in the liquid phase. The experimentally determined RTD curves were interpreted in terms of the diffusion type-model which proved to be a suitable means of describing axial dispersion in both phases. The model parameters (dispersion coefficient or Bodenstein number and mean residence time) were best determined by the time domain analysis of the response curves. The results indicated that the extent of axial dispersion was much greater in the liquid phase than the gas phase owing to the longer tails exhibited by the liquid-phase RTD curves. It was also found that axial dispersion in the gas phase increased with both gas and liquid flowrates whereas liquid-phase axial dispersion was a decreasing function of liquid rate and insensitive to gas flowrate up to the flooding point. Among the four packings, Sulzer(r) BX consistently produced the lowest mixing results in both phases. On the other hand, the largest deviations from plug flow in the gas and liquid phases were exhibited by 25.4-mm ceramic Raschig rings and Flexipac(r) 2, respectively. Various correlations were developed for reproducing the experimental mixing data obtained under one- and two-phase flow conditions. The major correlating variables were gas and liquid flowrates, packing size, surface area and inclination angle of the flow channels (structured packings). The agreement between experimental and correlated data appeared to be acceptable and within +20% of difference in most cases. An iterative procedure was proposed to correct the apparent number of transfer units due to axial dispersion. The procedure was applied to literature data for the case of gas absorption, stripping and water cooling using the present dispersion correlations. The results revealed that there was only a small detrimental effect of axial dispersion on the column performance within the range of operating conditions reported. A distillation system under high pressure conditions was also considered for correction purposes. The application of the present procedure predicted a large effect of axial dispersion on the column efficiency. This finding, however, requires further experimental verification either to support or invalidate the use of dispersion correlations based on air-water properties in the present correction procedure. Indicate on order, if 100 pp. Appendix should be included

F-95-10  PUBLISHED
Distillation: Still Towering over Other Options
Kunesh, J. G.; H. Z. Kister; M. J. Lockett; J. R. Fair
Chemical Engineering Progress 91(10):43-54 (1995)
Distillation dominates separations in the chemical process industries (CPI), at least for mixtures that normally are processed as liquids. We fully expect that distillation will continue to be the method of choice for many separations, and the method against which other options must be compared. So, in this article, we will put into some perspective just why distillation continues to reign as the king of separations, and what steps are being taken to improve its applicability and performance, as well as our basic understanding of the technique.

F-96-2
Entrainment - Efficiency Effects on Distillation Sieve Trays
Fair, J. R.
Presented at the AIChE Annual Meeting, Chicago, Illinois, November 15, 1996
The object of this paper is to convey a rational approach to the assessment of the level of entrainment and its effect on mass transfer efficiency. Its scope will be limited to sieve trays, although comparative data for valve trays will be discussed.

F-96-3
J. A. Rocha; Bravo, J. L.; Fair, J. R.
This is the second part of a two-part paper dealing with the fluid mechanics and mass transfer in structured packings for distillation column service. The first part elucidated pressure drop, flooding, and liquid holdup. The second part covers the generation of effective interfacial area and provides a general correlation for predicting the mass-transfer efficiency as a function of surface type, packing geometry, phase flow conditions, and fluid properties. The mass-transfer
model has been tested against a variety of commercial structured packings, for distillation pressures ranging from 0.33 to 20.4 bar. In all cases the fit of the data is excellent, with the possible exception of the highest pressures, where additional factors of axial mixing appear to have an effect.

F-96-4
Understand Distillation-Column Debottlenecking Options
Fair, J. R.; Seibert, A. F.
In this article, we explore the options for debottlenecking columns. The methodology is supported by research studies made in our laboratories. Because many, many situations simply do not fit any formula and are leveraged by local factors such as geography, marketing economics, and future plans, our approach necessarily is rather simplistic. It can be used to assess alternatives rather than as a basis for firm recommendations. Finally, the usual caveat must be invoked: Those in the position of selling and installing distillation devices are better prepared than we are to deal with the cost aspects of debottlenecking.

F-96-5
Entrainment - Efficiency Effects on Distillation Sieve Trays
Fair, J. R.
Presented at the AIChE Annual Meeting, Chicago, Illinois, November 15, 1996
The objective of the paper is to convey a rational approach to the assessment of entrainment level and its effect on mass transfer efficiency. Its scope will be limited to sieve trays, although comparative data for valve trays will be discussed.

F-96-6
Contacting Mechanisms on a Cocurrent Flow Tray
Fair, J. R.; A. F. Seibert
Presented at the AIChE Annual Meeting, San Francisco, California, November, 1994
Two series of tests of the cocurrent tray have been conducted at the larger-scale facilities of the Separations Research Program at the University of Texas at Austin, each series with a different design geometry. The tests were carried out under distillation conditions using the cyclohexane/n-heptane test mixture at four pressures. Since similar studies have been made of other devices, using the same test mixture and equipment, a ready means of comparison is available. The purposes of this paper are twofold: to present representation efficiency results for the cocurrent tray, and to present the results of mechanistic modeling of the mass transfer and hydraulic phenomena that occur on the tray.

F-96-7
Debottlenecking Distillation Columns D Technical and Economic Considerations
Fair, J. R.; A. F. Seibert
Presented at the AIChE Annual Meeting, Miami Beach, Florida, November 13, 1995
The purpose of this paper is to describe possible methodology and economic support for debottlenecking studies. This is a rather daring approach, since there are many, many situations which simply do not fit any formula and which are leveraged by local factors such as geography, marketing economics, and future plans. Thus, a rather simplistic approach will be used, which is more suggestive of alternate action than a basis for firm recommendations. The methodology will have some support in research studies made in our laboratories, and some of the data presented have not been published previously. Finally, the usual caveat must be invoked. Those in the position of selling and installing distillation devices are better prepared than we are to deal with the cost aspects of debottlenecking.
A New Ultracapacity Tray for Distillation Columns
Fair, J. R.; A. F. Seibert

Debottlenecking distillation columns is an activity that has the promise of large capital savings but in the usual sense has some severe limitations. A recent paper on the subject suggests that currently available replacement devices, suitable for retrofitting and for the purpose of increasing throughput capacity without loss of separating capability, offer capacity increases of the order of 25-30% when compared with modern designs of sieve trays or packings (Fair and Seibert, 1996). In this paper we will describe operating characteristics and performance results for a new device - the cocurrent tray. Also included in the paper will be details of a model which can be used to predict the efficiency of the device.

Mass Transfer in Beds of Modern High-Efficiency Random Packings
Wagner, I.; J. Stichlmair; J. R. Fair

The work described here has resulted from further investigations of the character of flow through the newer packings, particularly the work reported by Stichlmair et al. in 1989. In addition, a large amount of commercially important experimental data have become available in recent years, especially those from the Separations Research Program at The University of Texas at Austin, (SRP) and from Fractionation Research, Inc. (FRI). With these sources coupled with pertinent previously published information, a data bank of 326 experimental efficiency points has been assembled. This bank comprises the basis for evaluating the model to be described. The objective of the work was to develop a theoretical model taking into account the effect of irrigated pressure drop and liquid holdup on mass transfer.

Hydraulic Tests and Performance Evaluation of a Cocurrent Tray for Distillation
Brugger, M.

Diploma Thesis
The purpose of this work was to determine the performance of the cocurrent tray with regard to the hydraulic tests. For that determination, the achieved data was compared with a former hydraulic study of the cocurrent tray and with other distillation equipment. To predict the pressure drop for the cocurrent tray, a correlation was developed.

Pressure Drop in Structured Packing
Verschoof, Huib-Jan
Research Thesis

Four models to predict the pressure drop in structured packing have been thoroughly analyzed and validated against experimental pressure drop data for various sizes of Montz B1 and BSH packing. None of the investigated models was able to fit the experimental pressure drop data satisfactorily. An examination of the two-phase flow through he structured packing resulted in the proposal of a mechanism for the loading of the packing. This mechanism has been used together with a large databank covering a wide range of packings and systems in building a new generalized model, based on the dry pressure drop prediction of the Rocha, Bravo and Fair model, for the prediction of loading points and pressure drop in distillation columns containing structured packing over the entire operating range. The developed equations do not contain any packing or system specific constants that have to be determined experimentally. Physical properties of both phases, geometric properties of the packing, and the vapor and liquid load of the packing determine the hydraulic behavior of a packing operating on a system.
Sorpptive Removal / Recovery of Organics from Air
James R. Fair; A. Frank Seibert
Manuscript on file, Separations Research Program

The class of chemicals popularly known as volatile organic compounds (VOCs) represent for the most part contaminating materials often found in discharge water and air from manufacturing operations. In many cases these organics are used in the operations as solvents, the volatility of which gives rise to their presence in emissions from the manufacturing facility. In this paper we are concerned with the removal of such VOCs from discharge air and the economics of selecting a separation method for removal as well as possible recovery for recycle to the manufacturing operations. Two frequently-practiced methods for removing VOCs are scrubbing and adsorption, and they embody the potential for recovering the VOCs for re-use. In this study we made process and economic comparisons of these methods, and chose the following candidate VOCs: acetone (completely miscible with water), ethyl acetate (partially miscible with water), and toluene (immiscible with water). All three of these chemicals are well-known contaminants of air streams. Further, their equilibrium and kinetic (breakthrough) characteristics have been studied in our adsorption laboratories. Flow diagrams for the methods are given. Two air feed rates were used: 10,000 cfm and 50,000 cfm. Loadings of the VOC's were taken as 1.0 and 0.1 mole-% (10,000 and 1,000 ppmv). The VOC's were recovered at 98+ wt-% purity. Complete details of the designs and economic evaluations are included in the paper. The results show the following: At both flow rates and at low concentrations, and for all three organics, adsorption requires 40 to 80% of the capital investment needed for scrubbing. The equivalent direct and indirect operating costs for adsorption were 15 to 67% of those for scrubbing. At the higher concentrations, the valued of the recovered organics was more than the direct and indirect operating costs, and thus providing an economic advantage. At higher concentrations, adsorption is usually the winner, but this depends on the scrubbing solvent used, and whether water is introduced to the system. For example, toluene scrubbing with an organic solvent is cheaper than toluene adsorption on activated carbon, if steam is to be used for the carbon regeneration step.

Hydration of Isoamylenes in a Catalytic Distillation Column
Jose Castor Gonzalez Cortez, Ph. D
Ph.D. Dissertation
Manuscript on file, Separations Research Program

Tertiary amyl alcohol (TAA) is prepared by the liquid-phase reaction of isomylenes and water on a solid-acid catalyst. The exothermic reaction is limited by chemical equilibrium to an isamylenes conversion of less than 50%, even using a large excess of water. Reactive distillation has been identified as an alternative to obtain conversions that approach 100%. The objective of this research was to configure a reactive column capable of achieving high conversions to alcohol and then demonstrate it experimentally in a bench scale column. The first step was to develop a kinetic expression for the reaction. Acetone was identified as a convenient solvent, since it prevents liquid-phase splitting and enhances the rate of TAA formation. The reaction rate was measured and then modeled using an expression based on the Langmuir-Hinshelwood formalism, which accounts for the strong inhibiting effect of water. Chemical equilibrium and intraparticle mass transport were also evaluated. A bale-type packing, loaded with acid resin, was the device used to promote distillation and reaction in the column. An experimental evaluation revealed that its hydraulic capacity is 30% lower than that of a regular structured packing, while its vapor-liquid mass transfer efficiency is 2-3 times less. The catalytic column was simulated using a model based on vapor-liquid equilibrium stages. The model included the kinetic expression developed in this work. The column configuration and conditions that lead to high yields of alcohol were identified with the model. For an isoamylenes stream free of inert volatiles, the distillate stream from the catalytic column must be suppressed to prevent the early exit of unreacted olefins. This catalytic distillation scheme was demonstrated using a column of 5 cm diameter. At steady state, the TAA yield approached 100%, but small amounts of a by-product (mesityl oxide) were observed. This material is formed by the condensation of two molecules of acetone on the acid catalyst, and represents a loss of 0.6% of the solvent. This work demonstrates the efficiency of the
catalytic distillation concept and provides an important extension to difficult reactions, where the reactants are mutually insoluble and the equilibrium conversion is severely limited.

F-97-3  $20.00
Modeling, Simulation and Design of Reactive Distillation Columns.
Hoshang Eruch Subawalla, Ph.D.
Ph.D. Dissertation
Manuscript on file, Separations Research Program
Reactive distillation is a unit operation that combines reaction, using either liquid or solid catalyst, and separation in a single piece of equipment. This process is particularly useful for enhancing conversions of equilibrium-limited reactions. A comprehensive modeling study of mass transfer phenomena in solid-catalyzed reactive distillation processes is documented here. Transport resistance at the vapor-liquid, liquid-solid and within the catalyst pellet, were examined in detail using multicomponent reaction-diffusion and packing hydraulic models within a rate-based modeling framework. The multicomponent reaction-diffusion model examines intrapellet catalyst resistance and calculates an effectiveness factor that is used to modify intrinsic reaction rates calculated from bulk liquid compositions and temperatures. It uses the Generalized Maxwell-Stefan equations to determine molar flux. Model results were validated with experimental data from two systems, methyl tert-butyl ether (MTBE) and tert-amyl alcohol (TAA). Results from a parametric study were used to develop design heuristics for reactive zone location and operation. The packing hydraulic model which accounts for liquid flow in the form of rivulets, films and drops, determines liquid holdup, pressure drop, mass transfer coefficients and interfacial area for different packing. Two commercial geometries, that of bale packing and catalytic structured packing, were studied. Bale and structured packing results were validated with pilot-scale and commercial data from two binary non-reactive systems (cycloexane/n-heptane and acetone/MEK). A scale-up procedure based on wall effects was developed to calculate capacity and efficiency in large columns. A rate-based model was used to simulate a pilot-scale reactive column, and results validated with experimental data for the TAA system. Results from two design studies were used to develop heuristics for design and operation of reactive columns. Reactive distillation processes with and without a pre-reactor were compared. The results from a comparison between reactive distillation and conventional reactor-column processes highlight advantages and disadvantages of each process. This dissertation demonstrates the use of a rate-based model for reactive column design, and includes three unique features: a detailed discussion of reactive column devices and hydraulics, and examination of intrapellet and interpellet diffusion resistance for distillation conditions, and development of heuristics for design and operation of solid-catalyzed reactive distillation columns.

F-97-4  PUBLISHED
Preparation of Tertiary Amyl Alcohol in a Reactive Distillation Column. 1. Reaction Kinetics, Chemical Equilibrium and Mass Transfer Issues
Gonzalez, J. C.; J. R. Fair
The hydration of isoamylenes to produce 2-methyl-2-butanol (tert-amyl alcohol, or TAA) is strongly limited by chemical equilibrium to olefin conversions of less than 50%. The general goal of this work was to determine whether reactive distillation would be a valid method to enhance the yield of TAA. The first step was to study the reaction kinetics and chemical equilibrium, using a polymeric acid catalyst (Amberlyst-15). Acetone was identified as a suitable medium to enable single liquid phase operation and also to enhance the reaction rate. It was found that the antiparticle mass-transfer resistance is negligible at temperatures below 70°C. A kinetic expression, based on Langmuir-Hinshelwood formalism, is proposed. The forward and reverse reactions show first-order dependence on isoamylenes and TAA, respectively, while water is essentially an inhibitor of the reaction in both directions. The temperature effect on the forward reaction is quantified with an activation energy of 69.5 kJ/mol.
Preparation of tert-amyl Alcohol in a Reactive Distillation Column. 2. Experimental Demonstration and Simulation of Column Characteristics

Gonzalez, J. C.; H. Subawalla; J. R. Fair

Reactive Distillation has been proposed as a means of enhancing the conversion for reactions whose progress is limited by chemical equilibrium. In the present work, reactive distillation tests were carried out for the hydration of isoamylene (2-methyl-2-butene) to 2-methyl-2-butanol (tert-amyl alcohol or TAA) in a 5.3-cm column using a bale-type catalytic packing. Acetone was used as a solvent to avoid formation of a second liquid phase and also to enhance the rate of reaction. The experimental results showed TAA yields approaching 100% when the distillate stream from the top of the column was essentially suppressed. This yield is more than double that possible thermodynamically in a separate reactor. It was also found that an excess of catalytic packing can generate operational problems. The column was simulated using an equilibrium stage model together with the kinetic expression developed for this reaction and reported in Part 1 of this paper. The simulation and the experimental results matched reasonably well. Model results indicate that the TAA yield can be greater than 95% (at a pressure of 240 kPa) when the weight hour space velocity is lower than 30 kg/(h* kg). A parametric study elucidated the effect of varying feed composition and key operating variables.

Capacity and Efficiency of Reactive Distillation of Bale Packing: Modeling and Experimental Validation

Subawalla, H. J.; C. Gonzalez; A. F. Siebert; J. R. Fair

The geometry of catalyst-containing bale packing is characterized in this paper. The calculated packing parameters (specific surface area and void fraction) are employed in conjunction with a model to predict two-phase pressure drop, maximum capacity, and height equivalent to a theoretical plate (HETP). Experimental data obtained in a 5.3-cm (2.1-in.) column, operated at total reflux, are presented for two systems (cyclohexane/n-heptane and acetone/methyl ethyl ketone) at pressures of 138 and 241 kPa (20 and 35 psia). Model predictions for pressure drop and HETP are validated with experimental data obtained under nonreactive conditions. An appropriate procedure for scaleup of HETP and pressure drop, with associated limitations, is also discussed.

A General Correlation for Predicting the Loading Point of Corrugated Sheet Structured Packings

Verschoof, H. J.; Olujic, Z.; Fair, J.R.
Presented at the AIChE Annual Meeting, Los Angeles, California, November 1997

Comprehensive experimental studies have been carried out with Montz structured packings at Delft University (air-water system) and the SRP (cyclohexane/n-heptane system) to characterize hydraulic behavior based on geometry-imposed limitations. The resulting data have been used to support the development of a physically-sound, generally-valid empirical correlation for predicting the onset of loading in beds of structured packings. The correlation covers a wide range of operating conditions and variations in structured packing geometry. It is useful in establishing the limits of pre-loading models and in calculating pressure drop in the loading region.

Distillation Column Performance Testing: Continuous and Batch Approaches

Kalthod, V. G.; Joglekar, G.; Clark, S. M.; Fair, J. R.
Presented at the AIChE Annual Meeting, Los Angeles, California, November 1997

Performance tests were run on a new, four-foot column containing three 21-foot beds of Intalox 2T structured packing. The n-heptane/toluene test mixture was used. Samples were taken carefully and subjected to reliable analyses of composition. An equilibrium pinch at the top bed made the results for that bed somewhat unreliable, but results form the other beds provided consistent values of HETP that could be checked against SRP results for the same packing, using the
cyclohexane/n-heptane test mixture. It was found that a comparison between continuous (total reflux) and batch tests allowed a check on the suitable VLE data to use. Values of HETP were in the range of 15 to 20 inches, depending on loading.

**F-97-9**

**New Developments and Opportunities in Distillation, Absorption, and Extraction**
Fair, J.R.
Presented at the AIChE Annual Meeting, Los Angeles, California, November 1997

This review of the state-of-the-art of distillation, absorption and extraction is organized along the usual lines of analysis: phase equilibria, separation devices, indices of separability, hydraulic/mass transfer characteristics of devices, and energy economy. For convenience in presentation, extraction is handled separately from distillation/absorption. Special attention is given to "different" devices such as the rotating gas-liquid contractor and the membrane extractor. Also given some emphasis is the combination of two separation methods such as hybrid membrane/absorption and reactive distillation. Finally, some thoughts area offered on the current status of research in academia and industry regarding distillation, absorption and extraction.

**F-97-10**

**Tres Bien! Trays Are Still "In"!**
Fair, J.R.
Presented at the AIChE Annual Meeting, Los Angeles, California, November 1997

There is no denying that the use of packings for distillation columns has mushroomed in recent years. A main thrust of the packing popularity has been the low pressure drop / high efficiency ratio character of the newer "through-flow" random packings and the so-called structured packings. This does not mean, however, that the use of trays for new installations has been abandoned. In fact, vendors are busy developing new tray designs that provide low capital cost, high capacity, and the absence of axial mixing problems found in the counterflow devices. This paper outlines the relative merits of crossflow trays versus high-efficiency packings and points to areas where the crossflow tray is still the device of choice.

**F-98-1 $20.00**

**Steam Regeneration of Activated Carbon Beds: Mechanisms and Models**
Huggahalli, Madhusudhan
Ph.D. Dissertation

Thermal Swing Adsorption (TSA) processes using activated carbon adsorbers and incorporation steam as the regeneration fluid find widespread use throughout the chemical process industries for the gas phase recovery of organic solvents and volatile organic compounds (VOCs). Steam is a popular choice for regeneration mainly because it is a commonly available, inexpensive plant utility. Despite the extensive use of steam regeneration, present understanding of the process is subject to empiricism and vague rules of thumb, which inevitably lead to inaccurate adsorber designs using excessively wide margins of error. The present research was directed at gaining a fundamental understanding of the mechanisms involved in the regeneration of activated carbon with steam, and subsequently developing mechanistic models that describe the steam regeneration process.

**F-99-1**

**Liquid Flow over Textured Surfaces. 1. Contact Angles**
Nicolaiewsky, Elioni M.A.; James R. Fair

This research was directed toward a better understanding of the mass-transfer processes that occur in distillation columns containing structured packings. These packings are designed to create an extensive gas-liquid interfacial area, through a combination of packing surface texturing and geometrical arrangement in the column. Thus, the spreading tendencies of a liquid flowing over these special surfaces represent an important factor in the choice of packing for a given separation system. Part 1 of this series of papers deals with basic relationships between the liquid and the solid surface, as indicated by the contact angle. Various liquid-solid combinations were tested for
contact angle using the Wilhemy plate technique, which was found to be applicable for flat or
corrugated textured surfaces. Several variables thought to affect the contact angle were studied:
surface tension and viscosity of the liquid, type of metal, type of texturing, and shape of the
surface. Part 2 of the series will show how contact angle can be combined with liquid flow rate
and packing geometry for predicting the mass-transfer performance of a particular structured
packing application.

F-99-2
Macias, Ricardo; James R. Fair
An experimental study was conducted in a 0>43-m-ID packed column to determine the axial
mixing properties of air and water under single-phase flow conditions. The packings used were
25.4-mm ceramic Raschig rings, one modern random packing, 25/4-mm metal Pall rings; two
structured packings, Sulzer Bx and Flexiapac2. The column was operated at ambient conditions
with flow rates varying from 0.4 to 4kg/m2.s for the gas and from 3.25 to 8.5 kg/m2.s for the
liquid. Axial mixing was experimentally determined via dynamic response tubes based on the
pulse injection technique. The diffusion-type model served to reproduce the experimental
response curve satisfactorily and proved to be a suitable means of describing axial mixing in both
phases. The results confirm previous observations for first-generation packings.

F-99-3 $10.00
Liquid Entrainment from Spray Distributors for Packed Columns
Trompiz, Carlos Jose
Master's Thesis
A theoretical model has been developed for estimating the total entrainment from spray nozzles
used in liquid distributors of packed beds. The model is based on a mathematical representation of
the drop size distribution in sprays, and on the drop buoyancy equations. It takes into account
flow rates and physical properties of the gas and liquid as well as the orifice diameter of the spray
nozzles. An experimental investigation for measuring entrainment from sprays was conducted in a
17-inch air-water contactor with an 11.5-inch spray section using four types of spray nozzles at
different air and water flow rates. Good agreement between experimental values of entrainment
obtained in this work and the model predictions were generally observed.

F-99-4 $20.00
Fundamental Model for the Prediction of Distillation Sieve Tray Efficiency: Hydrocarbon and
Aqueous Systems
Garcia, Jose Antonio
PhD dissertation
Tray efficiency is a crucial factor in the analysis of sieve tray distillation columns. However, the
prediction of point efficiency and its relation to tray efficiency has remained as a largely
unresolved problem. A mechanistic model based on vapo-liquid mass transfer fundamentals,
developed for air-water by Prado and Fair (1990), was extended to apply to the prediction of tray
efficiency for distillation systems. Correlations were obtained to calculate the parameters that
characterize each individual mass transfer zone of the vapor-liquid contacting dispersion in a tray,
i.e., jet height, bubble formation, fraction of small bubbles in the froth, and bubble size
distribution. The hydrodynamic fundamentals for aerated vessels were used to represent a sieve
tray. In a similar fashion, the maximum bubble size was obtained from turbulent flow isotropic
theory as a function of turbulence and system physical properties. Flow visualizations in bubble
columns and the study of bubble stability were the basis for predicting bubble size distributions.
The fraction of small bubbles in the froth was found to depend upon the bubble stability, the
degree of turbulence, and the liquid viscosity. Murphree tray efficiencies from the open literature
were used to develop the model. For comparison purposes, Murphree efficiency was converted to
point efficiency by means of a mechanistic eddy diffusion model. Point efficiency data gathered
in a semi-industrial column with conventional and high viscosity liquid systems completed an
extensive data base. A total of 233 experimental points were used to validate the model. The

55
average deviation for the entire database was -10.8%. The man absolute deviation was 21.4%. These deviations were significantly less than those exhibited by the Chan-Fair model when compared with the same data base. In summary, the model properly accounted for the tray geometry (i.e. hole area, hole size and weir height), different liquid/vapor ratios, and the change in physical properties with a wide range. The extension of the model to the prediction of efficiency in new tray devices with similar hydrodynamics characteristics, was successfully investigated. These encouraging results indicate that the model takes into account the most important hydraulic and mass transfer mechanisms, and is able to describe the phenomena existing in a liquid-vapor mixture on a distillation tray. The model should be generally applicable to the prediction of tray efficiency for hydrocarbon and aqueous systems, applications that exist in the chemical and petrochemical refining industries.

F-99-5
Performance of the Montz Packings: A3-500, A350E, B1-250E, and B1-250ES
Fair, J.R.; F. Seibert; C. Lewis; B. Eldridge
Research Report
SRP engaged in a series of total reflux distillation studies to characterize structured packing referred to as Montz A3-500, A3-350E, B1-250E and B1-250ES. As in the earlier studies, the mass transfer performance was characterized using the cyclohexane/n-heptane test system under operating conditions of 0.33, 1.06, and 4.14 bar. In SRP9903, data were also obtained at 0.17 bar. The objective of the study was to determine the effect of packing geometry on mass transfer, capacity and pressure. The packing was supplied by Julius Montz and was installed according to its specifications. The packing was fabricated from type 316 stainless steel.

F-99-6 PUBLISHED
A New, Ultracapacity Tray for Distillation Columns
Fair, J.R.; W.R. Trutna; A.F. Seibert
TransIChemE, Vol 77, Part A: 619-626
The gas flow capacity of conventional crossflow distillation trays is normally limited by the propensity of the gas to entrain liquid from the tray. Only a slight amount of such entrainment can be permitted without serious degradation of mass transfer efficiency. The tray-type contacting device described here is designed to entrain all of the liquid entering the tray, and then separate that liquid by a device located with the tray zone. As a result, considerably more gas flow can be accommodated in a distillation column sized for conventional crossflow trays. Complete distillation test data, taken at a semi-works scale, are presented along with a mechanistic model which represents the data and which can be used for extension to other distillation conditions.

F-00-1 PUBLISHED
Entrainment from Spray Distributors for Packed Columns
Trompiz, Carlos J.; James R. Fair
Spray nozzles are widely used to provide a uniform liquid distribution to packed distillation and absorption columns. A disadvantage of such distributors is, however, the tendency for the atomized drops to be entrained by the upflowing gas. In some instances it is not convenient or even possible to remove the entrained liquid from the gas. A theoretical model has been developed for estimating the total entrainment from spray nozzle distributors. The model is based on drop size distribution and drop buoyancy relationships and has been confirmed by measurements in a 11/4-in. diameter spray contactor, using four different solid-cone nozzles and the air-water system. The model has also been confirmed by measurements of other using an air-paraffinic oil system. The model takes into account orifice diameter, phase flow rates, and phase physical properties. It predicts total entrainment and does not allow for partial removal of entrainment by walls, adjacent sprays, or target devices used to collect the entrained liquid. Thus, the predictions are conservative for multiple spray nozzle assemblies.
A comprehensive total reflux distillation study of sheet metal structured packings was carried out with the cyclohexane/n-heptane test mixture. The experiments covered a wide range of pressures, two corrugation angles, two surface areas, and two surface designs. Experimental results include pressure drop, capacity, and mass-transfer efficiency. The database generated has been used to evaluate generalized performance models developed independently at The University of Texas Separations Research Program (SRP model) and at Delft University of Technology (Delft model). This paper reports the experimental results and compares them with predictions from the two models. Deviations of predictions from measurements are discussed in terms of likely contacting mechanisms in the packed bed.

Comprehensive experimental studies have been conducted with several varieties of commercial structured packing to ascertain geometry-imposed effects on their hydraulic behavior. At Delft, the air-water system was used for hydraulic studies, and at the Separations Research Program (SRP) the cyclohexane/n-heptane distillation system was used to provide additional hydraulic and mass-transfer data for the same packings. These and other performance data available in the SRP database have been used to substantiate the development of a physically sound, generally applicable empirical correlation for predicting the onset of loading, where hydraulic characteristics of the packed bed change significantly. The correlation proposed in this paper covers a wide range of operating conditions and variations in structure packing geometry. It can be used with either Delft or SRP preloading models to provide an outgoing point for determining pressure drop, liquid holdup, and mass transfer in the loading region.

The results of an experimental study indicating a significant effect of column diameter on the pressure drop and capacity of corrugated sheet structured packing are presented. The experiments were carried out with Montz-pak B1-250, using an air/water system at ambient conditions in Perspex columns with internal diameters of 0.2 m, 0.45 m, 0.8 m and 1.4 m. The results clearly show that both the pressure drop increase and capacity decrease become significant when the column diameter approaches the value equal to that of the height of a packing element. This observation suggests that column diameter(s) based on small scale data can be too large.

Several correlations are available in the literature for the prediction of wetted area of the effective interfacial area in packed columns. A careful examination shows considerable discrepancies in the calculated areas and conflicting predictions concerning the influence of viscosity on the interfacial areas. In this work, the effect of physical properties of liquids and of surface treatment on wetted
area of structured packings was experimentally studied. Several wetting tests were performed on metallic and ceramic plates with flat, smooth or textured surfaces, using a circulation system, specially designed for this purpose. The liquid film width and thickness were measured for width, and hence the wetted area, decreased with liquid viscosity, contrary to earlier correlations in the literature. Also the influence of contact angle is not so strong as stated in the literature for random packings. In this study, a new statistical correlation for the estimation of the wetted area and for liquid film thickness is proposed, reflecting the measured variations with viscosity and advancing contact angles.

F-00-7  PUBLISHED
Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study
Fair, J.R.; A.F. Seibert; Z. Olujic
Chemical Engineering and Processing, 39: 335-342, 2000
While the utilization of corrugated sheet structured packings is well established, these gas-liquid-contacting devices are still not well understood. A contributing reason is the rather limited publicly available performance data, most of which have been obtained from relatively small columns. A recent comparison of data from the 1.2 m Fractionation Research, Incorporated (FRI) and from the 0.43 m Separations Research Program (SRP) columns show excellent agreement based on equivalent packings. This is significant since the FRI column is considered to be of industrial scale. As a result, we sought to create an expanded data base emphasizing packing geometric variations, using packings from a single manufacturer (J. Montz). Hydraulic characteristics of the same packings had been studied previously using air-water simulators at TU Delft. Total reflux distillation experiments were carried out a SRP using a bed height of 3.3 m for all packings. The cyclohexane-n-heptane system was utilized because of the availability of comparative data. The operating pressure was varied from 0.33 to 4.14 bar, to determine the effect of physical properties. the resulting data provided insight into the nature and effect of corrugation angle, specific surface area, and surface texture on pressure drop, capacity and efficiency. In this paper we report the results and also discuss the implications of the observations on model development and design.

F-00-8
The Effects of Free Water on the Performance of Packed Towers in Vacuum Service
Bravo, J.L.; Seibert, A.F.; Fair, J.R.
Manuscript on File

F-00-9
The Distillation Imperative
Fair, J.R.
Presented at the AIChE Meeting in November, 1998
This invited talk was given in November 1998 at the Miami Beach meeting of the American Institute of Chemical Engineers. It covers United States developments in distillation technology and traces them chronologically during the last half of the twentieth century, a period directly experienced by the speaker. the general conclusion reached by the speaker is that distillation is still the dominant separation method used by the chemical and petroleum industries, and merits more research than it is receiving as the century closes.

F-00-10
Distillation: State-of-the-Art and Future Trends
Fair, J.R.
Presented at the Annual Meeting of AIChE, Los Angeles, CA. Monday, Nov. 13, 2000
Any interpretation of the status and trends of distillation must reflect a particular viewpoint. Few will argue over the general health of distillation, which is robust with excellent actuarials. But the attitudes and views of different groups show variations. To a student entering a graduate program in chemical engineering, work in distillation is considered unrewarding, in the literal sense of the word. To the professor it offers little opportunity for financial support. To production people,
Distillation may very well provide life support. To those interested in exploiting, in an interesting and challenging way, the use of computers and mathematical modeling, several facets of distillation are especially attractive for study. It is this latter group that appears to be leading the way in journal publications. Of special note are efforts in batch, reactive and azeotropic distillation system and column control; and energy minimization.

F-00-11
Distillation References, 1995 - August 2000
Fair, J.F.; Seibert, A.F.; Fisher, Ernest
Manuscript on File
Distillation Bibliography for 1995-2000, Compiled September 1, 2000. Categories include: Phase Equilibria and Physical Properties; Stages/Transfer Units/Rate-Based Models; Hydraulics-Trays; Hydraulics-Packings and other Devices; Mass transfer-Trays, Packings and Other Devices; Systems, Devices; Dynamics and Control; Operation, scale up, Troubleshooting; Process Applications, Optimization and Economics; Batch Distillation; Absorption and stripping; Reactive Distillation; Azeotropic Distillation; Extractive Distillation; Energy Efficiency.

F-01-1
Distillation
Fair, J.R.

F-01-2
Don’t Forget the ChEs Who Really Run Things
Fair, J.R.

F-01-3
Absorption (Chemical Engineering)
Fair, J.R.; Kister, H.Z.
Encyclopedia of Physical Science and Technology 3rd Ed. Academic Press, 2001. Absorption is a unit operation in which a gas mixture is contacted with a suitable liquid for the purpose of preferentially dissolving one or more of the constituents of the gas. These constituents are thus removed or partially removed from the gas into the liquid. This article presents an overview of the method.

F-01-4 PUBLISHED
Distillation Sieve Trays Without Downcomers: Prediction of Performance Characteristics
Garcia, J.A.; Fair, J.R.

F-01-5 PUBLISHED
Axial Mixing Effects in Packed Gas-Liquid Contactors
Macias-Salinas, R.; Fair, J.R.

F-01-6
Performance of New Generation of Montz High Capacity Structured Packings
Presented at National AIChE Meeting, Houston, Texas April 2001

F-01-7
Performance of a New High Capacity Structured Packing
Chemical Engineering Processing, 2001
F-02-1  NEW
The Oldershaw Column: Useful for Solving Distillation Problems
Fair, J.R.; Reeves, Bobby; Seibert, A.F.
Presented at AIChE Spring Meeting, New Orleans, March 2002
The Oldershaw column is a bench-scale device that has been shown to be useful for predicting the
mass transfer efficiency of commercial sieve-tray distillation columns. By analogy, it has also
been used to predict the efficiency of columns containing bubble-cap trays and valve trays. In
this paper, uses of the device are extended to less-usual problems and valuable validation of
computer simulations of actual stages.

F-02-2  NEW PUBLISHED
The Workhorse Today & Tomorrow - Distillation
Fair, J.R.
Chem. Eng. 109 (8), 108-112
Distillation is, far and away, the predominant method for separating liquid mixture, and that
situation seems certain to continue.

F-04-1
Distillation
Fair, J.R.

F-04-3
Liquid-side Mass Transfer Resistance of Structured Packings
Ind. Eng. Chem. Research (43), 7113-7120, 2004

F-04-4
Fair, J.R., Couper, J.R., and Penney, R.
Amsterdam: Elservier, 2005

M-92-1
Preliminary Distillation Mass-Transfer and Pressure-Drop Results Using a Pilot Plant Scale High-
Gravity Contacting Unit
Martin, C. L.; M. Martelli
Presented at the AIChE Spring National Meeting,
New Orleans, Louisiana, March 29-April 2, 1992
The SRP has installed a high-gravity distillation unit (HGDU) that can be used for both
distillation and gas/liquid contacting operations. This paper describes the HGDU, some of the
operating problems encountered during the shakedown of the unit, and preliminary mass-transfer
and pressure-drop data that has been collected.

M-92-2
Trutna Tray
Trutna, W. R.; C. L. Martin; J. A. Garcia
Presented at the AIChE Spring National Meeting,
New Orleans, Louisiana, March 29-April 2, 1992
A method for predicting Trutna tray capacity based on entrainment rates was developed. It was
shown that the Trutna tray can meet a range of capacity requirements by altering the collector
design. The Trutna tray can be designed for low, medium, and high liquid rate systems with rates
30% to 60% higher than conventional equipment.
Electrical Separations

A-85-1 PUBLISHED
Electrochemistry in Near-Critical and Supercritical Fluids. 2. Water. Experimental Techniques and the Copper (II) System
McDonald, A. C.; F. R. F. Fan; A. J. Bard
An electrochemical cell and electrode system for investigation of aqueous systems under near-critical and supercritical conditions is described.

A-85-2 PUBLISHED
Electrochemistry in Near-Critical and Supercritical Fluids. 3. Studies of Br-, I-, and Hydroquinone in Aqueous Solutions
Flarsheim II, W. M.; Y.M. Tsou; I. Trachtenberg; K. P. Johnston; A. J. Bard
A new type of apparatus was constructed for studying electrochemistry in near-critical and supercritical aqueous solutions (A-85-2). This work provides a basis for future electro-organic synthesis in supercritical water.

A-86-1
Electrosorption as a Means of Separation
Bard, A. J.
Manuscript on file, Separations Research Program
State-of-the-art review for electrically controlled adsorption and regeneration.

A-86-2 PUBLISHED
Electrochemistry in Near-Critical and Supercritical Fluids. 4. Nitrogen Heterocycles, Nitrobenzene, and Solvated Electrons in Ammonia at Temperatures to 150°C
Crooks, R. M.; A. J. Bard
The electrochemistry of pyrazine, quinoxaline, phenazine, and solvated electrons in near-critical and supercritical ammonia was investigated by cyclic voltammetry and chronoamperometry and compared to that in liquid ammonia at -40°C. The reductions of pyrazine, quinoxaline, and phenazine at room temperature, and in the supercritical fluid, occur reversibly or quasi-reversibly and result in stable products (anion radicals or dianions) on the voltammetric time scale. The electrochemistry of nitrobenzene was investigated in the presence of water, and reactions of the dianion at higher temperature, similar to those previously reported at 40°C, were observed. The diffusion coefficient of the four aromatics increased by an order of magnitude between -40°C and 150°C in agreement with the Stokes-Einstein relationship over the temperature range studied. Solvated electrons were electrochemically generated in the supercritical fluid and found to be stable on the voltammetric time scale. The thermodynamics of electrode reactions in the SCF is discussed, and the apparatus for performing electrochemistry in the SCF is described.

A-87-1 PUBLISHED
Retention by Electrical Field-Flow Fractionation of Anions in a New Apparatus with Annular Porous-Vycor(r)-Glass Channels
Davis, J. M.; F.R. Fan; A. J. Bard
Analytical Chemistry 59(9):1339-48 (1987)
Polystyrenesulfonate and chromium phthalocyanine-tetrasulfonate were retained in Porous-Vycor(r)-Glass channels using high- and low-conductivity aqueous carriers. Retention ratios differ considerably from theoretical expectation, but measured and theoretical plate heights agree when the necessary parameters are estimated from experimental data.
Extraction

Mass-Transfer Studies in Liquid-Liquid and Supercritical Extraction Devices

B-86-6 PUBLISHED
Mass-Transfer Efficiencies of Column Contactors in Supercritical Extraction Service
Lahiere, R. J. and J. R. Fair
The mass-transfer performance of a small-scale continuous countercurrent extractor operating under high-pressure extraction conditions in the critical and near-critical regions for the solvent was investigated and characterized. Test systems were comprised of alcohol/water mixtures and the extractant was CO2. Experiments were carried out to determine mass-transfer efficiencies of a 2.5-cm (1-inch) extraction column with sieve trays and operating as a spray column. Limited data were also taken in a packed extractor for comparison purposes. A conventional model for predicting mass-transfer efficiencies in liquid-liquid extraction was applied to the data with good success.

B-87-3 PUBLISHED
Evaluation of Packed Columns in Supercritical Extraction Processes
Rathkamp, P. J.; J. L. Bravo; J. R. Fair
The purpose of the present work is to add to the base of knowledge in the use of packed columns when used in supercritical extraction service. Experimental studies were performed on a 2.54-cm-diameter supercritical fluid extraction column operated in both spray and packed-column arrangements. The packing used was 6.4 mm Raschig rings with a surface area of 722 m2/m3. The supercritical systems studied were CO2/ethanol/water and CO2/isopropanol/water at 102 atmospheres and 35°C, and 102 atmospheres and 40°C, respectively. In order to compare supercritical with conventional extraction, similar data were obtained in the same column with the toluene/acetone/water system at one atmosphere and 24°C.

E-87-1 PUBLISHED
Performance of Spray, Sieve Tray, and Packed Contactors for High-Pressure Extraction
Seibert, A. F. and D. G. Moosberg
The purpose of this paper is to provide hydrodynamic and mass-transfer efficiency data obtained from a pilot-scale supercritical fluid extractor. A comparison of the performance of various contactors operated under supercritical conditions is presented. The contacting devices investigated in this work include sieve trays, no. 15 metal Intalox(tm) saddles, and 1/2-inch ceramic Raschig rings. The spray or empty column was also studied as a base case to determine the effects of trays and packing. The high-pressure extraction column has an internal diameter of 3.88 inches and is capable of a contacting height of six feet. Glass windows in the extractor allowed visual observation and photography.

E-87-2
Supercritical Fluid Extraction-Process Simulation and Design
Martin, C. L. and A. F. Seibert
Presented at the Ninth Annual Industrial Energy Technology Conference, Houston, Texas, September 1987
This paper briefly discusses the previous experimental work done in the area of SFE, the experimental system and equipment currently being used at The University of Texas to study SFE, and our first attempt to simulate this process using our own experimental data. In this case study, the data used were taken from one experimental run to simulate process flows, energy requirements, and process conditions when separating isopropyl alcohol from water employing supercritical CO2 as the solvent. Experimental data were used to specify separations where these
data are currently unavailable. In addition, a standard data generation package was utilized from the process simulator to calculate these data when applicable conditions were met.

**E-87-3**

**Flooding in a Large Diameter Sieve Tray Extractor**

Rocha, J. A. and A. F. Seibert

Report on file, Separations Research Program

Modeling of sieve-tray liquid-liquid extractors has gained interest in recent years. Research emphasis has been placed on the mass-transfer efficiency of such devices, thus allowing the determination of the required column height. However, the study of flooding in sieve-tray columns appears to have been ignored, which is surprising since the column diameter is determined from such information. In fact, there is not a generally accepted correlation available in the literature to predict flooding velocities in sieve-tray extractors. The purpose of this study is to provide flooding data obtained from a large-diameter column (42.5 cm) using the isopar-m/water test system for future modeling efforts, as well as a compilation of flooding rates from other sources.

**E-87-4**

**Handouts for the Separations Research Program**

Study Group Meeting, October 1987

Includes copies of transparencies used by A. F. Seibert.

**E-87-5** PUBLISHED

**Hydrodynamics and Mass Transfer in Spray and Packed Liquid-Liquid Extraction Columns**

Seibert, A. F. and J. R. Fair


Mass-transfer efficiencies and hydraulic characteristics of a 10.2-cm packed extraction column have been investigated. The packings used were ceramic Raschig(tm) rings, metal Pall(tm) rings, ceramic Intalox(tm) saddles, corrugated sheet metal, and corrugated metal gauze. The performance of these packings was compared with that of an empty (spray) column. Two widely different chemical systems were used: toluene/acetone/water and n-butanol/ succinic acid/water. The influence of phase flow rates, direction of solute transfer, and phase dispersed was studied and found to be significant. Fundamental models were developed to account for flooding, dispersed-phase holdup, and mass-transfer efficiency.

**E-88-1**

**Handouts for the SRP Extraction Study**

Group Meeting, April 1988

Includes copies of transparencies used by Seibert, Little, and Wooten for the Extraction Study Group Meeting.

**E-88-2** PUBLISHED

**Spray, Sieve-Tray, and Packed High-Pressure Extraction Columns-Design and Analysis**

Seibert, A. F.; D. G. Moosberg; D. G., J. L. Bravo; K. P. Johnston

In Proceedings of the International Symposium on Supercritical Fluids, Societe Francaise de Chimie (1988)

Fundamental mass-transfer models applicable to spray, sieve-tray, and packed extractors are presented and compared with actual experimental data. The mass-transfer efficiency of sieve trays, ceramic Raschig(tm) rings, metal Intalox(tm) saddles, and a corrugated gauze ordered packing (Sulzer(tm) BX) was determined using a high-pressure extraction column with an internal diameter of 9.88 cm and a contacting height of 168 cm. The spray or empty column was also studied as a base case. Glass windows in the extractor allowed for visual observation and photography of the two-phase hydraulics. Supercritical and liquid CO2 were used to extract isopropanol or ethanol from water at pressures of 81 to 150 atmospheres and at temperatures of 297K to 318K. The sieve-tray extractor yielded the highest mass-transfer efficiency, followed in descending efficiency by Sulzer(tm) BX, Raschig(tm) rings, metal Intalox(tm) saddles, and the spray column. The dispersed CO2 phase was observed to preferentially wet the metal and ceramic packing surface instead of forming spherical drops.
E-89-1
Handouts for the Separations Research
Program Fall Conference, September 1988
Includes copies of transparencies used by Seibert and Barnicki for the Extraction Study Group Meeting.

E-89-2
Hydrodynamics and Mass Transfer in Supercritical Fluid Extraction Columns
Seibert, A. F. and C. T. Little
Presented at the AIChE Spring National Meeting, Houston, Texas, April 1989
Hydrodynamic and mass-transfer studies of packing, spray, and sieve-tray performance were conducted using a 10-cm-diameter column operated at high-pressure extraction conditions. Carbon dioxide/isopropanol/water, CO2/ethanol/water, and CO2/petroleum hydrocarbon/brine were used as experimental test systems. The latter system involved a multicomponent two-phase feed. The operating temperature and pressure were varied from 297-317K and 80-102 atmospheres. Windows in the column allowed for visual observation and photography of the extraction hydrodynamics. The Sauter mean drop diameters of the spray and sieve-tray extractor were observed to be dependent on the operating temperature and pressure and essentially independent of flow rates. The dispersed-phase holdups and mass-transfer efficiencies were determined to be dependent on the dispersed-phase flow rates. The hydrodynamic characteristics of the brine system were determined to be similar to the fresh water system. The reduction of the mass-transfer efficiency with column diameter is presented. These additional data will provide a reliable high-pressure hydraulic and mass-transfer data base for future correlating and design efforts.

E-89-3
Handouts for the Separations Research
Program Spring Conference, April 1989
Includes copies of transparencies used by Seibert for the Distillation/Extraction Study Group Meeting and by Little for the Environmental/Miscellaneous Study Group Meeting.

E-89-4
The Operating Characteristics of the Karr Reciprocating Column
Matthews, H.; R. Perrotta; C. Slade
Manuscript on file, Separations Research Program
An extensive, pilot-scale investigation was conducted on the performance characteristics of the Karr reciprocating column. The column was initially assembled and reworked to allow for complete recycle which was ideal for this experimental study because it allowed for continuous use. The holdup and the flooding velocity of the column were then found as a relationship of the water velocity, the isopar-m velocity, and the reciprocator speed. The holdup and the flooding velocity were needed to help find the most efficient operating conditions of the column. These conditions typically occurred at 70% of the flooding velocity. It was concluded that three types of flooding existed throughout the course of the experiments: entrainment flooding, phase inversion, and regular flooding. Entrainment flooding occurred at high water velocity and low isopar-m velocity. Phase inversion occurred at low water velocity and high isopar-m velocity. Regular flooding occurred at equal water and isopar-m velocities. Recommendations for further studies include obtaining automatic interface control, performing actual liquid/liquid extraction, changing reciprocator stroke length and plate spacing, and finding correlations between droplet size and mass transfer using photographic means.

E-89-5
Handouts from the Separations Research
Program Fall Conference, September 1989
Includes copies of handouts used by Seibert and Barnicki for the Extraction Study Group Meeting.
Design Manual-Liquid-Liquid Extraction
Seibert, A. F.; R. Macias; J. A. Rocha

This manual represents the SRP's current thinking on the design of spray, sieve-tray, or packed extraction columns for use in liquid-liquid or supercritical fluid extraction processes. The design manual and accompanying diskette use many of the fundamentally consistent models developed by the SRP over the past seven years. The majority of the equations have been verified under a wide range of conditions including supercritical fluid conditions. The packing and sieve-tray models have also been tested and verified with results obtained from a 16.75-inch (i.d.) liquid-liquid extractor. Since these models have only been compared with experimental data obtained from pilot-scale units, some precaution must be taken when designing a large commercial-scale column. Replaces F-86-10

Performance of a large-scale Packed Liquid-Liquid Extractor
Seibert, A. F; B. E. Reeves; J. R. Fair

The performance of commercial-size high-efficiency packings was determined using a 42.5-cm-diameter (i.d.) liquid-liquid extractor. Both random and ordered packings were studied to determine their effects on the fluid hydraulics and mass-transfer efficiency in a large-diameter extractor. These packings included #25 and #40 metal Intalox(tm) saddle random packing and Norton 2T ordered packing. Physical property effects were studied for three test systems, isopar-m/water, toluene/water, and toluene/acetone/water. The influence of packed height was also investigated and was observed to have a significant effect on the mass-transfer efficiency of the random packings. The experimental results were compared with models based on data obtained in small-scale columns. For the ordered packing, these models agreed favorably with the larger scale data; such was not the case with random packings. Based on these experimental results, it is evident that significant maldistribution can occur in large-diameter towers containing random packings. The apparent maldistribution was observed to increase with increasing packed height and column diameter. Maldistribution did not appear to be a problem with the ordered packings.

Critical Fluid Extraction of Hydrocarbons from Oil-Field Brines
Little, C. T.; A. F. Seibert; J. L. Bravo

This document summarizes the work that led to the development of a process to remove suspended as well as dissolved hydrocarbons from water by the action of an acid gas (CO2). The process can produce effluent waters that are well below the solubility limits of hydrocarbons and that meet current and expected discharge limitations. It also achieves the removal without the permanent addition of chemical agents to the water and is suitable for CO2 recycle with minimal losses. The process uses gaseous, liquid, or supercritical CO2 as the cleaning agent as dictated by the characteristics of the wastewater.

An update can be found in E-90-10

The Selection of Surfactants for Micelle Enhanced Ultrafiltration
Kandori, K. and R. S. Schechter

Presented at the Separation Research Program Spring Conference, April 1990

The selection of a surfactant is an important issue in designing separations processes based on micelle enhanced Ultrafiltration. The binding of hydrophilic solutes to ionic and nonionic micelles is considered and shown to be a function of molecular structure of the surfactants, concentration of surfactant, and electrolyte composition of the water. The passage of micelles is only partly restricted by polycarbonate membranes with 100Å pores but is effectively restricted by some cellulose acetate membranes. Swelling the micelles by cosolubilizing certain nonpolar compounds was found to only marginally improve the separation efficiency. There appears to be an optimum surfactant molecular structure but it will not be possible even under the best conditions to
completely remove a hydrophilic solute such as phenol in a single stage. Thus the process will necessarily be a multistage one.

**E-90-4**

**Handouts from the Separations Research**

Program Spring Conference, April 1990

Includes copies of transparencies used by Seibert and Little in the Extraction Study Group Meeting.

**E-90-5** $20.00

**Removal of Petroleum Hydrocarbons from Oil-Field Brines with Carbon Dioxide**

Little, C. T.

PhD dissertation

The objective of this research was to study the removal of dispersed and dissolved petroleum hydrocarbons from oil-field brines using CO2 in a sieve-tray extraction column. The studies involved phase equilibria mass transfer by extraction, hydrodynamics of bubble flow, and flocculation. Experimental data were obtained for a model system, water/toluene/CO2. A south Texas brine was used to test the effect of salinity on the hydrodynamics of bubble flow. Also, brine from a California steamflood was chosen; the California brine contained a nominal 700 mg/L of a heavy, asphalitic crude oil and had a total salinity of approximately 500 mg/L. The results from the south Texas brine hydrodynamic studies showed that salinity has a very minor effect on bubble flow hydrodynamics. The toluene phase equilibria runs verified the applicability of the phase equilibria part of the model. Problems with generating an aqueous solution of toluene prevented the verification of the mass transfer part of the model. A qualitative examination of several California brine experimental runs indicated that the removal by extraction was negligible compared to flocculation. Therefore, the flocculation studies with the California brine were continued. It was determined that the flocculation of the oil droplets was the result of two separate effects: a pH effect due to the acidity of CO2 and a shear effect due to the rising CO2 bubbles.

**E-90-6**

**Handouts from the Separation Research Program**

Fall Conference, September 1990

Includes copies of transparencies used by Seibert and Mshewa for the Extraction Study Group Meeting.

**E-90-7**

**Application of Supercritical Fluid Research Extraction for Energy Efficiency in Commercially Significant Separation Processes**

Bauer, D. L. and A. F. Seibert

Report prepared for the Energy Research in Applications Program, Texas Higher Education Coordinating Board

Four case studies are presented that demonstrate the energy efficiency of SFE when applied to important commercial separation processes. This report emphasizes the clean-up of water contaminated with emulsified and soluble oil because of the impact that this technology has in reducing the consumption of energy in the state of Texas and because of its importance to the environment. A detailed capital estimate is presented to aid in determining the feasibility of commercializing this process.

**E-90-8** PUBLISHED

**Dynamic Simulation of a Supercritical Fluid Extraction Process**

Ramchandran, B.; J. B. Riggs; H. R. Heichelheim; A. F. Seibert; J. R. Fair


A dynamic supercritical fluid extraction process simulator has been developed by modeling various units of a typical SFE process. Realism of the simulated results is enhanced by accounting for instrument noise, random drifts, transport delays, and analyzer deadtimes. The process
simulator has been compared with operating data from a pilot-scale SFE process and yields good agreement. The dynamic process simulator provides much needed insight into various process interactions and the nonlinearities that can exist in an integrated, multiunit process.

E-90-9
Removal of Petroleum Hydrocarbons from Oil-Field Brines with Carbon Dioxide
Bravo, J. L.; C. T. Little; A. F. Seibert
Presented at the Second International Symposium on High-Pressure Chemical Engineering, Erlangen, Germany, September 1990
The new treatment method described in this work is actually an enhancement of existing gas flotation technology. The enhancement results from the use of CO2 as the "sweeping" gas; the acid nature of CO2 causes a drop in the aqueous phase pH, which lowers the electrostatic charge on the surface of the oil droplets. With a lower surface charge, the repulsive potential between the droplets is reduced significantly. Under the influence of the shear field generated by the rising CO2 bubbles, the oil droplets flocculate and coalesce to form larger droplets which are subsequently swept by the CO2 bubbles.

E-90-10
Removal of Suspended and Dissolved Hydrocarbons from Water by the Use of Carbon Dioxide
Manuscript on file, Separations Research Program
An updated version of E-90-2.

E-90-11
Removal of Hydrocarbons from Oil-Field Brines by Flocculation with Carbon Dioxide
Little, C. T.; A. F. Seibert; N. E. Burke; S. Curtsy
Presented at the Society of Petroleum Engineers Conference, Anaheim, California, February 1991
The objective of this research was to develop a model to describe the removal of dispersed petroleum hydrocarbons from oil-field brines using CO2 in a sieve-tray extraction column. The model consists of two parts: hydrodynamics of bubble flow and flocculation. The flocculation part of the model is presented in this work. The system studied was a brine from a California steamflood. The brine contained a nominal 1000 mg/L of a heavy, asphaltic crude oil (13.2°API) and had a total salinity of approximately 500 mg/L. The flocculation model was tested with experimental runs at pressures of 83.75 and 97.54 bar and temperatures of 23.9, 37.8, and 65.6°C. Additional flocculation runs were made at pressures of 14.80, 42.38, and 69.96 bar at 65.6°C. The flocculation of the dispersed oil droplets was determined to be the result of two separate effects: a pH effect due to the acidity of CO2 and a shear effect due to the rising CO2 bubbles. An empirical flocculation efficiency in the model was needed to effectively predict removal efficiencies for each operating condition.

E-91-1 PUBLISHED
An Overview of Commercially Available Software for Distillation, Extraction, Adsorption, and Membrane Processes
Humphrey, J. L.; R. A. Koort; A. F. Seibert
This paper presents an overview of the commercially available software to solve distillation, extraction, adsorption, and membrane separation problems. The paper addresses hardware requirements, software characteristics and capabilities, and identifies the vendor of the software. Results from a case study are presented illustrating the application of one of the programs.

E-91-2
Handouts for the Separations Research
Program Spring Conference, April 1991
Copies of transparencies used by Seibert, Py, and Mshewa for the Extraction Study Group Meeting.
New Energy Efficient Method for Cleaning Oilfield Brines with Carbon Dioxide
Little, C. T.; A. F. Seibert; J. L. Bravo; J. R. Fair
Presented at the Thirteenth National Industrial Energy Technology Conference, Houston, Texas, June 1991

This paper describes an enhancement of an existing gas flotation technology that uses CO2 to clean oil-field brines. The enhancement results from the use of CO2 as the sweeping gas combined with its ability to lower the pH of the aqueous system. The reduction of pH neutralizes the charge on the surface of the drop, thus destabilizing the emulsion and enhancing phase separation. The water is simply neutralized by flashing the treated water to ambient pressure. The important discoveries of this study and an economic comparison of the CO2 treatment process with other potential processes are presented in this work.

Liquid-Liquid Extraction Using Microporous Hollow-Fiber Membranes
Mshewa, M. M.
Master's thesis

This research was based on a microporous hydrophobic hollow-fiber membrane module, which structurally resembles a shell and tube heat exchanger where the tube section is composed of a bundle of 7,500 small-diameter microporous hollow fibers. The module was 5.1 cm in diameter and 61.0 cm long. The main research objectives were to measure the mass-transfer efficiency of the module and subsequently provide an efficiency comparison with conventional extraction devices. In addition, the research sought to verify and/or modify a mass-transfer model for membrane extraction. Data were collected on four liquid-liquid extraction systems: toluene/acetone/water, methylisobutyl ketone/ acetic acid/water, n-butanol/succinic acid/water, and n-octanol/phenol/water.

Hydraulics and Mass-Transfer Efficiency of a Commercial-Scale Membrane Extractor
Seibert, A. F.; X. Py; M. M. Mshewa; J. R. Fair
Separation Science and Technology 28(1-3):343-59 (1993)

In recent years, there has been significant interest in using microporous hollow-fiber membranes for liquid-liquid extraction. In this process, the feed may be passed through the shell while the solvent is passed in the fiber side or vice versa. Mass transfer occurs across the liquid-liquid interface formed in the pores of the fiber wall. The advantages of this technology are high throughput capacities, the process is independent of the density difference between the feed and solvent, and a potentially high mass-transfer area is available. The mass-transfer performance of the commercial-scale membrane extractor modules was determined to be lower than expected based on the results obtained from smaller scale modules and flat film. Mass-transfer studies of a commercial-scale membrane extraction module at the SRP have shown that a significant portion of the fibers is bypassed by the shell-side fluid and consequently a fraction of the total fiber surface area may be used. A hydraulic study using a dye tracer technique verified these findings with an aqueous flow on the shell side. A model has been developed that incorporates mass-transfer correlations reported by others with the effect of shell-side bypassing. In this paper, the efficiency of the membrane extractor is compared with the conventional spray, sieve-tray, and packed column. The effect of fiber penetration or shell-side bypassing in a commercial-scale membrane extractor is also discussed.

Polymer Purification by Extraction with Supercritical Carbon Dioxide
Seibert, A. F. and J. R. Fair
Presented at the AIChE Meeting, Minneapolis, Minnesota, August 1992

In polymer purification, the removal of residual monomer is difficult and inefficient using conventional separation methods such as hot nitrogen purge or steam stripping. If the polymer is thermally labile, purification is generally limited to vacuum stripping. In the present work, a novel technique, one that uses supercritical CO2 to remove residual monomer from a polyethylene resin, has been investigated to determine the mass-transfer characteristics and process feasibility. In
addition to its enhanced solvating power as a supercritical solvent, CO2 has a high diffusivity in many polymers because of its small kinetic diameter. In this study, near-critical CO2 was used to purify a fixed bed of polyethylene powder having an initial concentration ranging from 10-15 wt% n-heptane. The mass-transfer studies were performed using a high-pressure pilot-scale extraction/distillation test system. In this process, over 95% of the heptane was removed from the polyethylene. However, the majority of the mass transfer occurred during the compression and decompression steps of the operation. The removal efficiency was also observed to increase when operating above the critical pressure and temperature of CO2. In this presentation, the mass-transfer characteristics of the process and the effects of different operating variables are reported.

**E-92-4  PUBLISHED**

**Mass-Transfer Efficiency of a Large-scale Sieve Tray Extractor**
Seibert, A. F. and J. R. Fair
The mass-transfer efficiency and phase flow capacity of a 42.5-cm-diameter sieve-tray extractor has been investigated. The extraction of acetone from water with toluene was chosen because of the large amount of data for comparison with the performance of other devices and particularly because of available data for a smaller sieve-tray extractor tested in the same laboratory. For capacity studies, the Isopar-m(r)/water system was also used. The performance of the sieve trays was compared with that of sprays and packings in the same column. Important parameters were found to be phase-flow rates, flow ratios, and column diameter. Mechanistic hydraulic and mass-transfer models, found to correlate well with experimental data, are presented in the paper. Replaces E-93-3

**E-93-1**

**Trutna Tray Performance Studies**
Trutna, W. R.; A. F. Seibert; J. A. García
Presented at the AIChE Spring National Meeting, Houston, Texas, March 1993
The Trutna Tray, or the cocurrent tray, is a new, unique gas/liquid contacting device. Since the operation is not limited by liquid entrainment, the cocurrent tray has the potential for high capacity with a relatively low HETP. The objectives of this research were to obtain semicommercial scale hydraulic and mass-transfer data on a new cocurrent tray and to compare these data with the conventional sieve tray and the original cocurrent tray. In addition, the performance of the distributor and collector were to be evaluated. In this study, the cyclohexane/n-heptane system was studied due to the availability of previous mass-transfer and hydraulic data. The new cocurrent tray provided twice the capacity with essentially the same efficiency as the conventional sieve tray. Relative to the original semicommercial cocurrent tray, the updated tray provided a 25% increase in capacity with essentially the same efficiency. The relative performance of the cocurrent tray also appeared to improve with increasing pressure. In this paper, an equipment description with comparable performance data are provided.

**E-93-2  PUBLISHED**

**New Dimensions in Distillation**
Humphrey, J. L. and A. F. Seibert
Chemical Engineering 99:86-98 (1992)
Separation processes play a variety of roles in industry: the removal of impurities from raw materials, the purification of products from byproducts, and the removal of contaminants from air and water effluents. Overall, these processes account for 40 to 70% of both the capital and operating costs of a broad range of industries. Separation technologies include distillation, extraction, adsorption, crystallization, and membrane-based technologies. Of these technologies, distillation is clearly the most widely used; it accounts for more applications than all the others combined. The purpose of this paper is to present a state-of-the-art review on distillation. Options for improving existing distillation columns are also discussed.

**E-93-3  NO LONGER AVAILABLE**
Membrane extraction is a process which has received a great deal of attention in recent years. Traditional roles for membranes utilize a membrane's species selectivity characteristic. One of the newer applications for membranes is liquid-liquid extraction. This report covers tests of a radial cross-flow microporous hollow-fiber membrane extractor. This extractor resembles a shell-and-tube heat exchanger with flow through the fibers being like flow through the tubes, and flow outside the fibers being like flow on the shell-side. The fibers are polypropylene; hence they are hydrophobic. When running the membrane extractor it is necessary to apply a pressure differential to form an interface at the pores of the hollow fibers. In this report, measured mass-transfer characteristics of a baffled radial-flow hollow-fiber membrane extractor are described. The performance of the system was analyzed by calculating volumetric mass-transfer coefficients, heights of a transfer unit, stage efficiencies, and heights equivalent to a theoretical stage. These characteristics were then compared to those of a membrane module tested earlier, as well as with conventional column-type contractors. Results from the test system n-butanol/ succinic acid/water were compared with those for two other systems using the same membrane module. The butanol was on the tube-side while the water was on the shell-side. It was determined that the shell-side resistance controlled the overall resistance. The overall stage efficiency of the module decreased as the shell-side velocity increased. The Liqui-Cel(r) Extra-Flow module clearly outperformed the earlier MHF module. During high shell-side velocities when the tube-side velocity was held constant, the water broke through. The Extra-Flow module has a much lower efficiency than a comparable differential contactor, however. The membrane did compare favorably with a spray extraction column run at low organic velocities. It was confirmed that the equilibrium distribution coefficient greatly affects the overall mass-transfer coefficient.

Liquid-liquid extraction is a process for the separation of one or more components of a liquid mixture through contact with a second immiscible liquid called a solvent. If the components in the original solution distribute themselves differently between the two liquid phases, separation will occur. With the availability of process simulators the number of equilibrium stages required for an extraction separation can be easily calculated. However, to complete the column design, it is necessary to estimate and apply mass-transfer efficiency so that equilibrium stages are corrected to actual ones. It is also necessary to estimate column flood rates so that column diameter and capacity can be determined. The efficiency and capacity of a liquid-liquid extractor will depend on flow rates, compositions, fluid mixing patterns, properties of the fluids, and column internals. In many extraction applications it may be advantageous to replace sieve trays with structured packings to enhance mass-transfer efficiency and capacity. Extractors equipped with structured packing are becoming more important, and this paper will present the information needed for design of this type of extractor.

Supercritical fluid extraction (SFE) has generated considerable research, development, and commercialization activity in recent years because of its potential to reduce overall energy use and eliminate the use of solvents with undesirable health and environmental characteristics. A bulletin by the Electric Power Research Institute (EPRI) describes the SFE process, applications, and energy savings potential.
E-94-2
Liquid-Liquid Extraction Studies on Semi-Commercial Scale Using Recently Commercialized Large Membrane Contactors and Systems
Sengupta, A.; B. Reed; A. F. Seibert
Presented at the AIChE National Convention, San Francisco, California, November 1994
The performance of a commercial-scale hollow fiber extraction system was investigated by the Separations Research Program at The University of Texas at Austin. The baffled radial flow hollow fiber membrane system and funding for this project were provided by the Hoechst-Celanese Corporation. The mass transfer characteristics of a new hollow fiber contactor for liquid-liquid extraction compared favorably to that of a packed column for the chemical system studied. In this work, n-hexanol was extracted from water into n-octanol. In the membrane contactor studies, the octanol-rich phase was fed on the tube-side while in the packed column studies, the octanol-rich phase was chosen as the dispersed phase. This chemical system was chosen because of its high solute distribution coefficient. For liquid-liquid systems of this type, the required solvent to feed ratio is very low which creates hydraulic problems for conventional dispersive extractors such as the packed column. Under identical operating conditions, the mass transfer performance of the hollow fiber extractor compared favorably with that of a commercial-scale type-2 structured packing. A height equivalent to a theoretical stage of 5 feet was obtained with the membrane contactor as compared to 50 feet for the type-2 structured packing. A staged hollow fiber extraction mass transfer model has been developed and was found to agree with data obtained in this work and with data obtained earlier with the n-butanol/succinic acid/water system. A final report summarizing all the experimental data and modeling work is provided.

E-95-1 PUBLISHED
Structured Packings in Liquid-Liquid Extraction
Seibert, A. F. and J. L. Humphrey
Extractors equipped with structured packing are becoming more important in the chemical process industries. These devices provide high mass transfer efficiency and capacity relative to random packings and sieve trays. At the present time, many sieve tray extractors are being retrofitted with structured packings to enhance mass transfer efficiency and capacity. This paper will present a comparison of the performance of structured packing with sieve trays, some background on the commercial development of structured packings, and fundamental models required to design a liquid/liquid extractor equipped with structured packing.

E-95-2
Performance and Economic Evaluation of the Cocurrent Tray
Seibert, A. F. and J. R. Fair
Presented at the AIChE Spring National Meeting, Houston, Texas, March 1995
The cocurrent tray is a contacting device for use in distillation and absorption columns. It performs on the principle similar to that of a conventional tray, except in the operation of the cocurrent tray, vapor is flowing at such a rate that liquid is purposely entrained. The cocurrent tray is designed with an entrainment separator located at the top of the tray. The separated liquid is collected and is fed to the inlet of the next downcomer. Two variations of the cocurrent tray have been studied at the Separations Research Program. These tests were carried out under distillation conditions using the cyclohexane/n-heptane test mixture at four pressures. A similar study of a conventional sieve tray was also made for comparison purposes. The cocurrent tray was observed to provide a higher mass transfer efficiency with twice the capacity of the sieve tray. The performance of the cocurrent tray has been shown to be amenable to mechanistic mass transfer and hydraulic modeling. The predicted results from these models agree with our experimental data. The enhanced capacity of the cocurrent tray suggests that this device may be of great value in the retrofit of conventional tray columns where a significant increase in capacity is desired. Two potential retrofit applications are presented in this paper: propylene/propane and ethylene/ethane separations.
Replaces F-95-3
Liqui-Cel(r) Membrane Contactors for Liquid-Liquid Extraction
Seibert, A. F.; J. L. Humphrey; A. Sengupta; B. W. Reed
To be presented at the International Solvent Extraction Conference, Melbourne, Australia, March 17-21, 1996

Liqui-Cel(r) Extra-Flow Membrane Phase contactors made with microporous hollow fibers have been used in the laboratory for extraction of organic solutes from aqueous feed phases into organic extractants. The recently developed contactors with "radial flow" design, based on flow across banks of hollow fibers inside a contactor, have been shown to have higher mass transfer efficiency and capacity compared to the previous "parallel flow" devices. In addition, new contactors with all olefinic components are being manufactured that are much more chemical resistant compared to the older products. Data on the extraction efficiency of membrane contactors are presented for two classes of organic solutes. Membrane contactors can have a number of advantages over conventional contactors, including dispersion-free contacting, efficient contacting of phases at widely different feed to solvent flow rates, ability to handle feed and solvents with the same density, and ease of scale-up. Two of the important parameters affecting the capacity and the efficiency of the membrane contactors are the distribution coefficient of the solute between the feed and the solvent phase, and the interfacial tension between the aqueous feed and the organic solvent. In general, higher distribution coefficient increases the efficiency, and higher interfacial tension improves the capacity. The performance of a Liqui-Cel(r) membrane unit with multiple contactors in modular forms has been compared with that of a packed extraction column with a type 2 structured packing under identical conditions for one test system. Based on actual data, an economic evaluation was conducted to compare capital and operating costs of the Liqui-Cel(r) technology vs. the conventional extraction technologies. It appears that there are potential applications where the membrane extraction technology would have very favorable performance-to-cost ratios compared to the competing technologies.

Performance of Trays and High Efficiency Packings for the Extraction of Methanol from Hexane with Water
Seibert, A. F.; J. A. Garcia; J. R. Fair,
Presented at the AIChE Meeting, Miami Beach, Florida, November 13, 1995

The purpose of this study was twofold: first to determine how various commercial size contacting devices would perform under conditions of high dispersed to continuous phase flow ratios, and secondly to determine how the column diameter and packing height would affect the overall extraction efficiency. The SRP large-scale extraction system was utilized to determine the performance of 1.5 inch Pall rings, no. 40 IMTP, SMVP-32, sieve trays and the spray column in extracting methanol from hexane with water. The Pall rings and no. 40 IMTP are random packings while the SMVP is a structured packing with a perforated plate located between each element.

Scale-Up of Hollow Fiber Extractors
Seibert, A. F. and J. R. Fair
Presented at the Separation Science and Technology Meeting, Gatlinburg, Tennessee, October 23, 1995

The performance of a commercial-scale hollow fiber extraction system was investigated by the Separations Research Program (SRP) at the University of Texas at Austin. In this work, hexanol was extracted from water into octanol using a large-scale extraction/distillation system. In the membrane contactor studies, the octanol-rich phase was fed on the tube-side while in the packed column studies, the octanol-rich phase was chosen as the dispersed phase. This chemical system was selected because of its high solute distribution coefficient. For liquid-liquid systems of this type, the required solvent to feed ratio is low which creates hydraulic problems for conventional dispersive extractors such as the packed column. Under identical operating conditions, the mass transfer performance of the hollow fiber extractor compared favorably with that of a commercial-scale type 2 structured packing. A height equivalent to a theoretical stage (HETS) of 1.5 meters was obtained with the membrane contactor as compared to 15 meters for the type 2 structured packing. A staged hollow fiber extraction mass transfer model for scale-up was developed and
E-96-1
Performance of High Efficiency Packings in Liquid Extraction
Seibert, A. F. and J. R. Fair
Presented at the AIChE Annual Meeting, Miami Beach, Florida, November 15, 1995

The debottlenecking of existing processes has become attractive because of the improving chemical and petrochemical markets. As a result, many older liquid-liquid extractors are being reevaluated to take advantage of the newer high efficiency packings. This has created a need for additional commercial-scale performance data for the development of flooding and mass transfer models. High efficiency packings may be random or structured. These packings provide high void fraction for capacity and high surface area for drop tortuosity and efficiency. In the present work, performance data and modeling information for no. 40 IMTP, 3.8 cm Pall rings, a type 2 structured packing and the SMVP packings are presented. The SMVP is a type 2 smooth sheet metal structured packing which incorporates dual flow plates between each element. Data on three chemical systems, toluene/acetone/water, octanol/hexanol/water and water/methanol/hexane, are included. The effect of system properties, mass transfer direction, and flow ratio are reported.

E-97-1
Performance of Dualflow and Sieve Trays in Liquid Extraction(revised to include coalescer results)
Seibert, A. F. and J. R. Fair
Manuscript on file, Separations Research Program, June 17, 1997

The mass transfer efficiency and phase flow capacity of sieve trays has been investigated using a 10.2 cm diameter glass extractor. The objective of this study was to determine the performance of sieve trays relative to dual flow trays for a possible retrofit application. The system studied in this work involved the extraction of an acid from an organic carrier with distilled water. The capacity of the sieve trays was observed to be approximately 80% greater than the dual flow trays. The average mass transfer efficiency of the sieve trays was observed to be approximately 15-20% lower than the dual flow trays. The measured efficiency was approximately 25% less than would be predicted using the mechanistic efficiency model of Treybal. The height of the uncoalesced layer was observed to be reduced 60-100% by adding a hydrophobic coalescer to the operating interface. Measurements of the height of the coalesced layer, drop diameter and flooding velocity agreed well with the predictive models.

E-98-1
Performance of Sieve Trays and Baffle Trays in Liquid Extraction
Seibert, A. Frank and J.R. Fair
Manuscript on file, Separations Research Program

The performance of sieve trays and special baffle trays has been investigated using an actual industrial feed and solvent system. A 10.2-cm diameter glass extraction system, located at an operating plant facility, was connected to slip streams from an industrial extraction process. The objective of this study was to compare the performance of sieve trays to donut-type baffle trays for a possible retrofit application. The system studied involved the extraction of a ketone component from an aqueous carrier using a hydrocarbon solvent. The capacity of the sieve trays was observed to be approximately 50% greater than that of the baffle trays. An equilibrium pinch at the bottom of the extractor was observed using the recycled solvent because of the presence of a significant concentration of solute in the feed solvent. As a result, separate runs were made using pure solvent. The average mass transfer efficiency of the sieve trays was observed to be approximately 50%, compared with approximately 40% for the baffle trays. The improved efficiency of the sieve trays may have resulted from complete utilization of the column cross-sectional area. The high tray efficiencies resulted from the system's unique physical properties of high-density difference and low interfacial tension, which provided many small and fast-moving drops. The measured sieve tray efficiency agreed very well with the SRP efficiency model. A hydrophobic structural packing, added as a coalescer, appeared to enhance phase separation at the operating interface.
Performance of a Sieve Tray and Spray Extractor with High Solute Transfer
Seibert, A. Frank and J.R. Fair
Manuscript on file, Separations Research Program

Hydraulic Study of a Sieve Tray Extractor Operated under High Dispersed to Continuous Flow Conditions
Seibert, A.F.
Manuscript on file, Separations Research Program
The Separations Research Program (SPR) engaged in a series of hydraulic studies to determine the hydraulic characteristics of an extractor operated under high dispersed to continuous flow conditions. A four-inch diameter (i.d.) glass column filled with sieve trays was utilized to observe average drop diameters, percent hole activity, and height of the coalesced layer. The effects of phase flowrate, flow ratio and downcomer length were determined. While the mass transfer efficiency was not obtained, the effect of mass transfer was noted. The experiments were videotaped to demonstrate the effect of mass transfer and phase rate.

Design Manual Liquid-Liquid Extraction
Seibert, A.F. and Jacinto Lopez-Toledo
This manual represents an update to our current thinking on the design of spray, sieve-tray, and packed extraction columns for use in liquid-liquid or supercritical fluid extraction processes. A membrane extraction option is also included. In Version 5.0, we have modified the programming language to utilize Excel 95 or 97. This design manual and accompanying diskette utilizes many of the fundamentally consistent models developed by the SRP over the past eleven years. The design equations have been verified under a wider range of physical properties including supercritical fluid conditions. The packing and sieve-tray models have also been tested and verified with results obtained from a 16.8 in (i.d.) liquid-liquid extractor. Since these models have only been compared with experimental data obtained from pilot-scale units, some precaution must be taken when designing a large commercial-scale column. Replaces E-89-6.

Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study
Seibert, A. Frank; J.R. Fair; Olujic, Z.
Paper for AIChE Spring National Meeting, March 14-18, 1999, Houston, TX.
While the utilization of corrugated sheet structured packings is well established, these gas/liquid contacting devices are still not well understood. A contributing reason is that rather limited publicly available performance data, most of which have been obtained from relatively small columns. Total reflux distillation experiments were carried out at SRP using a bed height of 3.3 m for all packings. The cyclohexane/n-heptaned system was utilized because of the availability of comparative data. The operating pressure was varied from 0.33 to 4.14 bar, to determine the effect of physical properties. The resulting data provided insight into the nature and effect of corrugation angle, specific surface area, and surface texture on pressure drop, capacity and efficiency. In the paper we report the results and also discuss the implications of the observations on model development and design.

Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study.
Seibert, A. Frank; J.R. Fair; Olujic, Z.
Manuscript on file, to be published in Chemical Engineering and Processing
Although the technology associated with the use of structured packing may be considered mature, there is still inadequate experimental evidence in the open literature to provide a firm basis for the development and validation of general and reliable models for predicting packing performance.
This article presents results from a study from J. Montz GmbH and Separations Research Program, using a conventional pilot scale distillation column at the SRP to determine the corrugation angle effect with its Bl- and BSH series packings. The revealing effects of packing geometry and corrugation angle on mass transfer and hydraulic performance are presented and discussed in this article.

**E-99-4**

**Design/Analysis of Wiped Film Evaporators**

Rocha, J. Antonio. Approved by James R. Fair and A. Frank Seibert

Manuscript on file

The wiped film evaporator (WFE) is a versatile device often used to process liquids having high viscosities, temperature sensitivity, fouling or foaming tendencies, or in general needing very short residence times in heated zones. It may be specified for evaporation, stripping or distillation services, often at low pressures. Wiped film evaporators may have advantages over more conventional evaporators when there are critical mass and/or heat transfer limitations.

**E-99-5**

**Continuous Phase Axial Mixing in Packed Large-Scale Liquid-Liquid Extraction Columns**

Becker, Oliver

Research Report

The scope of this work is to measure the axial dispersion coefficient of the continuous phase in different structured and random packings and in an industrial scale extraction column to enable more reliable design calculations of static spray and packed extraction columns.

**E-00-1**

**Axial Mixing in a Large-Scale Packed Extractor**

Seibert, A. Frank; Oliver Becker; R. Hardy


Interest in retrofitting existing tray-type extractors with structured packing continues to increase. Relative to typical tray devices, structure packings can provide an increased capacity, improved interface control, and improved mass transfer efficiency. However, since packings were developed for distillation to minimize pressure drop, they may be subject to axial mixing, which degrades the separation. In this paper, axial mixing data and models are presented based on four contacting devices: spray, SMV-32, SMVP-32 and SMP-16.

**E-00-2** PUBLISHED

**Mass-Transfer Efficiency of a Large-Scale Sieve Tray Extractor**

Seibert, A.F. and J.R. Fair


The mass transfer efficiency and phase flow capacity of a 425-cm-diameter (i.d.) sieve tray extractor has been investigated. The extraction of acetone from water with toluene was chosen because of the large amount of data for comparison with the performance of other devices, and particularly because of available data for smaller sieve tray extractor tested in the same laboratory. For capacity studies, the Isopar-m/water system was also used. The performance of the sieve trays was compared with that of sprays and packings in the same column. Important parameters were found to be phase flow rates, flow ratios, and column diameter. Mechanistic hydraulic and mass transfer models, found to correlate well the experimental data, are presented in the paper.

**E-00-3**

**Liquid-Liquid Extraction References**

Seibert, A.F.; Fair, J.R; Fisher, Ernest

Manuscript on File

Liquid-Liquid Extraction Bibliography compiled, October 1,2000. Categories include: Phase Equilibria and Physical Properties; Stages/Transfer Units/Rate-Based; Hydraulics-Trays; Hydraulics-Packing; Hydraulics-Mechanical Aided; Mass Transfer-Trays, Packings, Other
Sieve tray extractors continue to be highly utilized in the chemical and petrochemical industries. The trays are inexpensive, simple, and have demonstrated the ability to handle very high throughputs. Their mass transfer efficiency, while somewhat limited, is often adequate and may be compensated for by a modest increase in the solvent to feed ratio. However, the tray hydrodynamics are very complex and not well understood, especially in large diameter columns. As a result, expected throughputs may not be realized. Unfortunately, use of a single model or correlation developed from laboratory-scale equipment to predict sieve tray flooding velocities would likely be unreliable. A close look reveals that there are six significant and distinct mechanisms that limit capacity. These mechanisms have been observed in the Separations Research Program 10.2 and 42.8 cm diameter extractors and have also been reported by SRP industrial sponsors. The objective of this paper is to address briefly the important mechanisms that limit capacity of tray extractors. A collateral objective is to familiarize process engineers with these mechanisms.
**E-01-6**

Performance Characteristics of a New High Capacity Structured Packing
Paper submitted to Chemical Engineering Processing, June 2001

**E-01-7**

Pressure Drop in Packed Distillation Columns: Evaluation of Predictive Models
Sanchez, P.; Seibert, A.F.; Fair, J.R.
To be presented at the Fall AIChE Meeting in Reno, Nevada, November 2001.

**E-01-8**

Sieve Tray Extractors: A Closer Look at Capacity Limitations
Seibert, A.F.; Fair, J.R.; Bravo, J.L.
ISEC 2002, March 2001

Sieve tray extractors continue to be highly utilized in the chemical and petrochemical industries. The trays are inexpensive, simple and have demonstrated the ability to handle very high throughputs. Their mass transfer efficiency, while somewhat limited, is often adequate and may be compensated for by a modest increase in the solvent to feed ratio. However, the tray hydrodynamics are very complex and not well understood, especially in large diameter columns. As a result, expected throughputs may not be realized. Unfortunately, use of single model or correlation developed from laboratory-scale equipment to predict sieve tray flooding velocities would likely be unreliable. A close look reveals that there are six significant and distinct mechanisms that limit capacity. These mechanisms have been observed in the Separations Research Program (SRP) 10.2 and 42.8 cm diameter extractors and have also been reported by SRP industrial sponsors. The objective of this paper is to address briefly the important mechanisms that limit capacity of sieve tray extractors. A collateral objective is to familiarize process engineers with these mechanisms.

**E-01-9**

High-Capacity Bubble Columns
Seibert, A.F.; Fair, James R.
Presentation at the Separations Research Program, October 9, 2001.

The bubble column, or gas-sparged contactor, is a simple arrangement of a vessel containing a gas sparger - and little else. When operated on a continuous basis, liquid is fed to the column at some selected elevation, and gas is passed up through the vessel in the form of bubble swarms. It has been used extensively for gas-liquid reactions. Variations include the use of suspended solid catalysts and slurry feeds, in both cases taking on a more complex character because of the third phase. To deal with heat effects, cooling surfaces can be installed within the vessel. There are also cases on record where trays have been inserted to mitigate the strong trend toward complete mixing of liquid in the contactor. Some example process applications are fermentations, benzene hydrogenation, and cumene oxidation.

**E-02-1 NEW**

Ask the Experts, Extraction
Seibert, A.F
CEP Magazine, June 2002, p. 74
Discussion of when to consider liquid extraction.

**E-02-2**

Baffle Tray Performance in Liquid Extraction
Seibert, A.F.; Chris Lewis; James Fair
Presented at the 2002 Annual AIChE Meeting, Indianapolis, IN., November 8, 2002

In liquid extraction the presence of solids creates many challenges, not the least of which is the selection of an appropriate contacting device. While mixer-settlers can be used, this option may be unattractive if three or more equilibrium stages of separation are required. A static device that may have application for this service is the baffle tray column, with segmental and sloped baffles. However, very
little has been published on baffle tray performance in extraction. The hydraulic nature of the dispersed phase is unknown. The effects of variables such as system properties, tray overlap and tray spacing are also unknown. Studies were made to determine the effect of these variables on dispersed phase hydrodynamics, column throughput capacity and mass transfer efficiency. System property effects were investigated using the toluene(d)/acetone/water(c) and butanol(d)/succinic acid/water(c) systems. Solute was transferred from the organic to the aqueous phase. Tray spacings of 2, 4 and 12 inches were used together with tray overlaps of 0 and 62%. The objectives of this work were to obtain flooding and mass transfer data using a 4.0-inch i.d. baffle tray column. New baffle tray extraction models, developed from the new experimental data, are presented in this paper. (Keywords: baffle tray extraction, efficiency, capacity and models)

E-03-1
Trays Versus Packing: Selection of the Optimal Extractor
Seibert, A.F.; Fair, J.R.; Bravo, J.L.
Presented at the Annual AIChE Meeting, November 2003

E-04-1
The Oldershaw Column: Useful for Solving Distillation Problems
Seibert, A.F. and Fair, J.R.
Paper submitted to Chemical Engineering Progress, 2005

E-04-2
Liquid Side Mass Transfer Resistance of Structured Packings
Seibert, A.F.; Murrieta, C.R.; Fair, J.R.; Rocha-U, J.A.
Paper accepted by Industrial and Engineering Chemistry Research, 2004

E-04-3
Effective Gas/Liquid Contact Area of Packing for CO₂ Absorption/Stripping
Seibert, A.F.; Lewis, C.; Wilson, I.; Rochelle, G.
GHGT-7 Conference in Vancouver, September 2004

E-05-1
Extraction and Leaching
Seibert, A.F.

E-05-2
Effect of Viscosity on the Hydraulic performance of a Karr Extractor
Rocha, T., Rochelle, T. and Seibert, A.F.
SRP Technical Report, September 2005

E-05-3
Treatment of Air Pollutants Emitted from Corn-derived Ethanol Production Facilities
ASCE Journal of Environmental Engineering, Spring 2006, Submitted

E-06-1
Baffle Tray Extraction
Seibert, F., Lewis, C., and Fair, J.

E-06-2
Increasing Distillation Column Throughput
Dzyacky, G., Seibert, F., and Lewis, C.
Petroleum technology Quarterly, Q4 2005, pp. 99-104
EL-99-1
HETP and Pressure Drop Prediction for Structured Packing Distillation Columns Using a Neutral Network Model
Whaley, A.K., Bode, A., Ghosh, J., and Eldridge, R.B.
A neural net framework was used to predict the mass-transfer and hydraulic performance of a commercial structured packing operating in distillation service. The results indicated that the approach produced a more accurate prediction than a traditional semi empirical model. The neural net methodology was also used to yield a detailed sensitivity analysis of the operating variables.

EL-00-1
Neural Network Modeling of Structured Packing Height Equivalent to a Theoretical Plate
Pollock, G.S. and Eldridge, R.B.
The height equivalent to a theoretical plate (HETP) of nine types of structured packing was successfully modeled using a neural network. The network was trained on data similar to that used to develop semi empirical mass-transfer models. The HETP was then predicted using the trained network. The neural network model yields a very accurate prediction of experimentally determined HETP values, and it is also possible to rank the relative importance of input variables in determining the HETP. In particular, this work shows that the roughness of the structured packing surface is a very important input parameter.

EL-00-2
Process Tomography: An Option for the Enhancement of Packed Vapor-Liquid Contactor Model Development
Schmit, C.E., Cartmel, D., and Eldridge, R.B.
A multitude of packed vapor-liquid contactor mass-transfer and hydraulic models exist in the literature. With few exceptions, the development of these modes has been based on a very limited understanding of the microscale hydraulic phenomena inside the contacting column. Recently, the use of X-ray tomography has been shown to be an effective technique for imaging flow patterns in multiphase contactors. This paper describes the potential benefits that X-ray tomography analysis can bring to the understanding and modeling of the vapor-liquid contacting process. The technology has significant potential for enhancing the prediction of both mass-transfer efficiency and packing pressure drop of commercial packed columns.

EL-01-1
The Experimental Application of X-ray Tomography to a Vapor-Liquid Contactor
Schmit, C.E., Cartmel, D.B., and Eldridge, R.B.
Initial results obtained from the application of X-ray tomography to an operating vapor-liquid contactor indicate that the technology has the potential to provide insight into the underlying hydraulic behavior of a packed column. Experiments were performed with counter-current air-water flows in a 6-in-diameter contactor packed with random packing. Liquid and gas velocities typical of commercial column were tested. Liquid distribution patterns and holdup values were obtained for three tower elevations. The majority of liquid holdup values obtained from the tomography experiments were within 15% on the parity plot of model versus experiment. The experimental flow patterns for random packing showed a preference for the liquid stream to flow in rivulets.

EL-02-1
A Comparison of Steady-State Equilibrium and Rate-Based Models for Packed Reactive Distillation Columns
Peng, J., Lextrait, S., Edgar, T.F., and Eldridge, R.B.
A steady-state equilibrium model and a rate-based model were developed and compared for packed reactive distillation columns for the production of ter-amyl methyl ether (TAME) and methyl acetate. For the methyl acetate system, both models yield good agreement with experimental data. The results predicted by the equilibrium and rate-based models are similar with few differences found under all simulation conditions. However, the rate-based model is much more complicated than the equilibrium model and also more difficult to converge. The influence of the reflux ratio, the operating pressure, the catalyst amount, and the heat loss was studied. It was found that reactive distillation behaves very differently from ordinary distillation. The existence of an optimal reflux ratio and an optimal pressure is predicted by both models.

**EL-02-2**

Prediction of the Trayed Distillation Column Mass-Transfer Performance by Neural Networks
Olivier, E. and Eldridge, R.B.

The sieve-tray distillation column mass-transfer efficiency was successfully modeled using a neural network. The database developed by Garcia and Fair (*Ind. Eng. Chem. Res.* 2000, 39, 1809) was utilized to train and validate the neural network model. The results indicate that, if the system is similar to the data used to train the neural network, the purely empirical neural network model yields very accurate predictions. However, in areas where data are lacking, even if the input parameters are in the same range as those in the database, the neural network model must make extrapolations and will therefore make unreliable predictions. MS Excel programs based on the results from neural networks were developed for the prediction of the sieve-tray efficiency and structured packing height equivalent to a theoretical plate. These programs represent a convenient and easy to use tool. Moreover, they make better predictions than a single neural network and make it possible to detect extrapolations and misleading predictions.

**EL-03-1**

Dynamic Rate-Based and Equilibrium Models for a Packed Reactive Distillation Column
Peng, J., Lextrait, S., Edgar, T.F., and Eldridge, R.B.

Dynamic rate-based and equilibrium models were developed for a packed reactive distillation column for the production of ter-amyl methyl ether (TAME). The two types of models, consisting of differential algebraic equations, were implemented in gPROMS and dynamic simulations were carried out to study the dynamic behavior of reactive distillation of the TAME system. The dynamic responses predicted by the two types of models are similar in general, with some differences in steady-state values. The influence of manipulated variables, such as distillate flow rate, reflux ratio, and reboiler duty, on the dynamic responses of the controlled variables (reactant conversion and product purity) was studied. The dynamic response of reactant conversion is very nonlinear and unconventional, but the response of product purity is well approximated by a linear first-order differential equation. The CPU time required to complete a dynamic simulation of the rate-based model is at least an order of magnitude higher than that for the equilibrium model. Therefore, the dynamic rate-based model is much more complicated than the equilibrium model, and simplification of the rate-based model is necessary for the implementation of model-based control. A new approach was proposed to simplify the dynamic rate-based model by assuming that the mass transfer coefficients are time invariant. This approach was demonstrated to be superior to the conventional simplification methods. It can reduce the number of equations by up to two-thirds and still accurately predict the dynamic behavior.

**EL-04-1**

Use of Electrochemistry to Predict Ethylene Absorption Capacities of Reactive Absorption Systems

**EL-04-2**

Steady-State Rate-Based Simulation of Packed Reactive Distillation: Spatial Discretization
Lextrait, S., Edgar, T.F., and Eldridge, R.B.
**EL-04-3**
Investigation of X-Ray Imaging of Vapor-Liquid Contactors 1. Studies Involving Stationary Objects and a Simple Flow System
Schmit, C. and Eldridge, R.B.

**EL-04-4**
Investigation of X-Ray Imaging of Vapor-Liquid Contactors 2. Experiments and Simulations of Flows in an Air-Water Contactor
Schmit, C., Perkins, J., and Eldridge, R.B.

**EL-04-5**
Adsorption Equilibrium and Kinetics for Ethylene-Ethane Separation with a Novel Solvent
Reine, T.A. and Eldridge, R.B.

**F-86-1**
Interfacial Tension of Extractor Test Mixtures
Lehmann, L. K.; R. B. Eldridge; J. R. Fair
Manuscript on file, Separations Research Program
The purpose of this study was to make comparisons between the interfacial tensions of pilot-plant extraction mixtures, which are subject to normal contamination that might change interfacial tension, and those of clinically prepared mixtures of the same nominal composition. Replaces F-86-4

**F-86-3 $10.00**
Mass-Transfer Efficiency of a Supercritical Fluid Extraction Column
Rathkamp, P. J.
Master's thesis
Experimental studies were performed in a 1-inch-diameter supercritical fluid extraction column operated in both a spray-column arrangement and a packed-column arrangement using 1/4-inch Raschig rings. Mass-transfer and hydraulic characteristics of the SFE system were studied. It can be concluded from this work that SFE in spray and packed columns can be carried out at relatively high mass-transfer efficiencies. Approximate comparisons with conventional extraction data indicate that SFE efficiencies may be as much as ten times as great.

**F-86-5 $10.00**
Mass-Transfer and Hydraulic Characteristics of a Supercritical Fluid Sieve Tray Extractor
Lahiere, R. J.
PhD dissertation
The mass-transfer and hydraulic characteristics of a 2.54-cm-diameter sieve tray extraction column operating with supercritical and liquid solvents were investigated. A mechanistic mass-transfer model was developed to predict the overall efficiency of a sieve tray column operating with these solvents.

**F-86-6 $10.00**
Mixing Characteristics of a Crossflow Sieve Tray Extractor
Eldridge, R. B.
PhD dissertation
The degree of continuous-phase backmixing for a sieve tray extractor was determined to be a function of fluid physical properties, stream flow rates, and tray spacing. Hydraulic characteristics of the liquid-liquid contacting were also studied.
Hydrodynamics and Mass Transfer in Spray and Packed Liquid-Liquid Extraction Columns
Seibert, A. F.
PhD dissertation
The objective of this research was to develop fundamental hydraulic and mass-transfer models to be used in the design and scale-up of packed towers in liquid-liquid extraction service. Data were obtained for a variety of structured and random packings.

Efficiency of a Controlled-Cycle Extractor
Seibert, A. F.; J. L. Humphrey; J. R. Fair
Experimental studies were performed with a 4-inch-diameter extraction column containing ten dual flow trays and operating in a controlled cycling mode. A nonequilibrium model was developed to represent the experimental data. This paper is a summary of Seibert's thesis work (H-84-4).

Hydrodynamics and Mass Transfer in Supercritical Fluid Extraction
Handout for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Seibert for the Supercritical Extraction Study Group Meeting.

Liquid-Liquid Extraction: Possible Alternative to Distillation
Fair, J. R. and J. L. Humphrey
A tutorial paper on the liquid-liquid extraction process and equipment.

The Essentials of Extraction
Humphrey, J. L.; J. A. Rocha.; J. R. Fair
Chemical Engineering 91(19):76-95 (1984)
Comprehensive review article-includes liquid-liquid and supercritical fluid extraction.

Efficiency of Crossflow Sieve Tray Extractors
Fair, J. R.; J. A. Rocha; J. L. Humphrey
Existing mass-transfer models were evaluated and conclusions drawn on their accuracy. A data bank was presented. Conclusions were drawn regarding the importance of the Weber number in predicting mass-transfer efficiency.

Study and Prediction of Efficiency of a Controlled Cyclic Extractor
Seibert, A. F.
Master's thesis
Experimental studies were completed and a model was developed for a 4-inch diameter, controlled-cycle extractor containing 10 sieve trays. A manuscript summarizing the research is F-86-9.

Supercritical Fluid Extraction Applications in the Process Industries
Lahiere, R. J.; J. R. Fair; J. L. Humphrey
This paper is a review of the potential applications of this relatively new separation process.

**H-85-2**

**Mass-Transfer Efficiency of Sieve Tray Extractors**
Rocha, J. A.; J. L. Humphrey; J. R. Fair
Manuscript on file, Separations Research Program

A substantial amount of new data taken in a 4-inch-diameter, liquid-liquid extractor is presented. A new mechanistic model to predict mass-transfer efficiency as a function of extractor geometry, operating conditions, and system properties has been developed.

**H-85-3** $10.00

**Mass-Transfer Efficiency of Sieve Tray Liquid-Liquid Extraction Columns**
Rocha, J. A.
PhD dissertation

A substantial amount of experimental data was taken in a 4-inch-diameter extractor with 10 sieve trays. A new and generalized model for the prediction of mass-transfer efficiency in sieve tray extractors was developed. The model fits the total data bank with an accuracy of ±35%, a greater accuracy than can be achieved with other mechanistic models.

**H-85-4 PUBLISHED**

**Mass-Transfer Efficiency of Sieve Tray Extractors**
Rocha, J. A.; J. L. Humphrey; J. R. Fair

Report on an extensive study of variables affecting the efficiency of a small (4-inch) sieve-tray extraction column. Includes a new and improved model for predicting efficiency. Revised version of H-85-2.

**H-85-5 NO LONGER AVAILABLE**

**H-85-6 NO LONGER AVAILABLE**

**H-85-7 PUBLISHED**

**Evaluation of Packings for Use in Liquid-Liquid Extraction Processes**
Seibert, A. F.; J. L. Humphrey; J. R. Fair

Results of a study of several random and structured packings in a 4-inch column using two test systems. A tentative model for performance is included.

**H-85-8 PUBLISHED**

**Continuous-Phase Mixing on Crossflow Extraction Sieve Trays**
Eldridge, R. B.; J. L. Humphrey; J. R. Fair

Results of early axial mixing studies in a special sieve-tray simulator. Peclet number was found to be a suitable correlating parameter. Discussion of the influence of axial mixing on Murphree tray efficiency.

**H-85-9 PUBLISHED**

**Mass-Transfer in Countercurrent Supercritical Extraction**
Lahiere, R. J.; J. L. Humphrey; J. R. Fair

Experiments were made in a 1-inch column with packings and trays. Comparisons with extraction efficiencies for conventional conditions demonstrate the advantages of operating under supercritical conditions.

**H-86-2 NO LONGER AVAILABLE**
**Supercritical Fluid Extraction in Column Contactors**
Lahiere, R. J.; J. R. Fair; J. L. Humphrey
Presented at the International Solvent Extraction Conference, Munich, Germany, September 1986
This study used a 1-inch-column contactor fitted with a number of small sieve trays. Carbon dioxide/ethanol/water and CO2/isopropanol/water were the supercritical systems studied. To compare supercritical with conventional extraction, similar data were obtained in the same column with a toluene/acetone/water system. Preliminary experimental results indicate that favorable mass-transfer efficiencies are possible with commercial-scale supercritical extraction equipment. They also indicate that efficiency models for conventional extraction are not suitable for supercritical extraction. New models applicable to the supercritical case are being developed.

**Hydrodynamics of a Section of a Large Sieve Tray Extractor**
Eldridge, R. B.; J. L. Humphrey; J. R. Fair
Presented at the International Solvent Extraction Conference, Munich, Germany, September 1986
For this work a "slice" of a large extractor was constructed and equipped with windows for viewing drop mixing of the continuous phase were made by means of water-soluble or organic-soluble tracer dyes. The base systems for study were toluene/water and butanol/water. The results show that there is little enhancement of tray efficiency in either system. The enhancement is low in the toluene/water system because it exhibits characteristically low efficiencies and, even in the case of pure plug flow, only a small amount of enhancement would be possible. The enhancement in the butanol/water system was small because of the extent of backmixing in the continuous phase caused by a large and active population of very small drops. A model is being developed to predict values of the eddy diffusion coefficient as a function of the system properties, operating conditions, and geometry of the contactor.

**Flue Gas Desulfurization/Acid Gas Treatment**

**Buffer Additives for Limestone Scrubbing: A Review of R&D Results**
Rochelle, G. T.
A comprehensive review of lab, pilot, and demonstration activities in the development of organic additives. Includes quantification of effects on scrubber performance and required makeup rates of buffers such as adipic acid and dibasic waste acids.

**Limestone Dissolution in Stack Gas Desulfurization**
Toprac, A. J. and G. T. Rochelle
Environmental Progress 1(1):52-64 (1982)
Includes experimental studies with 19 types and grinds of CaCO3. Modeling by mass transfer is done using actual particle size distributions.

**Limestone Dissolution: Effects of pH, CO2, and Buffers Modeled by Mass Transfer**
Chan, P. K. and G. T. Rochelle
Experimental studies of the dissolution of reagent CaCO3 (calcite) show that dissolution is inhibited by dissolved sulfite. Includes primary modeling of mass transfer with equilibrium acid/base reaction.
Limestone Dissolution in Flue Gas Desulfurization Processes
Rochelle, G. T.; P. K. Chan; A. J. Toprac
EPA report including theses by Chan and Toprac, NTIS PB 83-252833 (1983)
Experimental studies and modeling of CaCO3 dissolution. Mass transfer with equilibrium reactions using actual particle size distributions.

Modeling of SO2 Removal by Limestone Slurry Scrubbing: Effects of Chlorides
Chan, P. K. and Rochelle, G. T.
Presented at the EPA/EPRI Flue Gas Desulfurization Symposium, New Orleans, November 1983
Integration of mass-transfer CaCO3 dissolution and sulfite oxidation was used to predict SO2 removal as a function of chemistry.

Flue Gas Desulfurization
Rochelle, G. T.
Chapter 12 of Coal Processing and Pollution Control, T. F. Edgar (ed.), Gulf Publishing (1983)
A comprehensive review of FGD processes; includes detailed review of chemistry in limestone slurry scrubbing.

Calcium Sulfite Hemihydrate: Crystal Growth Rate and Crystal Habit
Tseng, P. C. and G. T. Rochelle
Environmental Progress 5(1):5-11 (1986)
Experiments with calcium sulfite hemihydrate show that crystal growth is controlled by surface kinetics, and crystal habit depends on solution composition and temperature. These experiments were conducted under conditions typical of flue gas desulfurization (R-84-1) (FGD) processes.

Enhanced Oxygen Absorption into Bisulfite Solutions Containing Transition Metal Ion Catalysts
Ulrich, R. K.; G. T. Rochelle; R. E. Prada
Chemical Engineering Science 41(8):2183-91 (1986)
Project designed to analyze the effects of various metal desulfurization conditions. Goals of the project were to determine what factors are important in fixing the reaction rate and to elucidate aspects of the reaction mechanism when common catalysts and inhibitors are present.

Buffer Additives for Lime/Limestone Slurry Scrubbing: Sulfite Oxidation with Enhanced Oxygen Absorption Catalyzed by Transition Metals
Ulrich, R. K. and G. T. Rochelle
Includes Ulrich's dissertation. In-depth study of sulfite oxidation focused on measuring the rate of enhanced O2 absorption. Results of the experiments indicate that Fe is probably the most important catalyst in scrubbers and that the combination of Fe and Mn is a very strong synergistic catalyst.

Buffer Additives for Lime/Limestone Slurry Scrubbing: Synthesis, Mass Transfer, and Degradation
Rochelle, G. T.; R. J. Smith; W. T. Weems; M. W. Hsiang; Y. J. Lee.
Report prepared for the US Environmental Protection Agency, Office of Research and Development. EPA-600/7-84-052. 1984. Includes three MS theses.
Various experimental investigations provide data for the evaluation of buffer additive alternatives. Experimenters used inexpensive, nonvolatile acids as buffers and emphasized buffer synthesis, gas-liquid mass-transfer enhancement, and oxidative degradation.
Activity Coefficients Predicted by the Local Composition Model for Aqueous Solutions Used in Flue Gas Desulfurization
Taylor, C. E.
Master's thesis issued as an EPA report, December 1984
Theoretical correlation of activity coefficients for aqueous species in FGD using the local composition model developed by MIT/ASPEN. Includes model parameters derived from data correlation.

Modeling of SO2 Removal by Spray Dryers
Jozewicz, W. and G. T. Rochelle
Presented at the Pittsburgh Coal Technology Conference, September 1984
Discussion of the integration of heat and mass transfer to predict SO2 removal. Usually under predicts full-scale systems.

Calcium Sulfite Hemihydrate Dissolution and Crystallization Dissolution and Crystallization
Tseng, P. C.
PhD dissertation issued as an EPA report, August 1984
Experimental measurements using pH-stat and Coulter counter show that dissolution is modeled by mass transfer, and crystallization is inhibited by CaSO4 saturation. Results of this work are summarized in R-84-1 and R-86-2.

Sulfite Oxidation Inhibited by Thiosulfate
Owens, D. R. and G. T. Rochelle
Report prepared for the US EPA, February 1985
Experimental studies showed that thiosulfate stopped sulfite oxidation at levels of 1-5 mM. Thiosulfate degraded quickly but is still economically viable for use in limestone slurry scrubbing. See R-85-6 for a summary of this report.

Effect of Deliquescent Salt Additives on the Reaction of Sulfur Dioxide with Dry Ca(OH)2
Ruiz-Alsop, R. N. and G. T. Rochelle
Experimental studies in a packed-bed reactor at 50°C to 80°C with 15% to 90% relative humidity show that sodium chloride and other salts greatly enhance the reactivity of reagent Ca(OH)2 solids.

Activity Coefficients Predicted by the Local Composition Model for Aqueous Solutions Used in Flue Gas Desulfurization
Taylor, C. E. and G. T. Rochelle
This paper shows the correlation of activity coefficients by the MIT/ASPEN local composition model. Parameters are developed for FGD aqueous species. Summarizes Taylor's thesis work.
R-85-5 PUBLISHED
Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes: A Review of R&D Results
Rochelle, G. T.; D. R. Owens; J. C. S. Chang; T. G. Brna
Journal of the Air Pollution Control Association 36:1138-46 (1986)
Review of laboratory and pilot-plant work. Shows that thiosulfate can be used as an economic additive to eliminate gypsum scaling, enhance solids dewatering, and enhance SO2 removal (R-85-5).

R-85-6 PUBLISHED
Sulfite Oxidation Inhibited by Thiosulfate
Rochelle, G. T. and D. R. Owens
Sulfite oxidation and thiosulfate degradation kinetics are correlated in closed form. Summary of laboratory work by Owens (R-85-1).

R-85-7 PUBLISHED
Fly Ash Recycle in Dry Scrubbing
Jozewicz, W. and G. T. Rochelle
Environmental Progress 5:218-23 (1986)
Reagents for SO2 removal were prepared by reacting Ca(OH)2 with fly ash in aqueous slurry at 25°C to 92°C for 2 to 24 hours. The calcium silicate/aluminate product was found to be much more effective than the original Ca(OH)2 for gas-solid reaction with SO2.

R-85-8
Dry Scrubbing: Fly Ash Recycle
Jozewicz, W. and G. T. Rochelle
Final draft report prepared for the US EPA, September 1985
This report contains detailed results of the material covered in R-85-7.

R-86-1 $10.00
Oxidative Degradation of Organic Acids Conjugated with Sulfite Oxidation in Flue Gas Desulfurization
Lee, Y. J. and G. T. Rochelle
PhD dissertation issued as an EPA report
Experimental results are presented on the degradation of adipic acid, other dicarboxylic acids, hydroxycarboxylic acids, and sulfocarboxylic acids. Manganese, iron, halides, and thiosulfate were studied as catalysts and inhibitors. A free radical mechanism was developed based on the experimental observations.

R-86-2 PUBLISHED
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes
Tseng, P. C. and G. T. Rochelle
Experimental measurements using pH-stat and Coulter counter show that dissolution of agglomerates is modeled by mass transfer.

R-86-3 $15.00
Effect of Relative Humidity and Additives on the Reaction of Sulfur Dioxide with Calcium Hydroxide
Ruiz-Alsop, R. N. and G. T. Rochelle
PhD dissertation issued as an EPA report under cooperative agreement CR 812-454
Experimental studies in a packed-bed reactor at 50°C to 80°C with 15% to 90% relative humidity show that sodium chloride and other salts greatly enhance the reactivity of reagent Ca(OH)2 solids. Modeling of these data suggest that both reaction kinetics and diffusion through the product layer can affect the rate. The results are summarized in R-85-3 and R-86-4.
R-86-4
Modeling of the Reaction of SO₂ with Ca(OH)₂
Ruiz-Alsop, R. N. and G. T. Rochelle
Manuscript on file, Separations Research Program
A shrinking core model was developed to simulate reaction at 50°C to 80°C with 15% to 90% relative humidity. The results suggest that both reaction kinetics and diffusion through the product layer can affect the rate.

R-86-5 REPLACED BY R-87-9

R-86-6 PUBLISHED
Removal of SO₂ and NOₓ from Stack Gas by Reaction with Calcium Hydroxide Solids
Chu, P. and G. T. Rochelle
Previous workers have shown that simultaneous SO₂/NOₓ removal can be obtained in a dry-scrubbing system with Ca(OH)₂ promoted by an additive such as NaOH, and that fly ash and product recycle improve the reactivity of the solids toward SO₂. To test SO₂/NOₓ removal with fly ash and product recycle, bench-scale experiments with a packed-bed reactor were performed at bag filter conditions. The most reactive solid for NOₓ removal was prepared by slurring Ca(OH)₂ with fly ash, CaSO₃, and NaOH. The best conditions for NOₓ removal (R-86-6) were the greatest temperature (125°C) and greatest concentrations of SO₂ (1500 ppm) and O₂ (20%). At the best conditions, NOₓ removed in 1 hour was 3-4 moles per 100 moles Ca(OH)₂, compared to 5-10 moles SO₂ removed per 100 moles Ca(OH)₂. The best SO₂ removal (R-86-6) was obtained at the highest relative humidities/lowest temperatures (55% RH/65°C) with solids prepared by slurring Ca(OH)₂ with fly ash (R-86-6) and NaOH. At these conditions, SO₂ removed in 1 hour was 60-80 moles per 100 moles Ca(OH)₂, compared to 0.5 to 1 moles NOₓ removed per 100 moles Ca(OH)₂.

R-86-7
Thiosulfate Additives for Lime/Limestone Scrubbing
Rochelle, G. T.; Y. J. Lee; R. N. Ruiz-Alsop; J. C. S. Chang; T. G. Brna
Presented at the Tenth Symposium on Flue Gas Desulfurization, Atlanta, Georgia, November 1986
Bench- and pilot-scale experiments are reported on the use of powdered sulfur, ammonium thiosulfate, and sodium tetrathionate as alternatives to sodium thiosulfate for inhibiting sulfite oxidation in limestone slurry scrubbing (R-86-7). Powdered sulfur reacts in situ with calcium sulfate to produce thiosulfate at costs four to seven times less than sodium thiosulfate.

R-87-1
CO₂ Absorption into Aqueous MDEA and MDEA/MEA Solutions
Critchfield, J. E. and G. T. Rochelle
Presented at the AIChE National Meeting, Houston, Texas, March 1987
The rate of absorption of CO₂ was measured in 2 molal MDEA and in 1.36-m MDEA/0.61-m MEA at 9.5°C-62°C. The MDEA rate constant was 4.0 (Ms)-1 at 30.5°C with an activation energy of 9 kcal/gmol. In the mixed system, the data were predicted better by a mass-transfer model based on a shuttle mechanism than by one with two parallel reactions.

R-87-2
Evaluation of the Electrode Method for Measuring H₂S Vapor Pressure over Alkanolamine Solutions
Austgen, Jr., D. M. and G. T. Rochelle
Presented at the AIChE National Meeting, Houston, Texas, March 1987
A new electrode method for measuring the equilibrium vapor pressure of H₂S over any sulfide solution was tested. The method relates the electropotential difference produced between pH and silver/sulfide ion specific electrodes to the H₂S equilibrium vapor pressure of solution. H₂S equilibrium (R-87-2) vapor pressures were measured from 10-4 kPa to 10 kPa at 25°C in aqueous solutions of monoethanolamine (MEA) (2.5 N), diethanolamine (DEA) (2.0 N), and methyl...
diethanolamine (MDEA) (1.0 N and 4.28 N). Following electrode calibration to determine slope and standard potential, the method produced vapor/liquid equilibrium (VLE) measurements in agreement with published data.

R-87-3 NO LONGER AVAILABLE

R-87-4
Dissolution and Crystallization of Calcium Sulfite Platelets
Gleason, C. L. and G. T. Rochelle
Presented at the AIChE National Meeting, Houston, Texas, March 1987
The dissolution and crystallization rates of platelet-shaped calcium sulfite crystals were measured at pH 3.0 to 6.0. The effects of sulfate content in the solids and solution were also investigated. The platelet sample with a low solid sulfate content dissolved and crystallized slower than the sample with a high solid sulfate content and the agglomerated samples. The inhibiting effect of dissolved sulfate was also greater for the low solid sulfate sample.

R-87-5 $10.00
A Mass Transfer-Based Process Model of Acid Gas Absorption/Stripping Using Methyldiethanolamine
Hermes, J. E.
Master's thesis
A nonequilibrium stage model was developed for absorption/stripping of H2S and CO2 in tertiary amines. Enthalpy transfer, as well as mass transfer, is calculated for a stage of well-mixed liquid with gas in plug flow. Results were generated at Claus tail gas conditions using available equilibrium and rate data for MDEA. Reducing stripper pressure from 2 atm to 0.5 atm decreases the H2S leak from 176 ppm to 60 ppm because of higher lean loadings of CO2. Neutralization of 20% of the MDEA with a strong acid reduces the H2S leak to 91 ppm because of linearization of the H2S equilibrium.

R-87-6
A Mass Transfer-Based Process Model of Acid Gas Absorption/Stripping Using Methyldiethanolamine
Hermes, J. E. and G. T. Rochelle
Presented at the ACS National Meeting, New Orleans, New Orleans, Louisiana, August 1987
This paper is a summary of R-87-5.

R-87-7
Flue Gas Desulfurization and Acid Gas Treating Research Review Meeting
Handout for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Rochelle, Peterson, Trempel, Gage, Ruiz-Alsop, Gleason, Dunkley, Austgen, Critchfield, Glasscock, and Hermes.

R-87-8 PUBLISHED
Aqueous Reaction of Fly Ash and Ca(OH)2 Ca(OH)2 to Produce Calcium Silicate Absorbent for Flue Gas Desulfurization
Peterson, J. R. and G. T. Rochelle
Slurries of fly ash and Ca(OH)2 were monitored for dissolved metal concentrations with atomic absorption spectrophotometry. The solids produced were dried and tested for reactivity towards SO2 in a packed-bed reactor at bag filter conditions. The solids formed in slurries containing 10 ppm-100 ppm of dissolved calcium were up to 40% more reactive than the solids formed in slurries containing less than 10 ppm, or more than 100 ppm, of dissolved calcium. The dissolved calcium concentration was affected by NaOH concentration, fly ash loading [g fly ash/g Ca(OH)2], slurry temperature, fly ash type, and the presence of CaSO3 0.5 H2O.
**R-87-9**  
**SO2 and NOx Removal from Flue Gas Flue Gas by Reaction with Solids Prepared by Slurrying Fly Ash and Ca(OH)2**  
Rochelle, G. T.; P. Chu; J. R. Peterson  
Final report submitted to the US DOE under Grant no. DE-FG22-85PC81006  
The best NO/NOx removal in a packed-bed reactor was obtained using solids prepared by slurrying lime, fly ash, and calcium sulfite in a solution of NaOH. NOx removal was as high as 4 moles/hour per 100 moles of Ca(OH)2 at 125°C. Sulfur dioxide removal was as high as 80 moles/hour per 100 moles of Ca(OH)2 at 65°C. This report includes theses by Chu and Peterson summarized in R-86-6 and R-87-7.  
Replaces R-86-5

**R-87-10**  
PUBLISHED  
**Coprecipitation of Organic Acids with Calcium Sulfite Solids**  
Ruiz-Alsop, R. N. and G. T. Rochelle  
Coprecipitation of dicarboxylic acids with calcium sulfite was studied at conditions typical of limestone slurry scrubbing (R-87-10) for flue gas desulfurization (R-87-10). The driving force for coprecipitation was found to be the calculated activity of the ion pair of the calcium salt of the organic acid. The ratio of the organic acid concentration in (CaSO3)0.8(CaSO4)0.2 1/2H2O solids to ion pair activity at 55°C was 6.9, 13.2, and 194 for adipic, glutamic, and succinic acid, respectively. These relationships are reflected in reduced coprecipitation at lower dissolved calcium and pH.

**R-87-11**  
**Handouts for SRP Flue Gas Desulfurization and Acid Gas Treating Study Group**  
**and Acid Gas Treating Study Group; Meeting, October 1987**  
Includes copies of transparencies used by Rochelle, Peterson, Austgen, Critchfield, Glasscock, Dunkley-Timmerman, Gage, Gleason, Trempel, and White.

**R-88-1**  
**CO2 Desorption from DEA and DEA-promoted MDEA Solutions**  
Critchfield, J. E. and G. T. Rochelle  
Presented at the AIChE Spring National Meeting, New Orleans, Louisiana, March 1988  
The rate of CO2 desorption from solutions of DEA, MDEA, MEA-promoted, and DEA-promoted MDEA was studied as a function of loading at 25°C in a stirred tank reactor. Because the rate constants determined in absorption and desorption experiments agreed very well, a reversible rate model was applied to the data. The rate constants measured in the DEA system were well correlated with a two-step kinetic model. The DEA-promoted MDEA system demonstrated that MDEA interacts in the CO2-DEA reaction kinetics. MDEA has no special effect on the CO2-MEA reaction kinetics (R-88-1)

**R-88-2**  
$10.00  
**CO2 Absorption/Desorption in Methyldiethanolamine Solutions Promoted with Monoethanolamine and Diethanolamine: Mass-Transfer and Reaction Kinetics**  
Critchfield, J. E.  
PhD dissertation  
This dissertation is summarized by papers R-88-1 and R-87-1.

**R-88-3**  
**Transport of Carbon Dioxide in Nafion Membranes Enhanced by Relative Humidity and Ethylenediamine Content**  
Dunkley-Timmerman, T. and G. T. Rochelle  
Presented at the AIChE Spring National Meeting, New Orleans, Louisiana, March 1988  
Carbon dioxide transport through the cation exchange membrane Nafion 117 was studied as a function of ethylenediamine (EDA) concentration in the membrane and RH. Permeabilities up to
29,200 Barrers were measured in the EDA-loaded membranes, up to 37 times greater than those of the H+ form. CO2 permeabilities in the H+ form, compared to those in the literature of O2 and H2, imply selectivities for CO2 over nonpolar gases of 39 to 64. The diffusion coefficients in the EDA-loaded membranes were an order of magnitude less than the diffusion coefficient in the H+ form. The reaction stoichiometry was determined from the implied solubility data to be 0.5 gmol CO2/gmol EDA at conditions of EDA saturation.

**R-88-4** PUBLISHED
A Model of Vapor-Liquid Equilibria in the Aqueous Acid Gas-Alkanolamine System Using the Electrolyte-NRTL Equation
Austgen, Jr., D. M. and G. T. Rochelle
Adjustable parameters of the electrolyte-NRTL equation, representing short-range binary interactions, are fitted on binary and ternary system VLE data. Calculated H2S and CO2 equilibria (R-88-4) are in good agreement with most of the reported experimental data for aqueous solutions of a single acid gas in MEA and DEA in the temperature range of 25°C-120°C. Without fitting additional parameters, representation of experimental equilibria for mixture of H2S and CO2 in aqueous solutions of MEA or DEA is good.

**R-88-5** $10.00
Transport of Carbon Dioxide in Perfluorosulfonate Membranes Enhanced by Relative Humidity and Ethylenediamine Content
Dunkley-Timmerman, T.
PhD dissertation
The objectives of this study were to examine the transport of CO2 in Nafton 117 enhanced by relative humidity and EDA content (R-88-5) and to model the CO2-EDA system based on equilibrium considerations. This was to be accomplished by determining the diffusion coefficient and permeability, in situ. Loadings greater than one and conditions drier than 100% relative humidity were investigated. The goal was to clarify the diffusion process and the reaction chemistry between CO2 and EDA.

**R-88-6**
Handout for the Separations Research Program Spring Conference, April 1988
Handouts used by Rochelle, Austgen, Glasscock, Toman, Dunkley, Peterson, White, Trempel, Borgwardt, Gage, and Gleason for the Flue Gas Desulfurization and Acid Gas Treatment Study Group (R-88-6) Meeting.

**R-89-1**
Handouts for the Separations Research Program Fall Conference, September 1988
Includes copies of transparencies used by Rochelle, Austgen, Glasscock, Toman, Peterson, White, Borgwardt, Trempel, Gleason, and Gage for the Flue Gas Desulfurization/Acid Gas Treatment Study Group (R-89-1) Meeting.

**R-89-2**
Comparison of Steady- and Unsteady-State Theories for Multicomponent Diffusion/Reaction in Gas Absorption Processes
Glasscock, D. A. and G. T. Rochelle
Theories for modeling mass transfer with chemical reaction are quantitatively compared. The eddy diffusivity theory is a steady-state theory which gives results comparable to surface renewal theory, an unsteady-state theory.
Development of a Predictive Model for Limestone Dissolution in Wet FGD Systems
Jarvis, J. B.; F. B. Mesarole; T. J. Selm; G. T. Rochelle; C. L. Gage; R. E. Moser
Presented at the EPA/EPRI First Combined FGD and Dry SO2 Control Symposium, St. Louis, Missouri, October 1988
This paper reports cooperative work with Radian Corporation to measure and model limestone dissolution. The results suggest that limestone dissolution is inhibited by calcium sulfite saturation.

Handouts for the Separations Research Program Spring Conference, April 1989
Includes handouts used by Rochelle, Austgen, Glasscock, Toman, Peterson, White, Beaudoin, Trempel, Stromblad, Erickson, and Gage for the Flue Gas Desulfurization/Acid Gas Treating Study Group (R-89-4) Meeting.

Modeling the Solubility of H2S and CO2 in Aqueous Solutions of MDEA and Mixtures of MDEA with MEA and DEA Using the Electrolyte-NRTL Equation
Austgen, Jr., D. M. and G. T. Rochelle
Accepted by Industrial and Engineering Chemistry Research
Literature vapor-liquid equilibria data for the H2S-CO2-MDEA-water system were represented using a model of phase equilibria developed in previous work. Chemical equilibria were treated in a thermodynamically rigorous manner. The liquid phase nonideality was modeled with the electrolyte-NRTL activity coefficient equation accounting for physical interactions among various true species. The previous work covers H2S and CO2 equilibria with aqueous solutions of MEA and DEA. The model was further extended to represent CO2 solubility in aqueous mixtures of MDEA/MEA and MEA/DEA. As a part of this work, the solubility of CO2 in 4 M aqueous mixtures of MDEA/MEA and MDEA/DEA was measured at 40°C and 80°C over a wide range of CO2 partial pressures. These data have been successfully represented by the model.

Production of Calcium Silicate Reagent from Fly Ash and Ca(OH)2
Peterson, J. R. and G. T. Rochelle
Final report prepared for the US EPA, April 1989
High surface area solids, which are very reactive towards SO2 at bag filter conditions (i.e., low temperature and high RH), can be prepared by reacting fly ash with Ca(OH)2 in the presence of water. The solids produced by this reaction are believed to be calcium-silicate or calcium-silicate-aluminate materials. These solids have potential use in dry systems used for FGD (R-89-6). The use of these solids for FGD has been demonstrated up to the pilot-plant level, but the production of these solids is not well understood. The present study fundamentally investigates the chemistry of the fly ash-Ca(OH)2 reaction using bench-scale equipment. The study will determine the effects of fly ash type; the presence of CaSO3 0.5 H2O; the slurry temperature; and the effects of additives to the slurry.

Numerical Simulation of Diffusion and Reversibility Effects on CO2 Absorption into Aqueous Diethanolamine
Glasscock, D. A. and G. T. Rochelle
Presented at the AICHE 1989 Spring National Meeting, Houston, Texas, April 1989
This paper presents the simulation and interpretation of experimental data for the absorption of CO2 into 2M aqueous DEA (R-89-7). Previous work has concentrated on the interpretation of experimental data primarily at low CO2 loadings and conditions where the diffusion of DEA to the gas-liquid interface is not important. Neither of these conditions are met under a wide range of practical operating conditions. Therefore, a model has been developed which rigorously takes into account both the mass-transfer and thermodynamic effects. The electrolyte-NRTL model is used for the liquid-phase activity coefficients, and the simplified eddy diffusivity model is used to
account for the mass transfer of the reactants to the interface. The results show that the combined equilibrium/mass-transfer model can effectively simulate experimental data under a wide range of conditions. The sensitivity and relative importance of the absorption rate to both kinetic and thermodynamic parameters will also be discussed.

R-89-8
Carbon Dioxide Absorption Rates and Physical Solubility in 50% Aqueous Methyl-diethanolamine Partially Neutralized with Sulfuric Acid
Toman, J. J. and G. T. Rochelle
Presented at the AIChE 1989 Spring National Meeting, Houston, Texas, April 1989
Rates of absorption of pure CO2 into an aqueous 50% MDEA solution, and into another solution of equal strength for which 50% of the MDEA had been neutralized with sulfuric acid, were measured using a stirred-cell reactor. The physical and chemical solubility of CO2 (R-89-8), solution density, viscosity, and surface tension were also measured as a function of loading of CO2, expressed as mols CO2/mol MDEA. The apparent second-order rate constant was determined to be 5.5 liter/mol-s at 25°C and 9.5 liter/mol-s at 35°C and appeared to decrease very little with increasing ionic strength in the low to moderate region of loading. For the H2SO4 modified solution, the rate constant was slightly higher at 25°C than it was for the unmodified solution, indicating a weak catalytic effect, with a rate constant determined to be 6.5 liter/mol-s. The decrease in absorption rate in the low to moderate loading region is almost completely accounted for by the decrease in free MDEA and the decreased physical solubility of CO2. This was well correlated with the total ion concentration in the solution for both CO2 and N2O in solutions loaded with either H2SO4 or CO2. For the unmodified solution, the absorption rate diminished linearly with increasing loading up to loadings of about 0.5 mol CO2/mol MDEA and then rapidly thereafter. Rapid decrease in absorption rate for the partially neutralized solutions began at CO2 loadings of about 0.25 mols CO2/mol available MDEA. At higher loadings, effects of the reverse reaction, along with increased solution viscosity and density, which decrease diffusivity, are the likely causes of the drastic reduction in the apparent rate constant.

R-89-9
Theoretical Approach for Enhanced Mass-Transfer Effects in Duct Flue Gas Desulfurization Processes
Rochelle, G. T.
Manuscript on file, Separations Research Program
This report details work done under DOE support to characterize mass-transfer and reaction kinetic effects as they would happen in FGD performed by direct in-duct injection. Research into these effects is being done in three types of reactors: a stirred tank, a differential reactor, and a flow reactor. A computer model for direct slurry injection has been developed simultaneously with the mass-transfer/kinetic experiments. This report shows the experimental data on procedures for the reactor tests and describes the injection model. The last portion of the report describes research into the production of lime/fly ash absorbent solids for SO2 removal (R-89-9) at bag filters. The study shows the results of experiments to describe the chemistry of the fly ash/lime reaction.

R-89-10 $5.00
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds
White, W. B
Master's thesis
Previous work established that the reaction of SO2 with lime-based solids is a strong function of relative humidity at contact times of 20 to 60 minutes. The work also demonstrated that calcium silicate reagent produced from calcium hydroxide and fly ash is more reactive than calcium hydroxide. In the present study, reaction progress was measured at times (10 to 7200 seconds) approaching those typical of duct injection processes for FGD. Mississippi hydrated lime and a calcium silicate produced from Clinch River fly ash were studied at 0% to 85% RH and 450 ppm SO2. The conversion of calcium silicate varied from 3% at 0% RH and 10 seconds to 95% at 85% RH and 7200 seconds. The conversion of Mississippi hydrated lime varied from 1% at 24% RH and 10 seconds to 71% at 85% RH and 3600 seconds. At 10 seconds reaction time, the maximum
conversion was 4% and 11% for Mississippi hydrate and the calcium silicate, respectively. Therefore, these conditions would not be economically attractive for FGD. Presence of excess moisture on the sorbent increased conversion by 5% to 10% (of total reagent conversion) over the conversion attained under equilibrium moisture conditions. Increasing SO2 concentration from 450 to 2000 ppm had a limited effect only on conversion of calcium silicate for residence times under 600 seconds.

R-89-11
**Reaction of SO2 with Ca(OH)2 and CaO; at 100 to 800°C**
Trempel, D. P. and G. T. Rochelle
Calcium hydroxide is a potential reagent for FGD at 300°C to 600°C in a duct or a high-temperature baghouse. The calcination and sulfation kinetics of Mississippi hydrate lime were studied at 100°C to 600°C. The rate of calcination was half order in unreacted calcium hydroxide with an activation energy of 24.2 kcal/gmol. At 300°C, half of the hydrate was calcined in 316 seconds. The sulfation of Mississippi hydrate in the absence of O2 produced anhydrous CaSO3 with an activation energy of 32 kcal/gmol. The sulfation kinetics of calcium oxide were also studied in the absence of O2. With one and ten minute reactions, there was a linear increase in conversion from 100°C to 600°C. From 600°C to 800°C, the conversion decreased because CaSO4 was formed rather than CaSO3. The activation energy for CaO sulfation was only 10 kcal/gmol, suggesting a mechanism different from that of Ca(OH)2 sulfation.

R-89-12 $20.00
**A Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-Water Systems**
Austgen, Jr., D. M.
PhD dissertation
A physico-chemical model was developed to represent liquid-phase chemical equilibria and vapor-liquid (phase) equilibria of H2S-CO2-alkanolamine-water systems. Activity coefficients are represented with the electrolyte-NRTL equation treating both long-range electrostatic interactions and short-range binary interactions between liquid-phase species. Vapor-phase fugacity coefficients are calculated using the Soave-Redlich-Kwong equation of state. Adjustable parameters of the model, binary interaction parameters and carbamate stability constants, were fitted on published binary system (alkanolamine-water) and ternary system (H2S-alkanolamine-water, CO2-alkanolamine-water) VLE data. Ternary system measurements used in parameter estimation ranged in temperature from 25°C to 120°C, in alkanolamine concentration from 1 to 5 M, in acid gas loading from 0 to 1.5 moles per mole alkanolamine, and in acid gas partial pressure from 0.1 to 1000 kPa. Ternary system H2S or CO2 equilibrium partial pressures and liquid-phase concentrations were found to be in good agreement with measurements for aqueous solutions of MEA, DEA, diglycolamine (DGA), and MDEA. Without fitting additional parameters on quaternary system VLE data (H2S-CO2-alkanolamine-water), maximum likelihood estimates of H2S and CO2 equilibrium partial pressures and liquid-phase concentrations were found to be in satisfactory agreement.

R-89-13
**Report on Liquid/Liquid Equilibria of a Water/Isopar-M/Acetone System**
Hardy, R. D.
Manuscript on file, Separations Research Program
This report presents the results of a liquid/liquid equilibrium study for a water/isopar-m/acetone system at room temperature (24°C to 25°C). The primary objective of this study was to determine how acetone is distributed between phases in an equilibrium mixture of this system. The acetone concentration in each phase was determined by density measurement and by titration. The experimental results were developed theoretically with the van Laar activity coefficient equation to produce an activity coefficient model for an isopar-m/acetone system.
R-89-14
Handouts from the Separations Research Program Fall Conference, September 1989
Includes copies of transparencies used by Rochelle, Glasscock, Toman, Carey, Peterson, Trempel, Beaudoin, and Erickson for the Flue Gas Desulfurization and Acid Gas Treating Study Group (R-89-14) Meeting.

R-89-15 PUBLISHED
Numerical Simulation of Theories for Gas Adsorption with Chemical Reaction
Glasscock, D. A. and G. T. Rochelle
Steady- and unsteady-state theories for interfacial mass transfer are used to model gas absorption with second-order, reversible reaction and the absorption of CO2 into aqueous MDEA. The latter case represents a system of industrial interest, having both finite rate and equilibrium reactions. Steady-state theories studied are film theory, simplified eddy diffusivity theory, and an approximation to surface renewal theory. Higbie's penetration and Danckwert's surface renewal theories are the unsteady-state theories reviewed. The Nerst-Planck equations for diffusion and reaction in ionic systems are solved numerically using orthogonal collocation on finite elements. Comparisons are made between the absorption enhancement factor obtained for all theories. The applicability of approximate methods of solution for absorption with chemical reaction is also discussed.

R-90-1
Production of Lime/Fly Ash Absorbents for Flue Gas Desulfurization
Peterson, J. R. and G. T. Rochelle
Presented at the First Combined FGD and Dry SO2 Control Symposium, St. Louis, Missouri, October 1988
Previous workers have shown that fly ash can be reacted with Ca(OH)2 to produce solids, which are very reactive toward SO2 at bag filter conditions. The present study fundamentally investigates the important parameters of the fly ash-Ca(OH)2 reaction (R-90-1). The dissolution rate of fly ash, thought to be the rate limiting step of the overall reaction, was determined to depend on the fly ash type and on the pH of the slurry. It is shown that high calcium fly ashes dissolve faster than do low calcium fly ashes and that the dissolution rate for both types of fly ash increased with slurry pH. A new "selective dissolution (R-90-1)" method was formulated to determine the composition of the reactive surface layer of the fly ash-Ca(OH)2 reaction products. This method allows one to determine the conversion of the silica in the reaction products. These conversion data were correlated with the ability of the reaction product to remove SO2 in a packed-bed reactor that was designed to simulate bag filter conditions.

R-90-2 PUBLISHED
Nucleation and Crystal Growth of Calcium Sulfite Hemihydrate
Gleason, C. L. and G. T. Rochelle
Environmental Progress 10(3):225-33 (1991)
In slurry scrubbing processes for flue gas desulfurization, the precipitation rate of calcium sulfite affects scrubber solution composition, SO2 absorption, sulfite oxidation, and limestone utilization. Sludge quality and disposal costs are also a function of precipitation kinetics. The nucleation and crystal growth rates of calcium sulfite hemihydrate were measured in a continuous flow crystallizer at conditions that produced agglomerate crystals. At 28°C and 55°C, the nucleation rate, B°, varied from 0.25 to 23 ¥ 108 #/m3 - sec and was given at pH 5.5 by the correlation The suspension density, MT, was varied from 7 to 90 kg/m3. The linear growth rate, G(m/sec), varied from 0.5 to 9 ¥ 10-9 m/s as residence time was varied from 42 to 360 minutes. The nucleation rate constant had a maximum near pH 5.5 and was about 50% lower at pH 4.2 and pH 6.5. Gypsum saturation (R-90-2) in solution caused both the nucleation and growth rates to decrease.
Sulfation of Calcium Silicate-Aluminate and Calcium Oxide Below 800°C
Borgwardt, R. H. and G. T. Rochelle
Industrial and Engineering Chemistry Research 29:2118-23 (1990)

The sulfation rate of a calcium silicate-aluminate, consisting of the reaction product of Ca(OH)2 and fly ash, was measured as a function of temperature and the specific surface area of its calcination product. The maximum rate was found at 775°C and the presence of water vapor in the gas feed increased sulfation rate at all temperatures. Significant amounts of sulfite appeared in the reaction product at 580°C. Comparison with CaO sulfation showed faster reaction at all temperatures with CaO, partly due to a higher surface area, but also due to a higher equilibrium temperature for CaSO3 formation. The rate of CaSO3 formation from CaO in the presence of 5% O2 is much faster than the rate of CaSO4 formation; thus, the initial product of reaction is CaSO3 at temperatures as high as 665°C. The rate of sulfite reaction is fast enough to achieve 20% conversion within 2 sec at 538°C and is enhanced by the presence of water vapor. The proportion of sulfate to sulfite in the reaction product increases with time and temperature. In the presence of O2, the principal mechanism of CaSO4 formation (R-90-3) during the initial stage of reaction is the oxidation of CaSO3 rather than disproportionation of CaSO3.

R-90-4 $10.00
Nucleation and Crystal Growth of Calcium Sulfite Hemihydrate
Gleason, C. L.
PhD dissertation

The dissolution and precipitation rates of platelet-shaped calcium sulfite crystals were measured in a pH stat apparatus. The effects of sulfate content in the solids and solution were also investigated. The measured rates for the platelets were compared to the rates previously determined for agglomerates. It was determined that there are subtle differences between platelet and agglomerated calcium sulfite. The rate of dissolution and crystallization of the platelet sample with a low solid sulfate content was slower than with a high solid sulfate content. Low sulfate platelets also dissolved and crystallized slower than the agglomerated samples. The inhibiting effect of dissolved sulfate was also greater for the sample with low solid sulfate. The sample with high solid sulfate dissolved and crystallized at approximately the same rate as the agglomerates. Size distributions can be predicted if nucleation and growth rates are known. These rates can also be used to examine prospects for increasing the calcium sulfite particle size. This would lead to an improved sludge quality and lower disposal costs. The nucleation and crystal growth rates of calcium sulfite hemihydrate were measured in a continuous flow crystallizer. The effects of solution sulfate concentration, residence time, suspension density, and temperature on the rates were investigated. It was determined that the nucleation rate was directly proportional to the suspension density. The particle size distribution was observed to be independent of the suspension density. The growth rate was found to be directly proportional to the solids residence time in the reactor. Therefore, particle size distribution cannot be increased by increasing the residence time in the reactor. The activation energy for CaSO31/2H2O nucleation was estimated to be 4 kcal/mole within the temperature range of 25°C to 55°C. The nucleation rate constant was pH dependent and had a maximum near pH 5.5. Sulfate in solution inhibited nucleation. It was also observed that there was a maximum in the nucleation rate constant at pH 5.5, while sulfate in solution inhibited nucleation.

R-90-5 $10.00
Limestone Dissolution in Modeling of Slurry Scrubbing for Flue Gas Desulfurization
Gage, C. L.
PhD dissertation

Batch limestone dissolution experiments were carried out in a pH stat apparatus at 55°C with CO2 sparging and dissolved sulfite. Particle size distribution, utilization, sulfite in solution, limestone type, and the approach to calcite equilibrium were all found to contribute to the limestone reactivity. In the absence of sulfite, limestone dissolution was controlled solely by mass transfer. For a given stone under mass-transfer control, film thickness was found to be independent of pH. The dissolution rate in the presence of sulfite was controlled by a combined surface kinetics/mass-
transfer regime. A surface rate correlation was developed which accounted for observed inhibition by an inverse dependence on calcium sulfite concentration at the limestone surface. While the form of the rate expression was applicable to all stones, the surface rate constant was stone dependent. A computer code accounting for mass transfer with surface kinetics was tested against experimental observations of four limestone types. Changes in pH and the concentrations of calcium, carbonate, sulfite, sulfate, and adipic acid were accurately modeled. An overall slurry scrubber model was expanded to predict limestone reactivity from particle size and solution effects. This model predicts scrubber performance and hold-tank compositions from the chemistry of the limestone slurry process. Additional subroutines were written to predict particle size distributions from sieve data using the log gamma density function. The expanded model was tested against a limestone type and grind study that investigated utilizations of four limestone types at ten different grinds. The expanded slurry scrubber model was able to predict both SO2 removal and hold-tank composition of the limestone study. The effects of limestone type were handled through changes in the surface rate parameter. Within a given type, the effects of grind and utilization were well modeled.

R-90-6
Handouts from the Separations Research Program Spring Conference, April 1990
Includes copies of transparencies used by Rochelle, Glasscock, Toman, Carey, Dashti, Peterson, Beaudouin, Stroud, McGuire, and Agarwal for the Flue Gas Desulfurization/Acid Gas Treating Study Group (R-90-6) Meeting.

R-90-7 $20.00
Modeling and Experimental Study of Carbon Dioxide Absorption into Aqueous Alkanolamines
Glasscock, D. A.
PhD dissertation
A comprehensive model for the simulation of CO2 absorption and desorption with chemical reaction is presented. The activity coefficients for the alkanolamine systems studied are estimated using the electrolyte-NRTL equation (R-90-7). It takes into account both long-range and short-range interactions between the species in solution. A generalized framework is constructed for the diffusion and reaction of species in ionic solutions. The differential material balance equations are solved numerically to obtain liquid-phase concentration profiles and flux rates for CO2 at the gas-liquid interface. This general model is used to extract kinetic information from mass-transfer experiments and predict system behavior under industrially relevant conditions. The model has been used to study the reaction kinetics for CO2 with MEA, DEA, MDEA, and the mixtures MEA/MDEA, and DEA/MDEA. In addition to data taken by other authors, experimental data are presented for absorption of CO2 into 0.5 and 1.0 molal DEA at 40°C, 1.0 molal MDEA at 25°C and 40°C under a range of CO2 partial pressures up to 1 atm, and 0.1/0.9 and 0.3/0.7 molal DEA/MDEA mixtures at 40°C. The MDEA data indicate that the apparent reactivity of MDEA is a function of the CO2 partial pressure and loading. By detailed treatment of the reaction kinetics in nonideal solutions, absorption and desorption data for DEA have been successfully reconciled by assuming the reaction rate constants "increase" with ionic strength. It is also demonstrated that MDEA interacts in the DEA kinetic expression, but the model can simulate MEA/MDEA mixed amine data without kinetic interaction.

R-90-8 PUBLISHED
Approximate Simulation of CO2 and H2S Absorption into Aqueous Alkanolamines
Glasscock, D. A. and G. T. Rochelle
This work presents a comparison of rigorous and approximate methods for the simulation of CO2 absorption into aqueous alkanolamine mixtures of MDEA and DEA. In addition, data for the mixtures containing MEA and the simultaneous absorption of CO2 and H2S are presented. For the rigorous approach, the simplified eddy diffusivity theory is used to simulate the liquid-phase hydrodynamic characteristics. The approximation methods examined are the pseudo first-order approximation, an interpolation approximation, the algebraic combined flux approximation and the modified combined flux approximation (MCFLUX). The latter approximation uses the
reaction zone concept to determine the kinetic preference of the absorbing gas at the gas-liquid interface. Under the range of conditions studied, the MCFLUX approximation predicts very accurately the CO2 and H2S flux rates in mixed amine systems, as compared with the rigorous solution of the differential equations.

**R-90-9 PUBLISHED**

**CO2 Absorption/Desorption in Mixtures of Methyl diethanolamine with Monoethanolamine or Diethanolamine**

Glasscock, D. A.; J. E. Critchfield; G. T. Rochelle  

This paper presents a compilation of data and model interpretation of CO2 absorption/desorption with mixtures of MDEA, MEA, and DEA (R-90-9). The electrolyte-NRTL model is used to represent the activity coefficients of the species in solution. The simplified eddy diffusivity theory is used to simulate liquid-phase hydrodynamic characteristics. Binary interaction parameters for the equilibrium model and kinetic rate constants have been regressed from literature and currently obtained experimental data. The data presented in this work include both absorption and desorption conditions and temperatures ranging from 288K to 313K. The results indicate that the combined mass-transfer/equilibrium model can effectively represent CO2 mass-transfer rates for the mixtures MEA/MDEA and DEA/MDEA under a wide range of conditions. Using a generalized framework for consistency between kinetics and reaction equilibria in nonideal systems, absorption and desorption data have been reconciled by allowing the forward rate constants to "increase" with ionic strength. It is shown that MDEA promotes the DEA reaction rate but not the MEA reaction rate. Both of these phenomena can be explained in terms of the zwitterion mechanism for amine carbamate formation.

**R-90-10 $10.00**

**The Effect of Moisture on the Reactivity of Ca(OH)2-Based Sorbents for Flue Gas Desulfurization**

Beaudoin, S. P.

Ca(OH)2-based sorbents were investigated for application in tail-end FGD systems in coal-fired power plants. The effects of free moisture and surface area on sorbent reactivity (R-90-10) were studied at 0% to 85% RH and 1000 and 5000 ppm SO2. In 1000 ppm SO2 at 60% RH and 60 s reaction, the conversion of sorbent formed by slurrying Ca(OH)2 with Clinch River fly ash was found to increase from 0.15 in the absence of excess moisture (ambient reaction) to 0.3 with 30% free moisture. For the same reaction time and RH but in 5000 ppm SO2, the conversion of Mississippi hydrated lime increased from 0.12 at ambient conditions to 0.23 with 14% free moisture. The reactions between damp lime/fly ash sorbent (5%-50% moisture) and 1000 ppm SO2, and between damp hydrated lime sorbents and 5000 ppm SO2, were modeled successfully assuming gas-phase mass transfer of SO2 to the damp sorbent was rate-limiting. The reaction of damp lime/fly ash with 5000 ppm SO2 was not gas-phase controlled. During ambient reaction, hydrated lime sorbents of high surface area (74 m2/g) attained conversions up to 0.30 in 5000 ppm SO2 during 60 s reaction at 60% RH, compared to 0.12 for low surface area (17 m2/g) hydrated lime (R-90-10) at the same conditions. The reaction in the presence of excess moisture was independent of sorbent surface area.

**R-90-11**

**Handouts from the Separation Research Program Fall Conference, September 1990**

Includes copies of transparencies used by Rochelle, Toman, Carey, Peterson, Beaudoin, Stroud, Agarwal, and McGuire for the Flue Gas Desulfurization/Acid Gas Treatment Study Group (R-90-11) Meeting.
**R-91-1**

**Acid Gas Treating by Aqueous Alkanolamines - Review of Property Data**  
Rochelle, G. T.

Quarterly progress report prepared for the Gas Research Institute, contract no. 5090-260-2013, September-November 1990

This report reviews the data and research needs for thermodynamic properties, transport and rate properties, and modeling methods to contribute to the quantification of alkanolamine technologies. In this quarter, reviews were prepared for CO2 kinetics in tertiary amines, system modeling, and COS/CS2 absorption. A review has been initiated on equilibrium data for H2S/CO2 vapor pressures. A data base system has been set up to enter references and data. Regression results were analyzed to obtain a quantitative representation of the model and data accuracy.

**R-91-2**  **$15.00**

**Rate-Based Modeling of Acid Gas Absorption and Stripping Using Aqueous Alkanolamine Solutions**  
Carey, T. R.

Master's thesis

Two models for the simultaneous absorption and stripping of H2S and CO2 using aqueous alkanolamines were developed. The first model is a rate-based approach to modeling MDEA systems that uses DeCoursey's method to calculate the CO2 enhancement factor. The second model was developed within the framework of the process simulator ASPEN PLUS to model MEA, DGA, DEA, MDEA, and mixed amines. A kinetic subroutine was developed that contains complex kinetic expressions for each of these amine systems. The MDEA model was used to explore the effect of changing operating conditions on the system performance of a typical Claus-tail gas cleanup application. A reasonable liquid rate and steam rate resulted in an absorber H2S leak of 98 ppm. Addition of a strong acid to this system reduced the leak to 6 ppm. Similarly, reducing the stripper pressure from 2 atm to 0.5 atm increased performance to a leak of 4 ppm. In both cases, the improved performance is due to linearation of the H2S equilibrium. In the case of reducing the stripper pressure, an increase in the gas-phase mass-transfer coefficient and number of transfer units also contributes to the improved performance. The ASPEN PLUS model was used to generate equilibrium data for the various amine systems. This model satisfactorily represents the amine equilibrium, including data for mixed amine systems. The kinetic subroutine developed calculates reasonable reaction rates and can be used with either an equilibrium-based or a rate-based column model.

**R-91-3**

**Handouts for the Separations Research Program Spring Conference, April 1991**  
Copies of the transparencies used by Rochelle, Chakravarti, Chang, Kurimura, Stroud, Kind, Wasserman, Johnson, and Agarwal for the Flue Gas Desulfurization/Acid Gas Treating Study Group (R-91-3) Meeting.

**R-91-4**

**Acid Gas Treating by Aqueous Alkanolamines: Review of Property Data**  
Rochelle, G. T.

Quarterly progress report prepared for the Gas Research Institute, contract no. 5090-260-2013, December 1990-April 1991

In this quarter, a review of hindered amines was prepared and a sensitivity analysis of VLE was completed. Included is a paper reviewing research needs prepared for the Seventieth Annual Gas Processors Association convention, March 11-12, 1991, San Antonio, Texas.

**R-91-5**

**Novel Techniques for the Enhanced Utilization of Ca(OH)2 under Duct Injection Conditions**  
Jozewicz, W.; G. T. Rochelle; D. E. Stroud

Presented at the Seventh Annual Coal Preparation, Utilization and Environmental Control Contractors Conference, Pittsburgh, Pennsylvania, July 1991

The results of experimental work testing novel techniques for the enhanced utilization of Ca(OH)2 under duct injection (R-91-5) conditions are presented. Initial free moisture increased short-time
(<5 s) conversion of calcium silicate solids and of physically mixed Ca(OH)2/fly ash solids. The tendency of solids to agglomerate, as represented by the critical moisture content, was a function of surface area and pore volume. Wet grinding of spent Ca(OH)2/fly ash mixture in a bench-scale attritor resulted in the increase of Ca(OH)2 conversion with SO2 compared to unground solids. Several buffer additives were evaluated for their ability to enhance SO2 absorption in slurry injection (R-91-5). Only weak effect of additives (concentration of 50 mmol/L of slurry) on SO2 absorption was measured.

**R-92-1**

**Thermodynamic Parameters for Predicting Acid Gas Solubility in Methyldiethanolamine Solutions**

Chang, H.T. and G. T. Rochelle

Presented at the AIChE Spring National Meeting, New Orleans, Louisiana, March 30-April 2, 1992

The local composition model for electrolyte activity coefficients has been applied to the system MDEA/ water/ H2S/CO2. Parameters for the model were previously regressed from available H2S and CO2 solubility data. At low acid gas loading, model predictions of acid gas solubility are sensitive to parameters that quantify specific interaction between bisulfide or bicarbonate salt and amine solvent and to parameters that quantify interactions in the amine-water system. The water freezing point has been measured in several amine-water systems. The water activity coefficient derived from these measurements by regression with the NRTL model shows strong interactions in the MDEA-water binary system. The apparent solution nonideality sequence in the amine-water system is MDEA > triethanolamine (TEA) > DEA > MEA. The water activity in MDEA-H2O-CO2, MDEA-H2O-HCl, and MDEA-H2O-H2SO4 ternary systems has also been measured. The parameters for activity coefficients from regression of these data should be useful for predicting acid gas solubility (R-92-1) in these systems.

**R-92-2 $10.00**

**Research Needs for Acid Gas Kinetics and Equilibria in Alkanolamine Systems**

Rochelle, G. T.; H.T. Chang; S. Chakravarti

Final report prepared for the Gas Research Institute under contract no. 5090-260-2013

The published data on CO2 kinetics and acid gas equilibria in alkanolamine solutions have been reviewed for their adequacy for system design and troubleshooting. In a typical absorption/stripping system, the values of these properties are most important at the pinches, which occur at conditions of the absorber feed and overhead and near the stripper bottoms. The equilibrium data for most amines are most deficient in quality and quantity at the conditions of the stripper bottoms: lean loading and high temperature. Systems using tertiary amines for selective or customized absorption of H2S require accurate estimates of CO2 reaction rates. Data are generally available for dilute amines but are notably deficient for amine solutions at concentrations of industrial practice. There are practically no rate data at stripper bottom conditions.

**R-92-3 $15.00**


Jozewicz, W. and G. T. Rochelle

Final report prepared for the Environmental Control Division, Pittsburgh Energy Technology Center, US DOE, under contract no. DE-AC22-88PC88874

On the basis of fundamental mass-transfer investigation in the short-time differential reactor (STDR), gas-phase mass-transfer and chemical reaction steps could be excluded as rate limiting. This leaves solid-phase diffusion as a rate-limiting step in the reaction of Ca(OH)2 with SO2 under conditions of dry sorbent injection (DSI) into the duct. Global reactivity testing in the long-time differential reactor (LTDR) revealed that the conversion of a given calcium sorbent was most strongly affected by the flue gas RH. Given identical reaction conditions, conversion of the fly ash/Ca(OH)2 sorbent attained higher value than did the Mississippi Ca(OH)2. Recarbonation of Mississippi Ca(OH)2 took place as a result of CO2 presence in the flue gas and was enhanced by gas RH and sorbent surface area. For practical range of CO2 concentration (0-10 vol%), the effect of CO2 on reactivity of Ca(OH)2 with SO2 was insignificant. Novel techniques designed to enhance sorbent use that were investigated included sorbents with initial free moisture and
grinding of DSI recycle material. Presence of initial free moisture significantly increased sorbent reactivity with SO₂, compared with reactivity of sorbent with equilibrium amount of moisture. The initial free moisture content and corresponding level of maximum sorbent conversion with SO₂ varied with the surface area of the sorbent. A procedure was developed to measure the agglomeration of damp fly ash/Ca(OH)₂ sorbents. Exceeding the critical moisture caused sorbent agglomeration. Critical moisture increased with sorbent specific surface area independently of fly ash type, grinding, and recycle materials. Under conditions of the STDR, dry ground recycle solids were significantly more reactive with SO₂ than unground solids. Pilot-plant data indicated that the DSI recycle material lost its reactivity toward SO₂ after the first pass. Very little improvement in SO₂ removal (R-92-3) was accomplished by DSI recycle downstream of the humidifier. Significant SO₂ removal enhancement was achieved for DSI recycle upstream of the humidifier.

R-92-4 $15.00  
Theoretical Approach for Enhanced Mass-Transfer Effects in Duct Flue Gas Desulfurization Processes Volume II: Duct Spray Drying  
Jozewicz, W. and G. T. Rochelle  
Final report prepared for the Environmental Control Division, Pittsburgh Energy Technology Center, US DOE, under contract no. DE-AC22-88PC88874  
Removal of SO₂ from the flue gas of coal-burning power plants can be achieved by duct spray drying (DSD) using Ca(OH)₂ slurries. A primary objective of this research was to discover the aspects of mass transfer into Ca(OH)₂ slurries which limit SO₂ absorption. A bench-scale stirred tank reactor with a flat gas/liquid interface was used to simulate SO₂ absorption in a slurry droplet. The absorption rate of SO₂ from gas concentrations of 500 to 5000 ppm was measured at 55°C in clear solutions and slurries of Ca(OH)₂ up to 1.0 M (7 wt%). Results are reported in terms of the enhancement factor, Ø. This research will allow prediction of conditions where the absorption of SO₂ in Ca(OH)₂ slurries can be enhanced by changes to liquid-phase constituents (under which SO₂ absorption is controlled by liquid film mass transfer). Experiments in the stirred tank have shown that SO₂ absorption in a 1.0 M Ca(OH)₂ slurry was completely dominated by gas film mass transfer. For conditions of a slurry droplet, the model predicts that absorption of SO₂ is controlled by gas film mass transfer with a large excess of Ca(OH)₂ but becomes controlled by liquid film resistance at greater than 50% Ca(OH)₂ use. An algorithm using penetration theory for the SO₂ absorption and film theory for the Ca(OH)₂ dissolution has been developed to model the SO₂ absorption rate in a stirred tank reactor (R-92-4). This algorithm has been coded in FORTRAN and executed on a Cray computer. Results have been calculated for conditions representative of DSD. The results are expressed as the average fraction gas film resistance. With short contact times (0.1 sec), high slurry concentration [1000 mole Ca(OH)₂/m³], or low SO₂ concentration (500 ppm), gas film resistance approaches 100%. With a typical gas film transfer coefficient at 2000 ppm SO₂, gas film resistance decreases to less than 100% when the penetration distance of the absorption wave exceeds 10 to 20 µm.

R-92-5 $5.00  
Agglomeration of Damp Calcium Silicate Sorbents for Flue Gas Desulfurization  
Stroud, D. E.  
Master's thesis  
Calcium silicate sorbents were prepared by the hydrothermal reaction of coal fly ash with calcium hydroxide. Agglomeration of damp sorbents was investigated by sieving sorbents containing as much as 50% moisture. The critical moisture was determined for each sample. Critical moisture was defined as the moisture content that caused 50% of the sample to be retained by an 80 mesh sieve. Critical moisture was found to correlate with particle pore volume and with surface area. The correlation was the same for sorbents prepared from high-calcium and low-calcium fly ash as well as from ground fly ash. High-calcium fly ash slurried without calcium hydroxide was marginally effective as raw material for sorbent production. The addition of both calcium hydroxide and gypsum to slurries of high-calcium ash resulted in sorbent with greater values of critical moisture and surface area. High-calcium ash (R-92-5) appeared to require a catalytical amount of calcium hydroxide to initiate the formation of calcium silicate. Ground low-calcium fly
ash (R-92-5), slurried for eight hours with gypsum and calcium sulfite present, exhibited a maximum in both critical moisture and surface area when the calcium hydroxide loading was 1 g/g fly ash.

R-92-6 $5.00
Effects of Inorganic Salts on Calcium Silicate Sorbents for Flue Gas Desulfurization
Wasserman, P.D.
Master's thesis
The ADVACATE process uses high surface area solids, made by slurrying lime with fly ash, as a reagent for duct injection FGD in coal-fired power plants. These solids are very reactive with SO2. This reactivity correlates with surface area and moisture content of the solids. It is believed that additives to the ADVACATE process and impurities from within this process could have an effect on the solids' surface area and moisture content, thus effecting the reactivity with SO2. Earlier research was done on the effects of NaOH on ADVACATE solids. The results showed some possible enhancement of the solids reactivity with SO2 when NaOH was added to the slurry. Current research is focused on examining the effects on solids and solids preparation with other additives and impurities (such as CaCl2, NaNO3, and various inorganic salts) as well as continuing the work on NaOH. Several conclusions were reached in the current research. The addition of deliquescent salts to ADVACATE solids during preparation enhances the flowability of the solids as measured by critical moisture. Salts containing chloride enhance the equilibrium moisture content of solids and cause hysteresis in the water adsorption isotherms. The addition of CaCl2 increases the rate of growth of specific surface area and sorbent reactivity with SO2 gas.

R-92-7 $15.00
Thermodynamic Parameters for Predicting Acid Gas Solubility in Aqueous Alkanolamine Solutions
Chang, H.T.
Master's thesis
The local composition model for electrolyte activity coefficients has been applied to the system H2S/CO2/alkanolamine/water. Parameters for the model were previously regressed from available H2S and CO2 solubility data. At low acid gas loading, model predictions of acid gas solubility are sensitive to parameters that quantify specific interaction between bisulfide or bicarbonate salt and amine solvent and to parameters that quantify interactions in the amine-water system. The water freezing point has been measured in several amine-water systems. The water activity coefficient derived from these measurements by regression with the NRTL model shows strong interactions in the MDEA-water binary system near 0°C. The apparent solution nonideality sequence in the amine-water system is MDEA > DMMEA > TEA > DEA > MEA. The combined regression of freezing point depression and total pressure data predicts a significant temperature dependence of the solution properties. At 120°C, the expected solution nonideality sequence is DEA > DGA > MEA > MDEA. The water activity in MDEA/H2O/CO2, MDEA/H2O/HCl, and MDEA/H2O/H2SO4 ternary systems has also been measured. These data with the electrolyte-NRTL equation regression were used to quantify the interaction of chloride/sulfate salt with water. The model prediction for acid gas solubility in aqueous MDEA solution has been improved by regression of three parameters using fixed values of the MDEA/H2O parameters from the regression of freezing point data.

R-92-8 $10.00
Absorption of Carbon Dioxide in Aqueous Blends of Diethanolamine and Methyldiethanolamine
Chakravarti, S.
Master's thesis
Absorption of CO2 in aqueous alkanolamines is a phenomenon of gas-liquid mass transfer with chemical reaction at the interface. An attempt was made at modeling this problem in the framework of ASPEN PLUS. The effect of chemical reaction on mass transfer was accounted for by an enhancement factor. The feasibility of incorporating the enhancement factor approach into RATEFRAC, the rate-based model of ASPENPLUS, in order to model the gas absorption problem was investigated. Outside of RATEFRAC, two models of single-stage contactors were developed. One accounted for the effect of changing interfacial composition on activity coefficients while the
other used the activity coefficients calculated from equilibrium. Absorption rates of CO2 into 50 wt% aqueous alkanolamine solutions were measured at 25°C and 40°C. The amines considered in this work were pure MDEA, pure DEA, 10% DEA/90%MDEA, and 50% DEA/50% MDEA. Equilibrium data extracted from these rate measurements were compared to the predictions of the VLE model. Normalized fluxes and pseudo first-order rate constants were estimated from the rate data. The pseudo first-order rate constants were regressed to yield rate parameters. The predictions from the model with these parameters were compared with the experimental measurements to validate the obtained data.

**R-92-9 $15.00**

An Expert System to Select Acid Gas Treating Processes in Natural Gas Processing Plants

Kurimura, H.

Master's thesis

An expert system was developed to select near-optimum acid gas treating processes in natural gas processing plants using heuristic knowledge from experts and literature. The near-optimum processes are defined as highly applicable processes for given conditions. The following subtasks are carried out in order by the system:

- Determination of process combinations
- Selection of acid gas removal processes
- Selection of individual acid gas removal processes
- Selection of sulfur recovery units
- Selection of tail gas clean-up units

The selection of acid gas removal processes is performed with both fuzzy and "crisp" (conventional two-value) logic. The other subtasks are executed with "crisp" logic. The developed expert system can select near-optimum processes. For the selection of acid gas removal processes, the fuzzy logic provides more rigorous and realistic solutions than "crisp" logic. In addition to the development of the expert system, corrosion mechanisms in aqueous alkanolamine were investigated using semiquantitative analysis. Based on a literature review, the protective films FeCO3 and FeS may be considered as the most important factor. The semiquantitative analysis showed that chelating agents may increase iron solubility and, hence, corrosion rate and the solubility is significantly different among common amines.

**R-93-1 PUBLISHED**

Effects of Salts on Preparation and Use of Calcium Silicates for Flue Gas Desulfurization

Kind, K. K.; P. D. Wasserman; G. T. Rochelle


High-surface-area calcium-silicate hydrates that are highly reactive with SO2 can be made by slurring fly ash and lime in water at elevated temperatures for several hours. This concept is the basis for the ADVACATE process for flue gas desulfurization. This paper examines the impact of salts on such a system. Two low-calcium fly ashes, from the Shawnee and Clinch River power plants, were examined. The addition of gypsum or calcium chloride to the slurry system increased the dissolved calcium concentration allowing the reaction rate to increase and maximum surface area to more than double in some cases. This increase came despite a lower solution hydroxide level. The salts also enhanced the reaction of the sorbent with sulfur dioxide. This resulted from the higher equilibrium moisture on the sorbent at any humidity due to the deliquescent properties of some of the salts used (calcium chloride and calcium nitrate). Solids made without the deliquescent salts exhibited equilibrium moisture adsorption consistent with a type II Brunauer-Emmett-Teller (BET) isotherm while the deliquescent salts caused hysteresis in the adsorption/desorption isotherm.

**R-93-2 PUBLISHED**

Thermodynamics of Alkanolamine-Water Solutions from Freezing Point Measurements

Chang, H.T.; M. Posey; G. T. Rochelle


The water freezing point has been measured in several amine-water systems. The water activity coefficient derived from these measurements by regression with the non-random two-liquid
(NRTL) model shows strong interactions in the MDEA-water binary system near 0°C. The apparent solution nonideality sequence in the amine-water system at low temperature (about 0°C) and dilute amine solution (up to 13 mole%) is methyl diethanolamine (MDEA) > diglycolamine (DGA) > dimethyl monoethanolamine (DMMEA) > triethanolamine (TEA) > diethanolamine (DEA) > monoethanolamine (MEA). The combined regression of freezing point depression data and total vapor pressure data predicts a significant temperature dependence of the solution properties. At 120°C, the expected solution nonideality sequence is DEA > DGA > MEA > MDEA. The parameters for activity coefficients from regression of these data should be useful for predicting acid gas solubility in these systems.

R-93-3 $5.00
The Effect of Moisture on the Reaction of Sulfur Dioxide with Calcium Silicate Sorbents
Johnson, H. L.
Master's thesis
Calcium silicate reagents can remove sulfur dioxide (SO2) from the flue gas of coal-fired power plants when injected into existing ducts. The reaction of SO2 with a high surface area (84 m2/g) reagent has been measured as a function of the moisture content of the sorbent, the relative humidity, and the SO2 concentration. Using mass and heat transfer correlations, a relationship was developed to predict the SO2 reactivity as a function of the temperature and water in the solids. Increasing the initial moisture content of calcium silicate solids increases the effective Ca conversion. At high relative humidity, the Ca conversion was modeled best by assuming that the moisture was at the gas temperature. For long reaction times, the Ca conversion was modeled best assuming water was at the adiabatic saturation temperature. At low relative humidity and reaction times of 10 to 120 seconds, the Ca conversion was modeled best assuming the water temperature was between the gas temperature and the adiabatic saturation temperature.

R-93-4
Results of a Laboratory Investigation to Characterize Coprecipitation of Wet Limestone Flue Gas Desulfurization System Additives in Calcium Sulfite Crystals
Jarvis, J. B.; E. S. Roothaan; G. T. Rochelle; R. E. Moser
Manuscript on file, Separations Research Program
This paper presents interim results from a laboratory program designed to characterize coprecipitation of wet flue gas desulfurization (R-93-4) (FGD) system additives within the calcium sulfite waste solids. Coprecipitation can represent a major loss mechanism and impact the cost of using additives in FGD systems. The objectives of the program are to develop an understanding of the variables which influence coprecipitation, identify FGD operating conditions which minimize additive coprecipitation, and develop a general model to improve the predictive capabilities of EPRI's wet FGD process integration and simulation model (FGDPRISM). To date, experiments have been performed to measure coprecipitation of formate, thiosulfate, and sulfate. The experimental results show that both thermodynamic and kinetic factors influence coprecipitation. These factors include the calcium salt activity product for the coprecipitating species, the calcium sulfite precipitation rate, and interactions when more than one coprecipitating species are present. In addition, coprecipitation is influenced by the chemical characteristics of the coprecipitating species. Considerable work has been conducted at EPRI's High Sulfur Test Center (HSTC) on the applicability of sodium formate as an additive in wet FGD systems. Data are presented comparing the results from the HSTC tests with laboratory test results.

R-93-5 $10.00
Absorption of Carbon Dioxide in Tertiary Diamines
Kreutzer, S.
Master's thesis
Aqueous alkanolamines are used in the bulk removal of H2S and CO2 as well as selective removal of H2S. The selectivity to a large extent is governed by the CO2 kinetics. The absorption of H2S in alkanolamines enhances the absorption of CO2 and increases the H2S absorption as well as its equilibrium capacity. The purpose of this work is to find a suitable diamine for selective removal of H2S and to study the kinetics of CO2 absorption using a stirrer cell. We chose to work with two
amines, commercially available: tetramethylethylene diamine and 1, 2 bis(dimethylamino) propanol.

R-93-6  $5.00
Coprecipitation of Formate with Calcium Sulfite Hemihydrate
Roothaan, E.S.
Master's thesis

The quantity of formate which coprecipitates with calcium sulfite hemihydrate is important in slurry scrubbing processes for flue gas desulfurization. Formate is used in slurry scrubbing (R-93-6) to improve sulfur dioxide removal and the extent of coprecipitation directly affects the cost associated with utilizing this additive. Experiments were conducted to measure the coprecipitation of formate, sulfate, and thiosulfate with calcium sulfite hemihydrate in aqueous systems typical of flue gas desulfurization processes. The solution composition variables included the concentrations of calcium, formate, sulfate, sulfate, magnesium, and thiosulfate. The temperature was maintained at 50°C and the pH was maintained at 5.5. Empirical models were developed to predict both formate and sulfate coprecipitation as a function of solution composition. For formate and sulfate, coprecipitation was primarily controlled by the liquid-phase activity of the coprecipitating species. Formate coprecipitation was accurately modeled using the following relationship: $HCOOSO_3 (\text{mmol formate/mol sulfite}) = 1.25 \times a_{Ca(HCOO)}^{0.25}$, where $a_{Ca(HCOO)}$ is the liquid-phase activity product of calcium formate. The coprecipitation of sulfate was modeled using a similar expression: $SO_4 (\text{mmol SO}_4/\text{mol solids}) = 169 \times R_{CaSO_4}^{0.44}$, where $R_{CaSO_4}$ is the relative saturation of calcium sulfate hemihydrate. Limited testing of thiosulfate coprecipitation indicated that both formate and sulfate inhibit thiosulfate coprecipitation. In addition to measuring coprecipitation, the rate of calcium sulfite crystallization was measured. The rate of calcium sulfite crystallization is important in flue gas desulfurization systems because it affects the scrubber solution composition, SO2 absorption, sulfite oxidation, and limestone utilization. The crystal growth rate was found to be a strong function of the relative saturation of calcium sulfite and was inhibited by dissolved calcium sulfate. An empirical model was developed to predict the crystallization rate as a function of solution composition. The crystal growth rate per unit BET surface area, rate (mole/cm$^2$-min), was given by: $4.4 \times 10^{-5} \exp(-10250/RT) \times (R_{CaSO_3} - 2)^{2.6} \times R_{gypsum}^{0.95}$, where $R_{CaSO_3}$ and $R_{gypsum}$ are the relative saturations with respect to calcium sulfite hemihydrate and gypsum, respectively.

R-93-7
Absorption of Carbon Dioxide in Aqueous Blends of Diethane and Methyldiethanolamine
Mshewa, M.M.; S. Chakravarti; G.T. Rochelle
Submitted to Chemical Engineering Science

Rates of CO2 absorption and desorption by aqueous mixtures of methyldiethanolamine and diethanolamine were measured in a wetted wall column at 25°C and 37°C. Equilibrium CO2 solubility was determined by interpolating absorption/desorption to zero rate. The CO2 solubility was 10 to 70% lower than predicted by the ASPENPLUS NRTL Electrolyte model with Austgen parameters. The effective first-order rate constant was obtained with corrections for depletion of reactants in the boundary layer and the measured equilibrium partial pressure. At low CO2 loading the rate constants agree well with those previously published. At a CO2 loading of 0.5 mole/mole amine, the rate constants were factor of 2.7 times greater than at zero loading for methyldiethanolamine and diethanolamine.

R-93-8
Preparation of ADVACATE Reagent in a Flow Reactor
Kind, K.K. and G.T. Rochelle
Submitted for presentation at the 1993 SO2 Control Symposium, Boston, Massachusetts, August 1993

The ADVACATE (ADVANCED Silicate) process utilizes fly ash from power plants as a reactant with lime to form a high surface area material that can be injected into the flue gas to remove sulfur dioxide. The process has undergone bench and pilot testing but the sorbent has been prepared in batch reactions in most cases. The characteristics of the reaction between fly ash and hydrated lime in a flow reactor are examined in this study. Fly ash and reacted material from a
pilot scale test performed at the Shawnee test facility in the summer of 1992 are reacted in batch and flow reactors on the bench scale. The surface area of the product material was predicted using the batch data for flow reactor residence times of 10 hours or less. Reactions at long residence times performed with reacted pilot-plant material produced reagent without the high surface area needed for the process despite additional ash reaction. Grinding the ash dramatically increased the reaction rate. The addition of gypsum to the system to stimulate forced oxidation of the system had a negative impact on the product surface area for residence time less than 8 hours.

R-93-9
Chemistry of Limestone Slurry Scrubbing
Agarwal, R.S. and G.T. Rochelle
Submitted for presentation at the 1993 SO2 Control Symposium, Boston, Massachusetts, August 1993
Limestone slurry scrubbing is the dominant technology for the removal of SO2 from flue gases in coal based power plants. A fundamental, rate-based model to simulate the process has been developed at The University of Texas at Austin. This model incorporates principles of mass transfer with chemical reaction and electrolyte thermodynamics. The model has been used to simulate the effects of important operating variables such as inlet SO2 concentration, ratio of liquid to gas flow rate, hold tank residence time, and limestone utilization. This paper uses the model to explain the behavior of the system due to changes in the above operating variables.

R-94-1 $15.00
Hydrothermal Reaction of Lime with Fly Ash to Produce Calcium Silicates for Dry Flue Gas Desulfurization
Peterson, J.R.
PhD dissertation
Experimental work was performed to determine the important chemical interactions involved in the formation of lime/fly ash solids for flue gas desulfurization (FGD) (R-94-1). Three types of experiments were used: fly ash dissolution experiments, in which the fly ash dissolution rate was measured in the absence of any precipitation reactions which may alter the dissolution rate; lime/fly ash reaction experiments, in which hydrated lime was reacted with various sources of fly ash to determine the effect of fly ash type on the lime/fly reaction; and reagent chemical experiments in which the major components of fly ash were simulated with reagent chemicals to determine the relative importance of the various components of the fly ash. A significant amount of work was also performed to determine the effects of recycle (i.e., sulfite and sulfate) on the reaction of hydrated lime with fly ash. The fly ash dissolution experiments showed that the high-calcium fly ashes were much more reactive than the low- and medium-calcium fly ashes. A significant fraction of the high-calcium fly ashes dissolved instantly, while the other fly ashes dissolved uniformly. The aluminum present in the high-calcium fly ashes was much more reactive than the aluminum present in the low- and medium-calcium fly ashes. The dissolution rate of silica from the low-calcium fly ash was found to be first order in the hydroxide concentration of the solution. The activation energy for silica dissolution was determined to be 20.5 kcal/mol, comparable to previous results with the dissolution of quartz and amorphous silica. The dissolution rate of silica from the high calcium of fly ash was much more sensitive to the hydroxide concentration in the solution because the glass present in the fly ash is much different than that present in the low-calcium fly ash. The data from the lime/fly ash experiments showed a clear effect of fly ash type on the reaction of hydrated lime with fly ash. The solids produced with the high-calcium fly ash had a lower surface area and reactivity towards SO2 than the solids produced from low- and medium-calcium fly ashes. The data from the reagent chemical experiments showed that the reason for the low reactivity of the solids from the high-calcium fly ash is due to the very reactive aluminum content of the fly ash. The reagent chemical experiments showed that the calcium-silicates produced by the reaction of hydrated lime with silica fume were amorphous and had a high surface area. These solids were very reactive towards SO2. In contrast, the calcium-aluminate solids formed by reacting hydrated lime with A1(OH)3 were very crystalline, had a low surface area, and were unreactive towards SO2. The experiments investigating the effect of recycle materials showed that the addition of gypsum to the slurry inhibited the formation of the unreactive calcium-aluminate materials, but had no effect on the
formation of the calcium-silicate solids. The addition of calcium sulfite hemihydrate to the slurry changed the calcium-aluminate product, but the new product also had a low surface area and was unreactive towards SO2.

R-94-2
Kinetics of Carbon Dioxide Absorption/Desorption at Stripper Temperature in Mixtures of Aqueous Methyl diethanolamine and Diethanolamine
Mshewa, M.M. and G.T. Rochelle
Presented at the AIChE National Meeting, Atlanta, Georgia, April 21, 1994
Carbon dioxide absorption and desorption from aqueous solutions of alkanolamines occurs by a process of mass transfer enhanced by a fast, reversible chemical reaction in the boundary layer. Fundamental understanding of these reactions is important for efficient modeling, design, and retrofits of acid gas treatment processes. Satisfactory data is available in the literature for carbon dioxide reactions with single alkanolamines at low temperatures typical of the absorber. However, no significant kinetics data is available at stripper operating temperature for single alkanolamines and even less data is available for the blends. Rates of CO2 absorption/desorption by aqueous solutions of methyl diethanolamine (MDEA) and mixtures of MDEA and diethanolamine (DEA) were measured in a laboratory wetted-wall column at temperatures typical of the industrial stripper. Fifty-wt% amine solutions were used in the study (pure MDEA and a 25 wt% DEA/25 wt% MDEA). Temperature ranged from 25°C to 120°C. Solution CO2 loading was varied from 0 to 0.2 mol/mol amine. Vapor liquid equilibrium (VLE) and solution speciation were calculated by a VLE model developed in the frame work of AspenPlus. This model uses the electrolyte-nonrandom two-liquid equation to estimate the activity coefficient in the liquid phase. Lower rates than expected were observed for both 50 wt% MDEA and 25 wt% DEA/25 wt% MDEA solutions at high temperatures. Effective rate constants measured for pure MDEA were 6, 13.8, 16 m3/kmol-s for temperatures of 25, 105, and 120°C respectively. For the mixture solution, effective rate constants obtained for this case were 2090, 100, 32, and 18.7 m3/kmol-s for temperatures of 25, 80, 105, and 120°C, respectively.

R-94-3
Carbon Dioxide Absorption/Desorption Kinetics in Blended Amines
Mshewa, M.M. and G.T. Rochelle
Presented at the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, March 2, 1994
Carbon dioxide reacts at a finite rate with MDEA and DEA. The kinetics of these reactions have been measured by absorption and desorption of CO2 in 50 wt% MDEA at 25°C and 105°C. The rate constants obtained at 25°C and 105°C are 3 and 97 m3/kmol-s respectively. These constants correspond to an activation energy of 41 kJ/kmol. Extrapolation to 120°C gives a second-order rate constant of 150 m3/kmol-s. Literature values for DEA reactions were incorporated in the model for DEA and a blend of MDEA/DEA. The model was used to predict observed and expected trends in rates of CO2 absorption and desorption with commercial alkanolamines. With 50 wt% MDEA solution at absorber conditions, the absorption rate is nearly controlled by physical absorption. At stripper conditions, enhancement factors are between 2 and 3 and therefore the reaction is contributing to the absorption rate but not completely controlling it. With a blend of 10 wt% DEA and 40 wt% MDEA at the lean end of the absorber and throughout the stripped CO2, mass transfer is significantly enhanced by the fast chemical reaction. With a 50 wt% DEA solution, the rate of CO2 absorption is controlled by fast reaction both at the absorber and stripper conditions, and at the lean end of the stripper equilibrium, instantaneous reactions, may be approached.

R-94-4
Use of Excess Enthalpy Data to Improve Activity Coefficient Models for Water-Monoethanolamine Systems
Posey, M. and G.T. Rochelle
Manuscript on file, Separations Research Program
Natural-gas streams and refinery-process streams often contain hydrogen sulfide (H2S) and carbon dioxide (CO2) gases that must be removed. The traditional treating method is an
absorption/stripping system using aqueous solutions of alkanolamines. The common amines used are monoethanolamine (MEA), DEA, MDEA, and diglycolamine (DGA). Methyl diethanolamine and mixtures of MDEA with MEA or DEA are receiving wide use in today’s gas-treating systems. In order to better design these systems, a good model is necessary to predict equilibrium conditions at all possible combinations of amine concentrations and acid-gas loadings. It is believed, and will be shown here, that a model based on all types of data, not just pressure data, will perform better and the parameters will be known with more confidence. This benefit will be seen for any excess Gibbs energy model, not just the model we have chosen. In addition to vapor pressure data, we used freezing-point depression data and heat-of-mixing data to regress the model parameters.

**R-94-5**

**Nitrogen Dioxide Removal by Advocate Solids**

Nelli, C.H. and G.T. Rochelle

Final Report, EPA No. 3D2754NAEX

The purpose of this work is to provide science for new processes designed to remove nitrogen oxides from flue gases emitted by coal-fired electric power plants. Nitrogen dioxide (NO2) diluted with nitrogen was reacted with calcium silicate solids in a packed-bed reactor. The primary reagent was calcium silicate mixed with sand. Calcium silicate or ADVACATE solids (R-94-5); (ADVanced siliCATE) solids are comprised of varying amounts of reacted calcium hydroxide, fly ash, calcium sulfite, and sodium hydroxide. The reaction between silica in the fly ash and calcium hydroxide produces a calcium silicate material with high surface area and porosity. A process benefited by this work will be the ADVACATE process modified for NOx removal. This technology removes NOx by injecting methanol in the duct ahead of existing or new processes for FGD. As a result, NO is oxidized to more reactive and more soluble NO2. The flue gas is cooled and is contacted with injected damp calcium silicate solids. The sorbents react with the flue gas and are removed by a baghouse. Much of this reaction is expected to take place on the bag filter since moist, unreacted sorbent is contacted by oncoming flue gas. Some of the by-product coming off the filter bags is purged from the system while the rest is used to prepare the silicate solids.

**R-94-6**

**Limestone Slurry Scrubbing for SO2 Emission Control-Modeling and Parameter Estimation**

Agarwal, R.S. and G.T. Rochelle

Prepared for presentation at AIChE National Meeting, Denver, Colorado, August 14-17, 1994

Limestone slurry scrubbing; is the dominant technology for SO2 removal. A fundamental rate-based model has been developed for the simulation of this process. The model solves nonlinear algebraic and differential equations involving mass transfer, kinetics, and electrolyte thermodynamics. It uses three primary adjustable parameters, the number of gas-film mass-transfer units, the ratio of liquid to gas-film mass-transfer coefficients, and the limestone dissolution parameter. These have been estimated from field data for a turbulent contact absorber. The estimation procedure involves multivariate regression using the maximum likelihood estimate method. The calculated parameter values have been reported along with their respective confidence interval estimates as well as joint confidence regions. We have used statistical techniques to quantify the goodness of fit with respect to each parameter. The best parameter values were $N_g = 3.09\pm0.39$, $k^0/\text{kg} = 225\pm98$ atm-ml/gmol for the small scale contactor, and $N_g = 2.97\pm0.54$, $k^0/\text{kg} = 272\pm102$ atm-ml/gmol for the large-scale contactor. We also propose empirical correlations for the effects of liquid flow rate, gas flow rates, and the packing height.

**R-94-7** PUBLISHED

**An Expert System to Select Acid Gas Treating Processes for Natural Gas Processing Plants**

Kurimura, H.; G.T. Rochelle; K. Sephehrnoori


An expert system was developed to select near-optimum acid gas treating processes; in natural gas processing plants using heuristic knowledge from experts and literature. The near-optimum processes are defined as highly applicable processes for given conditions. The following subtasks are carried out in order by the system: determination of process combinations; selection of acid
gas removal processes; selection of individual acid gas removal processes; selection of sulfur recovery units; and selection of tail gas clean-up units. The selection of acid gas removal processes is performed with both fuzzy and "crisp" (conventional two-value) logic. The other subtasks are executed with the crisp logic. The developed expert system can select near-optimum processes. For the selection of acid gas removal processes, fuzzy logic is better than crisp logic because it provides more rigorous and realistic solutions.

**R-94-8: PUBLISHED**

**Preparation of Calcium Silicate Reagent from Fly Ash and Lime in a Flow Reactor**

Kind, K.K. and G.T. Rochelle


The batch reaction between fly ash and hydrated lime in water to produce high surface area calcium silicates for flue gas desulfurization (R-94-8) has been examined extensively. This paper examines the reaction in a flow reactor using two low-calcium fly ashes and introducing gypsum, calcium sulfite hemihydrate, and calcium chloride as additives to the reaction. The flow system is compared to the batch reaction at similar operating conditions and a segregated flow model is used to approximate flow reactor behavior. Experiments with calcium chloride and gypsum additives were modeled fairly well by the segregated flow approximation at residence times less than 12 hours. The flow reactor produced low surface area material at longer residence times when gypsum was present. Because the changing solution chemistry affected the batch reaction rate, the fly ash, and hydrated lime system without a gypsum or calcium chloride could not be approximated using batch reaction data. In this case, the flow reactor produced higher surface area product than the batch reactor for a given residence time due to the increased calcium hydroxide availability.

**R-94-9**

**A Nonrandom Two-Liquid Model for Alkanolamine-Water Systems**

Posey, M. and G.T. Rochelle

Submitted to the Canadian Journal of Chemical Engineering

Heat of mixing has been measured for pure methyldiethanolamine (MDEA), diethanolamine (DEA) and monoethanolamine (MEA) into 0.1 mol/L NaOH at 25°C and 70°C. Using data for total pressure, freezing point, heat of mixing and vapor-liquid equilibrium, parameters for the Nonrandom Two-Liquid (NRTL) model have been found for the binary alkanolamine-water systems. MEA-H2O, DEA-H2O and MDEA-H2O. Predictions are given and compared to experimental data for the MDEA-DEA-H2O mixed amine system. It is shown for the MEA-H2O system that heat of mixing data improves modeling for amine-water systems.

**R-94-10 $20.00**

**Modeling of Limestone Slurry Scrubbing in Plug Flow and Well-Mixed Contactors**

Vandekemp, R.

Master's thesis

Limestone slurry scrubbing, a dominant technology for removal of sulfur dioxide from flue gases, has been modeled by researchers at The University of Texas for several years. In a continuation of this effort, the model has been modified to simulate either tray or spray towers, and combinations thereof. The model first simulated a three staged contactor, with gas phase concentrations integrated through well mixed liquid. Several options have been added. The use of a log-mean average SO2 flux and arithmetic averages of O2 and CO2 fluxes were substituted for integration of the gas phase concentrations without significantly changing predicted SO2 removal. In this approach, SO2 gas composition was added as a fifth variable to the optimization routine, eliminating the need for gas phase integration. Computationally, the quickest approach for simulation of well-mixed stages combines the newer approach and a new optimization method written by Pepe. The approach using the average gas fluxes was modified to simulate plug flow liquid by using the arithmetic average of the solid-liquid mass transfer rates at the top and bottom of the stage. Finally, the numerical integration of concentrations in all three phases from the top of the scrubber to the bottom eliminated the need for optimization. Computation time required for the numerical integration approach was much less than that required for optimization; the Implicit
Euler's method showed the lowest convergence time. To model the effect of multiple spray headers, fresh slurry can be fed to any stage. By appropriately varying the solution method and other parameters used for each section in the simulation, a variety of scrubber configurations can be tested using the model.

R-95-1
Sulfur Dioxide Removal by Reagents Prepared from Lime and Recycled Glass
Arthur, L.F. and G.T. Rochelle
Manuscript on file, Separations Research Program

High surface area solids that are reactive toward sulfur dioxide (SO2) have been produced from recycled post-consumer glass and lime. Experimental results show that the rate of surface area formation is directly proportional to the initial surface area of the glass. Gypsum is shown to be an effective additive for reactions at 92°C to increase surface area after long times. For slurry reactions with gypsum, increasing the slurry temperature to 120°C produced a product with higher surface area than that produced at 92°C only, for reaction times <15 hours. Absorption of SO2 with solids made from recycled glass yield 80% utilization of available alkalinity when reacted with 1000-2000 ppm SO2 at 35°C and 64% relative humidity. The alkalinity was from both the lime (~86%) and the glass (~14%).

R-95-2
Sulfite Solutions as an Absorbent for Chlorine and Fluorine Gases - A Literature Review
Chisholm, P.N.
Manuscript on file, Separations Research Program

A literature review was conducted to investigate the feasibility of using sulfite solutions as scrubbers for chlorine and fluorine gas removal in waste streams. While molecular chlorine is a product in flue gases, it was found that molecular fluorine is not produced by microelectronics manufacturing (Trachtenberg, 1995). Plasma etching uses CF4, but has as its gaseous products-SiF4, H2SiO3, and HF. Considerable research has been done using hydroxyl and carbonate solutions to scrub waste streams for primarily molecular chlorine removal. Systems have been developed and have proven effective toward this end. The present literature review focuses on the feasibility of using sulfite solutions to scrub molecular fluorine and chlorine from waste streams. Included in this report are the mechanisms and kinetics of these halogens absorbing into just hydroxyl solutions presented to compare the projected performance of sulfite solutions to hydroxyl solutions.

R-95-3 $30.00
Hydrothermal Preparation of High Surface Area Calcium Silicate from Lime and Fly Ash in a Flow Reactor
Kind, K.K.
PhD dissertation

The ADVACATE process removes sulfur dioxide from flue gases by duct injection of calcium-silicate-hydrate sorbent with high surface area prepared by slurrying calcium hydroxide with fly ash and recycled material in water at temperatures between 90°C and 100°C. In this work, sorbent was prepared in bench scale batch and well-mixed flow reactors. Three low calcium ashes were studied with 1 to 8 g fly ash/g calcium hydroxide. Experiments were performed with additives including calcium sulfate hemihydrate, gypsum, calcium chloride, and sodium hydroxide. Reaction was enhanced at times through four hours by increasing hydroxide concentration to 0.1 M. Availability of calcium hydroxide to the ash reaction site was more significant than the hydroxide concentration in the bulk solution at reaction times greater than four hours. The addition of gypsum or calcium chloride to the slurry system increased the calcium concentration allowing for increased reaction rate and a maximum-product surface area more than double that of ash/lime reactions. The increase in surface area occurred despite lower solution hydroxide concentration. The impact of grinding ash prior to reaction was dependent on the reactivity of the base ash. Optimum product has a high surface area and this correlated to reacted ash silica. The product calcium to silicamole ratio was between 0.8 and 2.2 increasing with solution calcium concentration. This range is consistent with CSH, an amorphous calcium-silicate-hydrate species.
Aluminum and iron in the ash reacted to a lesser extent. No significant crystalline species were noted in any reaction products. A segregated flow model predicted product from the flow reactor in certain cases. The flow reactor provided better reaction of fly ash and calcium hydroxide due to the greater availability of fresh calcium hydroxide in the reactor. Product surface area decreased with residence time greater than ten hours in experiments with gypsum added despite additional ash reaction. Surface area of the pilot plant product material examined was predicted using the segregated flow model with continuously stirred tank reactor (CSTR) residence times of less than 11 hours. Experiments at longer residence times again produced sorbent without high surface area.

R-95-4
Nitrogen Dioxide Reaction with Alkaline Solids
Nelli, C.H. and G.T. Rochelle
Submitted to Industrial & Engineering Chemistry Research

At conditions typical of a bag filter in a coal fired flue gas, nitrogen dioxide (NO2) diluted with nitrogen was exposed to various alkaline and non-alkaline solids in a packed-bed reactor. On non-alkaline solids, three moles of NO2 reacted readily with water to produce two moles of nitric acid (HNO3) and one mole of NO. Alkaline solids such as calcium hydroxide or calcium silicate (from lime and fly ash) produced less NO and neutralized the nitric acid on the surface. A mathematical model developed to predict rates of NO2 removal on these surfaces successfully compared experimental and predicted rates. These results are relevant to technology for removal of NOx by addition of methanol to dry scrubbing systems for flue gas desulfurization.

R-95-5
Nitrogen Dioxide Removal by Hydrated Lime with SO2 Present
Nelli, C.H. and G.T. Rochelle
Manuscript on file, Separations Research Program

At conditions typical of a bag filter in a coal fired flue gas, nitrogen dioxide (NO2) reacted readily with surface water and sulfite ion (SO3=) on hydrated lime. The adsorption of water and the hydrolysis of SO2 on hydrated lime provided sufficient water and sulfite to react with NO2. The presence of oxygen in the synthesized flue gas reduced NO2 removal via sulfite oxidation on the hydrated lime surface. In addition, the presence of NO2 in the system improved total SO2 removal. A mathematical model developed to predict rates of NO2 removal by the NO2-water and NO2-sulfite reactions successfully compared experimental and predicted rates. These results are relevant to technology for removal of NOx by addition of methanol to dry scrubbing systems for flue gas desulfurization.

R-95-6
A Simple Semi-Empirical Model for Prediction of Hydrogen Sulfide and Carbon Dioxide Solubilities in Methyldiethanolamine
Posey, M.L. and G.T. Rochelle
Submitted to the AIChE Journal

Natural gas streams and refinery process streams often contain hydrogen sulfide (H2S) and carbon dioxide (CO2) gases that must be removed. The traditional treating method is an absorption/stripping system using aqueous solutions of alkanolamines. One of the most commonly used amines is methyldiethanolamine (R-95-6) (MDEA). Accurate equilibrium models for H2S and CO2 in alkanolamine solutions are needed to properly predict operating characteristics and behavior of absorption/stripping systems. However, any good equilibrium model must be partly based on good experimental acid gas equilibrium data. Several experimenters have collected data for the MDEA-CO2 and MDEA-H2S systems, with less data being collected for the MDEA-CO2-H2S system. Unfortunately, the data from different authors has been collected over different ranges of temperature, amine concentration, and acid gas loading, leaving no possibility for direct comparisons. In order to determine which data sets agree, and which data sets or points are far from the norm, a simple model was constructed.
Nitrogen Dioxide Absorption in Limestone Slurry for Flue Gas Desulfurization
Shen, C.H. and G.T. Rochelle
Manuscript on file, Separations Research Program
We have measured rates of NO2 absorption and sulfite oxidation in a highly characterized stirred cell contactor, at pH 4.5 to 6.0, 25°C to 55°C, and solution compositions typical of limestone slurry scrubbing (R-95-7). The rate constants of the reactions between NO2 and sulfite (SO3=), bisulfite (HSO3-) and water at 55°C were 11.2 x 10^5 M^-1s^-1, 2.8 x 10^4 M^-1s^-1, and 1.6 x 10^7 M^-1s^-1, respectively. NO2 absorption catalyzes sulfite oxidation in the presence of oxygen, which may lead to depletion of sulfite at the interface and reduce the rate of NO2 absorption. For every mole of NO2 absorbed, 4 to 160 moles of sulfite may be oxidized. Higher pH favors NO2 absorption, while additives such as Mg2+, Ca2+, and Cl- inhibit NO2 removal. The presence of buffer or oxidation inhibitor enhances the rate of NO2 absorption.

Limestone Slurry Scrubbing-Modeling and Parameter Estimation
Agarwal, R.S.
PhD dissertation
The Amendments to the Clean Air Act of 1990 require a reduction in the emission of sulfur dioxide (SO2) into the atmosphere. Electric power utilities are a major source of SO2 emissions and come under the purview of the Clean Air Act. Limestone slurry scrubbing is the dominant technology for controlling SO2 emissions generated by these utilities. The development of a FORTRAN model for simulation of the Limestone Slurry Scrubbing process has been an ongoing effort at The University of Texas at Austin for the past fourteen years. The present investigation is focused on calculating the adjustable parameters in the model. These parameters are calculated using data from bench-scale and pilot-scale absorbers. The estimated parameters can be used to describe mass-transfer characteristics of turbulent contact absorbers operated under similar hydrodynamic conditions, i.e., liquid velocity, gas velocity, and packed height. The uncertainty in the estimated values of the parameters has been quantified using statistics. The parameters were estimated using Generalized REGression (GREG, Caracotsios, 1986). The FORTRAN program used the Maximum Likelihood Principle to estimate adjustable parameters. The calculated values indicate that the parameters Ng and k°L/kg are similar for both the bench-scale and pilot-scale absorbers under similar hydrodynamic conditions. These estimates were found to be highly dependent on each other, due to the nature of the data and the parameters. More independent estimates could be obtained if the parameter set Ng and Ng k°L/kg was used. The effect of liquid phase chemistry on the absorption of SO2 was also investigated using the model. The investigations show that hydrolysis reaction plays a significant role in the enhancement of SO2 absorption. The alkalinity due to HCO3- and SO3= does not play a major role below pH of 5. The presence of high concentrations of buffer additives can lead to conditions of gas film control.

A Nonrandom Two-Liquid Model for Alkanolamine-Water Systems
Posey, M. and G.T. Rochelle
Manuscript on file, Separations Research Program
Heat of mixing has been measured for pure methyl-diethanolamine (MDEA), diethanolamine (DEA) and monoethanolamine (MEA) into 0.1 mol/L NaOH at 25°C and 70°C. Using data for total pressure, freezing point, heat of mixing and vapor-liquid equilibrium, parameters for the Nonrandom Two-Liquid (NRTL) model have been found for the binary alkanolamine-water systems, MEA-H2O, DEA-H2O and MDEA-H2O. It is shown for the MEA-H2O system that heat of mixing data improves modeling for amine-water systems. This effort is part of an ongoing project to model equilibrium in the alkanolaminewater-acid gas system using the electrolyte-NRTL model.
Processes for Removing Acid Components from Gas Streams
Rochelle, G.T.; C. Jorgensen; J.C.S. Chang; T.G. Brna; C.B. Sedman; W. Jozewicz
United States Patent 5,401,481 (March 1995)

The present disclosure relates to improved processes for treating acid gases to remove acid gas components therefrom. Processes in accordance with the present invention include preparing a calcium silicate hydrate sorbent in the form of a semi-dry, free-flowing powder, and treating the gas with the powdery sorbent, such as by injecting the sorbent into a stream of the gas. The powdery sorbents may be prepared by slurring/drying or pressure hydration techniques. Examples disclosed herein demonstrate the utility of these processes in achieving improved acid gas-absorbing capabilities in both lab-scale and pilot plant studies. Additionally, disclosure is provided which illustrates preferred plant design configurations for employing the present processes using conventional dry sorbent injection equipment. Retrofit application to existing plants is also addressed.

Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions
Posey, M.L.
Ph.D. Dissertation

Natural gas and refinery gas streams usually contain acid gases such as carbon dioxide and hydrogen sulfide that must be removed. The prevailing method for removing these gases is by chemical absorption into aqueous alkanolamine solutions. The common amines used are methyldiethanolamine (MDEA), diethanolamine (DEA), monoethanolamine (MEA) and their mixtures. To better design and operate these absorption systems, a good vapor-liquid equilibrium model of the chemical thermodynamics is needed. It is difficult to measure vapor-liquid equilibrium (VLE) data accurately at low acid gas concentrations. However, good predictions at these conditions are crucial to determining system performance and economics. Therefore, a primary goal of this work was to improve existing model predictions and understanding of low loading behavior. As acid gas approaches a loading of zero, the solution becomes a binary amine-water system. Freezing point data from the literature and heat of mixing data measured in this work have been regressed along with total pressure data to significantly improve modeling of the binary amine-water systems. Abundant VLE data exists at moderate to high loadings, but very little exists at low loading, and even then, discrepancies are seen between data sources. Therefore, pH and conductivity data have been measured to supplement the VLE data and improve confidence in model predictions at low acid gas loadings. The electrolyte-nonrandom two-liquid model has been used to represent thermodynamics in these solutions. The Data Regresion System (DRS) of Aspen Plus® was utilized to regress model parameters to the experimental data. DRS reports not only the regressed parameters, but calculates error in the parameter values and provides a parameter correlation matrix. These tools made it possible to critically analyze model sensitivity to the parameters. The important parameters and interactions are identified and provide the key to obtaining better model predictions. By comparing analogous parameters from MDEA and DEA systems, intelligent choices were made for mixed amine parameters in the MDEA-DEA-H2S-CO2 system. With the knowledge gained, reasonably accurate predictions can be made for other mixed amine systems for which experimental data does not exist.

A Simple Model for Prediction of Acid Gas Solubilities in Alkanolamines
Posey, M.L.; K.G.Tapperson; G.T. Rochelle

A simple model has been created for predicting acid gas vapor-liquid equilibrium (VLE) in alkanolamines. The model is simple enough to use in a hand held calculator, but its structure is derived from theory. Model parameters were obtained by regression of experimental VLE data. The model is valid for total acid gas loadings from 0.003 to 0.8 and over a wide range of temperatures and amine concentrations. Partial pressure predictions are shown to agree with a more complex model over seven orders of magnitude in pressure. Heat of absorption values
derived from the model are also shown to agree with literature sources. Parameters are given for the MDEA-H2O-H2S-CO2 and DEA-H2O-H2S systems.

R-96-3
Nitrogen Dioxide Reaction with Alkaline Solids
Nelli, C.H. and G.T. Rochelle
At conditions typical of a bag filter in a coal-fired flue gas, nitrogen dioxide (NO2) diluted with nitrogen was exposed to various alkaline and nonalkaline solids in a packed-bed reactor. On nonalkaline solids, 3 mol of NO2 reacted readily with water to produce 2 mol of nitric acid (HNO3) and 1 mol of NO. Alkaline solids such as calcium hydroxide or calcium silicate (from lime and fly ash) produced less NO and neutralized the nitric acid on the surface. A mathematical model developed to predict rates of NO2 removal on these surfaces successfully compared experimental and predicted rates. These results are relevant to technology for removal of NOx by addition of methanol to dry scrubbing systems for flue gas desulfurization.

R-96-4
Hg Absorption in Aqueous Permanganate
Zhao, L. and G.T. Rochelle
Accepted AIChE Journal (1996)
The absorption of elemental Hg vapor into acidic permanganate solution was measured in a stirred cell contactor at 25°C and 55°C. The gas film mass transfer coefficient was measured using concentrated acidic permanganate solution. The liquid film mass transfer coefficient was obtained by mercury desorption from HgCl2 injected into acidic stannous chloride solution. The absorption of Hg into permanganate occurs with simultaneous diffusion and fast irreversible reaction in the boundary layer. The reaction is first order in Hg and in KMnO4, respectively. The overall second order rate constant is (1.6 ± 0.2) × 107 M-1s-1 at 25°C and (12.6 ± 5.3) × 107 M-1s-1 at 55°C. The Arrhenius expression for the second order rate constant is 1.018 × 1017 exp (-6730/T). The activation energy was calculated to be 56.0 kJ/mole.

R-96-5 PUBLISHED
Modeling CO2 and H2S Solubility in MDEA and DEA: Design Implications
Rochelle, G.T. and M. Posey
The solubility of H2S and CO2 in aqueous alkanolamines affects solution capacity and the required circulation rate for acid gas absorption. These thermodynamics also determine the relationship of steam rate and the lean loading of the solution which in turn sets the leak of acid gas from the top of the absorber. Finally, the mechanics of mass transfer and the role of kinetics, especially in stripping, depend on the vapor/liquid equilibria. Published measurements of CO2 and H2S solubility in methyldiethanolamine (MDEA) and diethanolamine (DEA) are not in general agreement, especially at low loading of acid gas. The available sets of solubility data have been regressed with the AspenPlus electrolyte/NRTL model. All of the parameters and constants that make up this model have been carefully evaluated. Independent thermodynamic data such as freezing point and heat of mixing have been included in the regression to strengthen the estimates of model parameters. The parameters for each set of solubility data have been evaluated in an attempt to determine which set is correct. Each evaluated model has been used to calculate the acid gas capacity and minimum stripping steam rate for several industrial cases of acid gas absorption/stripping.

R-96-6
Electrolyte Nonrandom Two-Liquid Model for Methyldiethanolamine Solutions
Posey, M.L. and G.T. Rochelle
The Electrolyte Nonrandom Two-Liquid model has been applied to methyldiethanolamine solutions. Model parameters were regressed to fit experimental vapor-liquid equilibrium (VLE) data. Parameters are given along with plots showing how well the data was fit. Predicted solution
speciation is given along with insights into the observed trends. Differences between two data sets of hydrogen sulfide VLE are analyzed and discussed. Experimental pH data is presented in order to shed light on the differences.

**R-97-1**

**Nitrogen Dioxide Absorption and Sulfite Oxidation in Aqueous Sulfite**

Shen, C.H. and G.T. Rochelle  
Submitted to Environmental Science and Technology

Rates of NO2 absorption and sulfite oxidation were measured in a highly characterized stirred cell reactor. The relations between NO2 and sulfite (SO32-), bisulfite (HSO3-) and thiosulfate (S2O32-) were first ordered in NO2 concentration, and their respective rate constants at 55 °C were 11.2*10^5 M-1 s-1, 2.8*10^4 M-1 s-1, and 5.4*10^3 M-1 s-1. The NO2 hydrolysis reaction was second order in NO2 concentration, with a rate constant of 1.6*10^7 M-1 s-1 at 55 °C. NO2 catalyzes sulfite oxidation in the presence of oxygen, and this study quantified the effect of sulfite and oxygen concentration, the rate of NO2 absorption, the presence of thiosulfate and gas phase SO2 on the rate of sulfite oxidation. Areas of potential industrial application of this study are also discussed.

**R-97-2 $20.00**

**Nitrogen Dioxide Absorption in Aqueous Sodium Sulfite**

Chen H. Shen  
Ph.D. Dissertation May 1997  
Manuscript on file, Separations Research Program

The Clean Air Act of 1990 requires additional reduction of acid gases, sulfur dioxide, and nitrogen oxides released into the atmosphere from coal-fired electric power plants. In the case of older existing power plants, a possible retrofit strategy is to oxidize nitric oxide (NO, the major constituent of NOx in flue gas) to nitrogen dioxide (NO2) by the addition of methanol or other hydrocarbons into the duct at an optimum temperature regime. NO2 can then be by either modifying existing SO2 control equipment or by adding a limestone (CaCO3) slurry scrubbing process. Limestone reacts with SO2 to form CaCO3, and the free sulfite (SO32-) in solution is reactive toward NO2. The focus of this research is to study the reaction between NO2 and aqueous sulfite at an elevated temperature and in the presence of gas phase O2. The removal of NO2 by limestone slurry scrubbing involves the reaction between NO2 and SO32-, bisulfite (HSO3-) and water. The reactions between NO2 and SO32-/ HSO3- are first order in both reactants, while the NO2-water reaction is the NO2-thiosulfate (S2O32-) reaction were determined at 55 °C. SO32- was found to be the most reactive toward NO2, while the contribution of chemical reaction still dominated in the absorption of NO2 into water. The effect of gas phase SO2 and O2, and liquid phase additives such as S2O32-, Ca2+, Mg2+, and Cl- on NO2 absorption was also investigated.

The absorption of NO2 catalyzes free radical reactions that lead to sulfite oxidation. A semi-empirical model was proposed to relate the rate of sulfite oxidation to the rate of NO2 absorption. Thiosulfite inhibits sulfite oxidation by providing an alternative route for the termination of the free radical reactions, and a fundamental model was derived to quantify the effect of S2O32- on sulfite oxidation. The absorption of NO2 into aqueous bisulfite (HS-) was studied in an attempt to discover alternative scrubbing technologies. The reaction between NO2 and HS- is twice as fast as the NO2- SO32- reaction at 55 °C. A semi-empirical model was proposed to relate NO2 absorption to HS- oxidation. This study has shown that acceptable level of NO2 removal by a conventional limestone slurry scrubber is not probable. However, aqueous scrubbing of NO2 by Na2SO3 and Na2S solutions are viable options. Furthermore, significant reduction in hold tank liquid depth and/or oxidizing air stoichiometry is possible by NO2 injection.

**R-97-3**

**Preparation of Calcium Silicate Absorbent from Recycled Glass**

Arthur, L.F. and G.T. Rochelle  
Manuscript on file, Separations Research Program

Calcium silicate hydrates were prepared from hydrated lime and post-consumer recycled glass in an aqueous slurry. Surface area was monitored at a variety of reaction conditions. The rate of
surface area formation was found to be directly proportional to the initial surface areas of the glass. At 92°C, the addition of gypsum to the system had a significant positive effect, forming solids with surface areas up to 125 m²/g over long reaction times. Increasing the temperature from 92°C to 120°C increased the initial rate of surface area formation, however the rate decreased over time and the ultimate surface area was higher at 92°C. The addition of gypsum or calcium chloride to the reaction at 120°C increased the ultimate surface area, but not to the extent of the 92°C product. Up to a surface area of ~100 m²/g, sorbents formed at 92°C with gypsum were not affected by agitation, nor by solids content between 20-50% under non-agitated conditions. At reaction times after this point, surface area increased slightly with water content and more significantly with agitation. In addition, the dissolution of silica from glass was measured and was found to be faster than the rate of sorbent formation.

R-97-4 PUBLISHED
Mercury Absorption in Aqueous Oxidants Catalyzed by Mercury (II)
Zhao, Lynn L. and G.T. Rochelle
The absorption of elemental Hg vapor into aqueous solution containing Hg(II) was measured in a stirred cell contactor at 25 and 55°C. In 0.8 M HNO₃, the reaction is first-order in Hg and Hg(II) respectively. The overall second-order rate constant is given by \( k_2 = 2.90 \times 10^9 \times \exp(-1765/T) \). In 0.8 M HNO₃ with the addition of H₂O₂, the reaction is first-order in Hg, H₂O₂, and Hg(II), respectively. The overall third-order rate constant is given by \( k_3 = 2.13 \times 10^{23} \times \exp(-10110/T) \).
The addition of Fe²⁺ or Fe³⁺ has no immediate effect on mercury removal. In 0.8 M HNO₃ with the addition of K₂Cr₂O₇, the reaction is first-order in Hg, Cr₂O₇⁺, and Hg(II), respectively. The overall third-order rate constant is \( 4.3 \times 10^8 \text{ M}^{-2} \text{s}^{-1} \) at 25°C. For mercury absorption in Hg(II) obtained by HgCl₂ injection, the presence of HNO₂ greatly enhanced Hg absorption. H₂SO₄ had a comparable positive effect while HCl had a negative effect. Succinic acid-NaOH buffer solution greatly enhanced Hg absorption in Hg(II), but NaHCO₃-NaOH inhibited Hg absorption in Hg(II). MnSO₄ mildly enhanced Hg absorption in Hg(II). At MnSO₄ concentrations lower than 0.22 M, a constant overall third-order rate constant of \( 4.4 \times 10^7 \text{ M}^{-2} \text{s}^{-1} \) was obtained at 25°C. NaCl, MgSO₄, FeCl₃, CaCl₂ and MgCl₂ all inhibited Hg absorption in Hg(II). Under most conditions, oxygen in the gas phase did not have any effect on Hg absorption in Hg(II). However, oxygen had a positive effect on Hg absorption in Hg(II) when HCl or NaHCO₃/NaOH was present in the solution.

R-97-5
Rate-Based Modeling of Reactive Absorption of CO₂ and H₂S into Aqueous Methyl-diethanolamine
Pacheco, Manuel A. and G.T. Rochelle
Submitted to Industrial and Engineering Chemistry Research (Feb 1998)
A general framework was developed to model the transport processes that take place during reactive absorption when both rate and equilibrium-controlled reactions occur in the liquid phase. This framework was applied to the selective absorption of H₂S from fuel gas containing CO₂ using aqueous methyl-diethanolamine. A rate-based distillation column module, RATEFRAC(, was used for the column integration. The Maxwell-Stefan and enhancement factor theories were utilized. In packed columns CO₂ absorption is controlled by diffusion with fast chemical reaction; in trayed columns it is controlled primarily by physical absorption. Gas-film resistance is never significant for CO₂ absorption. For H₂S absorption gas and liquid-film resistances are important, and diffusion of bisulfide controls the liquid-film resistance. Heat effects produce temperature bulges which can cause equilibrium "pinches" at the maximum temperature. This gives an optimum packing height for the H₂S removal. Trayed columns perform better than packed columns for H₂S removal, primarily because of the larger number of mass transfer units.
Simultaneous Sulfur Dioxide and Nitrogen Dioxide Removal by Calcium Hydroxide and Calcium Silicate Solids

Nelli, Christopher H. and G.T. Rochelle
Manuscript on file, Separations Research Program

At conditions typical of a bag filter exposed to a coal-fired flue gas which has been adiabatically cooled with water, calcium hydroxide and calcium silicate solids were exposed to a dilute, humidified gas stream of nitrogen dioxide (NO2) and sulfur dioxide (SO2) in a packed-bed reactor. A prior study found that NO2 reached readily with surface water of alkaline and non-alkaline solids to produce nitrate, nitrite, and nitric oxide (NO). With SO2 present in the gas stream, NO2 also reacted with S(IV), a product of SO2 removal, on the exterior of an alkaline solid. The oxidation of S(IV) to S(VI) by oxygen reduced the availability of S(IV) and lowered removal of NO2. Subsequent acidification of the sorbent by the removal of NO2 and SO2 facilitated the production of NO. However, the conversion of nitrous acid to sulfur-nitrogen compounds reduced NO production and enhanced SO2 removal. A reactor model based on empirical and semi-empirical rate expressions predicted rates of SO2 removal, NO2 removal, and NO production by calcium silicate solids. Rate expressions from the reactor model were inserted into a second program, which predicted the removal of SO2 and NOx by a continuous process such as the collection of alkaline solids in a baghouse. The continuous process model, depending upon inlet conditions, predicted 30-40% removal for NOx and 50-90% removal for SO2. These results are relevant to dry scrubbing technology for combined SO2 and NOx removal that first oxidizes NO to NO2 by the addition of methanol into the flue duct.

Carbon Dioxide Absorption in Methyldiethanolamine with Piperazine or Diethanolamine: Thermodynamic Modeling and Rate Measurement

Kaganoi, S.
Masters Thesis

Natural gas usually contains acid gases such as carbon dioxide and hydrogen sulfide that must be removed. The prevailing method of removing these gases is by chemical absorption into aqueous alkanolamine solutions. Methyldiethanolamine is commonly used in these systems and is frequently blended with other primary or secondary alkanolamines to enhance performance. Recent approaches to simulate these absorber/stripper systems adopt rate-based modeling. To establish a rate-based model, a rigorous vapor-liquid equilibrium (VLE) model is essential, as well as information on the reaction and the mass transfer kinetics. In this work, a stand-alone VLE model was established to emulate the Flash routine of Aspen PlusTM for a blended alkanolamine system with multiple acid gases. Experiments were conducted with piperazine as an activator to measure absorption/desorption of CO2 in MDEA solution. Equilibrium partial pressures of CO2 were measured, and significant enhancement by piperazine was confirmed comparing with single MDEA or blended MDEA/DEA solution. These data can be also analyzed with rigorous piperazine chemistry in the future.

Simultaneous Dry Absorption of HCl and SO2 with Hydrated Lime from Humidified Flue Gas

Chisholm, P.N. and G.T. Rochelle
Submitted to Industrial and Engineering Chemistry Research (1998)

The simultaneous absorption of HCl and SO2 by hydrated lime in a fixed bed reactor has been studied at conditions simulating humidified flue gas dry scrubbing. At 120°C, an increase in relative humidity from 0 to 19% increased HCl removal and sorbent utilization. At 19% relative humidity (RH), the final conversion of hydrated lime was 82%. From 250 to 1000 ppm HCl, HCl removal and sorbent utilization were first order in HCl concentration. From 2000 to 3500 ppm, sorbent utilization decreased as HCl concentration increased. When SO2 was added to the feed gas, the total conversion of the sorbent by HCl and SO2 was not a function of gas concentration with 250 to 1000 ppm HCl and 0 to 2000 ppm SO2. However, the fraction of the hydrated lime converted by SO2 increased as the HCl/SO2 feed ratio decreased. With oxygen present in the feed, more SO2 was absorbed. The addition of 150 ppm NO to the feed gas had a slight negative
effect on SO2 reactivity. Adding 150 ppm NO2 to the gas stream increased conversion by SO2 from 6% to 17%. NO2 reactivity increased with SO2 and decreased with oxygen present in the feed gas. As the reactivity of SO2 and NO2 increased, the reactivity of HCl decreased slightly due to the competition for alkalinity with the other acid gases. When this competition was greatest (low HCl concentration and high SO2 concentration with NO2 and O2 present, the conversion by HCl dropped from its maximum value of 82% to 67%.

**R-98-2 $10.00**

**Modeling of Limestone Slurry Scrubbing in Spray Towers with Forced Oxidation**

DeVincentis, J.W. and G.T. Rochelle

*Masters Thesis*

The primary purpose of this work is to extend FGDTX to fully model the forced-oxidation spray tower system, and to then use the results of FGDTX to help provide a better understanding of the chemistry involved in this system, in part by creating simpler approximate models to represent the results of FGDTX. It has been observed that both the gas phase mass transfer and the liquid phase resistance can influence the performance of spray scrubber systems as concentrations of sulfate species build up. FGDTX attempts to model these effects based on the best sub-models available. Simple models designed to fit the predictions of FGDTX and actual scrubber data are used to give meaning to some of the many trends that may be observed between the many variables in the system.

**R-98-3 $20.00**

**Mass Transfer, Kinetics and Rate-based Modeling of Reactive Absorption**

Pacheco, M.A. and G.T. Rochelle

*PhD Dissertation*

A mass transfer model was developed to describe the rates of mass transfer of reactive absorbing gases. This model is based on the Danckwerts surface renewal model and uses the concept of time-mean concentrations. The diffusion of reactants and products through the liquid boundary layer, reversibility and interaction between the different chemical reactions is accounted for by the model. The model was applied to reactive absorption of CO2 into diglycolamine and methyldiethanolamine and blends of these reactive solvents. The electrolyte NRTL thermodynamic model was used to account for the non-ideality of the gas-liquid systems. The model was validated using rates of mass transfer measured in a wetted-wall column reactor at 25°C to 100°C with CO2 loading varying from 0.015 to 0.55 moles CO2/moles of reactive solvent. It was found that the reversibility of the chemical reactions affects the mass transfer rate at temperatures as low as 60°C. The interaction between the diffusion of reactants and products, the reversibility of the chemical reactions, and the electrolyte interaction parameter ([water, DGACOO-MDEAH+]) was found to be crucial for predicting the mass transfer rates, especially at temperatures above 60°C. The mass transfer model was integrated to simulate the selective absorption of H2S from a gas stream containing CO2 using aqueous methyldiethanolamine. A general framework was developed to model the transport processes that take place during reactive absorption when both rate and equilibrium-controlled reactions occur in the liquid phase. A rate-based distillation column module, RATEFRAC, was used for the column integration. The Maxwell-Stefan approach to multicomponent mass transfer and the enhancement factor theory were utilized. It was found that in packed columns CO2 absorption is controlled by diffusion with fast chemical reactions; in trayed columns it is controlled primarily by physical absorption. Gas-film resistance is never significant for CO2 absorption. For H2S absorption gas and liquid-film resistances are important, and diffusion of bisulfide controls the liquid-film resistance. Heat effects produce temperature bulges which can cause equilibrium "pinches" at the maximum temperature. This gives an optimum packing height for the H2S removal. Trayed columns perform better than packed columns for H2S removal, primarily because of the larger number of mass transfer units; however, this conclusion is subject to the accuracy of the models used for estimating the mass transfer coefficients and interfacial area for mass transfer in the contactors.
Silicate Sorbents for Flue Gas Cleaning
Arthur, L.F. and G.T. Rochelle
PhD Dissertation
Calcium silicate hydrates are effective alkaline sorbents for the removal of acid gases from humid flue gas streams. This work investigated the formation of calcium silicates from recycled consumer glass and iron blast furnace slag. The reaction between these high surface area solids and SO2 in a humid gas stream was also studied. The formation of high surface area solids was found to be highly dependent on both the pH and calcium concentration of the slurry. Even with a high concentration of lime intrinsic in slag, excess additional lime was required to maintain a sufficient pH. Gypsum was shown to be an effective additive for maintaining a high calcium concentration at 92°C. Increasing the temperature to 120°C, increased the surface area formation at short times, but produced a more crystalline product, with lower surface area at longer times. Neither agitation nor solids/water loading had any effect on the preparation of sorbents up to 80 m²/g. Above this surface area, only agitation had a clearly positive effect. The addition of CaCl2 maintained a higher calcium concentration and high rate of surface area formation at 92°C, however the solids were less reactive with SO2 than comparable solids prepared with gypsum. It is believed that the high chloride concentration may have resulted in a different solid phase that was visible on SEM but not with X-ray. The SO2 reactivity of high surface area glass sorbents was a strong function of the relative humidity of the gas, with temperature held constant. Sorbent surface area was also very important to the rate of SO2 removal and maximum solids conversion. However, while surface area was necessary for high SO2 reactivity, it was not sufficient, as seen with sorbents prepared with chloride. An empirical model for the SO2/glass sorbent system showed that for a baghouse filter cycle time on one hour at 58% relative humidity, a stoichiometric ratio of 1.0 will achieve 62% removal from a 1000 ppm SO2 gas stream. Increasing the stoichiometry to 2.0 increased the removal efficiency to 94%.

Physical and Chemical Solubility of Carbon Dioxide in Aqueous Methyldiethanolamine
Bishnoi, Sanjay and G.T. Rochelle
Master's Thesis
Data are presented for the solubility of nitrous oxide in methyldiethanolamine (MDEA) solutions and the solubility of carbon dioxide in neutralized MDEA solutions. The nitrous oxide analogy is verified in neutralized MDEA solutions based on the experimental data obtained in this work. The electrolyte-NRTL was successfully used to model chemical and physical solubility of carbon dioxide in MDEA solutions. The reference state for solutes was defined as infinite dilution in the aqueous phase. VLE data at high temperature and high loading are needed for industrially important MDEA concentrations. The N2O analogy need to be studied further in solutions at high and moderate loading as a function of temperature.

Physical and Chemical Solubility of Carbon Dioxide in Aqueous Methyldiethanolamine
Bishnoi, Sanjay and G.T. Rochelle
Manuscript on File
Data are presented for the solubility of nitrous oxide in methyldiethanolamine (MDEA) solutions and the solubility of carbon dioxide in neutralized MDEA solutions. The nitrous oxide analogy is verified in neutralized MDEA solutions based on the experimental data obtained in this work. The electrolyte-NRTL was successfully used to model chemical and physical solubility of carbon dioxide in MDEA solutions. The reference state for solutes was defined as infinite dilution in the aqueous phase. VLE data at high temperature and high loading are needed for industrially important MDEA concentrations. The N2O analogy need to be studied further in solutions at high and moderate loading as a function of temperature.
R-98-7
Modeling of Limestone Slurry Scrubbing in Spray Towers with Forced Oxidation
DeVincentis, Jr., Joseph W.; G.T. Rochelle
Manuscript on File
The FBDTX model of the limestone slurry scrubber simulates a staged or spray scrubber with a hold tank. The spray scrubber model can simulate multiple levels of spray headers, and works with natural or forced oxidation. This work simulates performance of a system with forced oxidation in a spray scrubber. Simple approximate models are proposed to summarize the calculations of FGDTX and to provide understanding of the chemistry involved. The input parameters have been varied over a wide range of conditions to represent the typical range of spray scrubber operation. The effects seen in FGDTX of inlet SO2 concentration, limestone utilization, liquid-to-gas ratio, and the number of gas-phase transfer units are compared to literature data. Three fundamental effects determine the performance of forced oxidation spray scrubbers: the enhancement factor for SO2 absorption, the gas-film mass transfer limit, and the equilibrium resistance to SO2 absorption. Spray scrubbers differ from turbulent contact absorbers by the importance of the equilibrium effect.

R-99-1  PUBLISHED
Nitrogen Dioxide Absorption and Sulfide Oxidation in Aqueous Sulfide
Shen, Chen H. and G.T. Rochelle
Rates of nitrogen dioxide (NO2) absorption and sulfide oxidation were measured in a highly characterized stirred cell contactor at 55°C, with O2 present in the gas phase. The rate constant of the reaction between NO2 and sulfide at 55°C was determined to be 26.4 x 10(5) M-1 sec-1. A reaction mechanism was proposed that is consistent with the kinetic data. NO2 absorption initiates sulfide oxidation in the presence of oxygen. The rate of sulfide oxidation increased with sulfide and oxygen concentration and with the rate of NO2 absorption. Furthermore, thiosulfate was an effective inhibitor of sulfide oxidation.

R-99-2  $10.00
Mobile Monitoring and Modeling of Ozone and Ozone Precursors in Texas
Pauly, Micole Marie and G.T. Rochelle
Master's Thesis
For the past thirty years, the primary focus of regulations designed to reduce concentrations of ground level ozone in the State of Texas has been to reduce emissions of hydrocarbons. Recently, however, the State of Texas has begun to propose reductions in NOx emissions as an ozone reduction strategy. This thesis begins an investigation of the ozone formation potential of nitrogen oxides (NOx) emissions in different settings in Texas. The first chapter summarizes the air quality monitoring observations in Victoria, Texas over the summer of 1999. The second chapter summarizes the air quality monitoring data collected in San Antonio over 3 days in the late summer of 1998. Together, this monitoring and modeling begins an investigation of the role of NOx in ozone chemistry in Texas.

R-99-3  $10.00
Nitrogen Dioxide Absorption in Aqueous Dithionite
Dutchuk, Michael J. and G.T. Rochelle
Master's Thesis
The Acid Rain Program (Title IV), Section 407, of the Clean Air Act Amendments calls for a reduction in the emissions of nitrogen oxides (NOx) from certain coal-fired utility units. Since NOx emissions are known precursors in the formation of ozone, it is expected that NOx emissions standards will become more restrictive as the Environmental Protection Agency pursues lower acceptable ambient ozone levels by the year 2000. It would be economically feasible to utilize air pollution control processes already existing at many of the coal-fired utility units, such as limestone slurry scrubbers. The addition of a reagent to existing limestone slurry scrubbers would be an attractive technology for NOx emission control if it reacts under scrubber conditions with either NO or NO2 or both. The focus of this research was to examine the potential for sodium
dithionite (NA2S2O4) to react with NO and NO2 and to quantify reaction kinetics. Experiments were performed using a highly characterized stirred cell reactor as the gas/liquid contactor.

**R-99-4 $20.00**

**Dry Absorption of Hydrogen Chloride and Sulfur Dioxide by Calcium-Based Sorbents from Humidified Flue Gas**  
Chisholm, Paul Norman and G.T. Rochelle  
PhD Dissertation

The objective of this work was to determine whether calcium silicate solids are a suitable replacement for hydrated lime using dry sorbent injection technology with flue gas from municipal waste combustors and coal-fired power plants. A secondary objective was to gain an understanding of and quantify the interactions on alkaline reagents between HCl, SO2, NO, NO2 and O2, and water vapor. This understanding then can be applied to systems utilizing not only dry sorbent injection but also spray dryer absorption and perhaps even furnace injection technologies. To reach these objectives, a two phase approach was used. During the first phase, bench-scale absorption data were obtained at various gas conditions with hydrated lime and a representative calcium silicate as the sorbent. Phase two of this study involved modeling of the bench-scale data using a parameter estimation package. The parameters estimated were then used to predict the performance of HCl and SO2 removal in a bag filter system employing either hydrated lime or calcium silicate solids.

**R-99-5**

**Dry Absorption of HCl and So2 with Hydrated Lime from Humidified Flue Gas**  
Chisholm, Paul N. and G.T. Rochelle  
Submitted to Industrial and Engineering Chemistry Research (May 1999)

Because of the passage of the Clean Air Act Amendments in 1990, many industrial processes must reduce acid gases emissions, including HCl and SO2. These two gases are emitted together primarily in municipal waste combustors (MWC), hazardous waste incinerators (HW1), and coal-fired power plants. The objective of this study was to gain a comprehensive understanding of the absorption of HCl alone and of HCl and SO2 simultaneously by hydrated lime at low temperature flue gas conditions. Experiments were performed simulating the reaction conditions of acid gases with hydrated lime on a fabric filter for a MWC.

**R-99-6**

**Absorption of HCl and So2 From Humidified Flue Gas with Calcium Silicate Solids**  
Chisholm, Paul N. and G.T. Rochelle  
Submitted to Industrial and Engineering Chemistry Research (June 1999)

Historically, SO2 emissions have received more attention than other acid gases because of the presence of high levels of sulfur in fuels, particularly coal. As a result of the Clean Air Act Amendments passed in 1990, emissions of these acid gases such as HCl are being more closely regulated. To meet acid gas control regulations, a variety of control strategies are employed. The objective of this work is to obtain an understanding of the absorption of HCl and SO2 with calcium silicate solids. An emphasis will be placed on understanding the interactions of other gases usually present flue gas -- NO, NO2, O2, and water vapor -- on HCl and SO2 reactivity.

**R-99-7**

**HCl and So2 Absorption with Calcium Silicate**  
Chisholm, Paul N. and G.T. Rochelle  

HCl and SO2 can be found in waste gases from municipal waste combustion1-2, hazardous waste incineration, and coal-fired boilers. The objective of this study was to gain an understanding of and quantify the interactions on calcium silicate between HCl, SO2, NO2, O2, and water vapor.
Nitrogen Dioxide Absorption in Aqueous Dithionite
Dutchuk, Michael J. and G.T. Rochelle

NoX emissions (specifically NO and NO2) are known precursors to the formation of ozone.

Modeling of Limestone Slurry Scrubbing in Spray Towers with Forced Oxidation
DeVincentis, Jr., Joseph W. and G. T. Rochelle

Limestone slurry scrubbing is one of the primary technologies for removing sulfur dioxide from the flue gas produced by coal-burning electric power plants. Models of limestone slurry scrubbing should be useful for optimizing the design of new scrubbers, troubleshooting problems in existing scrubbers, and redesign or optimization of existing scrubbers. The dominant technology for limestone slurry scrubbing uses a spray tower with forced oxidation in the hold tank. Slurry produced in the hold tank is pumped to 2 to 4 levels of spray nozzles, with 4 to 6 foot spacing between spray levels, with multiple nozzles on each level at 2 to 6 foot spacing.

CO2 Absorption into Aqueous Mixtures of Diglycolamine and Methyldiethanolamine
Pacheco, Manuel; Shoichi Kaganoi; G.T. Rochelle

Carbon dioxide can be removed from gaseous streams using reactive absorption with a basic alkanolamine solution. A desorption step follows where the reactions are reversed by increasing the temperature and/or decreasing the pressure. In this application the chemical reactions that take place in the liquid phase boundary layer are generally multiple, parallel (and/or consecutive) and reversible. This paper presents measurements of CO2 absorption and desorption in mixtures of DGA and MDEA. Previous researchers have studied Co2 absorption into aqueous solutions of DGA and MDEA but not in mixtures of these reactive solvents.

Preparation of Calcium Silicate Absorbent from Iron Blast Furnace Slag
Brodnax, Lia F. and G.T. Rochelle
Submitted to JAWMA, March 16, 1999

This research investigated the formation of calcium silicates using iron blast furnace slag as the amorphous silica source. Slag is the secondary product of an iron blast furnace, consisting of lime flux and the silica, sulfur, and other impurities separated by the flux from the iron ore. Slag was chosen for study due to the large intrinsic calcium concentration shown in Table 1, roughly equal parts calcium to silicon. Bench scale experiments conducted with slag focused on the effects of the lime/slag/additive recipe on the aqueous slurry chemistry, and therefore the final product solids.

Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility
Bishnoi, Sanjay and G.T. Rochelle
Presented at 49th annual CSChE Conference, October 3-6, 1999, Saskatoon, Saskatchewan

This work studies the absorption of carbon dioxide into aqueous solutions of piperazine in a wetted wall contactor.
Chlorine Absorption in Sulfite/Bisulfite Solutions
Roy, Sharmistha and G.T. Rochelle
Presented at the Eleventh Symposium on Separation Science and Technology for Energy Applications, October 18-21, 1999, Gatlinburg, TN.

The rate of chlorine (Cl₂) absorption into aqueous sulfite/bisulfite (S(IV)) solutions was measured at ambient temperature using a highly characterized stirred cell reactor. The reactor media were 0 to 10 mM S(IV) and pH ranging from 3.5 to 8.5. Experiments were performed using 150 - 200 ppm Cl₂ in nitrogen (N₂). Rate constants were extracted from the chlorine absorption rates by the theory of mass transfer with chemical reaction. Chlorine reacts with S(IV) to form chloride and sulfate with a rate constant of 2x10⁷L/mol-s at pH 4. Chlorine absorption is enhanced by increasing pH and S(IV) concentration. These results are relevant in the simultaneous removal of chlorine, sulfur dioxide (SO₂) and elemental mercury (Hg) from flue gas.

Co₂ and H₂S Thermodynamics and Kinetics in Aqueous Alkanolamines
Rochelle, Gary T.; Msafiri Mshewa; Mark Posey; Manuel Pacheco; Shoichi Kaganoi
Research Report, RR-167, A Joint Research Report by the Gas Processors Association and the Gas Research Institute

To provide the gas industry with accurate data and models for acid gas solubility and Co₂ kinetics in mixtures of diethanolamine (DEA) and methyldiethanolamine (MDEA). The report includes model parameters and calculated acid gas solubility in the system was-MDEA-DEA-H₂S-Co₂. These results effectively smooth and interpolate the available solubility data. Because the thermodynamic model has some theoretical basis, the results also extrapolate the available data to lower acid gas loading.

Physical and Chemical Solubility of Carbon Dioxide in Aqueous Methyldiethanolamine
Rochelle, Gary and S. Bishnoi
Fluid Phase Equilibria, 168: 241-258, 2000

Inconsistent trends for the physical solubility of carbon dioxide in aqueous methyldiethanolamine (MDEA) are presented. These inconsistencies are found between data sets for the chemical solubility of carbon dioxide in aqueous MDEA. In order to rationalize this inconsistency, data are presented for the solubility of nitrous oxide and carbon dioxide in MDEA solutions neutralized with sulfuric acid. The physical solubility is seen to decrease with increasing ionic strength. Previously published models show the incorrect trend for the physical solubility of carbon dioxide as a function of loading because of this discrepancy in the data. The electrolyte-NRTL model was successfully used to model the chemical and physical solubility of carbon dioxide in MDEA by defining the reference state for solutes as infinite dilution in the aqueous phase instead of the mixed solvent. VLE data at high temperature and high loading are needed for industrially important MDEA concentrations. The N₂O analogy needs to be studies further in solutions at high and moderate loading as a function of temperature.

Adsorption of Carbon Dioxide by Piperazine Activated Methyldiethanoline
Rochelle, Gary T.; Sanjay Bishnoi; Soichi Kaganoi
Prepared for Laurence Reid Gas Conditioning Conference, 12/15/00

Carbon dioxide absorption in a mixture of 0.6M piperazine (PZ) and 4M methyldiethanolamine (MDEA) was studied in a wetted wall contactor. A rigorous model that accounts for mass transfer and chemical reaction in the liquid boundary layer was developed based on eddy diffusivity theory. Data and model predictions suggest that PZ/MDEA blends absorb Co₂ faster than MEA or DEA blends with MDEA at similar concentrations. The reaction of PZ to form a mono-carbamate is dominant at low loading (<.14). The reaction of the mono-carbamate to form di-carbamate is dominant at high loading. All carbamate and dicarbamate formation reactions were found to approach instantaneous behavior at high loading. A combination of resistance due to pseudo first order and instantaneous carbamate formation was found to fit data throughout the entire loading.
range. A typical ammonia plant absorber is modeled using the rigorous model presented here at isothermal conditions. Gas film limitations are found to be very important (>50%) only at the top of the absorber.

R-00-4 $20.00
Carbon Dioxide Absorption and Solution Equilibrium in Piperazine Activated Methyldiethanolamine
Bishnoi, Sanjay and G.T. Rochelle
Ph.D. Dissertation
Solubility, rate of absorption and NMR data were taken for carbon dioxide in aqueous piperazine (PZ) and aqueous mixtures of PZ and methyldiethanolamine (MDEA). Solubility and rate data were acquired in a wetted wall contactor. 0.2 to 0.6 MPZ and 4 M MDEA concentrations were studied.

R-00-5 $10.00
Oxidative Degradation of Monoethanolamine
Chi, Qian Susan and G.T. Rochelle
Master's Thesis
Aqueous monoethanolamine (MEA) is used to remove CO2 from flue gas. MEA degrades in service in the presence of oxygen and CO2 resulting in extensive amine loss and equipment corrosion as well as generating environmental impacts. Oxidative degradation of MEA was studied under typical absorber condition of 55 degrees C.

R-01-1 PUBLISHED
Thermodynamics of Piperazine/Methyldiethanolamine/Water/Carbon Dioxide
Bishnoi, Sanjay and G.T. Rochelle
Ind. Eng. Chem. Res. 41, 604-612
Thermodynamics of aqueous amine systems are crucial to understanding their industrial use to remove acid gas from process gas streams. The equilibrium partial pressure of acid gas above a solution of the amine defines pinch conditions for the absorber and stripper. Speciation of the amine and reaction products defines the driving force for the forward and reverse reactions with CO2. An understanding of this is important since the reactions are usually rate controlling. Furthermore, a consistent thermodynamic model can quantify the energy required for regenerating the solvent and solvent losses due to amine volatility. This work studies piperazine (PZ)/methyldiethanolamine (MDEA)/H2O solvents that have been applied to synthesis gas and natural gas (Wammes et al., 1994)

R-01-2
Oxidative Degradation of Monoethanolamine
Chi, Susan and G.T. Rochelle
Oxidative Degradation of monoethanolamine (MEA) was studied under typical absorber condition of 55 degrees C. The rate of evolution of NH3, which was indicative of the overall rate of degradation, was measured continuously in a batch system sparged with air.

R-01-3 $10.00
CO2 Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water
Dang, Hongyi and G.T. Rochelle
Master's Thesis
The solubility and absorption rate of carbon dioxide into monoethanolamine/piperazine/water were measured in a wetted wall column at 40-60 degrees C. The total amine concentration was varied for 1.0 M to 5.0 M with monoethanolamine blends contain 0 to 1.2 M piperazine. CO2 solubility and solution speciation were simulated by 9 equilibrium reactions. Two of the equilibrium constants were adjusted to match literature data. The rate of absorption was predicted by the theory of diffusion with fast chemical reaction. Piperazine at 24 mol% of the total amine
decreases CO2 equilibrium pressure by 50% and enhances CO2 absorption rate by 50% to 100%. The CO2 enhancement factor decreases by a factor of 0.6 to 2 as loading decreases from 0 to 0.5 moles CO2/mole amine.

R-01-4 PUBLISHED
Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility
Bishnoi, S. and Rochelle, G.T.

R-01-5 PUBLISHED
Preparation of Calcium Silicate Absorbent from Iron Blast Furnace Slag
Broadnax, L.F. and Rochelle, G.T.
J. Air & Waste Manage. Assoc., 50, 1655-1662, 2000

R-01-6 PUBLISHED
CO2 Absorption into Aqueous Mixtures of Diglycolamine and Methyldiethanolamine
Pacheco, M.A.; Kaganoi, S.; Rochelle, G.T.

R-01-7
Absorption of Carbon Dioxide by Piperazine Activated Methyldiethanolamine
Bishnoi, S.; Kaganoi, S.; Rochelle, G.T.
Presented at Laurence Reid Gas Conditioning Conference, 2/26/01

R-01-9
Research Needs for CO2 Capture from Flue Gas by Aqueous Absorption Stripping
Rochelle, G.T.; Bishnoi, S.; Chi, S.; Dang, H.; Santos, J.

R-01-10
Chlorine Absorption in Sulfite Solutions: A Mechanism in Mercury Removal
Rochelle, G.T. and Roy, S.
Presented at the EPA/DPE/EPRI Combined Power Plant Air Pollutant Control Symposium, Chicago, IL, August 20-23, 2001

R-01-11
Liquid Phase Mass Transfer in Spray Scrubbers
Rochelle, G.T. and Yeh, N.
Presented at the EPA/DPE/EPRI Combined Power Plant Air Pollutant Control Symposium, Chicago, IL August 20-23, 2001

R-01-12
Absorption of CO2 in Aqueous Piperazine/Methyldiethanolamine Blends
Rochelle, G.T. and Bishnoi, Sanjay
Submitted to ACIhE Journal, August 20, 2001

R-01-13
Chlorine Absorption in S(IV) Solutions
Bishnoi, Sanjay and Roy, S.
Oxidative Degradation of Monoethanolamine
Rochelle, G.T. and Chi, S.
Ind. Eng. Chem. Res. 41, 4178-4186
Oxidative Degradation of Monoethanolamine (MEA) was studied at 55 degrees C, typical of absorbers for CO2 removal from flue gas. The rate of evolution is NH3, which was indicative of the overall rate of degradation, was measured continuously in a batch system sparged with air.

CO2 Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water
Rochelle, G.T. and Dang, H.
Submitted to Separation Science and Technology Journal August 20, 2001

Liquid Phase Mass Transfer in Spray Contactors
Yeh, Norman
Ph.D. Dissertation, 2002
Many separations and gas cleaning application rely on efficient mass transfer in gas-liquid contactors. Various unit operations have been employed to accomplish these separations by transferring a given component from one phase into another. The most common types of contactors include tray columns and packed columns, and a large body of data exists for mass transfer in these systems. Spray columns are also commonly used as gas-liquid contactors for certain separations, but the literature for mass transfer in spray contactors is fairly sparse compared to that for trays and packing. In particular, the liquid phase mass transfer characteristics of sprays have not been well described and further study is warranted.

Research Results for CO2 Capture from Flue Gas by Aqueous Absorption/Stripping
Rochelle, Gary; Goff, George; Cullinane, J. Tim; Freguia, Stefano
Presented at the Laurance Reid Gas Conditioning Conference, February 25-27, 2002
Alkanolamine absorption/stripping is an important technological option for CO2 sequestration to address global climate change. It has long been a commercial technology for CO2 removal from natural gas and hydrogen. Along with other technical challenges, application of this technology to coal combustion gasses must address lower CO2 particle pressures, large gas flow rates and solvent oxidation. Commercial systems using monoethanolamine (MEA) require potentially prohibitive quantities of steam for stripping. Solvents with a reduced heat of desorption have mixed benefits because they may also increase the stripping steam required, depending on the process configuration. An optimum design will probably have pinches at the lean and rich ends of the absorber and stripper.

Modeling Ozone Formation in a Central Texas Power Plant Plume
Hamlin, Dyron
Masters Thesis, 2002
This research focuses on two major aspects of modeling the ozone problem in Texas, and proposes methods for further analysis. -The ability of CAMx to accurately predict ozone production by a large NOx point source is validated by comparison to aircraft data taken in a plume of emissions from a grandfathered electric generating utility. Two different analysis techniques for performing such validation are proposed. -The diurnal variability of ozone production by this large utility is examined, and new methods are proposed. -Methods for further companion of modeled data and aircraft data are proposed.
**R-02-4 NEW**  
**Liquid Phase Mass Transfer in Spray Contactors**  
Yeh, N. and Rochelle, G.T.  
Manuscript, submitted to AIChE Journal, April 2002  
The liquid phase mass transfer in sprays has been measured with carbon dioxide desorption by collecting and analyzing samples of the spray. Experiments were conducted with laboratory (0.009 to 0.13 L/s) and pilot scale (6.4 to 12.8 L/s) centrifugal hollow cone spray nozzles at pressure drops from 34 to 138 kPa. Significant mass transfer occurred during sample collection, and quench sampling method was developed to minimize this effect. The number of liquid phase transfer units (NL) due to spray impact onto walls and liquid pools was often as much as the spray NL. Approximately 60% of the spray NL occurs in the liquid sheet before droplet formation, and the droplet region can account for less than half of the total NL of the spray.

**R-02-5 NEW**  
**Effect of Mixing on Efficiencies for Reactive Tray Contactors**  
Fisher, K.S. and Rochelle, G.T.  
Manuscript, submitted to AIChE Journal  
This paper describes the relationship between point efficiencies and Murphree tray efficiencies for systems where reactions take place in the liquid with a tray column. For nonreactive systems, several well-known mixing models are available for predicting Murphree tray efficiency from point efficiencies. For reactive systems, the magnitude and nature of the effect of mixing on tray efficiency are different. This paper develops an analytical representation of the mixed-pool and plug-flow mixing models for reactive systems with first-order kinetics and shows that there are different regimes, depending on the reaction kinetics.

**R-02-6 NEW**  
**Modeling of Co2 Capture by Aqueous Monoethanolamine**  
Freguia, S. and Rochelle, G.T.  
Manuscript, submitted to AIChE Journal  
The process for C02 removal from flue gases was modeled with Aspen RateFracTM. The process consists of an absorber, a stripper, and a cross heat exchanges. The solvent used in the model contains approximately 30 wt% monoethanolamine (MEA) in water. MEA reacts with Co2 in the packed absorber. The finite reaction rate requires a kinetic characterization. The RateFracTM absorbent model was integrated with a FORTRAN user kinetic subroutine to make the model consistent with the interface pseudo first order model and with a regressed Electrolyte-NRTL equilibrium model. The model was adjusted with laboratory wetted wall column data and with field data from a commercial plant.

**R-02-7 NEW $20.00**  
**Absorption of Chlorine and Mercury in Sulfite Solutions**  
Roy, Sharmi  
Ph.D. Dissertation, 2002  
The primary objective of this work is to understand the kinetics of systems containing mercury, chlorine, and S(IV). Mercury and chlorine absorption was measured in a gas/liquid contactor with known mass transfer properties. The absorption was modeled in order to extract kinetics. An understanding of these kinetics is needed in order to develop a technology that will remove both Hg and HgCl2 through aqueous scrubbing with chlorine. The gaseous chlorine oxidant should react with elemental Hg in the solution at the gas/liquid interface and greatly enhance the rate of absorption of Hg. This work provides kinetics data which may be important in other processes (than scrubbers in power plants) that contain mercury, chlorine, and/or S(IV).
Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperzine
Cullinane, J. Tim and G.T. Rochelle

Many commercial processes, developed for the removal of carbon dioxide from high-pressure gases, are facilitated by using aqueous potassium carbonate systems promoted by secondary amines. This paper presents thermodynamic and kinetic data for piperazine promoted potassium carbonate. Research has been performed at typical absorber conditions for the removal of CO2 from flue gas. Piperazine, used as an additive in 20 to 30 wt% potassium carbonate, has been investigated in a wetted-wall column using a concentration of 0.6M and at 40°C to 80°C. Equilibrium data indicates that the addition of 0.6M piperazine to a 20 wt% potassium carbonate system decreases the CO2 equilibrium partial pressure by approximately 85% at intermediate loading (absorbed CO2 concentration). Speciation of the solution was obtained through the use of proton NMR. Using the speciation data and relevant equilibrium constants, a model was developed to predict system speciation and equilibrium. Experimentally, promotion of potassium carbonate by piperazine increases the rate by a factor of approximately 10 at 60°C. The rate of CO2 absorption in the promoted solution compares favorably to that of 5.0 M MEA. The addition of piperazine increases the heat of absorption 3.7 kcal/mol in 20 wt% K2CO3 to 10 kcal/mol when 0.6 m PZ is added. The capacity ranges from 0.4 to 0.8 mol-CO2/kg-H2O for PZ/K2CO3 solutions, comparing favorably with other amines.

Properties of Concentrated Aqueous Potassium Carbonate/Piperazine for CO2 Capture
J. Tim Cullinane and Gary T. Rochelle

Information is presented on an innovative, aqueous K2CO3 and piperazine (PZ) blend for CO2 capture. The data, including PCO2*, PZ speciation, and CO2 absorption rate, have been collected at various solvent compositions and temperatures (40 to 80°C). A rigorous thermodynamic model of the CO2-solvent system has been developed. Concentrated PZ/K2CO3 blends have shown favorable PCO2* behavior at high partial pressures. Capacity demonstrates a dependence on total solvent composition. Heats of absorption depend strongly on the ratio of K+ to PZ and vary from 7 to 25 kcal/mol. Piperazine contributes to a CO2 absorption rate as much as four times faster than conventional absorbents such as MEA, DEA/K2CO3, and PZ/MDEA.

CO2 Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water
Hongyi Dang and Gary T. Rochelle

The solubility and absorption rate of carbon dioxide into monoethanolamine/piperazine/water were measured in a wetted wall column at 40–60°C. The total amine concentration was varied from 1.0M to 5.0 M, with monoethanolamine blends containing 0 to 1.2M piperazine. CO2 solubility and solution speciation were simulated by nine equilibrium reactions. Two of the equilibrium constants were adjusted to match literature data. The rate of absorption was predicted by the theory of diffusion with fast chemical reaction. Piperazine at 24 mol% of the total amine decreases CO2 equilibrium pressure by 50% and enhances the CO2 absorption rate by 50% to 100%. The CO2 enhancement factor decreases by a factor of 0.6 to 2 as loading decreases from 0 to 0.5 mol CO2/mole amine.

Innovative Stripper Configurations to Reduce the Energy Cost of CO2 Capture
Rochelle, G.T.

CO2 capture by absorption/stripping with aqueous monoethanolamine (MEA) is the state-of-the-art technology for CO2 capture from coal-fired power plants. The energy consumption in stripping can be 15 of 30% of the power plant output. A rigorous rate-based model was used to simulate several flowsheet alternatives that reduce the energy requirement by 5 to 20%: 1. A larger cross
exchanger to reduce the T approach from 10 to 5°C; 2. Vapor compression to recover latent heat from the stripper overhead; 3. Multipressure stripping to integrate with the CO₂ compressor; and 4. Intercooling in the Absorber. The model was also used to simulate the effects of using a more reactive solvent.

R-04.1
Carbon Dioxide Removal from Natural Gas by Membranes in the Presence of Heavy Hydrocarbons and by Aqueous Diglycolamine®/Morpholine
Mohammed Awad Al-Juaied, B.Sc.; M.S.
PhD dissertation, May 2004

Intrinsically defect-free asymmetric hollow fiber polyimide membrane modules were studied in the presence and absence of saturated and aromatic components. Results suggest that an essentially defect-free, non-nodular morphology offers advantages in stability under demanding operating conditions. Earlier work showed serious losses in performance of membranes comprised of similar materials, when the selective layer had a pronounced fused nodular nature as opposed to the intrinsically defect-free skin layers reported on here. Under some conditions for the ternary system, the permselectivity of the membrane is scarcely affected, while under other conditions, permselectivity is negatively affected by as much as 25%. In most cases, for the ternary feeds, significant depression in fluxes was observed due to competition between the CO₂, CH₄ and heavier hydrocarbons but the effect was even more pronounced for the toluene. In addition to steady state tests in the presence and absence of n-heptane and toluene, modules were conditioned for five days with ternary mixture of CO₂, CH₄ and one or the other of these heavy hydrocarbons. Following this conditioning process, the modules were studied with a simple binary 10% CO₂/90% CH₄ mixture. These conditioning studies provide insight into the fundamental effects induced in the membrane due to the long term exposure to the complex mixtures. Following exposure to the ternaries containing n-heptane, negligible CO₂ permeance increase was seen, while significantly increased permeances were seen under some conditions following toluene exposure even at low pressures of the ternary toluene/CO₂/CH₄ conditioning gas mixture. Although a more protracted process occurs in the case of heptane/CO₂/CH₄ at 35°C and 500 ppm, a serious loss in selectivity occurs in the actual ternary tests after exposure for five days. The problem caused by 300 ppm toluene at 35°C is more immediately apparent, but the ultimate selectivity loss is similar. In addition to the selectivity, in the presence of toluene the permeability is also depressed significantly, presumably due to a greater capability to toluene to compete for added free volume elements introduced in the conditioning process. The permeation enhancement due to toluene exposure is lost slowly when the module downstream is put under vacuum and the gas no longer in contact with the module for up to three weeks. The conditioning treatment has negligible effect at 55°C, suggesting that that the sorption affinity of toluene decreases with increasing temperature. It is seen from the sorption experiments that penetrant induced conditioning of toluene allows a significant increase in diffusivity than in solubility coefficients, thus allowing for higher permeability and lower selectivity. Solubility, rate of absorption and NMR data were obtained for carbon dioxide in aqueous morpholine (MOR), diglycolamine® (DGA) and aqueous mixtures of MOR and DGA®. Solubility and rate data were acquired in a wetted wall contactor. 23.5 wt%, 65 wt% DGA and 11 wt% MOR/53 wt% DGA concentrations were studied at 298K to 333K. MOR forms an unstable carbamate upon reaction with CO₂ compared to DGA which forms a very stable carbamate. Morpholine at 11 wt% of the total amine increases the CO₂ equilibrium partial pressure by a factor of 5 to 7 at high loading. The working capacity of 11 wt% MOR/53 wt% DGA was found to be 10% smaller compared to 65 wt% DGA under the conditions studied. The heat of reaction of 11 wt% MOR/53 wt% DGA® was found to be comparable to the 65 wt% DGA. MOR was found also to be more volatile than DGA. The second order rate constant of DGA was found to increase linearly with loading by a factor of 5 over a loading range from 0 to 4. Experiments with 65 w% DGA, glycolic acid and potassium formate suggest that rate constant increases with loading in the same way as in 65 wt% DGA. The second order rate constant for MOR (k₂5C =22000 L/mol s) is four times greater than DGA (k₂5C =6600 L/mol s). The MOR reaction with CO₂ was found to follow the zwitterion mechanism; DGA shows zwitterion mechanism in 25 wt% DGA and second order kinetics in 65 wt% DGA. Predictions made with a rigorous eddy diffusivity theory suggests that 11 wt% MOR/53 wt% DGA outperforms 65 wt%
DGA of the same concentration by 50% in terms of CO2 absorption rate. The CO2 enhancement decreases as CO2 loading increases.

R-04-2
Pilot Plant for CO2 Capture using Aqueous Piperazine/Potassium Carbonate
Chen, Eric and Gary T. Rochelle
Presented at Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004
The removal of CO2 typically uses an absorption/stripping system with an amine solvent, such as monoethanolamine (MEA). A new solvent, piperazine promoted potassium carbonate, has been developed. A solution of 2.5 m piperazine (PZ) and 5 m potassium bicarbonate (K+) has a CO2 absorption rate 1 to 3 times faster than 7 m MEA (30 wt%). The solvent also has a lower heat of CO2 absorption, which should reduce the heat requirement for stripping. A rigorous model absorber model has been developed to estimate absorber performance. The model predicts an equilibrium pinch in the absorber near the point of maximum liquid temperature. Experiments have been conducted on a pilot plant with solvent compositions containing 4.2 m K+/2.1 m PZ and 5 m K+/2.5 m PZ. The CO2 concentration was varied from 3 to 13%. The gas and liquid rates were varied from 120-800 cfm and 2.4-10 gpm, respectively. The CO2 removal rates ranged from 85 to 99.8 percent.

R-04-3
Aqueous Piperazine/Potassium Carbonate for Enhanced CO2 Capture
J. Tim Cullinane (presenter), Babatunde A. Oyenekan, Jennifer Lu, and Gary T. Rochelle
Presented at the Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004
Experimental and modeling results are presented for aqueous piperazine (PZ)/potassium carbonate (K2CO3) for enhanced CO2 capture from flue gas. CO2 removal by aqueous absorption/stripping is a mature technology currently used in the manufacture of ammonia and syngas. The use of aqueous K2CO3 promoted by PZ should enhance rates of CO2 absorption and reduce the heat requirement for stripping. The thermodynamic and rate properties of this new solvent have been measured in a wetted wall column. Simple models have been developed to estimate absorber and stripper performance. The new solvent, 5 m K+/2.5 m PZ (m ß mol/kg water), provides CO2 solubility and capacity comparable to 7 m (30 wt%) monoethanolamine (MEA). The heat of CO2 absorption is less than that in MEA solvents (22 kcal/mol) and decreases from 16 to 9 kcal/mol as temperature increases from 40 to 80°C and rich CO2 vapor pressure increases from 100 to 5000 Pa. CO2 absorbs 5 m K+/2.5 m PZ 1 to 5 times faster than into 7 m MEA. This faster rate can provide a rich solution from the absorber that has CO2 vapor pressure 1.4 to 2.6 times greater than with MEA. The piperazine solvent can also be used to provide 90% CO2 removal with a rich loading and packing height that would give only 75% removal with MEA. Because 5 m K+/2.5 m PZ provides a richer solution and greater optimum capacity, the reboiler duty with 5 m K+/2.5 m PZ in a simple absorption/stripping process can be 25 to 46% less that that with 7 m MEA. Additional heat savings up to 6% may be achieved by operating the stripper at greater pressure.

R-04-4
Concentrated Potassium Carbonate/Piperazine/Potassium Carbonate for Enhanced CO2 Capture
Cullinane, J. Tim and Gary T. Rochelle
Presented at the Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004
This work presents CO2 absorption performance for blends of aqueous piperazine (PZ) and potassium carbonate (K2CO3) in traditional absorber/stripper processes. Experiments have been performed at conditions representative of CO2 removal from flue gas (40 to 120°C) with a broad range of solvent concentrations (0 to 6.2 m K+ and 0 to 3.6 m PZ). Results show that concentrated K+/PZ mixtures increase the rate of absorption by as much as a factor of four over that of MEA. Ionic strength effects were also examined with the addition of non-reactive salts, such as NaCl and K2SO4, and are shown to significantly enhance the absorption rate. To explain the complex behavior observed in experiments, a rigorous model of the boundary layer is required. Using
both a simple and rigorous rate model, kinetics of CO2 absorption by PZ was quantified both with and without K+ present. The rate substantially increases with the inclusion of K+ in the solvent. The apparent rate constants are approximately five times higher than in aqueous PZ at 60°C.

**R-04-5** PUBLISHED

Oxidative Degradation of Aqueous Monethanolamine in CO₂ Capture Controlled by the Physical Absorption of O₂

Goff, George F. and G.T. Rochelle


**R-04-6**

Oxidative Degradation of Monoethanolamine in CO₂ Capture: O₂ Mass Transfer

Goff, George F. and Gary T. Rochelle

Presented at the Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004

This study examines the rate of oxidative degradation of MEA under conditions typical of a CO₂ capture process. Experiments examined the effects of amine concentration, CO₂ loading, O₂ concentration, and agitation rate at 55°C. Degradation rates were quantified by measuring the rate of NH₃ evolution from the amine solutions using FT-IR analysis. Results show that degradation rates are controlled by the rate of physical absorption of O₂ and NH₃ evolution rates ranged from 0.2 mM/hr to 8.0 mM/hr. Previous studies were re-examined and compared to the current study, and appear to have been performed under conditions that were mass transfer limited. This would indicate the previous literature values for degradation kinetics were actually O₂ absorption rates.

**R-04-7**

Thermodynamics of Aqueous Piperazine/Potassium Carbonate/Barbon Dioxide Characterized by the Electrolyte Nonrandom Two-Liquid Model in Aspen Plus

Hilliard, Marcus D. and Gary T. Rochelle

Presented at the Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004

The Electrolyte Nonrandom Two-Liquid (NRTL) Activity Coefficient model in Aspen PlusTM v11.1 was used to develop a rigorous thermodynamic representation of an aqueous piperazine (PZ) and potassium carbonate (K₂CO₃) mixed-solvent electrolyte system for the application of carbon dioxide (CO₂) absorption/stripping from power plant flue gas. The model predicts the speciation and carbon dioxide solubility as a function of solvent composition, temperature, and pressure. These results provide the capacity of the solvent, the heat of absorption, and the concentration of reactive species (e.g. piperazine and piperazine carbamate (PZCOO−)). Binary adjustable parameters for the potassium carbonate/piperazine mixed-solvent electrolyte system were obtained through the regression of water vapor pressure and calorimetry over potassium carbonate and potassium bicarbonate (KHCO₃) solutions, CO₂ solubility in potassium carbonate/piperazine, and proton nuclear magnetic resonance (NMR) of K₂CO₃/PZ speciation. As a result, the model satisfactorily correlates the experimental data of this mixed-solvent electrolyte system over a wide range of temperature, mixed-solvent concentration, and CO₂ loading.

**R-04-8**

Stripper Models for CO₂ Capture by Aqueous Solvents

Oyenekan, Babatunde A. and Gary T. Rochelle

Presented at the Seventh International Conference on Greenhouse Gas Control Technology, Vancouver, Canada, September 5-9, 2004

Aqueous amines have been the conventional method used for CO₂ removal in ammonia, natural gas and refinery streams for decades. The growing interest in CO₂ capture from large point sources, presents another opportunity for the use of this technology. The steam requirement for stripping is estimated to be about 20 – 40 % of the power plant output. We have developed a model that estimates the steam requirements for stripping of CO₂ from two aqueous solvents, 7m monoethanolamine (MEA) and 5m K+/2.5m PZ. It uses simple relationships to represent the VLE and enthalpies and can be used to simulate stripper performance for a variety of solvents and
operating conditions (e.g. pressure, approach temperature, rich and lean loading). The results show that energy savings of 29-33% can be achieved by using 5m K+/2.5m PZ over MEA at a stripper pressure of 160 kPa with a 5oC temperature approach. The reboiler duty has also been expressed in terms of equivalent work that can quantify work output from the turbines in the power plant. The stripper can be operated at any convenient pressure at which steam can be extracted from the power plant.

**R-04-9**
**Selection of Internals for Carbon Dioxide Absorption/Stripping**
Rochelle, G.T.
Presented at the AIChE 2004 Spring National Meeting, New Orleans, LA., April 25-29, 2004

**R-04-10**
**Chlorine Absorption in Sulfite Solutions**
Roy, Sharmistha and Gary T. Rochelle
Accepted for publication in Separation Science & Technology July, 2004
The rate of chlorine (5 to 300 ppm Cl2) absorption into aqueous sulfite/bisulfite (0 to 10 mM S(IV)) was measured using a stirred cell reactor and a wetted wall column at pH 4.7 and 5.7. Chlorine absorption was modeled using the theory of mass transfer with fast reaction. Chlorine reacts quickly with S(IV) to form chloride and sulfate near the gas/liquid interface. The rate constant for the reaction of chlorine with S(IV) at 25°C was determined to be 1.1 x 109 L/mol-s. The enhancement of the succinate buffer on the chlorine hydrolysis rate was quantified. The addition of sodium chloride (NaCl) did not affect the rate of Cl2 absorption in S(IV). Oxygen did not affect the rate of chlorine absorption or catalyze S(IV) oxidation. These results are relevant in the simultaneous removal of chlorine, sulfur dioxide, and elemental mercury from flue gas and may also be applicable to scrubber design for removal of chlorine in the pulp and paper and other industries.

**R-04-11**
**Simultaneous Absorption of Mercury and Chlorine in Sulfite Solutions**
Roy, Sharmistha and Gary T. Rochelle
Simultaneous absorption of mercury (Hg) and chlorine (Cl2) into aqueous sulfite/bisulfite (0 to 1 mM S(IV)) at pH 4.7 and 5.7 was measured in a wetted wall column. Experiments were performed at ambient temperature and pressure using 5–40 ppm Cl2 and 46 ppb Hg. Absorption was modeled using the theory of mass transfer with chemical reaction. At the gas/liquid interface, chlorine oxidizes the elemental Hg to a more soluble form. The rate constant for the reaction of mercury and chlorine was determined to be 6:1 x109 l/mol s. Mercuric chloride and sodium hypochlorite also enhanced Hg absorption. The addition of sodium chloride did not affect the rate of Hg=Cl2 absorption with S(IV). When no S(IV) was present, the chloride significantly enhanced Hg absorption. Possible reaction pathways are discussed. These results are relevant in the simultaneous removal of chlorine, sulfur dioxide, and elemental mercury from flue gas. A model was developed to predict the expected Hg removal in a limestone slurry scrubber. Mercury removal decreases as the S(IV) concentration increases. The process feasibility will depend on the SO2=S(IV) concentration of the scrubber, the desired Hg removal, and the amount of Cl2 which can be tolerated.

**R-04-12**
**Gas-Liquid Contact Area of Random and Structured Packing**
Wilson, I
Thesis, May 2004
R-04-13
Monoethanolamine Degradation: O2 Mass Transfer Effects Under CO2 Capture Conditions
Goff, George S. and Gary T. Rochelle
This study examines the rate of oxidative degradation of MEA under conditions typical of a CO2 capture process. Experiments examined the effects of amine concentration, CO2 loading, O2 concentration, and agitation rate at 55°C. Degradation rates were quantified by measuring the rate of NH3 evolution from the amine solutions using FT-IR analysis. Results show that degradation rates are controlled by the rate of physical absorption of O2 and NH3 evolution rates ranged from 0.2 mM/hr to 8.0 mM/hr. Previous studies were re-examined and compared to the current study, and appear to have been performed under conditions that were mass transfer limited. This would indicate the previous literature values for degradation kinetics were actually O2 absorption rates. An estimate of the degradation rate for a CO2 absorber was made assuming the degradation was controlled by the rate of O2 absorption, and was shown to be equal to or less than values reported in the literature.

R-04-14
Oxidative Degradation of Monoethanolamine: O2 Mass Transfer & Degradation Inhibitors
Goff, G. and Rochelle, G.T.
Presented at the International CO2 Test Capture Network: 7th Workshop, Vancouver, Canada, September 10, 2004

R-05-1
Thermodynamics of Diglycolamine®/Morpholine/Water/Carbon Dioxide
Al-Juaied, Mohammed and Rochelle, G.T.
Carbon dioxide solubility and 13C NMR speciation were measured and modeled in aqueous solutions with 23.5 wt% morpholine (MOR), 65 wt% diglycolamine® (2-aminoethoxyethanol, DGA®) and 11 wt% MOR/53 wt% DGA. CO2 solubility was determined by dynamic measurements with a wetted wall contactor. The concentrations of carbamate and bicarbonate species were determined by 13 C NMR in solutions loaded with 13CO2. The data are represented by a stand-alone implementation of the electrolyte NRTL model. At a given CO2 loading (mole/mole amine), the CO2 vapor pressure over 23.5 wt% MOR is 10 to 1000 times greater than 65% DGA. In 11 wt% MOR/53 wt% DGA, the CO2 vapor pressure is 5 to 7 times greater than in 65 wt% DGA at high CO2 loading, but the same below 0.2 loading. MOR carbamate is less stable than DGA carbamate by a factor of 7 to 10 from 27°C to 60°C. DGA carbamate is the major reaction product at loading <0.4. MOR carbamate, protonated MOR, and protonated DGA are the major reaction products at high loading. The model predicts MOR vapor pressure is 100 times greater than DGA over 11 wt% MOR/53 wt% DGA from 40°C to 60°C. The heat of CO2 absorption in the blend is equivalent to 65 wt% DGA up to 0.35 loading, but is 40% lower at 0.5 loading. The solvent working capacity of the blend is 17% less than 65 wt% DGA.

R-05-2
Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine
Cullinane, Tim J. and Rochelle, G.T.
The absorption rate of CO2 was measured in a wetted-wall column in 0.45 to 3.6m piperazine (PZ) and 0.0 to 3.1m potassium carbonate (k2CO3) at 25 to 110°C. A rigorous kinetic model was used to model the data and interpret diffusivities and rate constants. The rate approaches second-order behavior with PZ and is highly dependent on other strong bases. In 1M PZ, the overall rate constant is 102,000s⁻¹, 20 times higher than in monoethanolamine. The activation energy is 35k J/mol, similar to other amine-CO2 reactions. Rate constants for contributions of carbonate, PZ carbonate, and water to the rate were determined according to base catalysis theory. The addition of neutral salts to aqueous PZ increases the apparent rate constant. In 2.7M NaCl/0.6M PZ, the overall rate constant is increased by a factor of 7. Ionic strength effects were accounted for within the rigorous model of K+/PZ mixtures. The absorption rate in concentrated K+/PZ mixtures is up to 3 times faster than in 30 wt% monoethanolamine. At low temperatures and low CO2 loadings, a pseudo-first order approximation adequately represents the absorption rate. At high loadings, the reaction approaches
instantaneous behavior, but is still influenced by reaction kinetics. Under industrial conditions, gas film resistance may account for >80% of the total mass transfer resistance at low loadings.

**R-05-3**  
**Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine**  
Cullinane, Tim J. and Rochelle, G.T.  
*Chemical Engineering Science* 59, (2004), pp. 3619-3630

Many commercial processes for the removal of carbon dioxide from high-pressure gases use aqueous potassium carbonate systems promoted by secondary amines. This paper presents thermodynamic and kinetic data for aqueous potassium carbonate promoted by piperazine. Research has been performed at typical absorber conditions for the removal of CO₂ from flue gas.  

Piperazine, used as an additive in 20-30 wt% potassium carbonate, was investigated in a wetted-wall column using a concentration of 0.6m at 40-80°C. The addition of 0.6m piperazine to a 20 wt% potassium carbonate system decreases the CO₂ equilibrium partial pressure by approximately 85% at intermediate CO₂ loading. The distribution of piperazine species in the solution was determined by proton NMR. Using the speciation data and relevant equilibrium constants, a model was developed to predict system speciation and equilibrium.  

The addition of 0.6m piperazine to 20 wt% potassium carbonate increases the rate of CO₂ absorption by an order of magnitude at 60°C. The rate of CO₂ absorption in the promoted solution compares favorable to that of 5.0M MEA. The addition of 0.6m piperazine to 20 wt% potassium carbonate increases the heat of absorption from 3.7 to 10 kcal/mol. The capacity ranges from 0.4 to 0.8 mol-CO₂/kg-H₂O for PZ/K₂CO₃ solutions, comparing favorably with other amines.

**R-05-4**  
**Thermodynamics of Aqueous Potassium Carbonate, Piperazine, and Carbon Dioxide**  
Cullinane, Tim J. and Rochelle, G.T.  

CO₂ solubility was measured in a wetted-wall column in 0.6-3.6 molal (m) piperazine (PZ) and 2.5-6.2m potassium ion (K⁺) at 40-110°C. Piperazine speciation was determined using 1H NMR for 0.6-3.6m piperazine (PZ) and 3.6-6.2m potassium ion (K⁺) 27-70°C. The capacity of CO₂ in solution increases as total solute concentration increases and compares favorably with estimates for 7m (30wt%) monoethanolamine (MEA). The presence of potassium in solution increases the concentration of CO₃²⁻/HCO₃⁻ in solution, buffering the solution. The buffer reduces protonation of the free amine, but increases the amount of carbamate species. These competing effects yield a maximum fraction of reactive species at a potassium to piperazine ratio of 2:1.  

A rigorous thermodynamic model was developed, based on the electrolyte nonrandom two-liquid (ENRTL) theory, to describe the equilibrium behavior of the solvent. Modeling work established that the carbamate stability of piperazine and piperazine carbamate resembles primary amines and gives approximately equal values for the heats of reaction, ΔH rxn (18.3 and 16.5 kJ/mol). The pKₐ of piperazine carbamate is twice that of piperazine, but the ΔH rxn values are equivalent (~5kJ/mol). Overall the heat of CO₂ absorption is lowered by the formation of significant quantities of HCO₃⁻ in the mixed solvent and strongly depends on the relative concentrations of K⁺ and PZ, ranging from -40 to -75kJ/mol.

**R-05-5**  
**Oxidation Inhibitors for Cu Catalyzed Degradation of Monoethanolamine in CO₂ Capture Processes**  
Goff, George S. and Rochelle, G.T.

This study examines the effect of a number of additives on the oxidative degradation of monoethanolamine (MEA) in the presence of dissolved Cu. Additives were selected from three categories: O₂ scavengers and reaction inhibitors, chelating agents, and stable salts. Three proprietary inhibitors have been identified that significantly inhibit the rate of degradation at concentrations below 100mM. Inhibitor A is a stable compound, while Scavengers B and C are stoichiometrically degraded to products that must be removed in an industrial application. Hydroquinone, ascorbic acid, manganese sulfate, and potassium permanganate all increased the rate of oxidative degradation. EDTA (ethylene-diamine-tetra-acetic acid) was an effective
chelating gent, but lost inhibiting capacity over time. Phosphate was a weak chelating agent. Heat stable salts, including potassium chloride, potassium bromide, and potassium formate were also ineffective oxidation inhibitors. Potassium formate was the strongest of the stable salts tested, and decreased degradation by 15% at 0.55M.

R-05-6
Oxidative Degradation of Piperazine in the Absorption of Carbon Dioxide
Alawode, A.,
The University of Texas at Austin (2005)
Masters Thesis

R-05-7
Absorption of CO₂ in Aqueous Diglycolamine
Al-Juaied, M. and Rochelle, G.T.
I & ECR-Special Issue on CO₂ Capture, May 10, 2005, submitted

R-05-8
Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption
Cullinane, J.T.
Ph.D. Dissertation, The University of Texas at Austin, 2005

R-05-9
Oxidative Degradation of Aqueous Monoethanolamine in CO₂ Capture Processes: Iron and Copper Catalysis, Inhibition, and O₂ Mass Transfer
Goff, G.S.
Ph.D. Dissertation, The University of Texas at Austin, 2005

R-05-10
Innovative Absorber/Stripper Configurations for CO₂ Capture for Aqueous Monoethanolamine
Jassim, M. and Rochelle, G.T.
I & ECR-Special Issue on CO₂ Capture, May 11, 2005, submitted

R-05-11
Energy Performance of Stripper Configurations for CO₂ Capture by Aqueous Amines
Oyenekan, B.A. and Rochelle, G.T.
I & ECR-Special Issue on CO₂ Capture, May 11, 2005, submitted

R-06-1
Pilot Plant for CO₂ Capture with Aqueous Piperazine/Potassium Carbonate
Chen, E., Seibert, F. and Rochelle, G.T.
The University of Texas at Austin 78712

R-06-2
CO₂ Capture Performance of an MEA Pilot Plant
Dugas, R.E., Seibert, F. And Rochelle, G.T.
The University of Texas at Austin 78712

R-06-3
Thermodynamics of Carbon Dioxide in Aqueous Piperazine/Potassium Carbonate at Stripper Conditions
Hilliard, M.D., Kim, I., Rochelle, R.T., Svendsen, H.F. and Hoff, K.A.
The University of Texas at Austin, 78712
R-06-4
Alternative Stripper Configurations to Minimize Energy for CO2 Capture
Oyenekan, B.A. and Rochelle, G.T.
The University of Texas at Austin, 78712

R-06-5
Oxidation Products of Amines in CO2 Capture
Sexton, A., Alawode, A. and Rochelle, G.T.
The University of Texas at Austin, 78712

---

General

B-84-1 $15.00
Assessment of Potential Energy Savings in Fluid Separation Technologies: Technology Review and Recommended Research Areas
Bravo, J. L.; J. R. Fair; J. L. Humphrey; C. L. Martin; A. F. Seibert; S. R. Joshi
An in-depth review of energy consideration, technology state of the art, and future research needs is presented for distillation with high-efficiency devices (B-84-1), membrane separations (B-84-1), adsorption (B-84-1), extraction (conventional and supercritical) (B-84-1), and crystallization (B-84-1).

B-86-2
Potential Energy Savings by Using Alternative Technologies for the Separation of Fluid Mixtures
Bravo, J. L.
Presented at the Industrial Energy Technology Conference, Houston, Texas, June 1986
This report compiles some very preliminary information on possible energy savings offered by combinations of separation technologies in the separation of ethanol/ water, O2/N2, and ethyl/benzene/styrene mixtures (B-86-2).

B-86-7
Alternative Separation Processes for Fluid Mixtures
Bravo, J. L.
This report is a collection of studies on the energy-saving potential of some separation technologies in the process industries. It is a compilation of preliminary information that was developed during the execution of another DOE-sponsored project. Three industrially important fluid mixtures were studied: ethanol-water, air, and ethylbenzene-styrene. Current technology for the separation of these mixtures involves distillation as the main step. The minimum energy requirements for various fluid separations are presented and applied to alternative separation schemes for the three processes under consideration.

B-87-4
Analytical Techniques for Very Dilute Mixtures of Chlorinated Hydrocarbons in Water
Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Bravo for the Chromatography Study Group Meeting.
B-87-9
Development of a Knowledge-Based Expert System for the Synthesis of Separation Sequences
Barnicki, S. D.
Proposal on file, Separations Research Program
This proposal outlines the SRP's research plans in the area of expert systems technology as it applies to the synthesis of separations processes. It describes briefly the different approaches that have been used in the past and our proposed research efforts in the development of specific separation process heuristics and in the implementation of an expert system that would provide the best combination of separation processes for a given task.

B-89-6 $30.00
Distillation and Extraction Videotape
Bravo, J. L.; A. F. Seibert; C. Tischler
This twenty-minute VHS video presentation shows some of the research in distillation, extraction, and supercritical extraction that has taken place in the various test systems of the SRP. Emphasis is on phase contacting and hydraulics. Images of film flow in structured packings and drop motion in extraction are presented. The tape includes narration by SRP talent.

F-85-6
Thermosiphon Reboilers-Performance Modeling
Fair, J. R.
Presented at the August 1985 Meeting of Heat Transfer Research, Inc.
Overview of approaches to modeling both vertical and horizontal reboilers (for distillation columns).

F-85-7 PUBLISHED
Sprays
Fair, J. R.
Concise summary of characteristics of sprays from pressure and two-fluid nozzles. This is a condensation of a longer article in the full encyclopedia.

F-87-3 $10.00
Heat Transfer by Direct Gas-Liquid Contacting
Huang, C. C.
Master's thesis
The heat transfer by direct gas-liquid contacting was studied in a packed-bed simulator with a cross-sectional area of 0.85 sq. ft. Water and mineral spirits were heated and contacted with air to transfer heat. Seven different dumped-type packings were tested including Raschig rings, Intalox saddles, Pall rings, and Hypack rings. The Mickley graphical method was applied to calculate the experimental data for the air/water system. The heat transfer/mass-transfer analogy was used to predict the transfer coefficients for the air/mineral spirits system. It is worthy to note that the values of transfer coefficients predicted by the heat transfer/mass-transfer analogy approach appear to be conservative when compared with experimental data. This work was completed in 1982 but is now available through the SRP.

F-87-5
Separations: Essential to Life and Well Being
Fair, J. R.
Manuscript on file, Separations Research Program
A general information treatise on the field of separations technologies. The booklet contains the text and illustrations presented by Dr. Fair at the Joe J. King Professional Engineering Achievement Award Ceremony held at The University of Texas at Austin in February 1987.
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column
Huang, C. C.; J. R. Fair

Heat transfer by direct gas-liquid contacting was studied in a packed bed with a cross-sectional area of 0.079 sq. m. Water and a nonvolatile oil were contacted with air in beds containing seven different random packings: ceramic Raschig rings (two sizes), metal Pall rings (two sizes), ceramic Intalox saddles (two sizes), and metal Hypak rings. The Mickley graphical method was used to calculate individual heat transfer coefficients for the air/water system. Volumetric heat transfer coefficients were found to be simple functions of gas and liquid flow rates. The heat transfer/mass-transfer analogy was used to predict heat transfer coefficients for the air/oil system. It was found that the predicted coefficients were in close agreement with measured values.

Novel Technique to Measure Equilibria of Supercritical Solvents and Liquid Mixtures
Lahiere, R. J.; J. R. Fair

A new flow method was developed to measure supercritical and near-critical phase equilibria. Equilibrium data for the CO2/ethanol/water system at 35°C and 102.0 atm and the CO2/2-propanol/water system at 25°C and 81.6 atm and at 40°C and 102.0 atm were determined using this technique. The equilibria compared favorably to work reported previously.

A Half-Century of Progress in Separations Technology
Fair, J. R.

Several key separation methods used by the Chemical Process Industries (CPI) have been reviewed in the context of developments over the past 50 years. It is clear that for all of them there is much useful research and development work in progress. In most instances, 1988 practice is very different from that used in 1938. A combination of improved understanding of basic mechanisms, full use of computer power, and innovations in equipment design has been the key to what is regarded as great success in one of the most important areas of the CPI.

Energy Recovery by Direct Contact Gas-Liquid Heat Exchange
Fair, J. R.; J. L. Bravo
Presented at the Industrial Energy Technology Conference, Houston, Texas, September 1988

Energy from hot gas discharge streams can be recovered by transfer directly to a coolant liquid in one of several available gas-liquid contacting devices (F-88-9). The design of the device is central to the theme of this paper, and experimental work has verified that the analogy between heat transfer and mass transfer can be used for design purposes. This enables the large amount of available mass-transfer data for spray, packed, and tray columns to be used for heat transfer calculations. Additional information is provided on flow arrangements for integrating direct contact exchangers into systems for recovering the energy transferred to the liquid.

Energy Savings by Use of Disk/Donut Baffling in Tubular Heat Exchangers
Taborek, J. J.; D. E. Klein; J. R. Fair
Presented at the Industrial Energy Technology Conference, Houston, Texas, September 1988

Using segmental baffling in shell-and-tube heat exchangers has become standard design practice, and process heat transfer specialists recognize that such baffling is the basis for most design procedures. Data from earlier work at The University of Texas indicate that disk/donut baffling can provide equivalent heat transfer rates at significantly reduced pressure drops. In this paper estimates are made of the potential for energy savings by this change of baffle arrangement, and methods are provided for executing designs that involve disk/donut features.
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery
Fair, J. R.
Energy from hot gas discharge streams can be recovered by transfer directly to a coolant liquid in one of several available gas-liquid contacting devices. The design of the device is central to the theme of this paper, and experimental work has verified that the analogy between heat transfer and mass transfer can be used for design purposes. This enables the large amount of available mass-transfer data for spray, packed, and tray columns to be used for heat transfer calculations. Recommended methods for designing the several types of gas-liquid contacting devices are summarized.

Separation System Synthesis: A Knowledge-Based Approach
Barnicki, S. D.; J. R. Fair
This paper describes a task-oriented, or problem decomposition, approach to the selection and sequencing of separation methods for multicomponent gas and liquid mixtures. The design expert's knowledge is organized into a structure query system, the Separation Synthesis Hierarchy (F-89-4) (SSH). This hierarchy divides the overall separation synthesis problem into subproblems or "tasks." Each task can be solved essentially independently from the other tasks. The SSH presented here is being developed explicitly for implementation in a knowledge-based system, the Separation Synthesis ADvisor (F-89-4) (SSAD). The Separation Synthesis ADvisor is currently in the prototype stage of development. In its current implementation, SSAD is limited to the preliminary sequencing of multicomponent liquid mixtures using one of the following methods: 1) simple distillation, 2) azeotropic/extractive distillation, 3) liquid-liquid extraction, 4) stripping, 5) adsorption, 6) membrane permeation, or 7) crystallization.

Separation of Gas Mixtures
Fair, J. R.
This paper provides a discussion of the three main methods used industrially to separate gas mixtures: adsorption, absorption, and membranes. The basic technology of each method is discussed, and areas of application are outlined. Selection criteria are included. For most industrial separations, more than one of the methods is feasible. Sometimes, combinations of the methods provide favorable economics. References are provided.

Separation System Synthesis: A Knowledge-Based Approach
Barnicki, S. D.
PhD dissertation
A systematic, comprehensive approach to the preliminary synthesis of separation sequences for fluid mixtures, the SSH was developed. The knowledge-structuring approach of the SSH has been implemented for liquid mixtures as a knowledge-based expert system, the SSAD. The validity of the synthesis methods is demonstrated for several industrially significant separation problems. The use of the SSH and the SSAD results in a limited number of optimal to suboptimal preliminary process flowsheets. Further optimization must be carried out on a process simulator. The SSH decomposes the overall separation synthesis problem into four similarly structured problem-solving activities dealing with phase separation as well as distillation, liquid-phase, and gas-phase separations. These activities are further divided into distinct separation method selection, separation sequencing, and separation design subproblems. The problem-solving structure of each of the three types of subproblems is explicitly developed and presented with the pertinent separation synthesis domain knowledge.
This paper is the second of a series on the development of the Separation Synthesis ADvisor (SSAD). Part 1 concentrates on separation system synthesis for liquid mixtures and Part 2 focuses on the parallel problem for gas/vapor mixtures. This paper briefly summarizes the structure of the manager subtasks, concentrating on the particulars of the Gas Split Manager; presents the concepts involved in separation method selection for gas/vapor mixtures; and presents several industrially significant gas/vapor separation examples that illustrate the capabilities of the Separations Synthesis Hierarchy (SSH).

S-88-5 $25.00
Separations Research Program Annual Report 1987
Contains an overall description of the structure and operation of the SRP and detailed reports on all of the research projects of the program during 1987.

S-89-4 $25.00
Separations Research Program Annual Report 1988
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1988.

S-89-5 $25.00
Separations Research Program Annual Report 1988
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1988.

S-90-1 $25.00
Separations Research Program Annual Report 1989
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1989.

S-91-1 $25.00
Separations Research Program Annual Report 1990
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1990.

S-92-1 $25.00
Separations Research Program Annual Report 1991
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1991.

S-93-1 $25.00
Separations Research Program Annual Report 1992
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1992.

S-94-1 $25.00
Separations Research Program Annual Report 1993
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1993.

S-95-1 $25.00
Separations Research Program Annual Report 1994
Contains an overall description of the structure and operation of the SRP. Includes detailed reports on all the research projects of the program during 1994.
Membrane Technology

F-92-5  PUBLISHED
Membrane Separations Research
Fair, J.R.
Among the potential application areas of membranes (F-92-5) is that of waste minimization. This paper emphasizes this area, with recognition that a combination of membranes and other separation techniques may represent the optimal design from a cost-energy point of view. It is concluded that the use of membranes will expand further into the field of industrial separations, with membrane materials being tailor-made to provide both high selectivities and large throughputs.

FR-01-3  PUBLISHED
Mixed Gas Permeation Properties of Synthesis Gas Components in Polymers
Merkel, T.C.; Jiang, X.; Lin, H.; Patel, N.P.; Spontak, R.J.; Freeman, B.D.; Gupta, R.; Turk, B.
Polymeric Materials: Science & Engineering 2001, 85, 100

FR-01-4  PUBLISHED
Nanocomposites for Gas Separations
Merkel, T.C.; Freeman, B.D.; Hez, X.; Morisato, A.; Pinnau, I.
Polymeric Materials: Science & Engineering 2001, 85, 301

FR-01-5  PUBLISHED
Effect of Fluorocarbon-Hydrocarbon Interactions on Solubility and Permeability Properties of Polymers
Prabhakar, R.; Merkel, T.C.; Freeman, B.D.; Imizu, T.; Higuchi, A.; Sarti, G.C.; Doghieri, F.
Polymeric Materials: Science & Engineering 2001, 85, 253

FR-01-6  PUBLISHED
CO₂/H₂ Separation Using Polymers
Lin, H.; Jiang, X.; Patel, P.; Spontak, R.J.; Freeman, B.D.
Polymeric Materials: Science & Engineering 2001, 85, 146

FR-01-7  PUBLISHED
Solubility and Diffusivity of Sodium Chloride in Phase-Separated Block Copolymers of Poly(2-dimethylaminoethyl methacrylate), Poly(1,1'-dihydroperfluorooctyl methacrylate), and Poly(1,1,2,2-tetrahydroperfluorooctyl acrylate)
Polymer, 42 (25), 9941-9948 (2001)

FR-01-8  PUBLISHED
Mixed Gas Permeation of Syngas Components in Poly(dimethylsiloxane) and Poly(1-trimethylsilyl-1-propyne) at Elevated Temperatures
Merkel, T.C.; Gupta, R.; Turk, B.; Freeman, B.D.
FR-01-9  PUBLISHED
Gas Permeation Properties of Poly(1,1’-dihydroperfluorooctylacrylate) (PFOA), Poly(1,1’-dihydroperfluorooctylmethacrylate) (PFOMA) and Poly(styrene-b-FOA) (PS-b-FOA) Copolymers
Arnold, M.E.; Nagai, K.; Freeman, B.D.; Spontak, R.J.; Betts, D.E.; DeSimone, J.M.; Pinnau, I.
Macromolecules, 34 (16), 5611-5619 (2001)

FR-01-10  PUBLISHED
Gas and Vapor Sorption and Diffusion in Poly(ethylene terephthalate)
Serad, G.E.; Freeman, B.D.; Stewart, M.E.; Hill, A.J.
Polymer, 42, 6929-6943 (2001)

FR-01-11  PUBLISHED
Gas Permeability and Free Volume of Highly Branched Substituted Polyacetylenes
Macromolecules, 34 (6), 1788-1796 (2001)

FR-01-12  PUBLISHED
Propane and Propylene Sorption in Solid Polymer Electrolytes Based on Poly(ethylene oxide) and Silver Salts
Sunderrajan, S.; Freeman, B.D.; Hall, C.K.; Pinnau, I.
J. Membrane Sci., 182 (1-2), 1-12 (2001)

FR-01-13  PUBLISHED
Sorption and Transport of Linear Alkane Hydrocarbons in Biaxially Oriented Polyethylene Terephthalate
Dhoot, S.N., Freeman, B.D., Stewart, M.E., and Hill, A.J.

FR-01-14  PUBLISHED
Poly[1-(trimethylsilyl)-1-propyne] and Related Polymers: Synthesis, Properties, and Functions
Nagai, K., Masuda, T., Nakagawa, T., Freeman, B.D., and Pinnau, I.
Progress in Polymer Science, 26, pp. 721-798 (2001)

FR-02-1  PUBLISHED
Sorption and Diffusion of Gases and Vapors in a Perfluorinated Rubber
DeAngelis, M. G.; Maurizio, C.; Freeman, B.D.; Doghieri, F.; Sarti, G.C.
Polymeric Materials: Science & Engineering 2002, 86, 133

FR-02-2  PUBLISHED
Polyether-polyamide Block Copolymers: Versatile Materials for Membrane Separations
Pinnau, I. and Freeman, B.D.

FR-02-3  PUBLISHED
Membranes for Vapor Separations: Recent Advances and Future Directions
Freeman, B.D. and Pinnau, I.

FR-02-4  PUBLISHED
Modeling the Relationship Between Free Volume and Transport in Polymers: Theory and Experiment
Hill, A.J.; Meakin, P.; Freeman, B.D.
Polymeric Materials: Science & Engineering 2002, 86, 128
Gas Sorption and Dilation in Poly(2, 2-bistrifluoromethyl-4, 5-difluoro-1, 3-dioxole-co-tetrafluoroethylene): Comparison of Experimental Data with Predictions of the Nonequilibrium Lattice Fluid Model

DeAngelis, M.G.; Merkel, T.C.; Bondar, V.I.; Freeman, B.D.; Doghieri, F.; Sarti, G.C.
Macromolecules 2002, 35, 1276-1288

The sorption and dilation properties of a series of n-alkanes and the corresponding perfluorinated compounds have been examined in two amorphous copolymers of tetrafluoroethylene (TFE) and 2, 2-bis(trifluoromethyl)-4, 5-difluoro-1, 3-dioxole (BDD), commercially available under the names Teflon AF1600 and AF2400. The analysis was made at three different temperatures: 25, 35, and 45°C, to test the effect of temperature on solubility and to evaluate the sorption enthalpies. The partial molar volumes of most penetrants have also been determined in both copolymers. The experimental data have been satisfactorily compared with the sorption isotherms predicted or correlated using the nonequilibrium lattice fluid model.

Ultrapermeable Reverse-Selective Nanocomposite Membranes

Merkel, T.C.; Freeman, B.D.; Spontak, R.J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A.J.
Science Reprint, 19 April 2002, Volume 296, pp. 519-522

Polymer nanocomposites continue to receive tremendous attention for application in areas such as microelectronics, organic batteries, optics, and catalysis. We have discovered that physical dispersion of nonporous, nanoscale, fumed silica particles in glassy amorphous poly(4-methyl-2-pentyne) simultaneously and surprisingly enhances both membrane permeability and selectivity for large organic molecules over small permanent gases. These highly unusual property enhancements, in contrast to results obtained in conventional filled polymer systems, reflect fumed silica-induced disruption of polymer chain packing and an accompanying subtle increase in the size of free volume elements through which molecular transport occurs, as discerned by positron annihilation lifetime spectroscopy. Such nanoscale hybridization represents an innovative means to tune the separation properties of glassy polymeric media through systematic manipulation of molecular packing.

Gas and Vapor Sorption, Permeation, and Diffusion in Glassy Amorphous Teflon AF 1600

Alentiev, A.Y.; Shantarovich, V.P.; Merkel, T.C.; Bondar, V.I.; Freeman, B.D.; Yamposlkii, Yu.P.

Sorption and permeation parameters of light gases, C1-C12 hydrocarbons, and C1-C7 perfluorocarbons were determined in a random, amorphous, glassy copolymer containing 65 mol % 2, 2-bis(trifluoromethyl)-4, 5-difluoro-1, 3-dioxole (BDD) and 35 mol % tetrafluoroethylene (TFE) (TFE/BDD65 or AF 1600). AF 1600 results were compared to those of another copolymer, AF 2400, which contains 87 mol % BDD. As the amount of bulky, packing-disrupting BDD increases, solubility coefficients increase systematically, primarily due to increases in the nonequilibrium excess volume of the glassy polymer. Permeability and diffusivity also increase with increasing BDD content, AF 1600 is easily plasticized by larger, more soluble penetrants and is susceptible to penetrant-induced conditioning. As penetrant size increases, permeability and diffusivity coefficients decrease. The rates of decrease of permeability and diffusivity with increasing penetrant size, which characterize permeability and diffusivity selectivity, are intermediate between those of conventional glassy polymers and exceptionally high free volume glassy materials such as poly(1-trimethylsilyl-1-propyne) (PTMSP). Positron annihilation lifetime spectroscopy (PALS) results suggest unusually large free volume elements and a bimodal distribution of free volume element size: this is consistent with similar results obtained earlier for other high free volume glassy polymers such as AF 2400 and PTMSP. Inverse gas chromatography and PALS estimates of free volume element size distributions were consistent.
Microphase-Separated Block Copolymers Comprising Low Surface Energy Fluorinated Blocks and Hydrophilic Blocks: Synthesis and Characterization
Macromolecules 2002, Vol. 35, No. 9, 3697-3707

The synthesis and characterization of diblock and triblock copolymers produced by a two-component iniferter system is reported. These materials, designed for possible water treatment applications, consist of a hydrophilic poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) block and a very low surface energy poly(1,1'-dihydroperfluorooctyl methacrylate) (PFOMA) or poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN) block. Angle-dependent X-ray spectroscopy results and water contact angle measurements indicate that the surfaces of PDMAEMA-b-PFOMA diblock copolymers consist primarily of PFOMA. Transmission electron microscopy reveals that the block copolymers are microphase-separated, exhibiting either cylindrical or layered morphologies that do not change appreciably upon exposure to water. Both water uptake and water flux increase with increasing PDMAEMA content.

Application of Hydrocarbon-Fluorocarbon Interactions in Membrane-Based Gas Separations
Prabhakar, R. and Freeman, B.D
Presented at the International Congress on Membranes and Membrane Processes (ICOM), Toulouse, France, July 7-12, 2002

To control membrane plasticization in natural gas streams containing higher hydrocarbon compounds, we propose to coat a hydrocarbon-based polymer gas separation membrane with a fluoropolymer layer to reduce the hydrocarbon penetrant partial pressure to which the hydrocarbon membrane is exposed. A theoretical analysis is presented which addresses the trade-offs between reducing membrane plasticization, reduction in gas flux through the composite membrane and reduction in product purity due to the fluoropolymer layer. The analysis reveals that an effective plasticization-resistant, hydrocarbon-fluorocarbon composite membrane would consist of a fluoropolymer that has a lower ratio of hydrocarbon gas to CO$_2$ solubility and a higher size-selectivity than the hydrocarbon polymer. Model cases are presented to illustrate the possibilities and limitations of this approach.

Novel Block Copolymers as Nanofiltration Materials
DiGiano, F.A.; Roudman, A.; Arnold, M.A.; Freeman, B.D.
Env. Eng. Sci., 19 (6), 497-511, 2002

Nanocomposites for Vapor Separation
Freeman, B.D.; Merkel, T.C.; Pinnau, I.; He, Z.; Hill, A.J.; Meakin, P.
Proceedings of the American Chemical Society, Polymer Division for the 224th ACS National Meeting, POLY-371 2002

Gas Permeability and n-Butane Solubility of Poly(1-trimethylgerml-1-propyne)
Nagai, K.; Toy, L.G.; Freeman, B.D.; Teruguchi, M.; Kwak, G.; Masuda, T.; Pinnau, I.

Removal of Acid Gas Components from Coal-Derived Syngas using Novel, Reverse-Selective Membranes
Merkel, T., Toy, L., Coker, D., Gupta, R., Freeman, B.D., and Fleming, G.
Sorption, Transport, and Structural Evidence for Enhanced Free Volume in Poly(4-methyl-2-pentyne)/Fumed Silica Nanocomposite Membranes
Merkel, T.C.; Freeman, B.D.; Spontak, R.J.; Pinna, I.; He, Z.; Meakin, P.; and Hill, A.J.
Chem. Mater. 2003, 15, 109-123
In contrast to the performance of traditional filled polymer systems, penetrant permeability coefficients in high-free-volume, glassy poly(4-methyl-2-pentyne) (PMP) increase systematically and substantially with increasing concentration of nonporous, nanoscale fumed silica (FS). For instance, the permeability of PMP containing 40 wt % FS to methane is 2.3 times higher than that of the unfilled polymer. Gas and vapor uptake in the PMP/FS nanocomposites is essentially unaffected by the presence of up to 40 wt % FS, while penetrant diffusion coefficients increase regularly with increasing filler content. This increase in diffusivity is responsible for elevated permeability in the PMP/FS nanocomposites. The addition of FS to PMP augments the permeability of large penetrants more than that of small gases, consistent with a reduction in diffusivity selectivity. Consequently, vapor selectivity in the nanocomposites increases with increasing FS concentration. Activation energies of permeation in PMP decrease with increasing FS content, suggesting that penetrant diffusive jumps require less energy at higher filler concentrations. Positron annihilation lifetime spectroscopy (PALS) reveals that FS subtly increases the free volume in PMP available for molecular transport. The accessible free volume measured by PALS correlates favorably with relative penetrant permeability in the nanocomposites. Transmission electron microscopy confirms that the FS nanoparticles are relatively well dispersed in PMP.

Sorption and Transport in Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) Containing Nanoscale Fumed Silica
Merkel, T.C.; He, Z.; Pinna, I.; Freeman, B.D.; Meakin, P.; and Hill, A.J.
The addition of nanoscale, nonporous fumed silica (FS) particles to size-selective poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) [AF 2400] systematically increases penetrant permeability coefficients, similar to behavior previously observed in vapor-selective polyacetylenes, but contrary to results in traditional filled polymer systems. Permeability coefficients of large penetrants increase more than those of small molecules in filled AF 2400, thereby decreasing the size selectivity of this polymer. AF 2400 is readily plasticized by n-butane, whereas AF 2400 containing 40 wt % FS exhibits antiplasticization behavior, suggesting that filler addition alters AF 2400 to allow n-butane molecules to be accommodated in the polymer without significant swelling and subsequent plasticization of the matrix. Both filled and unfilled AF 2400 have essentially the same gas solubility coefficients, so all of the increase in penetrant permeability in filled AF 2400 is a result of increased diffusion coefficients. There is reasonable agreement between diffusion coefficients obtained from transient sorption and steady-state data, both of which increase regularly with increasing FS content. Positron annihilation lifetime spectroscopy reveals that FS addition increases the size of free volume elements in AF 2400. Thermal analysis of filled AF 2400 shows that FS has no detectable effect on the polymer’s glass transition temperature, indicating that FS has little impact on long-range chain mobility.

Gas Separation Using Polymers
Coker, D.T.; Prabhakar, R.; Freeman, B.D.
Chemical Engineering Education Winter 2003
Gas Separation Properties of Aromatic Polyimides
Ayala, D.; Lozano, A.E.; de Abajo, J.; Garcia-Perez, C.; de la Campa, J.G.; Peinemann, K.V.; Freeman, B.D.; and Prabhakar, R.
A series of aromatic polyimides have been investigated for their permeation properties to oxygen, nitrogen, helium, carbon dioxide and methane. The polymers are soluble, film-forming polyimides
Based on new anhydride monomers containing carbonyl groups as connecting linkages of phenyl rings and bulky side groups like phenyl and t-butyl. To assist in explaining the experimental results, molecular modeling was performed to calculate density, free volume and chain parameters that could account for the behavior of the polymers as selective barriers for gas penetrants. High values of O2/N2 selectivity and good permeabilities were observed for some polymers; their properties lie near the upper bound for this gas pair. Gas permeability typically increased with increasing free volume, and, in general, free volume could be related to the chemical composition of the polymer backbone and to the nature of the pendant groups.

**FR-03-5 PUBLISHED**

**Effect of Nanoparticles on Gas Sorption and Transport in Poly(1–trimethylsilyl-1-propyne)**

Merkel, T.; He, Z.; Pinnau, I.; Freeman, B.D.; Meakin, P.; and Hill, A.J.

Macromolecules 2003, 36, 6844-6855

Penetrant permeability coefficients in high-free-volume, glassy poly(1-trimethylsilyl-1-propyne) [PTMSP] increase systematically with increasing concentration of nonporous, nanoscale fumed silica [FS]. For example, the permeability of PTMSP containing 40 wt % FS to methane is 180% higher than that of the unfilled polymer. Gas and vapor solubility in the nanocomposites are unaffected by FS at concentrations of up to 50 wt %. Penetrant diffusion coefficients in PTMSP increase with increasing FS content, and the enhanced permeability in the nanocomposites is due to this rise in diffusivity. These results are qualitatively similar to behavior previously observed when FS was added to another stiff-chain polyacetylene, poly(4-methyl-2-pentyne) [PMP]. However, in contrast to PMP, the permeability of PTMSP to relatively small gases increases more upon filling than that of larger penetrants. This results in a reduction in vapor/permanent-gas selectivity for filled PTMSP. In fact, mixed-gas n-butane/methane selectivity is 64% lower in PTMSP containing 50% wt % FS than in pure PTMSP. These results, combined with penetrant diffusion coefficients on the order of 10^3 cm^2/s in filled PTMSP, suggest an escalating influence of free phase transport mechanisms such as Knudsen diffusion as FS concentration in the polymer increases.

**FR-03-6**

**Kinetic Gravimetric Sorption of Low Volatility Gases and Vapors in Polymers**

Dhoot, S.N. and Freeman, B.D.


**FR-03-7**

**Barrier Polymers**

Dhoot, S.N., Freeman, B.D., and Stewart, M.E.


**FR-04-1**

**Membrane Materials to Remove CO2 from Gas Mixtures**

Lin, H. and Freeman, B.D.

*J. Molecular Structure*, 739(1-3), 57-74 (2005)

**FR-04-2**

**Gas Solubility, Diffusivity, and Permeability in Poly(ethylene oxide)**

Lin, H. and Freeman, B.D.


**FR-04-3**

**Reverse-Selective Membranes for Hydrogen Purification, Polymer Preprints**

Lin, H.; Freeman, B.D.; Toy, L.G.; Bondar, V.I.; Gupta, R.P.; Pas, S.J.; Hill, A.J.

American Chemical Society, Division of Polymer Chemistry, 45 (2), 22-23 (2004)
FR-04-4
Cavity Size Distributions in High Free Volume Glassy Polymers by Molecular Simulation
Wang, X.-Y.; Lee, K.M.; Lu, Y.; Stone, M.T.; Sanchez, I.C.; Freeman, B.D.
Polymers, 45 (11), 3907-3912 (2004)

FR-04-5
Modeling Transport Properties in High Free Volume Glassy Polymers
Wang, X.-Y.; Lee, K.M., Lu, Y.; Stone, M.T.; Sanchez, I.C.; Freeman, B.D.

FR-04-6
Fluoropolymer/Hydrocarbon Polymer Composite Membranes for Natural Gas Separation
Prabhakar, R.S. and Freeman, B.D.

FR-04-7
Gas and Vapor Sorption and Permeation in Poly(2,2,4-trifluoro-5-trifluoromethoxy-1, 3-dioxole-co-tetrafluoroethylene)
Prabhakar, R.S.; Freeman, B.D.; Roman, I.
*Macromolecules*, 37 (20), 7688-7697 (2004), (available on-line at journal website)

FR-04-8
Self Consistent Model of Concentration and Temperature Dependence of Permeability in Rubbery Polymers
Prabhakar, R.S.; Raharjo, R.; Toy, L.G.; Lin, H.; Freeman, B.D.

FR-04-9
Sorption and Transport of Propane and Perfluoropropane in Poly(dimethylsiloxane) and Poly(1-trimethylsilyl-1-propyne)
Prabhakar, R.S.; Merkel, T.C.; Freeman, B.D.; Imizu, T.; Higuchi, A.

FR-04-10
Gas and Vapor Sorption, Permeation and Diffusion in Poly(tetrafluoroethylene-co-perfluoromethyl vinyl ether)
Prabhakar, R.S. and Freeman, B.D.

FR-04-11
Fundamentals of Membranes for Water Treatment
Sagle, A. and Freeman, B.D.

FR-04-12
Influence of Methanol Conditioning and Physical Aging on Carbon Spin-Lattice Relaxation Times of Poly(1-trimethylsilyl-1-propyne)
Hill, A.J., Pas, S.J., Bastow, T.J., Burgar, M.I., Nagai, K., Toy, L.G. and Freeman, B.D.

FR-04-13
Reverse-selective Polymeric Membranes for Hydrogen Purification
Lin, H., Freeman, B.D., Toy, L., Bondar, V., Gupta, R., Gupta, S., and Hill, A.
FR-04-14  
Effects of Physical Aging on Solubility, Diffusivity, and Permeability of Propane and n-Butane in (Poly(4-methyl-2-pentyne))  
Nagai, K., Sugawara, A., Kazama, S., and Freeman, B.D.  

FR-04-15  
Sorption and Transport of Linear and Branched Keytones in Biaxially Oriented Polyethylene Terephthalate  
Dhoot, S.N., Freeman, B.D., and Stewart, M.E.  

FR-04-16  
Sorption and Transport of Linear Esters and Branched Alkanes in Biaxially Oriented Poly(ethylene terephthalate)  
Dhoot, S.N., Freeman, B.D., and Stewart, M.E.  

FR-05-1  
Pure Gas and Vapor Permeation Properties of Poly(1-phenyl-2-[p-(trimethylsilyl)phenyl]acetylene] (PTMSDPA) and Its Desalinated Analog, Poly[diphenylacetylene](PDPA)  
Raharjo, R.D., Lee, H.J., Freeman, B.D., Sakaguchi, T., and Masuda, T.  
*Polymer*, 46(17), pp. 6316-6324 (2005)  

FR-05-2  
Translation and Rotation of Penetrants in Ultrapermeable Nanocomposite Membrane of Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) and Fumed Silica  
Zhong, J., Lin, G., Wen, W.-Y., Jones, A.A., Kelman, S., and Freeman, B.D.  

FR-05-3  
Synthesis and Properties of membranes of Poly(diphenylacetylenes) Having Fluorines and Hydroxil Groups  
Shida, Y., Sakaguchi, T., Shiotsuki, M., Fumio, S., and Freeman, B.D.  

FR-05-4  
Relaxation Characteristics of Crosslinked Poly(ethylene glycol) Diacrylates and Their Relation to Gas Transport Properties  
Kalakkunnath, S., Lin, H., Freeman, B.D., and Kalika, D.S.  

FR-05-5  
Chlorine Resistance Studies on Membranes  
Sagle, A.C., Gin, D.L., Sharma, M., and Freeman, B.D.  

FR-05-6  
A Molecular Simulation Study of Cavity Size Distributions and Diffusion in para and meta Isomers  
Wang, X.-Y., in’tVeld, P.J., Lu, Y., Freeman, B.D., and Sanchez, I.C.  
*Polymer*, 46, pp. 9155-9161 (2005)
FR-05-7
Transport of Gases and Vapors in Glassy and Rubbery Polymers
Yampolskii, Yu, Freeman, B.D., Pinnau, I., and Matteucci, S.

FR-05-8
Gas and Vapor Transport Properties of Perfluoropolymers
Merkel, T.C., Pinnau, I, Prabhakar, R., and Freeman, B.D.

FR-05-9
The Effect of Crosslinking on Gas Permeability in Crosslinked Poly(ethylene glycol diacrylate)
Lin, H., Kai, T., Freeman, B.D., Kalakkunnath, S., and Kalika, D.S.

FR-05-10
Permeation and Diffusion
Lin, H. and Freeman, B.D.

FR-05-11
Gas and Liquid Separations Using Membranes: An Overview
Freeman, B.D. and Pinnau, I.

FR-05-12
Tailoring Nanospace
Hill, A.J., Freeman, B.D., Jaffe, M., Merkel, T.C., and Pinnau, I

FR-05-13
Modeling Transport Properties in High Free Volume Glassy Polymers
Wang, X.-Y., Lee, K.M., Lu, Y., Stone, M.T., Sanchez, I.C., and Freeman, B.D.

FR-05-14
Synthesis and Properties of F-Containing Poly(diphenylacetylene) Membranes
Sakaguchi, T., Shiotsuki, M., Sanda, F., Freeman, B.D., and Masuda, T.

FR-05-15
Segmental Relaxation Characteristics of Crosslinked Poly(ethylene oxide) Copolymer Networks
Kalakkunnath, S., Kalika, D.S., Lin, H., and Freeman, B.D.

FR-05-16
Gas and Vapor Solubility in Crosslinked Poly(ethylene glycol diacrylate)
Lin, H. and Freeman, B.D.
FR-06-1  
**Plasticization-Enhanced H2 Purification using Polymeric Membranes**  
Lin, H., vanWagner, E., Freeman, B.D., Toy, L.G., and Gupta, R.P.  

FR-06-2  
**Transport and Structural Characteristics of Crosslinked Poly(ethylene oxide) Rubbers**  
*Journal of Membrane Science*, available online

FR-06-3  
**Gas Permeation and Diffusion in Crosslinked Poly(ethylene glycol diacrylate)**  
Lin, H. and Freeman, B.D.  
*Macromolecules*, in press

FR-06-4  
**Viscoelastic Characteristics of U.V. Polymerized Poly(ethylene glycol) Diacrylate Networks with Varying Extents of Crosslinking**  
Kalakkunnath, S., Kalika, D.S., Lin, H., and Freeman, B.D.  
*Journal of Polymer Science: Part B, Polymer Physics*, in press

FR-06-5  
**Enhancement of Track-etched Membrane Performance via Stretching**  
*Purification Technology*, in press

FR-06-6  
**Water Sorption, Proton Conduction, and Methonal Permeation Properties of Sulfonated Polyimide Membranes Crosslinked with N,N-Bis(2-hydroxyethyl)-2-aminooethanesulfonic Acid (BES)**  
Lee, Chang Hyun; Park, Ho Bum; Chung, Youn Suk; Lee, young Moo; and Freeman, B.D.  

FR-06-7  
**High Performance Polymer Membranes for Natural Gass Sweetening**  
Lin, H., vanWagner, E., Freeman, B.D., and Roman, I.  

K-83-1  **PUBLISHED**  
**Multicomponent Gas Sorption in Glassy Polymers**  
Koros, W.J. and E.S. Sanders  
The complex behavior observed for mixed gases sorbing in glassy polymers is explained. Data for CO2/N2O are presented for PMMA.

K-84-1  
**Gas Separations Using Membranes**  
Handout for SRP Membrane Study Group Meeting, May 1984  
A review of plans for SRP-related research including equipment and new projects for students beginning research. Includes copies of all transparencies used in talks by Koros, Muruganandam, Fleming, Story, and Barbari.
K-84-2 PUBLISHED
Material Selection for Membrane-Based Gas Separation
Chern, R.T.; W.J. Koros; H.B. Hopfenberg; V.T. Stannett
A review of the basic principles governing the operation of gas separation membranes. Also included are suggestions for novel directions that may lead to markedly improved "second generation" membrane materials with high permeabilities and high selectivities.

K-84-3 PUBLISHED
Simplified Analysis of Gas/Polymer Selective Solubility Behavior
Koros, W.J.
Factors controlling the inherent solubility selectivity of a polymer membrane (K-84-3) are discussed. The basic principles introduced are illustrated for the CO2/CH4 system.

K-84-4 PUBLISHED
Selective Permeation of CO2 and CH4 through Kapton(r) Polyimide: Effects of Penetrant Competition and Gas-Phase Nonideality
Chern, R.T.; W.J. Koros, B. Yui; H.B. Hopfenberg; V.T. Stannett
Permeabilities and solubilities of CO2 and CH4 are presented and discussed for Kapton(r), a polyetherdiimide, at 60°C. Complex effects in mixed gas permeation cases are explained in terms of a combination of gas phase nonideality and so-called dual-mode sorption effects.

K-84-5 PUBLISHED
Gas Separations Using Membranes
Koros, W.J.; D.R. Paul
A historical review of the field of membrane-based gas separation (K-84-5) with a brief overview of current areas of application for this technology.

K-84-6 PUBLISHED
A Simple Apparatus for Measurement of Liquid Permeabilities through Polymeric Films
Al-Hussaini, H.; W.J. Koros; M. Howard; H.B. Hopfenberg
Describes a device for gravimetric measurements of the permeation of liquid solvents (K-84-6) through polymer films. The cell eliminates inherently leaky polymeric seals (O-rings of gaskets) by using opposing metal O-rings that produce uniform deformation of the test membrane. The cell is best suited for studying rubbery polymer materials.

K-84-7 PUBLISHED
Current Aspects of Membrane-Based Separation of Gases
Koros, W.J. and D.R. Paul
Commercial membrane-based applications of gas separation are reviewed. Technical developments leading to the current popularity of membranes are traced and research directions are suggested to meet future market opportunities.
K-84-8
Membrane Program Update and Overview Information
Koros, W.J.
Handout for the SRP Membrane Study Group Study Group Meeting, October 1984
Discusses additions to SRP personnel and equipment in the membrane area since the last group
meeting. Also reviews recent membrane meeting activities.

K-84-9 PUBLISHED
Simulation of a Hollow-Fiber Gas Separator: The Effects of Process and Design Variables
Chern, R.T.; W.J. Koros; P.S. Fedwick
Presents case studies of design considerations for hollow-fiber gas permeation modules. The
interplay between fiber diameter, membrane permeability (K-84-9), and overall separator
performance is treated. The paper also treats the effects of bore-side resistance induced by volume
contractions of epoxy potting materials used in manifolds. The effects are shown to be small for
commonly used fiber bore diameters unless fiber permeabilities are extremely high.

K-85-1 PUBLISHED
The Effects of Morphology and Hygrothermal Aging on Water Sorption and Transport in Kapton(r)
Polyimide
Yang, D.K.; W.J. Koros; H.B. Hopfenberg; V.T. Stannett
Discusses permeation, sorption, and diffusion properties (K-85-1) of water vapor in Kapton(r)
polyimide for films of two different thicknesses. Solubility differences are small, but diffusivity
and permeability differences are about a factor of three higher for the thick (2 mil) film compared
to the thin (0.3 mil) film. These effects are attributed to the complex morphology of Kapton(r)
which is known to be produced during curing to its diimide form from its polyamic acid precursor
form.

K-85-2 PUBLISHED
Separation of Gaseous Mixtures Using Polymer Membranes
Koros, W.J. and R.T. Chern
& Sons (1987)
Summarizes the historical development and the fundamental basis and design of gas permeation
modules (K-85-2). Also reviews experimental methods for characterization of dense and
asymmetric membranes (K-85-2). A reasonably comprehensive summary of the subject.

K-85-3 PUBLISHED
Sorption and Dilation of Glassy Polymers by Gaseous Penetrants
Koros, W.J. and G.K. Fleming
The simultaneous volume dilation and mass uptake associated with exposure of bisphenol-A
polycarbonate to CO2 pressures up to 900 psia are reported. Analysis of the data in terms of the
so-called dual-mode sorption model explains the dilation data for the system. Hysteretic responses
(K-85-3) for volume and mass sorbed are found during the depressurization of the sample back to
vacuum.

K-85-4 PUBLISHED
Dual-Mode Analysis of Subatmospheric Pressure CO2 Sorption and Transport in Kapton H(r)
Polyimide Film
Uragami, H.; H.B. Hopfenberg; W.J. Koros; D.K. Yang; D.K.; V.T. Stanett; R.T. Chern
Discusses the application of the dual-mode sorption and transport model (K-85-4) to low-pressure
gas-polymer systems.
K-85-5  PUBLISHED
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate
Fleming, G.K and W.J. Koros
Macromolecules 19:2285 (1986)
Sorption/desorption and volume dilation/consolidation measurements are reported for silicone rubber and bisphenol-A polycarbonate at 35°C for CO2 pressures up to 900 psia. The combined sorption and dilation measurements are analyzed to determine the volume change upon mixing and the partial specific volumes of both the gaseous and polymeric material as a function of pressure. Marked differences are observed for the partial specific volume of CO2 in the rubbery and glassy media. The differences in responses between the two media can be rationalized to a large degree in terms of the nonequilibrium nature of glassy polymers (K-85-5).

K-85-6
Handout for the SRP Membrane Study Group Study Group Meeting, October 1985
Koros, W.J.
Describes progress on three major projects:
1. Polymer synthesis and characterization of two series of high glass transition polyimides for gas separation membrane applications.
2. Chemical modification of PPO to improve its permselectivity in CO2/CH4 separation applications.
3. Characterization of the effects on permeability and permselectivity of polycarbonate caused by high-pressure preconditioning of films with CO2 followed by partial removal of the conditioning gas.
Also summarizes observations concerning the activities of the Japanese membrane community (K-85-6) in the area of gas separation. These observations are the result of a visit to Japan by W. J. Koros.

K-85-7  PUBLISHED
Gas and Liquid Separation Membrane Activity in Japan
Koros, W.J.
This report summarizes Japanese governmental, industrial, and academic research and development activities in the field of membrane separation of liquids and gases (K-85-7). This report can be obtained by contacting Science Applications International Corporation, 1200 Prospect Street, La Jolla, California 92037.

K-86-1  PUBLISHED
A New Technique for the Measurement of Multicomponent Gas through Transport Polymeric Films
O'Brien, K.C.; W.J. Koros; T.A. Barbari; E.S. Sanders
This article describes a simple apparatus to measure mixed gas permeation through polymer films. The system is based on a combination of manometric and gas chromatography techniques and permits determination of permeabilities and selectivities over a wide range of feed pressures and compositions. Pure and mixed gas permeation data in polycarbonate films are reported for CO2 and methane to illustrate the use of the equipment.

K-86-2  PUBLISHED
Material Selection Considerations for Gas Separation Processes
Koros, W.J.; B.J. Story; S.M. Jordan; K.C. O'Brien; G.R. Husk
Polymer Engineering and Science 27(8):603 (1987)
This article considers advantages and disadvantages associated with common membrane types used in gas separation operations. Trade-offs between the use of rubbery and glassy polymers are considered first, followed by a treatment of the optimization of glassy membrane permeability and permselectivity properties. Material optimization principles are defined in terms of the basic thermodynamic solution and kinetic transport properties of polymers. Applications of these
principles are illustrated for a modified poly(phenylene oxide) (PPO) and a homologous series of polyimides derived from pyromellitic dianhydride.

K-86-3
Gas Separations Using Membranes
Koros, W.J.
Handout for SRP Membrane Study Group Study Group Meeting, April 1986
Copies of transparencies used in the above meeting are in the collection. Detailed summaries of projects by three graduate students are included along with a brief program highlight section describing the students in the group and their projects.

K-86-4 PUBLISHED
The Effects of CO2 Exposure on Pure and Mixed Gas Permeation Behavior: Comparison of Glassy Polycarbonate and Silicone Rubber
Jordan, S.M.; W.J. Koros; G.K. Fleming
Pure and binary mixture permeabilities were investigated for the CO2/CO4 system in polycarbonate and silicone rubber. Upstream pressure conditions ranging from zero up to the critical point of CO2 were investigated. No permeability hysteresis was observed for the silicone rubber sample with pure or binary feeds of CO2 and CH4. On the other hand, perturbation treatments with CO2 resulted in long-lived increases in the permeability of the conditioned polycarbonate films compared to untreated films.

K-86-5 PUBLISHED
Membranes and Membrane Process
Koros, W.J.
This chapter deals with a range of topics involving the moderation of passage of small molecules between two regions separated by a high polymer membrane. The chapter gives an overview of the following application areas:
- Pressure and simple concentration-driven gas and liquid separations
- Gas permeable contact lenses
- Barrier packaging
- Controlled release
- Microporous reactors, membrane lungs, and breathable moisture barriers

K-86-6 PUBLISHED
Influence of Casting and Curing Conditions on Gas Sorption and Transport in Polyimide Films
O'Brien, K.C.; W.J. Koros; G.R. Husk
Polymer Engineering and Science 27:211 (1987)
Carbon dioxide and methane gas permeabilities, solubilities, and diffusivities for poly[N,N'- (phenoxophenyl)-pyromellitimide] films synthesized in our laboratory are contrasted with values measured for a chemically identical commercial polyimide film, Kapton H(r). The synthesized samples exhibited greater permeabilities, solubilities, and diffusivities than those of the commercial sample. At the same time, the higher CO2 permeability is associated with only a moderate reduction in permselectivity for the CO2/CO4 system. The increased sorption and transport coefficients (K-86-6) for the synthesized sample are attributed to a lower degree of aggregation and orientation of this film as compared to the Kapton H(r) sample.

K-86-7
Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications
Koros, W.J. and D.R. Paul
Proposal submitted to DOE in September 1984 and approved for a three-year period.
The proposal describes a concerted experimental program to develop advanced polymeric membranes (K-86-7) for gas separation applications (K-86-7). The program focuses on the
interpretation of high-pressure pure and multicomponent gas sorption and transport data to be collected for a series of novel polymers to be synthesized as part of the project.

K-86-8
W.J. Koros Research Group Report
Handout for SRP Membrane Study Group Study Group Meeting, October 1986
A review of research projects including copies of transparencies used by Koros, Kim, and Moe in their presentations.

K-86-9 PUBLISHED
The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders. Part 1. Lower Alcohol and Water Sorption in Poly(methylmethacrylate)
Connelly, R.N.; N.R. McCoy; W.J. Koros; H.B. Hopfenberg; M.E. Stewart
Sorption kinetics and equilibria for methanol, ethanol, and n-propanol in 0.544-mm-diameter PMMA microspheres were determined at 35°C over a wide range of relative pressures. Sorption isotherms (K-86-9) were concave to the pressure axis at low relative pressures and convex to the pressure axis at higher relative pressures. These results, considered in the context of recently reported data for high-pressure sorption of gases in polymeric glasses, suggest that the S-shaped isotherms reported here are examples of a generalized isotherm which describes sorption behavior of all penetrants in glassy polymers if an appropriate range of concentration is traversed by the experimental protocol. The effects of dilating the microspheres by preswelling with methanol were studied by subsequent low-pressure sorption of water, methanol, ethanol, and n-propanol at 35°C. The preswollen microsphere exhibited initially higher sorption capacities than the as-received samples but tended to consolidate with time following the preswelling treatment. The aging process, monitored by periodic short-term sorption with the various penetrant probes, was arrested by contacting the microspheres with an activity of n-propanol sufficient to maintain a sorbed concentration of approximately 1 wt%. The aging was significantly retarded by the presence of low concentrations of water and ethanol. Conversely, the aging process appeared to be essentially unaffected by the presence of correspondingly low concentrations of methanol.

K-86-10 PUBLISHED
The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymers Powders. Part 2. n-Propane Sorption in Polystyrene
Stewart, M.E.; H.B. Hopfenberg; W.J. Koros; N.R. McCoy
Both the rate and apparent equilibrium of propane sorption in glassy PS were increased after swelling the polymer by exposure to a highly sorbing vapor. Cyclic sorption experiments revealed that the increase in rate and apparent equilibrium of sorption due to the preswelling treatment decayed only during vacuum aging. The presence of low levels of propane in the polymer during aging, however, appeared to arrest the decay in sorption capacity. These composite results, taken in conjunction with the results of previous work in our laboratory, suggest that the component of the total sorption which resides in nonequilibrium, distended interchain gaps, retards the chain motions that otherwise lead to consolidation of the dilated glass.

K-86-11 PUBLISHED
Comments on Measurements of Gas-Induced Polymer Dilation by Different Optical Methods
Fleming, G.K and W.J. Koros
Several reports of gas-induced polymer dilation measurements have appeared in the literature recently. Direct dilatometric measurements made by observation of dimensional changes of polymer films provide straightforward determinations of the length and width dimensional changes; however, the thickness changes are difficult to measure using this technique. Optical interferometry of a film cast on a quartz window allows indirect measures of the thickness dimensional changes. To use the interferometry technique, one must know how the refractive index of the polymer film is changed by the presence of sorbed gas to convert apparent optical
thicknesses into actual thicknesses. In this manuscript, we examine both methods used for
determination of dimensional changes in unconstrained films. The optical interferometry and
length dilation results are shown to be in good agreement if the appropriate values of the refractive
index of the gas-laden polymer are used in the analysis of the optical interferometry data.

K-87-1
Abstracts
Abstracts of papers presented at the Second International Conference on Pervaporation Processes

K-87-2
Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Fleming, Jordan, Segura, Story, and Koros for the Gas
Separations (K-87-2) Using Membranes Study Group (K-87-2) Meeting.

K-87-3 PUBLISHED
Reverse Perme selectivity" of N2 over CH4 in Aromatic Polyimides
Kim, T.H.; W.J. Koros; G.R. Husk; K.C. O'Brien
The presence of significant supplies of natural gas containing N2 contamination in the range of
5%-15% makes it desirable to have membranes which preferentially pass N2 while rejecting CH4
as a high-pressure nonpermeate product. Upgrading of the heating value of such gas supplies
without the need to recompress the resultant product stream would be a significant advantage.
Unfortunately, the permeability of N2 is lower than that of CH4 for most polymer materials, as
indicated in this paper. A series of polymers have, however, been synthesized in our laboratory
which show so-called "reverse perme selectivity" of N2 over CH4. The detailed synthesis of such
materials, all of which are aromatic polyimides, has been described in detail in other papers. The
purpose of the present note is to clarify the apparent cause of such an unusual phenomenon. The
N2 permeabilities and the perme selectivities of N2 over CH4 for the polyimides are reproduced.
The equipment and procedures for the gas permeation and sorption experiments are the same as
described in other papers.

K-87-4 PUBLISHED
Relationship between Gas Separation Properties and Chemical Structures in a Series of Aromatic
Polyimides
Kim, T.H.; W.J. Koros; G.R. Husk; K.C. O'Brien
Gas permeabilities and perme selectivities for various gas pairs (He/CH4,CO2/CH4, N2/CH4, and
O2/N2) are reported for a series of aromatic polyimides synthesized in our laboratory. Gas
solubility and diffusivity (K-87-4) data are also reported for some of the polyimides. Systematic
variations in chemical structure were found to lead to significant changes in permeabilities and
selectivities. Further analysis shows that the permeability and selectivity changes in these cases are
primarily due to the alteration of diffusivity factors. Generally, increases in permeability are
attended by losses in permeselectivity; however, some of the polyimides in the present series of
materials were found to deviate very favorably from this typical behavior. Specifically, materials
were discovered having simultaneously higher permeabilities and permselectivities than
commercial polymers currently being used as membrane materials. The relationship between gas
separation properties and chemical structures is discussed in terms of intrasegmental mobility and
intersegmental packing of the constituent polymers. The experimental data and their physical
implications suggest the possibility that many new polymers having both high permeability and
selectivity can be designed by tailoring the intrasegmental mobility and intersegmental packing of
membrane polymers.
Polyimide Materials Based on Pyromellitic Dianhydride for the Separation of Carbon Dioxide and Methane Gas Mixtures
O'Brien, K.C.; W.J. Koros; G.R. Husk

The sorption and transport of CO2 and methane in a series of dense polyimide films were examined to evaluate these materials for gas separation applications. The polyimides described in this study are based on the reaction of pyromellitic dianhydride (PMDA) with oxadiazoline (ODA), methylene dianiline (MDA), or isopropylidene dianiline (IPDA). The CO2 permeabilities for this series of compounds increased in the order: PMDA-ODA < PMDA-MDA < PMDA-IPDA, while the permselectivity increased in the opposite order: PMDA-IPDA < PMDA-MDA < PMDA-ODA. Sorption studies, coupled with mixed gas permeability measurements, demonstrated that the trends in permeabilities and permselectivities were due primarily to differences in the mobilities of the gases in the various films. The trends observed for permeabilities and selectivities were correlated with trends in the macroscopic densities and average intersegmental distance for each film as measured by wide-angle x-ray diffraction (WAXD). These results indicated that in addition to intrachain motions, interchain spacing differences are contributing, if not dominating, factors in understanding differences in the transport behavior of gas through these polyimide films.

Gas and Liquid Separations Using Membranes
Koros, W.J.
Handout from the Separations Research Program European Meeting, June 1987
Includes all transparencies used by Koros for the Membranes Study Group Meeting.

Solubility Properties in Polymers and Biological Media: 10. The Solubility of Gaseous Solutes in Polymers in Terms of Solute-Polymer Interactions
Abraham, M.H.; P.L. Grellier; R.A. McGill; R.M. Doherty; M.J. Kamlet; T.N. Hall; R.W. Taft; P.W. Carr; W.J. Koros
Polymer 28:1363-69 (1987)

A general correlation equation based upon the so-called "solvatochromic" method has been used to describe solubility properties of a wide range of gaseous solutes in polymers. Difficulties in using the solvatochromic method for glassy polymers are noted.

Characterization of CO2-Induced Conditioning of Polycarbonate Films Using Penetrants with Different Solubilities
Jordan, S.M.; W.J. Koros; J.K. Beasley

Past work has shown that hysteresis in sorption, volume dilation, and permeation can be produced when a glassy bisphenol-A polycarbonate film was first conditioned with CO2 at 900 psia and then exposed to lower pressures of CO2 as a pure gas or in a mixture with methane. In this study it is shown that once a polycarbonate's permeability has been increased by the CO2 conditioning treatment, the material retains a state of high permeability, even if the CO2 is replaced with pure methane or air without any intervening exposure to vacuum. On the other hand, the conditioning treatment is not apparent even after very short times following exposure with CO2, if the CO2 is replaced by helium without any intervening exposure to vacuum.

Polymeric Membrane Materials for Solution-Diffusion Based Permeation Separations
Koros, W.J.; G.K. Fleming; S.M. Jordan; T.H. Kim; H.H. Hoehn

The present discussion provides an update on current theory and practice involving separation of gases and liquids with polymeric membranes for solution-diffusion based permeation separations.
mechanism for separation involves a thermodynamic solution and a kinetic diffusion process. In a practical sense, several levels of structure determine the ultimate performance of a membrane. The principal focus of this discussion is on the most basic levels of structure, involving the primary chemical segment composition and the steric relationships between the segmental repeat units comprising the selective polymer skin. Clearly, changes in these basic levels of chemical and steric factors can impact additional structure levels involving skin morphology and the overall relationship between skin and porous support in an asymmetric membrane. These most basic levels of structure, therefore, are critically important and lie at the interface between polymer science and the practical field of membrane technology. A "new" polymeric membrane material exists when a novel molecular-level environment is generated, through which the transport process occurs.

**K-87-10 PUBLISHED**

**Effects of Film History on Gas Transport in a Fluorinated Aromatic Polyimide**  
Moe, M.B.; W.J. Koros; H.H. Hoehn; G.R. Husk  

The effects of film formation procedures on transport properties are reported for a rigid-chained, fluorinated, aromatic polyimide. Residual dimethylacetamide (DMAC) solvent present in films formed under certain casting protocols produces complexities in the permeation behavior of He and CO2. Significant differences in transport properties are also observed between films prepared using two different casting techniques. These differences appear to be due to differences in organization of chain segments within the films. Rigid-chained polymers are attractive for membrane-based gas separation applications. The results of this study emphasize the considerable care needed in formation and post-formation processing of these materials to ensure optimum flux/selectivity properties in such applications.

**K-87-11 PUBLISHED**

**Effects of Molecular Structure and Thermal Annealing on Gas Transport in Two Tetramethyl Bisphenol-A Polymers**  
Moe, M.B.; W.J. Koros; D.R. Paul  

The effects of molecular structure and thermal history on the gas transport properties of TMPC and TMPSF are reported. The presence of the bulky methyl side groups on the aromatic rings of TMPC and TMPSF inhibits both chain packing and molecular motions in these polymers as compared to standard polycarbonate and PSF. The methyl substitution results in significant increases in permeability with little or no loss of selectivity, making these materials promising candidates for membrane-based gas separation applications. Thermal annealing produces a densification of the materials, resulting in decreased permeabilities. Selectivities increased upon annealing at temperatures slightly below the glass transition temperature.

**K-87-12 PUBLISHED**

**Advanced Gas Separation Membrane Materials: Rigid Aromatic Polyimides**  
Kim, T.H.; W.J. Koros; G.R. Husk  
Separation Science and Technology 23:1611 (1988)

Permeabilities, solubilities, diffusivities, and selectivities for He/CH4 and CO2/CH4 gas pairs are reported for four aromatic polyimides having systematic variations in intersegmental packing and intrasegmental mobility. As intersegmental packing is disrupted by bulky substituents, gas diffusivities are generally increased, but diffusivity selectivities of He/CH4 and CO2/CH4 are correspondingly decreased. Simultaneous suppression of intrasegmental mobility and intersegmental packing, however, yields significant increases in both diffusivity and diffusivity selectivity, and consequently in permeability and permselectivity.
The Effects of CO2 Conditioning on the Transport Properties of Glassy Polycarbonates
Jordan, S.M.; W.J. Koros; G.K. Fleming
Presented at the AIChE Meeting, November 1987
Sorption, volume dilation, and permeation results are presented for CO2 conditioning pressures significantly below the previously studied 900 psia which was near the critical point of CO2. Lower CO2 conditioning pressures are able to produce the same type of hysteretic behavior in these properties, although of a lower magnitude compared to that observed at 900 psia. Previous testing of the effect of CO2 exposure has been performed using standard permeation techniques where the downstream face was maintained at a vacuum, while the upstream face was exposed to the high-pressure CO2. We have modified the permeation equipment to allow measurements when the downstream face is exposed to nonzero pressures of CO2. Pure gas results for this equipment are presented using both an unconditioned polycarbonate film and a film that had been uniformly conditioned on both sides with CO2 at 600 psia, without total depressurization.

Development of a Gas Permeation Membrane Minimodule Testing System
Segura, C.J.
Master's thesis
A large-scale testing system was developed for testing small asymmetric membrane modules, or minimodules. The system's capabilities include determining gas permeation rates for one or two minimodules in series or in parallel under various pressures and temperatures. Gases are recycled enabling long-term compaction and conditioning studies with a minimum loss of gas. Future capabilities include condensate introduction into the feed gas stream and adaptive control strategies. Permeation rates are reported for a proprietary minimodule. In separate experiments, a proprietary minimodule was conditioned with CO2 at 125 psig. Permeation rates for air through the minimodule membrane more than doubled over the rates for the unconditioned sample for at least two days, with a negligible drop in the O2/N2 separation factor. On depressurization to air at atmospheric pressure, periodic air permeation rate tests indicated that the membrane appeared to approach its original state. These tests indicate that productivity improvements due to conditioning with CO2 can occur in asymmetric membrane modules, as they have previously been shown to occur in dense films. The tests also indicate that the conditioning effect can occur with some polymers after a relatively short conditioning period for CO2 at relatively low pressures.
Effects are also presented. Specifically, pressure dependencies of gas permeabilities, solubilities, and diffusivities are discussed in terms of pre-established dual-mode sorption and partial immobilization theory. Temperature dependency was also characterized for two of the eight members of this polyimide family. More complex history-dependent effects were seen due to perturbation treatments of high-pressure CO2 in one of the films. Specifically, hysteretic behavior of permeabilities between increasing pressure and decreasing pressure runs occurred. The hysteretic behavior is discussed in terms of CO2 conditioning-induced defects in polymer segmental packing and the segmental re-arrangement tending to recover from the defects, especially in the depressurization process.

K-88-4 $10.00
Effects of Annealing Below the Glass Transition Temperature on Transport Properties of Three Aromatic Glassy Polymers
Moe, M.B.
Master's thesis
The effects of annealing of glassy polymers on permeability and selectivity are discussed. The polymers used were TMPC and sulfone, which show increased permeabilities with little or no accompanying loss in selectivity when compared to the unsubstituted aromatic rings. Annealing of TMPC and TMPSF causes a slight degree of densification. Sizeable enthalpic endotherms are developed upon annealing near the glass transition. The degree of relaxation in both volume and enthalpy is much greater for annealing near the glass transition than for annealing near the glass transition.

K-88-5 $10.00
Sorption of Low Molecular Weight Organic Penetrants in Protective Polymeric Coatings
Kollaja, R.
Master's thesis
Sorption data for nine organic saturated vapors in several military paint coatings; at 40°C are reported. Sorption measurements for whole paint formulations and polymeric resins excluding pigment and filler materials were conducted. A simple, inexpensive, yet relatively accurate direct gravimetric sorption method was used and a description of the technique is given. Sorption equilibria are analyzed using the solvatochromic comparison method. Linear solvation energy relationships obtained from solubility data provide insight into the important physiochemical parameters controlling solvation effects. An interpretation of the solubility results is based upon consideration of resin, pigment/ filler, and penetrant molecular structures and properties. The effect of varying coating cure conditions on solvent resistance was conducted and significant differences in sorption equilibria were found. The results are interpreted in terms of both the amount and type of crosslinks occurring in the polymeric resin as a function of cure conditions. The presence of residual solvents in the resin is believed to play an important role in sorption equilibria and kinetics for some of the less stringent curing conditions studied.

K-88-6 $15.00
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption
Fleming, G.K.
PhD dissertation
Gaseous sorption/desorption and polymeric volume expansion/consolidation measurements are reported for both rubbery and glassy polymers in the presence of various gases at pressures up to 1000 psia. The polymers studied were silicone rubber and glassy bisphenol-A polycarbonate, TMPC, and HFPC. The gases used were He, N2, CH4, CO2, and C2H4. The equipment for the volume dilation measurements was based on direct optical observation of sample dimensions. The dilation data and the sorption data were used to determine the volume change upon mixing and the partial specific volumes of both the gaseous and polymeric materials as functions of sorption level. Marked differences were observed for the partial specific volumes of gases in the rubbery and glassy media. In the rubbery polymer, the partial specific volumes of the gases were similar to the corresponding values in low molecular weight solvents and showed little pressure dependence. For the glassy polycarbonates, the partial specific volumes of the various gases were markedly lower.
than their corresponding values in the rubbery material and showed a much stronger dependence on the external gas pressure. Large hysteresis was also observed in both sorption and volume dilation when comparing the pressurization and depressurization responses of the glassy samples in the presence of CO2 and ethylene. Very small sorption and volume dilation hysteresis was observed for glassy samples in the presence of CH4, and essentially no hysteresis was observed for N2 and He exposure. The magnitude of the sorption and volume dilation hysteresis was found to increase as the maximum sorption level in the glassy polymers was increased.

Vapor Sorption and Blend Miscibility Studies of Alkyd Resin and Poly(vinyl chloride)

Kuse, R.J.
Master's thesis
Polymer miscibility of an alkyd resin and PVC was investigated over the entire span of composition ranges at 10 wt% increments. Blends containing 10 to 80 wt% poly(vinyl chloride) (PVC) were found to be essentially immiscible using differential scanning calorimetry (DSC). No conclusion could be reached for the blend containing 90% PVC due to difficulties in discriminating glass transition behavior for the alkyd at these dilute concentrations. Equilibrium sorption measurements were made for the alkyd resin with nine saturated organic vapors at 40°C. Substantial amounts of organic were sorbed into the resin. In three cases, the sorption level in grams of penetrant per gram of alkyd exceeded unity. The solvatochromic comparison method was used to correlate the data. The resulting equation suggested that significant H2 bonding and dipole-dipole effects between the sorbate molecules and alkyd were responsible for the observed sorption levels. Sorption measurements were also performed for PVC and for two of the alkyd/PVC blends. Equilibrium uptake in the immiscible blends appeared to be a composition-weighted average of the sorption levels for the pure components, as expected.

Handouts for the Separations Research Program Fall Conference, September 1988

Koros Research Group Report
Includes copies of transparencies used by Hellums, Story, Walker, and Koros for the Gas Separations Using Membranes Study Group (K-89-1) Meeting.

NASA Project-Permeation Studies

Wooten, C.
Report on file, Separations Research Program
The objectives for this project were to make permeation measurements on engineering resins using various pure and water saturated gases over a range of pressures and temperatures. The sweep gas system constructed to make the permeation measurements as well as the analytical procedures used are described. Results are reported on O2 and H2 permeation in PSF for a range of temperatures and pressures. The difficulties encountered in making O2 permeation measurements with a sweep gas system are discussed, and the preliminary work done with water saturated gases is described.

The Use of Bench-Scale and Pilot-Scale Testing Systems to Investigate the Effects of Carbon Dioxide Conditioning on the Permeation Behavior of Asymmetric Membranes

Henson, M.A.
Master's thesis
Hollow-fiber modules conditioned with CO2 are shown to have significantly enhanced permeation rates when tested with air as compared to their unconditioned values. The conditioning treatment is shown to have little or no effect on the O2/N2 selectivity. A flat polycarbonate asymmetric film conditioned with CO2 is shown to have an enhanced permeability when tested with air as compared to its unconditioned value. The enhancement is not stable, however, and the permeability drops below the unconditioned value as the film remains exposed to the air feed. The initial permeability enhancement is accompanied by a decrease in the O2/N2 selectivity. A pilot-
scale testing system has been altered to facilitate long-term conditioning studies (K-89-3) of modules tested with air. The system was interfaced with a personal computer to automate data acquisition and control functions.

**K-89-4 $20.00**

**The Effects of Carbon Dioxide Exposure on Permeation Behavior in Silicone Rubber and Glassy Polycarbonates**

Jordan, S.M.
PhD dissertation

Permeation measurements are reported for both rubbery and glassy polymers in the presence of various pure (He, CH4, CO2, C2H4) and mixed gas (O2/N2, CO2/CH4, He/CO2, CO2/N2) feed streams up to 1000 psia. The polymers studied were silicone rubber and glassy bisphenol-A polycarbonate, TMPC, and HFPC. Large hysteresis was observed in permeation when comparing the pressurization and depressurization responses of the glassy samples in the presence of CO2 above 300 psia exposure pressure. The conditioning treatment resulted in long-lived increases in the permeability of the conditioned films and appeared to be "semipermanent" if the conditioning agent was not totally removed. For CO2/CH4 mixed gas feed streams, the conditioning treatment resulted in enhancements in flux without significant loss in permselectivity. Hypothetical explanations are offered to rationalize the increase in permeability in the context of solubility and diffusivity contributions. For the silicone rubber sample, no permeability hysteresis was observed. Exchange experiments showed that it was possible to condition a glassy polymer with CO2 to increase its permeability and maintain a state of increased permeability even if the CO2 was replaced by another gas of sufficient solubility such as CH4 or air. In addition to permeation results with a vacuum maintained at the downstream face of the membrane, results from a modified permeation system are presented for conditions where the downstream face is exposed to nonzero pressures of CO2. Uniformly conditioned films generated using this system showed a significant increase in permeation flux above the unconditioned value and even above those for single-side conditioned films.

**K-89-5 PUBLISHED**

**Study of Ultramicroporous Carbons by High-Pressure Sorption: Part 1. N2, CO2, O2 and He Isotherms**

Koresh, J.E.; T.H. Kim; W.J. Koros


Adsorption-desorption isotherms for N2, CO2, O2, and He on as-received TCM-128 ultramicroporous carbon are reported for pressures up to 60 atm at 35°C. Evidence is presented that suggests that there are regions in the carbon that have closed porosity which is composed of tiny hydrophobic constrictions in series and more open pores inside. At room temperature, water molecules cannot penetrate these constrictions in reasonable time due to a clustering effect, while the much bigger, but unclustered N2 and CO2 molecules do penetrate these constrictions at a measurable rate. The closed porosity is responsible for unexpected hysteresis observed for N2 and CO2 at 35°C and the unusually large amount of He adsorbed.

**K-89-6 PUBLISHED**

**Study of Ultramicroporous Carbons by High-Pressure Sorption, Part 2. Nitrogen Diffusion Kinetics**

Koresh, J.E.; T.H. Kim; D.R.B. Walker; W.J. Koros


Sorption-desorption kinetics for N2 in the as-received TCM 128 ultramicroporous carbon fiber are reported at 35°C over a wide range of pressures. The N2 sorption kinetics at low pressures follow the Fickian model. As the pressure increases, the deviations from the model become more pronounced, and at high enough pressure a sigmoid kinetic response shape is observed which is indicative of a non-Fickian diffusion process. An additional time scale must be active to account for the non-Fickian transport behavior. This second time scale process may correspond to adsorbate surface rearrangements leading to locally time-dependent clearing of constrictions at a rate with a characteristic kinetic constant. The N2 desorption kinetics are found to be less affected by the non-Fickian transport, thus leading to higher apparent diffusion coefficients for the same
average pressures. At high pressure and very long sorption times, slow protracted uptake becomes apparent into regions of "closed porosity." The kinetics for this process can be described by a barrier model and are sufficiently slow to allow treatment independent of the processes occurring in the more open pore system.

K-89-7 PUBLISHED
Study of Ultramicroporous Carbons by High Pressure Sorption. Part 3: Complex Transport Phenomena as Sensed by CO2 and N2 Kinetics
Koresh, J.E.; T.H. Kim; D.R.B. Walker; W.J. Koros
High-pressure sorption kinetics for N2 and CO2 in as-received TCM carbon, introduced in part 2 of this series, is elaborated here. Fickian processes are apparent for both gases and provide the background over which the following complicated transport phenomena are overlaid. The most dramatic of these additional phenomena is CO2-induced constriction dilation, which causes over four orders of magnitude decrease in the equilibration time as pressure increases from 0 to 60 atm. Desorption equilibration times at lower pressures following the CO2 exposure also reflect residual dilation after exposure. Higher desorption rates compared to adsorption rates were also observed for N2; however, the differences are much less extreme and believed to be due to immobilization of adsorbate near constrictions instead of constriction dilation. Evidence is presented to indicate the existence of a weak, transient barrier at the pore entrances at the beginning of sorption runs if appropriate conditions are chosen for each of the two gases.

K-89-8 PUBLISHED
Study of Ultramicroporous Carbons by High-Pressure Sorption. Part 4: Isotherms and Kinetic Transport in Activated Carbons
Koresh, J.E.; T.H. Kim; D.R.B. Walker; W.J. Koros
Low-pressure hystereses shown to exist for both N2 and CO2 on as-received TCM carbon disappear upon slight activation. These hystereses are related, in the case of N2, to protracted penetration of restricted regions and, in the case of CO2, to dilation of tiny constrictions. A highly oxygen-activated carbon (19% weight loss) showed minute hysteresis in CO2 sorption experiments while the more activated carbon (32% weight loss) formed by nitric acid activated extreme hysteresis. These hystereses are related to swelling of the progressively weakened carbon matrix. Nitrogen, which is a poor swelling agent, does not show any hysteresis with these highly activated carbons. A series of TCM carbons which were progressively activated by O2 showed a maximum in their sorption affinity constant with respect to the degree of activation. This maximum is related to either the greater accessibility of new small pore regions or to the gradual opening of tiny constrictions that regulate transport into these regions. The lack of internal pore resistance to transport in a slightly activated carbon (K-89-8) provides conditions conducive to observation of transient barriers formed in the entrances to the outermost pores immediately after applying a pressure step.

K-89-9 PUBLISHED
Fluorinated Polycarbonates for Gas Separation Applications
Hellums, M.W.; W.J. Koros; G.R. Husk; D.R. Paul
Gas sorption and transport properties of two aromatic polycarbonates with hexafluoroisopropylidene moieties have been characterized for a variety of gases at 35°C at pressures up to 60 atm. These materials have structural features that hinder interchain packing and intrachain rotational mobility. Wide angle x-ray diffraction measurements of the average segmental spacings in a series of polycarbonates, including the fluorinated materials, reflect the hindrance to packing caused by systematic variation in structure within the series. Hindrance to interchain rotational mobility is apparent from the higher glass transition temperatures and from the sub-Tg transition behaviors of the substituted materials. These fluorinated polycarbonates exhibit a very significant increase in permeability relative to conventional bisphenol-A polycarbonate without a significant loss in permselectivity. The permeability of the higher flux
fluorinated material is over 200 Barrers for He and over 100 Barrers for CO2, representing an increase of a factor of 15 relative to standard polycarbonate. The higher permeabilities and permselectivities of the rigid substituted polycarbonates occur due to both solubility and diffusivity factors.

K-89-10 PUBLISHED
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption
Fleming, G.K. and W.J. Koros
Mass sorption/desorption and volume dilation/consolidation measurements are reported for tetramethyl and hexafluoro polycarbonate samples in the presence of CO2 pressures up to 900 psia at 35°C. These results are combined with previous results for bisphenol-A polycarbonate. The combined sorption and volume dilation measurements are used to analyze the thermodynamics of the three gas-polymer systems, and the partial specific volumes of CO2 and the polymer are reported as functions of sorption level. Desorption and subsequent resorption measurements with the substituted polycarbonates show large and long-lived hysteretic effects similar to those unseen with standard bisphenol-A polycarbonate. Finally, assumptions inherent in the dual mode model are shown to provide a satisfactory description of the volume dilation behavior for the substituted polymers.

K-89-11 PUBLISHED
Carbon Dioxide Conditioning Effects on Sorption and Volume Dilation Behavior for Bisphenol-A-Polycarbonate
Fleming, G.K. and W.J. Koros
Macromolecules 23:1353-60 (1990)
Sorption/desorption and volume dilation/consolidation measurements are reported for bisphenol-A polycarbonate in the presence of CO2 pressures up to 900 psia at 35°C. Second exposure sorption and desorption isotherms are presented after conditioning samples at 300 psia, 600 psia and 900 psia. The sorption and volume dilation data are used to calculate the partial specific volumes of the polymer and penetrant as functions of sorption level. Qualitative physical arguments concerning the nature of the conditioning effect are presented based on this thermodynamic analysis of the gas-glassy polymer system. A fugacity based dual mode sorption model is shown to be very useful for describing the sorption and volume dilation results. The increase in solubility observed during the desorption hysteresis cycle does not appear to be due to the simple introduction of additional packing defects responsible for the Langmuir-like sorption in the as-received sample. Specifically, more subtle and generalized intersegmental, residual dilation appears to be responsible for the enhanced sorption during the desorption process. After total removal of the sorbed gas, however, evidence of a small amount of additional packing defects can be detected with subsequent resorption. This small conditioning effect is shown to be reversed by annealing the polycarbonate sample at 135°C.

K-89-12 PUBLISHED
Permeability of Pure and Mixed Gases in Silicone Rubber at Elevated Pressures
Jordan, S.M. and W.J. Koros
The transport properties of silicone rubber are reported at 35°C for a series of pure gases (He, N2, CH4, CO2, and C2H4) and gas mixtures (CO2/CH4 and N2/CO2) for pressures up to 60 atm. The effects of pressure and concentration on the permeability of various gases have been analyzed to consider plasticization (K-89-12) and hydrostatic compression effects. Over an extended pressure and concentration range, both compression of free volume and eventual plasticization phenomena were observed for the various penetrants. In pure component studies, plasticization effects tended to dominate hydrostatic compression effects for the more condensible penetrants (C2H4 and CO2), while the reverse was true for the low sorbing N2 and He. These issues will be discussed in terms of penetrant diffusion coefficients versus pressure to clarify the interplay between the opposing effects for the penetrants of markedly different solubilities. Additional insight into the somewhat complex interplay of the plasticization and hydrostatic compression effects is given by
mixed gas permeation results. It was found that the permeability of N2 in a 10/90 CO2/N2 and a 50/50 CO2/N2 mixture was increased by the presence of CO2 because the plasticizing nature of CO2 is able to overcome N2's compression effect.

K-89-13  PUBLISHED
Gas Separation Membrane Material Selection Criteria: Differences for Weakly and Strongly Interacting Feed Components
Koros, W.J. and M.W. Hellums
Insights into the basic principles governing sorption and transport in glassy polymers (K-89-13) have recently led to large improvements in the materials used for membrane-based gas separation processes. Examples of such materials are compared to conventional membrane materials to illustrate the value of a systematic structure-property approach to this topic. The current thinking regarding optimization strategies for gas separation applications will be summarized in two apparently simple rules for selecting candidate materials for gas separation membranes in the absence of strong interactions between the polymer and penetrating gas mixture. Preliminary insights into cases where interactions cannot be neglected are also discussed. The most familiar example of such interactions, "plasticization," is generally undesirable because it leads to a loss in selectivity of the membrane from the different permeating components. Plasticization and more complex interaction phenomena will be discussed for a series of well characterized glassy polymers (K-89-13).

K-89-14  PUBLISHED
Transport Properties
Koros, W.J. and M.W. Hellums
In Encyclopedia of Polymer Science and Engineering, New York: John Wiley & Sons, Inc. (1989) Transport properties are discussed for rubbery, semicrystalline, and glassy polymers. The treatment is subdivided according to the types of penetrants: gases and low activity vapors, intermediate sized penetrants, and macromolecular penetrants. The effects of crystallinity, orientation, and micromolecular penetrants. The effects of crystallinity, orientation, and more subtle history-dependent phenomena are also discussed. Transport properties of particular importance in are discussed. These include the permeability, diffusivity, and solubility coefficients, and the separation factor or permselectivity. Various theories for predicting these parameters including free volume and dual mode theories are discussed. Relationships between transport and mechanical properties in polymers are also presented. The topic of non-Fickian transport is covered briefly. This subject encompasses cases in which the assumption of a concentration dependent diffusion coefficient and constant system boundary conditions is insufficient to describe the time dependent behavior of the system. Physical interpretations of the causes of the non-Fickian behavior are discussed for crystalline and amorphous materials.

K-89-15
Handouts for the Separations Research Program Spring Conference, April 1989
W.J. Koros Research Group Report
Includes copies of transparencies used by Koros, Pope, Jordan, and Miller for the Membrane Technology Study Group (K-89-15) Meeting.

K-89-16
Handout from the Separations Research Program Fall Conference, September 1989
W.J. Koros Research Group Report
Includes copies of transparencies used by Koros, Hellums, Coleman, Walker, Pinnau, Pesek, and Wooten for the Membrane Technology Study Group (K-89-16) Meeting.
A series of structurally related polycarbonates are shown to retain a state of high permeability, induced by exposure to high-pressure conditioning with CO₂, even if the pure CO₂ is completely replaced by CH₄ or CO₂/CH₄ and O₂/N₂ mixed gas feed streams. Reductions ranging from 0% to 15% in the CO₂/CH₄ and O₂/N₂ separation factors occur for the substituted polycarbonates, while as much as a 30% enhancement in the flux of the various gases was observed. On the other hand, as was the case for standard polycarbonate, if the conditioning agent is completely replaced by He, the conditioning treatment is not detectable, even after short times. The magnitude of the increase in permeability following an exchange experiment for a given penetrant is qualitatively smaller for the substituted materials as compared to standard polycarbonate because their less efficiently packed matrices experience smaller increases in reaction free volume.

Past work has shown that hysteresis in sorption, volume dilation, and permeation results when standard bisphenol-A polycarbonate is conditioned by exposure to 900 psia CO₂ at 35°C. This article reports hysteretic permeation results for the same polycarbonate exposed to other CO₂ conditioning pressures. In addition, permeation results are reported for tetramethyl and hexafluoro polycarbonate following conditioning with CO₂. Permeation measurements with these structurally related polycarbonates show qualitatively similar, but quantitatively smaller, long-lived hysteretic effects compared to standard polycarbonate dilated to similar volume percentages. The percentage increase in permeability following conditioning treatments is discussed in terms of FFV considerations.

A technique for chemical modification of 40Å g-alumina membranes with tridecafluoro-1,1,2,2,-tetrahydrooctyl-1-trichlorosilane (TDFS) is presented. The modification is carried out in order to reduce the membrane's pore size so that the selective separation of low molecular weight liquid mixtures may be possible. It is shown that the extent of modification can be monitored by measuring the evolution of HCl due to the reaction of silane with the membrane's hydroxyl group. Pure gas permeability measurements with He, H₂, Ar, and SF₆ are reported for one unmodified and two modified membranes which varied in their reactions times from one day to two weeks. The permeability measurements indicate that the short-term modification produced a membrane that still had an appreciable amount of surface flow, while the membrane modified for two weeks had a hindered surface transport. Data are also reported on the separation of toluene from a high molecular weight (M ~ 660) lube oil. The data indicate an increase in selectivity due to the short-term modification; however, after the two-week modification, the selectivity drops to near unity. An interpretation of the gas and liquid data leads to the conclusion that selective separations may be possible using short reaction times and long chain silanes that extend across the width of the pore.
The Effects of Carbon Dioxide Conditioning on the Permeation Behavior of Hollow Fiber Asymmetric Membranes
Jordan, S.M.; M.A. Henson; W.J. Koros
Journal of Membrane Science 54:103 (1990)
Asymmetric hollow-fiber membrane modules conditioned with 125 psig CO2 are shown to have significantly enhanced air permeation rates as compared to their unconditioned values. Permeation increases as great as 100% are reported for modules conditioned for 48 hours with CO2. The conditioning treatment has negligible effect on the O2/N2 selectivity. The permeation enhancement is permanent as long as air remains in contact with the module, but is slowly lost when the module is depressurized. Neither air nor He were able to induce the conditioning response but were able to maintain the module in a state of enhanced permeability as long as they remained in contact with the module. The permeation enhancement observed for air following CO2 conditioning (K-90-1) treatments is much greater in asymmetric modules than in dense films composed of the same polymer. It is proposed that the difference between the dense film and hollow-fiber module conditioning results is due primarily to the morphology of the asymmetric membranes.

Effect of Various Exposure Histories on Sorption and Dilation in a Family of Polycarbonates
Pope, D.S.; G.K. Fleming; W.J. Koros
Methane sorption and dilation isotherms along with their dependence on sample exposure history are presented for three systematically varied polycarbonates. Sorption and dilation levels of CH4 in the various polycarbonates are shown to be increased by two methods of exposure to CO2 termed "conventional-conditioning (K-90-2)" and "exchange-conditioning (K-90-2)." The exchange-conditioning procedure produces the largest increases for all three polycarbonate samples. The largest percentage changes in properties are noted for the well-packed unsubstituted bisphenol-A polycarbonate, which displays a 44% increase in sorption and a corresponding 58% increase in dilation using the conventional conditioning protocols. This polymer also showed the largest changes in properties for the exchange-conditioning procedure with a 79% increase in sorption and a corresponding 167% increase in dilation over unconditioned values. Qualitatively, the substituted materials, with less efficiently packed matrices and higher Tg values, showed smaller increases under both conditioning protocols as compared to standard PC, indicating a trend smaller sorption and dilation enhancements for samples that experience smaller increases in FFV as induced by the conditioning treatments (K-90-2).

Gas Permeability and Chain Packing in Aromatic Polycarbonates
Hellums, M.W.; W.J. Koros; G.R. Husk; D.R. Paul
The gas transport properties in a series of four polycarbonates is characterized for CO2, CH4, O2, and N2. The permeability of gases in the highest flux material, tetramethyl hexafluoro bisphenol-A polycarbonate (TMHFPC) is roughly fifteen time higher than in conventional PC. Mixed gas permeation (K-90-3) results indicate plasticization tends to lower permselectivity for the CO2/CH4 pair below the values from pure gas data. Wide-angle x-ray diffraction measurements of the average segmental spacings in the series of polycarbonates reflect hindrance to chain packing caused by variations in structure. Relationships between dynamic-mechanical property transitions and the permselectivity are proposed. Hindrance to intrachain rotational mobility is apparent from the sub-Tg transition temperatures measurements in the substituted materials. Support is given to the concept that simultaneous inhibition of chain packing and inhibition of intrachain rotational mobility can lead to improved membrane performance (K-90-3).
Gas Transport in Halogen-Containing Aromatic Polycarbonates
Hellums, M.W.; W.J. Koros; G.R. Husk; D.R. Paul

The gas permeability and permselectivity of a series of halogen-containing polycarbonates are discussed in terms of the fundamental solubility and diffusivity factors. These materials have been structural features that hinder interchain packing and intrachain rotational mobility. Both diffusion and solubility coefficients are higher in materials with higher FFVs. Diffusivity selectivities tend to increase with increasing restriction of intrachain torsional mobility. The materials with four bromine atoms substituted on the phenyl rings ortho to the carbonate linkages display a significantly increased diffusivity selectivity relative to conventional PC. This improvement in the ability of the polymer matrix to discriminate between gas molecules of different sizes is due to a reduction in intrachain torsional mobility. The reduction in chain mobility is indicated by higher glass transition and higher sub-Tg transition temperatures in the bromine-substituted materials. The materials with hexafluoroisopropylidene moieties have high FFVs and exhibit a very significant increase in permeability relative to conventional bisphenol-A polycarbonate. The material with both the hexafluoro- and the tetrabromo-substitutions displays significant simultaneous increases in permeability and permselectivity relative to conventional polycarbonate.

Transport Characterization of a Polypyrrolone for Gas Separations
Walker, D.R. and W.J. Koros

The gas sorption and permeation properties of a polypyrrolone step-ladder polymer have been characterized with a variety of pure gases and one gas mixture at 35°C and for feed pressures up to 60 atm. The transport properties of the soluble prepolymer have also been characterized with pure gases up to 30 atm. The polypyrrolone shows simultaneously increased permeability and selectivity (K-90-5); over the analogous polyimide. Wide-angle x-ray diffraction measurements of the average segmental spacing of the materials and FFV calculations characterize the packing of the different polymer types. Hindrance to intrasegmental motion is apparent in the polypyrrolone by the lack of a glass transition temperature prior to decomposition and by the limited plasticization by high-pressure CO2. The permeability of the polypyrrolone is 89 Barrers for He, 7.9 Barrers for O2, and 27.6 Barrers for CO2.

Separation of Oil/Water Emulsions Using Ceramic and Polymeric Micro- and Ultrafiltration Membranes
Warmuth, W.
Master's thesis

In this study the performance of ceramic alumina membranes was compared with poly(vinylidene fluoride) (PVDF) membranes for the separation of oil/water emulsions. The alumina membranes used had rated pore sizes of 0.1 µm (microfiltration) and 100 Å (ultra-filtration). They came as tubes and were asymmetric, having a g-alumina skin on an a-alumina support. The PVDF membranes came as flat sheets or tubes, in either standard or surface-modified versions, having a molecular weight cut off of 20,000-50,000 daltons. The membranes were compared in terms of oil concentration in the permeate, permeate flow, and flux stability over time. The experiments were carried out in a test system that held three membranes in parallel. The model emulsion used in this study was created out of a lube oil and a nonionic surfactant. It was shown that the permeate flow of the ceramic microfiltration membrane became independent from the transmembrane pressure beyond a certain pressure, indicating that a gel layer is formed on the surface of the membrane.
Temperature has a significant influence on the permeate flow. It has been found that the membrane is affected by fouling, adsorption, or plugging, leading to a decrease in permeate flow over time. Due to the relatively large pore size, the oil rejection was around 97%, leading to high oil concentrations in the permeate. After the emulsion runs, the membrane was cleaned. Rinsing at high temperatures and using a surfactant as a cleaning agent gave the best results in terms of recovering water permeability. Membrane fouling had little effect on the ceramic Ultrafiltration membrane. A very low total organic carbon (TOC) content in the permeate led to the conclusion that only the dissolved surfactant passed through the membrane. The same behavior in terms of permeate flux stability and oil rejection was shown by the modified PVDF membrane. Due to its hydrophobicity, the unmodified PVDF membrane was very susceptible to fouling. This lead to a significant decrease in permeate flow over time and to high oil concentrations in the permeate. When comparing the membranes in terms of the resistance in series model the modified PVDF membrane is shown to be even less affected by membrane fouling than the ceramic Ultrafiltration membrane. Due to a lower membrane resistance, the permeate flow is at a higher level than found with the ceramic membrane. This makes the modified PVDF membrane a suitable membrane for the separation of oil/water emulsions.

K-90-8 PUBLISHED
Isomeric Polyimides Based on Fluorinated Dianhydrides and Diamines for Gas Separation Applications
Coleman, M.R. and W.J. Koros
Gas sorption and transport properties of two isomeric polyimides with hexafluoroisopropylidene moieties in the diamine and dianhydride monomers were characterized for a variety of gases at 35°C at pressures up to 60 atm. These materials have structural properties that inhibit intrasegmental rotational mobility and intersegmental chain packing. The effect of isomerism on the physical and gas separation properties of these rigid materials was investigated. The effect of isomerism on the hindrance to packing is reflected in the WAXD measurements of the average spacing between adjacent polymer chains. The para-connected polyimide showed significant increases in permeability relative to a series of polyimides studied earlier with less packing disruptive substituents on the polymer backbone. The permeability of the higher flux material was 64 barrers for CO2 and 16 barrers for O2. The meta-connected polyimide showed large decreases in permeability with corresponding increases in permselectivity when compared to its para counterpart. For example, the permselectivity of the meta material for O2 relative to N2 is 6.9, which is 50% greater than that of the para-connected material. Differences in permeability and permselectivity (K-90-8) are due to both penetrant solubility and diffusivity effects.

K-90-9 $20.00
Gas Permeation and Sorption in a Series of Aromatic Polycarbonates
Hellums, M.W.
PhD dissertation
Gas sorption and transport properties in a family of polycarbonates including a series of halogen-containing aromatic polycarbonates have been characterized for a variety of gases. Gas permeation and gas solubility data were collected for He, H2, N2, O2, CH4, and CO2 in the various materials. Polymers with structural features that hinder interchain packing and intrachain rotational mobility were studied. Several of the monomers as well as the polymers were not commercially available and were synthesized for the study. The structural changes that inhibited chain packing lead to high permeabilities through increases in both solubility and diffusion coefficients. The structural changes that inhibited torsional mobility lead to increases in permselectivity through the diffusivity selectivity. Detailed pressure dependence of the transport properties of some of the polycarbonates was also studied. The packing inhibited materials with substitutions that hinder chain packing are subject to plasticization by CO2 at lower pressures than the other materials. This plasticization lead to a lower permselectivity determined by mixed gas measurements than initially indicated by pure gas measurements. Interestingly, the local concentration in the matrix at the point of plasticization is higher in the more packing inhibited materials.
**K-90-10**

Handouts from the Separation Research Program Fall Conference, September 1990

Includes copies of transparencies used by Koros, Miller, Pinnau, Jones, Pessan, Coleman, and Walker for the Membrane Technology Study Group (K-90-10) Meeting.

**K-91-1 PUBLISHED**

The Formation of Chemically Modified g-Alumina Microporous Membranes

Miller, J.R. and W.J. Koros


A technique for the chemical modification of 40Å g-alumina membranes with TDFS is presented. The modification is carried out to reduce the membrane's pore size so that selective separation of low molecular weight liquid mixtures may be possible. Pure gas permeability measurements with He, H2, Ar, and SF6 are reported for one unmodified and two modified membranes which varied in their reaction times from one day to two weeks. The permeability measurements indicate that the short-term modification produced a membrane that still had an appreciable amount of surface flow, while the membrane modified for two weeks had a hindered surface transport. Also reported are data on the separation of toluene from a high molecular weight (M ~ 660) lube oil. The data indicate an increase in selectivity due to the short-term modification; however, after the two-week modification, the selectivity drops to near unity.

**K-91-2**

Handouts for the Separations Research Program Spring Conference, April 1991

Koros Research Group Report

Copies of transparencies used by Miller, Jakobs, Coleman, Costello, Pope, Pinnau, Pesek, Pfromm, Rezac, and Järvelin for the Membrane Technology Study Group (K-91-2) Meeting.

**K-91-3 $5.00**

Influence of Iron (III) Hydroxide on Oil-Water-Separation in Ultrafiltration Systems

Jakobs, E.

Master's thesis

Dynamic membranes were formed on an alumina ceramic support from an iron hydroxide solution. The objective of this study involved the characterization of the effects of various operating conditions on the formation of gel layers and on the separation characteristics of the membranes, such as permeation rate, flux stability, and oil or iron rejection. In order to determine basic information, all experiments were first conducted in a stirred-cell system. The results were then transferred to a tubular Ultrafiltration system.

**K-91-4 $20.00**

The Effects of Conditioning on Sorption and Volume Dilation in Rubbery and Glassy Polymers

Pope, D.S.

PhD dissertation

Penetrant sorption and penetrant-induced dilation measurements were performed on a variety of glassy polymers (K-91-4) with various exposure histories. Penetrants included C3H8, CO2, C2H4, CH4, and N2. Polymers included PC, TMPC, TMHFPC, PS, poly(methyl silyl propyne), and PMP. Penetrant sorption and dilation isotherms in most of the glassy materials subsequent to exposure at high penetrant concentrations were substantially higher than the isotherms for as-received materials. Correlations of these increases with FFV increases and Tg depression indicated that larger sorption and dilation increases occur for larger FFV increases and larger percentage Tg depressions. The sorption and dilation data were analyzed quantitatively through the dual-mode model and the lattice fluid equation of state. The dual-mode model described the data satisfactorily while the lattice fluid equation of state may aid in a totally predictive method. Sorption and dilation measurements were performed on semicrystalline PMP. Previous reports of sorption into areas other than the traditional amorphous regions are supported.
Preparation of Polymer-Ceramic Composite Membranes with Thin Defect-Free Separating Layers
Rezac, M.E. and W.J. Koros

Polymer-ceramic composite membranes with essentially defect-free separating layers have been prepared by a solution deposition technique. Rigid polymers were used for the selective organic layer. These included high molecular weight samples of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl) ethyldiene] bis-1,3-isobenzofuran-dione, isopropylidene dianiline, 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl) ethyldiene] bis-1,3-isobenzofuran-dione, methylene dianiline, TMHFPC, and TMHFPSPF. Unsuccessful attempts were made to prepare composite membranes from lower molecular weight samples of PC and tetrabromo hexafluoro bisphenol-A polycarbonate (TBHFPC). A microporous ceramic membrane was used as the support layer and provided minimal resistance to gas flow. The composite membranes were found to have high gas fluxes and gas separating abilities essentially equivalent to that of a dense isotropic film. The estimated, effective skin layer thicknesses for these membranes are on the order of 0.2 to 1.0 mm. The formation of these composites is believed to occur through a sieving process in which large swollen polymer chains are sieved out of solution by the ceramic support. Polymer chains whose swollen diameter was smaller than that of the ceramic membrane did not produce selective composite membranes.

Structures and Gas Separation Properties of Asymmetric Polysulfone Membranes Made by Dry, Wet, and Dry/Wet Phase Inversion
Pinnau, I. and W.J. Koros

Integrally skinned asymmetric gas separation membranes were prepared by dry, wet, and dry/wet phase inversion processes. The membranes were cast from a PSF/methylene chloride/1,1,2-trichloroethane/2-methyl-2-butanol casting system. Wet and dry/wet phase inversion membranes were quenched in methanol. Membranes made by dry/wet phase inversion using convective evaporation showed optimum gas separation performance. The average O2/N2 and He/N2 selectivities of these membranes were within 85% of those determined for a dense, solution-cast PSF film, suggesting that the ultra thin skin layers were essentially defect free. The average apparent skin layer thickness of all samples tested was 270Å. Scanning electron photomicrographs revealed that optimum membranes made by dry/wet phase inversion consist of an ultra thin skin layer, a tightly packed nodular transition layer, and an open-cell, sponge-like substructure. Dry/wet phase inversion membranes (K-91-6) prepared by free-standing evaporation resulted either in high flux and low selectivity membranes or essentially defect-free membranes with fluxes lower than those made by convective evaporation. Dry-phase inversion membranes exhibited extremely low gas fluxes due to thick (17.5 mm) skin layers. On the other hand, wet phase inversion membranes showed O2/N2 selectivities < 1, indicating that gas transport was determined by pore flow through skin layer defects.

Transient Length Dilation vs. Transient Increase in Permeability of Natural Rubber Films
Pope, D.S.; W.J. Koros; J. Jagur-Grodzinski

Air dissolved under pressure in a film, made from natural rubber, causes its slight dilation. Sudden decompression of this film leads to its large transient dilation (K-91-7) that afterwards vanishes within less than a minute (t ≈ 20 s). Such transient expansion is apparently caused by internal stresses due to over saturation. This behavior is analogous to the previously reported transient increase in the permeability to gases of the suddenly decompressed polymeric membranes. A clear correlation between results derived from the dilation and the permeability (K-91-7) measurements seems to be evident.
Relationship Between Substructure Resistance and Gas Separation Properties of Defect-Free Integrally Skinned Asymmetric Membranes

Pinnau, I. and W.J. Koros

Integrally skinned asymmetric membranes consist of an ultra thin skin layer supported by a microporous substructure. Optimum membrane properties are obtained if the skin layer is defect-free and its thickness is minimized. A series resistance model shows that the minimum desirable skin thickness of defect-free integrally skinned asymmetric membranes having the intrinsic selectivity of the membrane material is limited by the resistance of the microporous substructure. Asymmetric membrane substructures show selectivities essentially equal to those predicted by Knudsen flow. However, pressure-normalized fluxes of substructures can vary by several orders of magnitude. Model calculations reveal that the pressure-normalized flux of the fast-permeating gas component through the substructure has to be ~10 times higher than that of the component through the skin layer to achieve at least 90% of the intrinsic selectivity of the membrane material. The validity of the model is demonstrated for defect-free asymmetric polysulfone and polyimide membranes. These considerations become increasingly important as higher performance polymeric materials are employed in membrane separation applications (K-91-8).

Skin Formation of Integral-Asymmetric Gas Separation Membranes Made by Dry/Wet Phase Inversion

Pinnau, I
PhD dissertation

The formation of integrally skinned asymmetric gas separation membranes; made by a dry/wet phase inversion process has been studied. The influence of solvents, quench medium, polymer concentration, and evaporation-induced phase separation phenomena on the structures and gas separation properties of polysulfone membranes was investigated. Optimized polysulfone membranes made from ternary casting systems via dry/wet phase inversion were essentially defect-free and showed apparent skin layer thicknesses of only a few hundred Angstroms. The structures of the asymmetric polysulfone membranes were elucidated by field emission SEM. Optimum dry/wet phase inversion membranes consist of an ultra thin, dense skin layer, an interconnected nodular transition layer, and an open-cell, sponge-like structure. A novel qualitative skin layer formation mechanism resulting in simultaneously ultra thin and defect-free asymmetric membranes made by dry/wet phase inversion is presented. It is suggested that the formation of the ultra thin skin layer is the result of phase separation processes and surface tension phenomena that occur during the evaporation step. The guidelines obtained from the preparation of optimized polysulfone membranes made by the dry/wet phase inversion process were successfully applied to form ultra thin, essentially defect-free polycarbonate, polyester carbonate, and fluorinated polyimide membranes. The gas transport properties of the asymmetric membranes were determined as a function of the temperature and the feed pressure. Asymmetric membranes formed by dry/wet phase inversion can show higher selectivities than those determined for thick isotropic films. It is suggested that the molecular polymer packing density in the ultra thin skin layers can be somewhat higher compared to those of solvent-cast or extruded films. The resistance of the substructure to gas transport can lead to a dramatic decline in the selectivity of defect-free, integrally skinned asymmetric membranes. Series resistance model calculations suggest that the substructure resistance can limit the full potential of highly permeable polymers for the preparation of advanced asymmetric membranes.

Influence of Quench Medium on the Structures and Gas Permeation Properties of Poly(sulfone) Membranes Made by Wet and Dry/Wet Phase Separation

Pinnau, I. and W.J. Koros
Journal of Membrane Science 71-81 (1992)

Essentially defect-free integrally skinned asymmetric polysulfone membranes were fabricated by a dry/wet phase inversion process (K-91-10) using forced-convective evaporation. The choice of the
quench medium is of utmost importance for the formation of gas separation membranes having high selectivities combined with high gas fluxes. The integrally skinned asymmetric membranes were characterized by gas permeation measurements and field emission SEM. This study indicates that the phase separation and vitrification processes occurring during the wet phase inversion step should be as rapid as possible to generate the highest performance gas separation membranes (K-91-10).

**K-91-11 PUBLISHED**

Gas Transport Through Homogeneous and Asymmetric Polyester Carbonate Membranes  
Pinnau, I.; M.W. Hellums; W.J. Koros  
Polymer 32:2612 (1991)

Permeabilities, solubilities, and diffusivities of N2, O2, CO2, and H2 are reported for a polyester carbonate at 35°C and 4.4 atm. Constant activation energies of permeation were determined for dense films and defect-free asymmetric polyester carbonate membranes over a temperature range of 25°C to 55°C. Activation energies of permeation were 10% and 20% higher for N2 and O2, respectively, in the asymmetric membrane samples as compared to the dense films. Permselectivities for the gas pairs O2/N2, H2/N2, and CO2/N2 were found to be higher in the asymmetric membranes compared to those of the dense films. The detailed cause of the higher permselectivities and activation energies in the asymmetric membranes is currently not known. Possible orientation-induced increases in segmental packing density in the asymmetric membrane skin are discussed as a potential explanation for the differences between the asymmetric and dense films.

**K-91-12 PUBLISHED**

Gas Permeation Properties of Asymmetric Poly(carbonate), Poly(ester carbonate), and Fluorinated Poly(imide) Membranes  
Pinnau, I. and W.J. Koros  

Essentially defect-free, ultra thin asymmetric polycarbonate, polyester carbonate, and 6FDA-IPDA polyimide membranes were prepared by a dry/wet phase inversion process (K-91-12) using forced-convective evaporation. The pure gas permeation properties of these membranes were determined for N2, O2, He, CO2, and CH4. The average apparent skin layer thicknesses of the membrane samples varied between 330Å and 580Å, which is substantially thinner than for previous defect-free membranes formed by the conventional wet phase inversion process. This study indicates that the dry/wet phase inversion process appears to be universally applicable to form ultra thin, defect-free asymmetric membranes from hydrophobic, glassy polymers.

**K-91-13 PUBLISHED**

Gas Transport in Spirobiindane Polycarbonate  
Hellums, M.W.; W.J. Koros; J.C. Schmidhauser  

The gas permeability and solubility of various gases in spirobiindane polycarbonate (SBIPC) are compared to the properties of bisphenol-A polycarbonate. Spirobiindane polycarbonate has high FFV and severe steric hindrance to torsional motion resulting from the presence of the spirobiindane ring in the chain backbone. These factors combine to produce oxygen permeabilities roughly four times higher in SBIPC than in PC, with slightly higher O2/N2 permselectivities. Although CO2 and He permeabilities are also roughly four times higher than in PC, markedly lower CO2/CH4 and He/CH4 permselectivities are observed for the SBIPC compared to PC. The causes of these trends are interpreted in terms of the component solubility and diffusivity contributions to overall selectivity. Also, the results for SBIPC are compared to earlier data for other polycarbonates with complex connector groups replacing the isopropylidene unit in standard polycarbonate.
The complex and interacting issues involved in effectively separating commercially important gas mixtures using membranes are summarized. The detailed issues determining success in the various applications make it clear that the technology of gas separation membranes (K-91-14) is highly dependent on basic support from polymeric materials science. Membrane module construction and system design are also crucial to the successful implementation of this technology. Nevertheless, the breakthroughs in new materials for making membranes and the protocols for forming ultra thin-skinned asymmetric structures to provide high productivity have been responsible for the burgeoning interest in this topic. By far the most popular materials for membrane-based gas separation applications are polymeric in nature. Four specific families of polymers and representative membranes of these families are used throughout the discussion in this review.

The transport properties of gases in glassy polymers are determined by contributions from several polymer properties, including the (1) total free volume, (2) distribution of free volume, (3) intersegmental resistance to chain motions, and (4) intrasegmental resistance to chain motions. The importance of these factors in determining the gas transport properties for a family of six fluorine-containing polyimides was reported. The structure of the dianhydride residue was modified and the location of the bond linking the diamine and dianhydride residues was changed from a meta connection (6FmDA) to a para connection (6FpDA) in these six polyimides. The substitution of packing resistant groups within the diamine or dianhydride residence, which increased the free volume and the resistance to chain motions, increased the permeability with little loss in selectivity. The permeabilities and selectivities in the para-connected polyimides correlated well with the total free volume. The distribution of free volume between well packing regions and the penetrant-scale packing defects may also determine the solubility and diffusivity. The permeabilities were consistently lower and the permselectivities were higher in the meta-connected polyimides than in the para-connected polyimides. The decrease in permeability and increase in permselectivity in the meta-connected polymers was attributed to an increased intrasegmental and intersegmental resistance to chain motions relative to the para-connected polyimides. The meta and para isomers of these polyimides formed miscible blends over a wide range of concentrations. The permeabilities and selectivities of the miscible blends of 6FDA-6FpDA and 6FDA-6FmDA were approximately log averages of the pure component properties. Preconditioning of these glassy polyimides with CO2 at 60 atmospheres resulted in six- to ten-fold increases in permeability relative to an untreated sample. Exchange conditioning of 6FDA-6FpDA with CO2 increased the permeabilities of CO2 and methane with little loss in the permselectivity. The permeability enhancement in the conditioned polymers was dependent on the procedure used to pretreat the film. Thermal quenching of the 6FDA polyimides from above the glass transition temperature increased the permeability with little decrease in the selectivity relative to the untreated film. The transport properties of the glassy polymers were time dependent because of physical aging of these out-of-equilibrium materials.
Transport Properties of Native and Chemically Modified Gamma-Alumina Membranes
Miller, J.R.
PhD dissertation

Liquid- and gas-phase transport measurements are reported for native and chemically modified 40Å Membralox(r) g-Al2O3 membranes (K-92-3). Modification of the native membranes was performed with organotrichlorosilanes having nominal lengths of 5Å and 10Å in order to decrease the pore size and change the chemical nature of the membrane surface from hydrophilic to hydrophobic, thereby improving the rejection capabilities of the membrane and altering its adsorption properties. High surface area g-Al2O3 powders were modified as well to facilitate determination of the silane layer thickness and surface coverage. The test liquids used to evaluate the performance of the native and modified membranes were pure water and toluene along with dilute, single-solute mixtures of poly(ethylene glycol) (PEG) 400, 1000, 1500, 2000, 3000, 4000, and 6000 in water and PEG 400, 2000, and 6000 in toluene. Runs were performed at 25°C and pressures up to 30 bar. The pure gases He, H2, Ar, and SF6 were run at ambient temperature and 0.35 bar. As few fundamental transport studies have been performed on these membranes, the transport data of the native membranes have not only served as a basis for comparison, but have contributed as well to a better understanding of the material. For both water and toluene, the native membranes followed Darcy's Law behavior in terms of pressure dependency; however, toluene displayed a lower permeability than water. This is inconsistent with pure viscous flow behavior and indicated a dependence of molecular size on flow. With PEG/water mixtures, a reversible 10%-30% decrease in permeability was observed, while an irreversible 70%-95% decrease in permeability was observed for PEG/toluene mixtures. The rejection of all PEG/water mixtures followed hindered transport theory in that the rejection increased with increasing flux (pressure) for a given molecular weight and increased from 0 to 1 as the solute molecular weight increased. For PEG 2000 and 400/toluene mixtures, however, negative rejections were observed. With modified membranes, the degree of fouling was less for PEG 6000/toluene mixtures. Additionally, the modified membranes showed a decrease in pure liquid permeability of 1-2 orders of magnitude, depending on the size of the silane. However, this was met with an overall decrease in solute rejection. It was revealed through bubble-point measurements that this may be a result of defects present in the native membrane. The reaction itself was quite successful. Nitrogen adsorption measurements revealed a silane layer thickness consistent with CPK space filling molecular models. Elemental analysis showed that the surface coverage was consistent with a monolayer of coverage. Furthermore, a computer model was developed of the modified surface, which agreed well with experimental data. This model can possibly be used to predict the outcome of other modifications.

Permeation of Several Gases through Elastomers, with Emphasis on the Deuterium/Hydrogen Pair
Fitch, M.W.; W.J. Koros; R.L. Nolen; J.R. Carnes

The diffusion and permeation coefficients for He, H2, D2, O2, and N2 in a variety of elastomers were measured by simple manometric methods. The elastomers (K-92-4) studied were butyl rubber; Hypalon(r) 40 and 45; Viton(r) E60 and GF; Hydrin(r) 100 and filled Hydrin 100; Kraton(r) G, FG, and KG VTEOS; ethylene-propylene diene monomer; epoxidized natural rubber; and neoprene. Consistent with earlier studies, elastomers with higher Tgs exhibited lower diffusion coefficients. The ratio of diffusion coefficients of the hydrogen isotope pair differed from the purely molecular weight-based prediction. Deuterium (K-92-4)'s slightly smaller size relative to hydrogen is consistent with observed deviations from the molecular weight-based diffusion coefficient ratio.
Optimized membranes made by a dry/wet phase inversion process using forced-convective evaporation consist of an ultra thin and pore-free skin layer supported by a nodular transition layer and an underlying open-cell, sponge-like substructure. It is suggested that the outermost region of such cast membranes undergo phase separation by spinoidal decomposition in the initial stages of the evaporation process. As a result of the small scale of phase separation present in polymer-solvent systems, an appreciable capillary pressure (K-92-5) occurs in the interstitial space filled with the polymer-poor phase in contact with air. The resulting force acts normal to the membrane-air interface, which tends to consolidate the polymer-rich phase to form a nonporous surface layer.

Gas Transport through Integral-Asymmetric Membranes: A Comparison to Isotropic Film

Pressure-normalized gas fluxes for defect-free integral-asymmetric membranes prepared according to a dry/wet phase inversion (K-92-6) process were measured as a function of temperature and pressure and compared to measurements on thick isotropic films (K-92-6). Asymmetric membranes were prepared from polysulfone (K-92-6), polycarbonate (K-92-6), and polyestercarbonate (K-92-6). The activation energies of permeation (K-92-6) for O2 and N2 in the range of 25°C to 55°C were higher for the asymmetric polysulfone membranes than for a thick isotropic film. Oxygen/nitrogen selectivities of the asymmetric membranes are higher than those for isotropic films. The asymmetric membranes did not show the typical dual mode behavior for the CO2 flux as a function of pressure as determined for thick films. Differences in the free volume and its distribution in the ultra thin skin layer of the asymmetric membranes compared to isotropic films may be responsible for these results.

Isomer Effects on Transport Properties of Polyesters Based on Bisphenol-A

Pure gas sorption and transport properties of polyesters based on bisphenol-A and both pure isophthalic and pure terephthalic acid chloride were obtained for He, N2, O2, CH4, and CO2 at 35°C. The polymers were synthesized in our laboratory and amorphous films were prepared with a specialized solvent casting procedure. The polymer containing m-phenylene groups shows higher permselectivity for most of the gas pairs. The ideal selectivity of O2/N2 was increased by 33% when p-phenylene units were replaced by m-phenylene units. On the other hand, the polyester containing only p-phenylene groups shows higher permeability to all the gases studied. The polymer based on pure terephthalic acid chloride has a 75% higher oxygen permeability and a 1.1-fold higher CO2 permeability than the isophthalic acid derivative. The polyester containing m-phenylene units has lower Tg, higher permselectivity, lower permeability, lower FFV, and lower d-spacing. The values of FFV and d-spacing were only slightly different between the two isomers. Moreover, for the sub-Tg g transition, the maximum in tan d occurred at essentially the same temperature (-55°C). The polymer with a higher concentration of p-phenylene units shows a somewhat larger area under the g-peak, indicating slightly more sub-Tg motion. The distribution of FFV is considered to be the determining factor for the differences in transport properties observed.
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer
Gou, M.M.; W.J. Koros; G.W. Goldman
A study of the interaction of solvent in a urethane/urea/ether copolymer belonging to the spandex family of materials is presented. Sorption and desorption isotherm data for N,N-dimethylacetamide (DMAC) in spandex solutions are used to determine thermodynamic parameters of solvent/polymer interaction (K-92-8). Isosteric enthalpies for sorption of DMAC tend to approach the heat of evaporation of DMAC at high sorbed concentrations. A qualitative mechanism for the assemblage of hard-segment domains in the polymer during desorption is presented and interpreted in terms of the sorption isotherms and isosteric enthalpy data. The study provides useful insights into the influence of particulate additives, such as titanium dioxide in the solution.

Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer
Gou, M.M.; W.J. Koros; G.W. Goldman
Polymer solvent interactions in a block polyurethane/urea/ether polymer belonging to the spandex family are considered in this paper. Independent analysis of the sorption isotherms for DMAC in the spandex polymer as a function of vapor activity and temperature was presented in a previous paper. A second aspect in understanding solvent/polymer interactions is the kinetics of desorption. Characterization of the solvent devolatilization is an important aspect of the drying procedure to guide processing protocols to eliminate residual solvent in the final spandex products, especially for medical applications. This paper reports data for desorption kinetics under nominally isothermal conditions to provide diffusion coefficients as a function of polymer phase concentration and temperature. Desorption curves were found to be Fickian at least up to the half-time of desorption. Diffusion coefficients were therefore calculated using a half-time method. Temperature effects on sorption or desorption were measured to obtain corrected diffusion coefficients and found to be significantly different than the apparent diffusion coefficient measured from a conventional McBain sorption cell.

Temperature Dependence of Gas Sorption and Transport Properties in Polymers: Measurement and Applications
Costello, L.M. and W.J. Koros
Equipment for determination of gas sorption and transport properties of polymer membranes at elevated temperatures is described in detail. To illustrate the utility of the equipment, permeability and solubility data for five gases in bisphenol-A polycarbonate are reported for temperatures up to 175°C and 120°C, respectively. Activation energies for permeation and diffusion and the heat of sorption for each penetrant in polycarbonate are also presented and interpreted. The temperature dependencies of both solubility and diffusivity selectivity and their contributions to the overall selective behavior of polycarbonate are discussed for CO2/CH4 and He/N2 separations at temperatures up to 120°C.

Aqueous Quenched Asymmetric Polysulfone Membranes Prepared by Dry/Wet Phase Inversion
Pesek, S.C. and W.J. Koros
A process for producing ultra thin and defect-free selecting layers on asymmetric membranes using dry/wet phase separation (K-92-11) has been reported earlier for organic coagulation media. The present study generalizes this process by focusing on the important parameters necessary for the formation of equally thin defect-free polysulfone (K-92-11) membranes using an aqueous coagulation (K-92-11) medium. In addition, this study presents the fundamental issues involved in altering low viscosity, flat-sheet casting solutions to produce viscous solutions, potentially useful
for hollow-fiber spinning, without losing the desirable thin selective layer. Transport properties of integrally skinned asymmetric polysulfone membranes coagulated in water are reported for the separation of various gases at 24°C and upstream driving pressures of 50 to 100 psig. These asymmetric membranes have essentially the intrinsic permselectivities of dense polysulfone films formed by simple solvent casting techniques. The novel aspect of both the organic and the aqueous-quenched structures is their ultra thin selective layers, which can be made as thin as 200Å to 800Å under optimum formation conditions without introducing defects that reduce permselectivity. Unlike other thin-skinned structures reported recently, the present membranes do not require any post-formation solvent treatments or silicone coatings to achieve essentially the intrinsic separation factors of the material. High resolution scanning electron photomicrographs of the membrane structures are presented to clarify the morphologies responsible for their desirable properties.

**K-92-12 PUBLISHED**

**Gas Permeation and Selectivity of Poly(organophosphazene) Membranes**

Allcock, H.R.; C.J. Nelson; W.D. Coggio; I. Manners; W.J. Koros; D.R.B. Walker; L.A. Pessan


A series of poly(organophosphazenes) and the ferroncenyl polymer \([\text{N3P3(OCH2CF3)}_4 \text{(h-C5H4)2Fe}]n\) were synthesized. Molecular structural characterization for these polymers; was achieved by 1H and 31P NMR, gel permeation chromatography, elemental microanalysis, and DSC. Films of these polymers were examined with respect to their permeability to \(\text{O}_2, \text{N}_2, \text{CO}_2, \text{He}, \text{and CH}_4\), and selectivity ratios were established. The effect of cross-linking on both the permeation and selectivity values for films of the silyl-bearing polymers were also investigated. The change in permeability and selectivity as a function of side group structure variations, free volume effects, gas pressure, and \(T_g\) is discussed. Poly[bis(trifluoroethoxy)phosphazene] was found to have oxygen permeabilities comparable to those of poly(dimethylsiloxane) but with higher permselectivities.

**K-92-13**

**Material Science of Polymeric Membranes**

Pessan, L.A. and W.J. Koros

Presented at the First Brazilian Polymer Conference, Sao Paulo, Brazil, November 1991

The variety of sophisticated polymers available nowadays makes possible the application of polymeric membranes (K-92-13) in diverse processes such as pressure and concentration-driven separations, gas permeable contact lenses, barrier packaging, controlled release devices, and gas separation (K-92-13). Insights are given into the basic principles that govern permeability and selectivity of gases in glassy polymers. The technique of simultaneous modification of intrasegmental mobility and intersegmental packing for controlling the absolute diffusivity and diffusivity ratio of binary gas pairs in glassy polymers is illustrated.

**K-92-14 S5.00**

**Benzene Sorption from Dilute Aqueous Solutions by Crosslinked Polystyrene/Divinylbenzene Microspheres**

Abukhadr, R.K.

Master's thesis

Removal of dilute quantities of organics from aqueous streams is done mainly by the use of granular activated carbon (K-92-14) (GAC) as an adsorptive material. Benzene, an important pollutant is soluble in water up to 1710 mg/liter at room temperature. A water stream having a large amount of benzene; in it would exhaust a carbon bed in a short time, thereby resulting in frequent costly bed regeneration. This study focuses on developing preliminary data for a continuous separation process for the removal of organic matter from water using crosslinked polymeric microspheres. The process involves a sorption stage followed by a filtration stage to separate the swelled polymer from the treated water stream. Polystyrene microspheres crosslinked with DVB have been synthesized by surfactant-free dispersion polymerization (K-92-14) in the presence of methanol. Divinylbenzene content varied from 0% to 50% by weight in the initial monomer mixture. The polymerization results in microspheres about 0.5 micrometers in diameter.
The dried microspheres have a powdery texture that can be redispersed in water with the aid of a small amount of surfactant. Sorption equilibrium isotherms for microspheres having various crosslink densities have been developed for the benzene/water system. Both ceramic and poly(tetrafluoroethylene) (PTFE) filters were used to separate the microspheres from water. It was found that at relatively high activities, these microspheres can sorb a substantial amount of benzene from the water phase. These isotherms have been compared with isotherms developed for benzene sorption into polystyrene in a benzene vapor sorption cell. Few people have done sorption experiments for both the water/benzene system and the benzene vapor system and quantified their results thermodynamically on the basis of experimental data. The kinetics of sorption for the water/benzene system have also been studied using a stirred cell that works on-line with an ultraviolet spectrophotometer. Kinetic data have been collected at different activities for two different crosslink activities.

**K-92-15 PUBLISHED**

**The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders. IV**

Osborne, J.L.; H.B. Hopfenberg; W.J. Koros


Uniform, submicron-diameter PS and PMMA microspheres were dilated by preswelling with pure organic vapors followed by rapid removal of the preswelling penetrant by protracted evacuation of the preswelling chamber to a pressure of 10-3 mm Hg. Aging of the preswollen polymers (K-92-15) was carried out both in vacuum and in the presence of various penetrants at sorbed concentrations typically less than 2 wt%. Inferences about relaxations of the polymers were based on changes in concentrations of the penetrants within the microspheres, at a given temperature and penetrant activity, which result from aging in vacuum or in the presence of penetrant. The kinetics of the relaxations were monitored by probing the expanded glasses with relatively low concentrations of penetrants. In general, the continuous presence of these low concentrations of probe molecules either arrested or retarded the ensuing relaxations as compared with the aging that occurred in vacuum. A series of lower monohydric alcohols, lower n-alkanes, and some other similar penetrants were used as probes to test explicitly and systematically the effects of size and structure of the penetrant contacting the polymer during aging on the decay of excess sorption capacity of the preswollen glassy polymers. Decay of excess sorption in the presence of penetrant was evident only when molecularly small penetrants with interactive functional groups, alcohols for example, were sorbed into preswollen PMMA. This result suggested that the relaxation occurring in the presence of penetrant involved specific interactions between the penetrants and the carbonyl groups in the PMMA.

**K-92-16 PUBLISHED**

**Sorption and Transport of CO2 and CH4 in Chemically Modified Poly(phenylene oxide)**

Story, B.J. and W.J. Koros


The sorption and permeability of CO2 and CH4 in PPO and several of its derivatives are reported. Three modified PPOs were synthesized containing carboxyl (CPPO), methyl esterified carboxyl (MeCPPO), and bromine substituents (BPPO). The carbonyl-containing derivatives, substituted at the methyl side chain site of the PPO backbone, were chosen to increase the CO2/CH4 solubility selectivity of PPO. The brominated PPO, substituted at the phenylene ring position, was prepared in order to study the effect of substitution position on permselective properties. The modified PPOs were characterized via FTIR, FTNMR, DSC, density, and wide-angle x-ray measurements. The differences in permeability and CO2/CH4 selectivity of the modified polymers are explained in terms of the effect of each substituent on the solubility and diffusivity factors that govern the transport of gases in glassy polymers (K-92-16). The solubility selectivity of the carbonyl-containing PPO derivatives increases, with the greatest increase (41%) observed for CPPO with 1.0 carboxyl group per repeat unit. The methyl-substituted polymers are significantly less permeable but more selective than PPO. The observed decreases in gas sorption, diffusivity, and permeability in these materials are attributed to decreases in free volume and decreased segmental rotation in the polymer. Simultaneous decreases in Tg suggest a reduction in sub-Tg motions at low concentrations of methyl substituents that are analogous to diluent-induced antiplasticization.
effects. Internal plasticization is observed at higher levels of carboxylation. Brominated PPO shows a 150% increase in CO2 permeability, with no change in CO2/CH4 selectivity. These changes are explained by bromination-induced stiffening of the polymer molecules. An increase in chain stiffness results in, but is offset by, an increase in the average diffusional jump length of dissolved gas molecules.

**K-92-17 PUBLISHED**

**Effect of Various Pre-exposure Agents on Methane Sorption and Dilation; in Tetramethyl Polycarbonate**

Pope, D.S. and W.J. Koros


The effects caused by pre-exposure of TMPC to CO2, C2H4, and C3H8 on subsequent apparent equilibrium CH4 sorption and dilation are explored. Three exposure histories are studied: (1) no pre-exposure (unconditioned); (2) pre-exposure to CO2, C2H4, and C3H8, respectively, followed by depressurization to vacuum (conventionally conditioned); and (3) pre-exposure to high swelling levels, with the same three agents, followed by exposure to CH4 without depressurization (exchange conditioned). The unconditioned samples exhibit the lowest CH4 sorption and dilation levels while the exchange-conditioned samples exhibit the highest CH4 sorption and dilation levels. The increases above the unconditioned levels for the exchange-conditioned samples depend only on the swelling level achieved during the conditioning step and are independent of the conditioning agent. On the other hand, the increases seen for the conventionally conditioned samples show a slight dependence on the conditioning agent, possibly due to the occurrence of an effective "templating" of the free volume distribution during the conditioning procedure.

**K-93-1 $10.00**

**Aqueous Quenched Asymmetric Polysulfone Flat-Sheet and Hollow-Fiber Membranes Prepared by Dry/Wet Phase Separation**

Pesek, S.C.

PhD dissertation

A dry/wet phase separation process and an aqueous coagulation medium have been used to prepare integrally skinned, asymmetric polysulfone flat-sheet and hollow-fiber membranes for gas separations (K-93-1). Multicomponent casting solutions consisting of polymer, a primary volatile solvent, a secondary less-volatile solvent, and a less-volatile nonsolvent allowed "dry" evaporation-induced permeation of pure CO2 and CH4 and their 50/50 mixtures (at 5 and 20 atm partial pressures) were measured at 35°C in a series of styrene/methyl methacrylate copolymers (K-93-2) (SMMA) and a series of miscible blends of bischloral polycarbonate (BCPC) and poly(methyl methacrylate) (PMMA). PMMA is significantly plasticized by CO2 at 20 atm; whereas BCPC and, to a lesser extent, polystyrene, are not. Thus, by incorporating MMA units into the copolymer or in the blend, a varying extent of plasticization response was built in. Mixed gas separation factors were found to be well-predicted by pure gas measurements for CO2 and CH4 at 5 atm partial pressure for all copolymers and all blends. However, at 20 atm partial pressure of CO2, the actual mixed gas separation factors are much lower than that predicted by pure gas measurement as the MMA content of the copolymers or the blends increased. Significant history or conditioning effects accompany plasticization in glassy polymers so the results obtained depend on the measurement protocol. For this reason, no attempt was made to fit these data to current models since they do not allow for this fact.

**K-93-3 $10.00**

**Improving Ceramic Ultrafiltration Membrane Properties: Gelation of Colloidal Silica in Defects of Alumina Membranes**

Trocha, M.

Master's thesis

Previous studies by Miller and Koros (1990) have shown that commercially available 40Å Membralox(r) alumina ultrafiltration membranes; have a small number of large defects of a size up to approximately 2000Å. After applying a chemical vapor deposit (CVD) process using organosilanes, the 40Å pores of the Membralox(r) membrane decreased down to a size of 20Å
However, the polyethylene glycol (PEG) rejection and the gas selectivity was lower for the modified membrane than for the native membrane. Miller and Koros attributed these highly surprising results to previously unrecognized defects which become much more apparent after reducing the flux through the selective pores by the CVD. In this work a caulking treatment with aqueous colloidal silica has been developed in order to reduce the impact of such defects. Instead of using the conventional slipcasting process, a diffusion controlled casting device has been established. This procedure is able to selectively caulk 2000Å pores, while deposit on the surface can largely be avoided. Thus, the productivity of the ultramicroporous layer tends not to be affected, whereas the flow through the defects can be tremendously reduced. The feasibility of the caulking procedure has been shown for 2000Å Anodisc(r) membranes. The chemical properties of this type of membrane are similar to those of the 40Å Membralox(r), but the Anodisc(r) membrane is experimentally more accessible. Single treatment with silica sols reached a relative weight gain of approximately 20%. Scanning electron microscopy (SEM) has proven that the established caulking procedure specifically plugs the 2000Å pores but largely prevents silica deposit on the surface. The gas and water permeability of the membrane decreases one and two orders of magnitude, respectively. A progressive liquid displacement technique based on the difference in capillary force for pores of different size has been further developed to probe the pore-size distribution of the caulked membranes. The results lead to the conclusion that the average pore diameter in the modified membrane is approximately 100Å, which was expected based on literature values of packing properties of silica gels. PEG rejection measurements showed a high selectivity of the dried silica gel. PEG12000 (particle size ~57Å) was rejected up to 97%. The rejection results have been interpreted by a theoretical approach ( Hindered Transport Model), and indicate an average pore diameter of approximately 100Å. In longtime runs over several days with both water and organic solvent, the gas permeability did not change more than ±6% proving the stability of the dried silica gel.

**K-93-4 PUBLISHED**

Effect of Mild Solvent Post-Treatments on the Gas Transport Properties of Glassy Polymer Membranes
Rezac, M.E.; J.D. Le Roux; H. Chen; D.R. Paul; W.J. Koros
This study examines the effect of treatment of defective glassy polymer membranes with a variety of vapors and liquids which have varying solvency power for the polymer. The pure-gas oxygen/nitrogen selectivities of defective, asymmetric membranes are shown to be permanently increased, in special cases, by treatment with certain solvents which has adequate solvency power to cause a critical level of swelling in the membrane skin layer. Three distinct types of membranes have been treated: asymmetric polysulfone membranes formed by dry-wet phase inversion; spin-coated polyphenylene oxide-ceramic composite membranes; and solution deposited polyimide-ceramic composite membranes. While the detailed fundamental processes controlling the elimination of surface defects are complex, our results suggest that plasticization of the selective skin layer, coupled with surface-tension driven cohesive forces are likely to be the key factors at play.

**K-93-5 PUBLISHED**

Sorption Equilibrium Isotherms for Volatile Organics in Aqueous Solution: Comparison of Head-Space Gas Chromatography and On-line UV Stirred Cell Results
Simpson, E.J.; R.K. Abukhadra; W.J. Koros; R.S. Schechter
Sorption equilibrium isotherms from aqueous solution of benzene, toluene, chlorobenzene, p-xylene, carbon tetrachloride, trichloroethylene, and chloroform for various sorbents have been measured by two independent techniques: head-space gas chromatography (HSGC) and a stirred cell with on-line UV detection. Isotherms obtained by each technique showed close agreement at all concentrations. Isotherms are presented for XAD4, XAD2, AC-F400, and solid poly(styrene/divinylbenzene) copolymer microspheres. For solution concentrations <25% of the aqueous solubility of the organic, activated carbon was found to have the highest sorption capacity; however, activated carbon was surpassed in capacity by XAD4 at high thermodynamic
activities for each organic solute. Thus, for concentrated (>25% saturated in organic) industrial waste streams, XAD4 would appear to be an attractive alternative to activated carbon. Sorption data for this study were best represented for solutes onto XAD4 by normalized volumetric isotherms and AC-F400 by a Polanyi potential theory correlation plot.

K-93-6 PUBLISHED
Aqueous Transport Properties of Mesoporous g-Al2O3 Membranes
Miller, J.R. and W.J. Koros
The transport properties of 40Å Membralox(r) g-Al2O3 membranes were determined using pure water and dilute, single-solute aqueous mixtures of PEG 400, 1000, 1500, 2000, 3000, 4000, and 6000. Runs were performed at 25°C and transmembrane pressures up to 30 bar. Darcy's Law behavior and minimal fouling were observed for pure water flow with an average pure water permeability of 6.5 L/m2 hr bar. Runs with 0.1% PEG/water mixtures showed no evidence of concentration polarization, and although fouling reduced the permeability 10-30%, the reduction was completely reversible with pure water rinsing. The rejection behavior of all PEG/water mixtures followed hindered transport theory, and by fitting the transport data to a hydrodynamic model, a pore slit width of ~27Å was found, in excellent agreement with other measurements.

K-93-7 $10.00
Synthesis and Characterization of Polypyrrolones for Gas Separation Membranes
Walker, D.R
PhD dissertation
A family of four step-ladder type polymers, polypyrrolones, were synthesized and characterized by gas sorption and permeation up to 1600 psia. Polypyrrolones are produced by the thermally induced ring closure of poly (amide amino acid)s that are initially produced by the reaction of aromatic dianhydrides with aromatic tetraamines. The dianhydride residue was kept constant as 6FDA, while the tetraamine residue was varied to study the effects of different connector groups on the transport properties within this family of polymers. Transport properties of two of the polypyrrolones and two of the precursor polyamides were compared to study the effects of ring closure on the transport properties. The transport properties of similar polypyrrolones and polyimides were also compared to examine the effects that increasing the rigidity of the repeat unit has on the transport properties of polymers. The polypyrrolones, polyamides, and polyimides were examined additionally with wide-angle x-ray diffraction, differential scanning calorimetry, density measurements, and free volume analysis. Polypyrrolones have higher glass transition temperatures and greater fractional free volumes than similar polyimides and greater fractional free volumes than the precursor polyamides.

K-93-8 PUBLISHED
Aging of Thin Polyimide-Ceramic and Polycarbonate-Ceramic Composite Membranes
Rezac, M.E.; P.H. Pfommm; L.M. Costello; W.J. Koros
The gas-transport properties of several polymer-ceramic composite membranes with glassy polymer layers having effective thicknesses of approximately 4000 Å exhibit strongly time-dependent behavior. The membranes, prepared from polyimide and polycarbonate, demonstrated decreases in gas flux of 40-60 percent in the first twenty days following manufacture. The pure-gas selectivity of these membranes for the He/N2 separation increased over the same period to values approximately 50% higher than those of a thick film of the same material. Substructure compaction of these membranes is nonexistent, unlike integral-asymmetric polymeric membranes, so transport property changes are less ambiguous to interpret. We suggest a true glassy-state drift in the properties of the selective layer of the composite membranes as the cause for our observations. Our observations show that transport properties determined on thick films of glassy polymers may differ significantly from the properties of thin gas permeation membranes. Replaces K-93-23
Blends of polyimide isomers containing hexafluoroisopropylidene in the central moiety of the diamine residue have been studied. The isomers differed by having either a meta or a para linkage between the diamine and dianhydride residues. The miscibility of these materials was investigated by studying the glass transition temperature behavior using differential scanning calorimetry. Mixtures of isomer pairs, such as 6FDA-6FmDA and 6FDA-6FpDA, exhibited one glass transition temperature, Tg, and were therefore miscible. Mixtures of nonisomer pairs exhibited two Tg's and were immiscible. The gas sorption and transport properties of the blends of the 6FDA-6FmDA and 6FDA-6FpDA isomers were characterized for a variety of gases at 35°C for pressures up to 60 atmospheres. The permeabilities and permselectivities in the miscible blends fell between those of the pure components and were approximately logarithmic averages of the pure component properties. The miscibility of the polyimide isomers enables one to tailor the composition of the material to optimize the gas separation and mechanical properties.

**Comparison of Pure and Mixed Gas CO2 and CH4 Permeabilities in Polycarbonate: Effect of Temperature**
Costello, L.M. and W.J. Koros
Pure and mixed gas permeabilities in polycarbonate films (K-93-10) are reported and compared for temperatures from 35 to 125°C. The effect of competition among penetrants and the temperature dependence of pure and mixed gas sorption and transport properties in the polymer membranes are discussed. Also, permeation activation energies of pure CO2 and CH4 in polycarbonate are compared with those obtained from the gas mixture studies.

**Sorption and Transport of Sulfur Dioxide in Polysulfone**
Pfromm, P.H. and W.J. Koros
The sorption and transport of sulfur dioxide (SO2) in polymers is important in areas such as food packaging, polymer degradation, and sensors and monitoring devices. Another possible application is in pollution control for exhaust gases from power plants. Polysulfone is a polymer that is widely used for commercial gas separations with membranes. We have investigated the sorption and transport of SO2 in a commercially available BPA polysulfone (K-93-11) near room temperature. The results were interpreted using the dual-mode sorption model with partial immobilization. Although similar data on other polymers have been published in the literature, we are not aware of any studies of sorption and transport of SO2 in polysulfone.

**Measurement of Thickness Dilation in Polymer Films**
Pope, D.S.; W.J. Koros; G.K. Fleming
For several years, gas sorption into polymers has been measured using a pressure decay method. Recently these measurements have been combined with corresponding volume dilation data to determine partial molar volumes. Previously, the volume dilation values were obtained from length and width measurements of the sample as determined from direct optical measurements with a cathetometer, assuming an isotropic expansion. This note presents a method to measure the thickness change of a polymer sample by optical/electronic means which eliminates the need to assume isotropic expansion, thereby allowing three-dimensional dilation measurements when combined with the previous length and width measurement approach.
Temperature Effects on Gas Permselection Properties in Hexafluoro Aromatic Polyimides
Kim, T.H. and W.J. Koros

Temperature dependencies of gas permeabilities, solubilities, diffusivities, and selectivities for various gas pairs (He/CH4, CO2/CH4, O2/N2, and N2/CH4) are reported for two hexafluoro-substituted aromatic polyimides prepared in our laboratory. The activation energies for gas permeation and diffusion, and the heats of sorption are also reported. These polyimides have exceptionally high permeabilities and permselectivities as compared to typical glassy polymers used in gas separation membrane applications. The temperature dependency of the permeabilities of all penetrants in these polyimides also is smaller than in other standard glassy polymers having more flexible backbones. The differences in activation energies between larger and smaller penetrants in these packing-disrupted rigid matrices, however, are more extreme than in standard glassy polymers, thereby causing a stronger temperature dependency of the permselectivity than for more flexible backbone glassy polymers.

Characterization of Physical Aging of Poly(methyl methacrylate) Powders by a Novel High-Pressure Sorption Technique
Stewart, M.E.; H.B. Hopfenberg; W.J. Koros,

High-pressure CO2 sorption isotherms were measured at 35°C in previously dilated PMMA microspheres, which were subsequently aged in vacuum at 35°C. The dilation was induced by preswelling with high activity methanol vapor at 13°C, or alternatively with CO2 at a pressure of 20 atm and a temperature of 5°C. The state of the samples during long-term aging was probed by rapid and intermittent determination of complete high-pressure CO2 isotherms. The dilation increased the sorption levels observed in the sorption experiments compared to those observed in untreated samples and, as the aging time increased, the sorption level progressively decreased. The isotherms under all conditions were well described by the dual mode sorption model. The observed time dependence of the isotherms was successfully described by confining all changes in sorption capacity to a systematic decay of the Langmuir capacity parameter. The equilibrium parameters of the model, however, were essentially unaffected by the preswelling and aging histories.

Comparison of Three Models for Permeation of CO2/CH4 Mixtures in Poly(phenylene oxide)
Story, B.J. and W.J. Koros

Two models for the permeability of pure gases (K-93-15) have been extended to include binary gas mixtures. The first is an extension of a pure gas permeability model, proposed by Petropoulos, which is based on gradients of chemical potential. This model predicts the permeability of components in a gas mixture solely on the basis of competition for sorption sites within the polymer matrix. The second mixed gas model follows an earlier analysis by Barrer for pure gases which includes the effects of saturation of Langmuir sites on the diffusion as well as the sorption processes responsible for permeation. This generalized "competitive sorption/diffusion" model includes the effect of each gas component on the sorption and diffusion of the other component in the mixture. The flux equations from these two models have been solved numerically to predict the permeability of gas mixtures on the basis of pure gas sorption and transport parameters. Both the mixed gas Petropoulos and competitive sorption/diffusion model predictions are compared with predictions from the earlier simple competitive sorption model based on gradients of concentration. An analysis of all three models is presented for the case of CO2/CH4 permeability in poly(phenylene oxide) (PPO). As expected, the competitive sorption/diffusion model predicts lower permeability than either of the models which consider only competitive sorption effects. The permeability depression of both CO2 and CH4 predicted by the competitive sorption/diffusion model is roughly twice that predicted by the competitive sorption model, whereas the mixed gas Petropoulos model predictions for both gases lie between the other two model predictions. For the
PPO/CO2/CH4 system, the methane permeability data lie above the predictions of all three models, whereas CO2 data lie below the predictions of all models. Consequently, the competitive sorption/diffusion model gives the most accurate prediction for CO2, while the simple competitive sorption model is best for methane. The effects of mixed gas sorption, fugacity, and CO2-induced dilation were considered and do not explain the inaccuracies of any of the models. The relatively small errors in mixed gas permeability predictions using either of the three models are likely to be related to "transport plasticization" of PPO owing to high levels of CO2 sorption and its effect on polymer segmental motions and gas diffusivity.

**K-93-16 Published**

Study of Ultramicroporous Carbons by High-pressure Sorption  
Koresh, J.E.; T.H. Kim; D.R.B. Walker; W.J. Koros  

Sorption-desorption kinetics and the isotherm for CH4 in as-received TCM 128 ultramicroporous carbon fiber (K-93-16) are reported at 35°C up to 15 atm. The CH4 isotherm exhibits a similar hysteresis to that seen for N2 and CO2 on the carbon but at a much lower pressure. The low-pressure hysteresis might reflect adsorption in restricted regions composed of constrictions analogous to the tiny constrictions which were the cause of the hystereses seen with N2 and CO2. For the larger CH4, however, some of the regions that were easily accessible to N2 may be behaving as "restricted" to CH4 owing to a molecular-sieving phenomenon. Analysis of the diffusion kinetics indicates that the large CH4 molecules cause a slow barrier build-up over a few constrictions in series at the outer pores of the carbon. The desorption kinetic response, which is much faster than the adsorption, follows the Fickian model and thus reveals diffusion coefficients of the order 10-13 cm2 s⁻¹.

**K-93-17 Published**

Barrier Polymers and Structures: Overview  
Koros, W.J.  

This introductory chapter provides an overview of the papers presented at the symposium on Barrier Polymers and Barrier Structures that was sponsored by the Polymer Chemistry Division of the American Chemical Society at the Spring 1989 meeting. A total of nineteen papers from the symposium are included in this volume. Topics covered include barrier transport fundamentals, advanced composite structures, reactive surface treatments and the effects or orientation on barrier properties. Relationships between polymer molecular structure and barrier efficacy are also treated in detail. Time and history dependent phenomena associated with retorting of barrier laminates are discussed from the standpoint of theoretical modeling and experimental characterization of the barrier layers. The effects of concentration dependent diffusion, flavor scalping and non-Fickian transport phenomena are also discussed. The coverage, therefore, is broad while providing sufficient depth to provide a state-of-the-art update on the major technical issues facing the barrier packaging field.

**K-93-18 Published**

Gas Transport Properties of Polysulphones: 1. Role of Symmetry of Methyl Group Placement on Bisphenol Rings  
McHattie, J.S.; W.J. Koros; D.R. Paul  

Gas sorption and transport properties are reported for a series of polysulphones having either two or four phenylene hydrogens per repeat unit replace with methyl groups. The results for tetramethyl bisphenol A polysulphone (TMPSF), dimethyl bisphenol A polysulphone (DMPSF) and dimethyl bisphenol Z polysulphone (DMPSF-Z) are compared to unsubstituted bisphenol A polysulphone (PSF). The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and differential scanning calorimetry were used to judge chain mobility, while X-ray diffraction and free-volume calculations give information about chain packing. Permeability measurements were made for He, H2, O2, N2, CH4 and CO2 at 35°C over a range of pressures up to 20 atm. Sorption experiments
were also done for N₂, CH₄, and CO₂ under the same conditions. The permeability coefficients of these polymers rank in the order: TMPSF > PSF > DMPSF > DMPSF-Z for all of the gases. This order correlates well with free volume as well as with the g transition temperature. The symmetric methyl substitution of TMPSF yields a relatively open structure with improved separation characteristics over PSF. The asymmetric substitution results in tightly packed structures for the dimethyl materials that are highly selective but less permeable than PSF or TMPSF. The flexible cyclohexyl substituent of DMPSF-Z further reduces the gas permeability and improves the selectivity.

**K-93-19 PUBLISHED**

Sorption of CO₂/CH₄ Mixtures in Poly(phenylene oxide) and a Carboxylated Derivative

Story, B.J. and W.J. Koros


The sorption of CO₂ and CH₄ and their binary mixtures in poly (phenylene oxide) (PPO) and its carboxylated derivative (CPPO) is reported. All mixed gas data are accurately described by the dual mode sorption model, which predicts mixed gas sorption on the basis of pure gas sorption parameters. The present paper extends the mixed gas sorption data base to include polymers having a wide range of permeabilities and chemical structures. The confirmed accuracy of the model for these systems provides strong support for applying the mixed-gas dual-mode sorption model (K-93-19) to any gas/polymer system. A numerical simulation of the mixed gas sorption experiment is also presented which greatly simplifies the experimental procedures used to maintain the partial pressure of one of the gas components at a constant value over the course of a sorption isotherm measurement. By establishing the appropriate amounts of each gas component which are added to the polymer sample chamber of the sorption cell, the mixed gas apparatus simulator (MIGAS) can be used to maintain the partial pressure of one of the components to within 1% of the desired value.

**K-93-20 PUBLISHED**

Gas Separation Membrane Material Selection Criteria: Weakly and Strongly Interacting Feed Component Situations

Koros, W.J. and D.R.B. Walker


Materials from the polyimide and polycarbonate families with an attractive combination of productivity and perme selectivity for important gas pairs have been reported recently. A systematic group of materials from both of these families will be considered in this paper. Material optimization strategies in the absence of strong interactions between the membrane material and the penetrating gas mixture will also be discussed in the context of these materials. In addition, a material from a relatively unexplored family of rigid chain polymers, the polypyrrolones, will be compared to the behavior of the polycarbonates and polyimides. Performance for mixtures such as carbon dioxide and methane that interact relatively strongly will be contrasted by those such as oxygen and nitrogen that interact weakly with the membrane materials.

**K-93-21 PUBLISHED**

Statistical Thermodynamic Interpretation of Sorption/Dilation Behavior of Gases in Silicone Rubber

Pope, D.S.; I.C. Sanchez; W.J. Koros; G.K. Fleming


The lattice-fluid equation of state is used to predict sorption isotherms for nitrogen, methane, carbon dioxide, and ethylene in silicone rubber (K-93-21) at 308 K. In addition, partial molar volumes for each of these gases in the silicone rubber are predicted as a function of pressure and concentration. Model parameters are determined from pure component PVT values without the use of any mixing data. The sorption and partial molar volume predictions are then compared with experimental data. The predictions of the lattice-fluid model are in good agreement with the experimental data.
Temperature Dependence of Gas Sorption and Transport Properties in Polymers: Measurements and Applications
Costello, L.M. and W.J. Koros
Equipment for determination of gas sorption and transport properties of polymer membranes at elevated temperatures is described in detail. To illustrate the utility of the equipment, permeability and solubility data for five gases in bisphenol-A polycarbonate are reported for temperatures up to 175 and 120 °C, respectively. Activation energies for permeation and diffusion and the heat of sorption for each penetrant in polycarbonate are also presented and interpreted. The temperature dependencies of both solubility and diffusivity selectivity and their contributions to the overall selective behavior of polycarbonate are discussed for CO2/CH4 and He/N2 separations at temperatures up to 120 °C.

Analysis of a Thermally Stable Polypyrrolone for High-Temperature Membrane-Based Gas Separations
Costello, L.M.; D.R.B. Walker; W.J. Koros
A rigid polypyrrolone material that exhibits excellent thermal and chemical stability has been studied to determine its potential for novel applications in membrane-based gas separations at elevated temperatures. Operation at high temperatures produces favorably high membrane productivities; however, losses in permselectivity usually occur as well. Gas transport and sorption measurements have been obtained for this polypyrrolone at temperatures up to 200 °C. The loss of permselectivity with increasing temperature that occurs for most gas pairs is discussed in terms of both solubility and diffusivity selectivity. The temperature dependences of productivities and permselectivities for various gas pairs are also compared to those of other materials thought to be attractive for high temperature gas separations. In most cases, the structurally rigid polypyrrolone outperforms these other materials, demonstrating favorable productivities and permselectivities over the entire range of temperatures studied.

Gas Sorption and Transport Properties of Bisphenol-I-Polycarbonate Properties
Hägg, M.B.; W.J. Koros; J.C. Schmidhauser
Gas sorption and transport characterization of a new polymer in the polycarbonate family, based on the bisphenol of 3,3,5-trimethylcyclohexane-1-one (BPI) is reported at 35°C. By comparison with properties of other known polycarbonates, the effects of inhibition of both packing and segmental motion due to the introduction of the bulky substituent in the backbone are elucidated. The Tg of the material was measured with differential scanning calorimeter (DSC) and found to be unusually high for a polycarbonate (233°C). This indicates a successful inhibition of the large scale segmental mobility of the polymer. Variable 13C NMR analysis indicated that rotation of one phenylene ring has an unusually high (ca. 10 kcal) energy barrier, whereas the other phenylene ring has a more typical rotation profile (barrier < 3 kcal). The density was measured and found to be low, 1.107 g/cm3, indicating a high fractional free volume (FFV) for the polymer. Consistent with expectations, the introduction of the bulky substituted cyclohexane-group gave high permeabilities for the various gases tested (N2, O2, He, CH4, CO2) compared to most standard polycarbonates. On the other hand the permselectivities were typical for standard polycarbonates. The solubility coefficients of all gases were rather high, as expected for a polymer with such an open structure.
The Transport Properties of Polyimide Isomers Containing Hexafluoroisopropylidene in the Diamine Residue

Coleman, M.R. and W.J. Koros


The effect of modification of the central moiety of the dianhydride residue and isomerism on the gas transport and physical properties were compared for six polyimides containing the hexafluoroisopropylidene group in the diamine residue. Substitution of bulkier groups within the dianhydride residue resulted in disruption of chain packing and slight increases in resistance to chain motions which led to an increase in permeability with little loss in selectivity. The permeabilities and diffusivities in the meta connected polyimide isomers were considerably lower than in the para connected polyimide isomers. Similarly, the permselectivities in the meta connected isomers were consistently higher than in the para connected isomers. These lower permeabilities and higher permselectivities were a result of the more dense packing and a significant suppression to small scale motions in the meta connected isomers. The suppression to segmental mobility in the meta connected isomers was indicated by a increase in the sub Tg transition temperatures in these materials relative to the para connected isomers. The differences in transport properties for these polyimides were attributed to contributions by several factors, including: (i) total free volume (ii) distribution of free volume (iii) intersegmental resistance to chain motions and (iv) intrasegmental resistance to chain motions.

Multiloop Control of a Pilot-Scale Membrane System for Gas Separations

Henson, M.A. and W.J. Koros


A multiloop control system for a pilot-scale membrane separation process is designed and evaluated. The process employs hollow fiber membrane modules and is representative of air separation systems in industry. The decentralized control system originally consists of five PID controllers which regulate feed flow rate and pressure, permeate pressure, suction pressure, and module temperature. This configuration yields poor performance as a result of interactions between the feed flow rate and feed pressure controllers. By disabling the flow rate controller and proper tuning of the remaining control loops, satisfactory control is achieved during 4 days of continuous operation.

Sorption and Dilation of Poly(1-Trimethyl Silyl-1-Propyne) by Carbon Dioxide and Methane

Pope, D.S.; W.J. Koros; H.B. Hopfenberg

Accepted by Macromolecules, in press (1994)

Poly(1-trimethyl silyl-l-propyne) (PMSP) is known to absorb large amounts of fixed gases such as carbon dioxide and methane, presumably due to the inherently large free volume of PMSP. Exposure to carbon dioxide at pressures as high as 1000 psia apparently increases chain mobility allowing for relaxation of excess volume in the polymer matrix induced by toluene solution casting. These volumetric relaxations, determined with a three dimensional dilatometer, appear in the form of a time-dependent decrease in the overall polymer volume upon depressurization of the carbon dioxide. Repeated exposures to carbon dioxide show no further decrease in sorption capacity and essentially no further decrease in overall volume. The PMSP did not exhibit the typical conditioning behavior in which volume and sorption capacity increase upon subsequent repressurization following desorption. This absence of "normal" conditioning behavior was attributed to residual "pre-conditioning" by the toluene casting solvent. The PMSP stiff chain backbone relaxes so slowly after casting that the polymer retains massive amounts of excess volume even after initial exposure to plasticizing carbon dioxide.
Synthesis and Gas Transport Properties of Aromatic Polyester Membrane Materials
Pessan, L.A.
PhD dissertation
A family of aromatic polyesters has been synthesized and characterized by pure gas sorption and transport properties for helium, oxygen, nitrogen, methane, and carbon dioxide at 35 °C and at pressures up to 50 atm. A series of polymers with a systematic variation of chemical structure was selected to study the effects of inhibition of molecular packing and mobility on gas permeability and selectivity of polymeric membranes. Another series of polyester was chosen to test the hypothesis that alternating packing disruptive units and flat and packable moieties can provide a more favorable free volume distribution in the polymer matrix for gas transport properties. This dissertation involved the synthesis of monomers not available commercially and the synthesis of all the polyester materials studied. The gas transport properties of the polymeric membranes were interpreted in terms of physical properties determined by differential scanning calorimetry, wide angle x-ray diffraction, density measurements, free volume analysis, and dynamic-mechanical thermal analysis.

Temperature Dependence of Gas Sorption and Transport Properties in Glassy Polymers
Costello, L.M.
PhD dissertation
An in-depth characterization of the temperature-dependent gas-transport properties of several membrane materials is provided, thereby improving the fundamental understanding of this complex separation process. The permeabilities and solubilities of gaseous penetrants in various polymers have been determined using permeation and sorption systems that were designed to operate at temperatures up to 315°C and 200°C, respectively. From these data, the activation energies for permeation, heats of sorption, and activation energies for diffusion were calculated and analyzed for each polymer-penetrant pair. The materials studied range from the basic engineering materials to novel thermally stable membrane materials. Initially, a series of substituted polycarbonates bisphenol-A polycarbonate [PC], tetramethyl bisphenol-A polycarbonate (tetramethyl polycarbonate) [TMPC], tetramethyl hexafluoro [TMHFPC] were studied. By analyzing the thermal and selective behavior of polymers within a family, the specific structures that respond most favorably to increases in temperature were identified. Next, gas-sorption and gas-transport properties over a large temperature range were determined for a novel polypyrrolone material hexafluoro dianhydride tetraamino diphenyl ether polypyrrolone (6FDA-TADPO). Polypyrrolones have a great deal of potential for use in separation processes at elevated temperatures since they display exceptional strength and oxidation resistance to 400°C. The 6FDA-TADPO results were promising since it was able to achieve extremely high productivities while retaining very reasonable permselectivities at temperatures up to 200°C. Thermally stable derivatives of the polymeide family have also been characterized since they are attractive candidates for use in high-temperature gas-separation applications. Gas permeabilities and solubilities in two fluorine-containing polyimide isomers (6FDA-6FpDA and 6FDA-6FmDA) were determined at temperatures exceeding 300°C. These studies provided insight into the effect of a seemingly small structural variation on the ability of a material to retain favorable separation characteristics at high temperatures. At the present time, most industrial gas separations utilizing polymer membranes occur at temperatures only slightly elevated above ambient conditions. The identification of thermally stable, chemically resistant materials that retain favorable separation characteristics at elevated temperatures, along with the fundamental conclusions drawn from this research, will hopefully lead to important new applications of membranes for gas separations.

K-94-1 REPLACED BY K-93-29
Gas Transport Properties in Amorphous Glassy Polymers and Aging of Thin and Thick Films Made from Amorphous Glassy Polymers
Pfromm, P.H.
PhD dissertation

The physical aging of thin (~0.5 µm), intermediate (~2.54 µm), and thick (~25 µm) amorphous glassy polymer films has been investigated. The goal was to discover evidence of accelerated physical aging in the thin films. All films were free of solvents and had identical thermal histories. The polymer samples included a polysulfone (UdelTM 1700-Amoco, Ridgefield, CT) and a polyimide-hexafluoro dianhydride isopropylidene dianiline (6FDA-IPDA). Gas permeabilities of thin films decreased and selectivities increased with time, while intermediate and thick films showed virtually constant values. Gas selectivities of the thin films exceeded by far the values for intermediate and thick films. Activation energies of permeation were found to be much higher in aged thin films. The typical dual-mode characteristics were much less pronounced in the aged thin films. Sorption kinetics showed evidence of decreased diffusion coefficients in the thin films. The densities of thin films were found to be increasing with time and exceeded the constant densities of intermediate and thick films. Differential scanning calorimetry measurements did not show conclusive evidence of differences between thick, intermediate, and thin films. Wide-angle x-ray diffraction results showed no significant differences for the polyimide, but additional time-dependent peaks were found for the thin polysulfone films. The experimental results provide strong evidence for a thickness dependence of physical aging in polymeric glasses, resulting in an accelerated approach of thin films to the densified equilibrium state.

Polymer-Ceramic Composite Membranes in Reactor Applications
Rezac, M.E.
PhD dissertation

Essentially defect-free polymer-ceramic composite membranes with skin thicknesses as thin as 1200Å were prepared via a solution-deposition method and used at temperatures up to 300°C to selectively remove hydrogen from a dehydrogenation system and improve the overall product quality. Polymers which had swollen coil diameters larger than the surface pores of the ceramic support formed thin, defect-free surface coatings. No migration of the polymer into the pore structure of the support was apparent. The interfacial adhesion strength of the membranes appears sufficient and for use in membrane-assisted dehydrogenation systems. The properties of 6FDA-IPDA polyimide-ceramic composite membranes as a function of temperature were investigated and compared to those of thick dense films of this polymer. The permeabilities increased and the pure-gas selectivities decreased with increasing temperature in both the membrane and the thick film, but the hydrogen/butane selectivity remained over 100 even at 300°C. The ability of these membranes to affect the yield of normal butanes in a butane dehydrogenation was evaluated for reactor temperatures from 480 to 540°C and membrane temperatures from 25 to 300°C. In the presence of a correctly sized membrane, the normal butane conversions achieved in the membrane-assisted dehydrogenation system were up to 15% higher than those achieved in the conventional system. These values are in good agreement with the maximum predicted conversion. At 480°C, the selectivity of the catalyst for the production of normal butanes was unaffected by the membrane and was stable for nearly 600 hours. The stability of the membrane in the presence of the reaction mixture and expected impurities at elevated temperatures were evaluated. The membranes were quite stable at temperatures just below the polymer's glass-transition temperature; however, the membranes do not appear suitable for use at temperatures above 310°C or in the presence of oxygen.

Part 1: Ultramicroporous Carbon Membranes Produced from a Polylimide Precursor
Jones, C.W. and W.J. Koros

Carbon molecular sieving (CMS) membranes; are new, high-performance materials for gas-separations. The selectivities of these membranes are much higher than those typically found with
polymeric materials, and the selectivities are achieved without sacrificing productivity. Ultramicroporous carbon membranes can be produced by pyrolyzing various thermosetting polymeric materials under a variety of pyrolysis conditions. The membranes described in this paper were produced from the pyrolysis of a hollow-fiber polyimide precursor under conditions found to yield membranes with good air-separation properties. Membranes were produced by two different temperature protocols and were evaluated with mixed-gas feeds at pressures ranging up to 200 psig. The lower-temperature protocol yielded membranes with O2/N2 selectivities ranging from 8.5 to 11.5, while a higher temperature pyrolysis yielded membranes with selectivities ranging from 11.0 to 14.0. These membranes were found to be quite stable over time periods of several days with high purity, dry feeds. Limited studies also showed that these membranes were highly effective for the separation of other mixed-gas pairs including CO2/N2, CO2/CH4, and H2/CH4.

K-94-6 PUBLISHED
Part 2: Effects of Organic Contamination on Ultramicroporous Carbon Membranes
Jones, C.W. and W.J. Koros
Carbon molecular sieving membranes; have been found to have exceptional gas-separation properties with high-purity feeds. The basic nature of the carbon itself, however, makes these membranes vulnerable to compounds typically found in industrial process streams. Because of their organophillic nature, CMS materials are excellent adsorbents for organics and this results in significant problems in membrane applications. The studies detailed in this paper show that CMS membranes are vulnerable to adverse effects from exposure to organic contaminants. Membrane-performance losses were severe and occurred with feed-stream concentrations as low as 0.1 ppm. The pattern was consistent and observed for a number of different organic compounds. For various reasons, regeneration techniques used for carbon adsorbents were not suitable for the CMS membranes. However, a very promising regeneration process has been identified that uses pure propylene at unit or near-unit activity as a cleaning agent. This property appears to be unique to propylene and may have significant implications for a number of application areas.

K-94-7 PUBLISHED
Part 1: Characterization of Ultramicroporous Carbon Membranes with Humidified Feeds
Jones, C.W. and W.J. Koros
Carbon molecular sieving membranes; offer many advantages for difficult gas separations. The selectivities achieved with these membranes are much higher than those typically found with polymeric materials without sacrificing productivity. While they perform very well with high-purity dry feeds, the work in this paper will show that they are vulnerable to adverse effects from exposure to water vapor. Tests made with humidified air feeds ranging from 23 to 85% relative humidity show that some performance losses occur at all levels, with the losses increasing as the humidity level increases. In addition, most of the performance loss occurs in the initial period of exposure to water vapor. Despite this vulnerability, it was observed that significant membrane function was maintained at the lower levels of exposure. The effects of other factors, including feed pressure, membrane orientation and the nature of the carbon itself, are also considered

K-94-8 PUBLISHED
Part 2: Carbon Composite Membranes A Solution to Adverse Humidity Effects
Jones, C.W. and W.J. Koros
While the gas-separation properties of carbon molecular sieving membranes are superior to those of other materials, a significant drawback has been their vulnerability to adverse effects from exposure to water vapor. Since significant membrane function is maintained at low levels of exposure, efforts were focused on devising a means to lower the water activity at the carbon surface. This was successfully accomplished with the development of carbon composite membranes. These membranes consist of a hollow-fiber carbon membrane coated with a thin layer of certain unique polymeric materials. The polymers are highly hydrophobic but don't
prohibitively reduce the flux of other permeating species, and the resulting composite membranes are much more resistant to water-vapor effects. The performance of the composite membranes is analyzed in terms of the series-resistance model. While small losses in selectivity and productivity occur as a result of the resistance added by the polymer layer, the composite membranes are still very attractive as compared to conventional polymer membranes. The polymer barrier type and thickness, and the resulting degree of protection, are variables that can be tailored in a controlled manner for specific applications.

K-94-9
Composite Carbon Fluid Separation Membranes
Koros, W.J. and C.W. Jones
US Patent Number 5,288,304 (February 1994)

The invention provides carbon membranes for use in fluid-separation processes, particularly gas separations, which are treated with a coating that provides a protective barrier which significantly limits permeation of water vapor or other impurities such as hydrocarbons without significantly inhibiting permeation of the faster fluid component or lowering selectivity. The composite membranes retain good fluid separation properties and are resistant to the adverse effects on membrane performance commonly observed in environments having high humidity. The coating is preferably an amorphous polymer of perfluoro-2,2-dimethyl-1,3-dioxole. The membranes can be of a varied configuration: sheet-form, hollow-fiber, asymmetrical membranes, and the like.

K-94-10 PUBLISHED
Effect of Structure on the Temperature Dependence of Gas Transport and Sorption in a Series of Polycarbonates
Costello, L.M. and W.J. Koros

The permeabilities and solubilities of five gases are reported for PC, TMPC, and TMHFPC at temperatures up to 200°C. The temperature dependence of permselectivity is discussed in terms of solubility and diffusivity selectivity changes with temperature for CO2/CH4 and He/N2 gas separations. The activation energies for permeation and diffusion, and the heats of sorption are also reported for each gas in the three polycarbonates. Analysis of these values provides a better fundamental understanding of the effect of polymer-penetrant interactions and polymer backbone structure on the temperature dependence of the transport and sorption properties of gases in membrane separation processes. Important factors affecting the solubility and diffusivity selectivity losses or gains with increased temperature are also identified through correlation of these data with physical properties of the gases and polymers. These conclusions provide a framework for choosing the most promising membrane materials for particular gas separations at elevated temperatures.

K-94-11 PUBLISHED
Thermally Stable Polyimide Isomers for Membrane-Based Gas Separations at Elevated Temperatures
Costello, L.M. and W.J. Koros

The temperature dependence of gas sorption and transport properties (K-94-11) are examined for two polyimide isomers (K-94-11). The permeabilities and solubilities of five gases in these materials are reported over an extensive temperature range from 35 to 325°C. Also, the activation energies for permeation, the heats of sorption, and the activation energies for diffusion obtained for both polyimides are compared and correlated with physical properties of the polymers and penetrants. The influence of temperature on the selective properties of these membrane materials is discussed for three gas separations: He/N2, CO2/CH4, and O2/N2. Thorough analysis of these data provides insight into the influence of the subtle difference in chain structure of the two isomers. The performance of the 6FDA-6FpDA as a separation membrane at high temperatures suggests that it is an outstanding candidate for use in novel elevated temperature applications.
**K-94-12 PUBLISHED**

**Solubilization Isotherms of Aromatic Solutes in Surfactant Aggregates**

Gadelle, F.; W.J. Koros; R.S. Schechter


Several factors affecting solubilization of aromatic solutes in surfactant micelles have been investigated. Solubilization isotherms (K-94-12) of benzene, toluene, and chlorobenzene in various aqueous micellar solutions were determined using head space gas chromatography (HSGC). Cationic surfactants such as cetyl pyridinium chloride or cetyl trimethylammonium bromide present high solubilization capacities. Comparable anionic surfactants exhibit lower solubilization and a greater tendency to precipitate. It was observed that nonionic surfactants show high solubilization on a molar basis. Solubilization in mixed cationic-anionic micelles was also investigated. It also appears that the molecular size of the solute determines the extent of the solubilization. Finally, the shape of the different isotherms indicates that knowing the amount solubilized at saturation of the micellar solution is not sufficient to estimate solubilization at solute concentrations lower than the solute-aqueous solubility.

**K-94-13 PUBLISHED**

**Effects of Orientation on the Transport of d-Limonene in Polypropylene**

Moadeb, M. and W.J. Koros


Kinetics and equilibria of sorption and desorption of d-limonene in three polypropylene films (unoriented polypropylene [UN], uniaxially oriented polypropylene [UA], and biaxially oriented polypropylene [BA]) were studied at 30°C and various penetrant activities. The weight percent uptake of a saturated vapor of limonene in UN, BA, and UA films ranged from 12.5% to 19.0%. The kinetics of sorption of a saturated vapor of limonene in these polymers exhibits an increasing tendency toward Fickian transport as the degree of orientation increases, with the highly oriented BA approaching a Fickian response. As the penetrant activity is lowered, sorption kinetics tend to show a Fickian response more closely even for the UN and the UA films. Desorption of limonene (K-94-13) from the three samples appears to be Fickian and considerably faster than sorption in the initial stages; however, the process decelerates after roughly half of the penetrant has desorbed. Subsequent exposure of the three oriented films to a saturated vapor of limonene resulted in identical sorption kinetics, suggesting the absence of crazing or other irreversible damage often associated with anomalous sorption in glassy polymers. These results illustrate that the concentration-dependent anomalies in kinetics of sorption of a large penetrant such as limonene in the unoriented polypropylene film may be influenced by orientation to yield Fickian transport even at the highest external surface concentration. Thus, the orientation processes appear to affect large-scale, swelling-induced relaxations to a larger degree than it does the diffusional processes which are dependent on smaller scale segmental motions.

**K-94-14 PUBLISHED**

**Silica-Treated Ceramic Substrates for Formation of Polymer-Ceramic Composite Membranes**

Moadeb, M. and W.J. Koros


Fabrication of composite membranes from a highly porous substrate and a thin polymeric permselective layer allows achieving both high flux and selectivity in a single structure. In practice, formation of such composites is difficult due to the presence of large pores on the surface of highly permeable substrates. A novel approach to the formation of composite membranes was examined in this work to avoid this difficulty with large, hard-to-coat pores. Anopore-microporous aluminum oxide membranes with 2000 Å were used as model systems and were treated with 100Å spherical, colloidal silica particles to reduce their pore diameter while maintaining low-flow resistance through them. The silica-treated ceramics were then used as substrates for formation of thin defect-free polymer-ceramic composite membranes by a solution-coating method. The treatment protocols and characterization of the treated substrates, and gas permeation results for the composites formed are discussed.
K-94-15
Gas Transport Properties of Polymers Based on Spirobiindane Bisphenol
Pessan, L.A.; W.J. Koros; J.C. Schmidhauser; W.D. Richards
Accepted by Journal of Polymer Science: Part B: Polymer Physics, in press
Transport properties of pure gases in polycarbonates, polyesters, and polyetherimides based on 6,6'-dihydroxy-3,3',3'-tetramethyl-1,1'-spiro biindane (SBI) and bisphenol-A (BPA) are compared at 35°C. The SBI monomer contains two spiro-linked five-membered rings which are fused to the phenyl rings at the meta and para positions to the hydroxyl groups. This molecular structure gives SBI-based polymers a higher fractional free volume (FFV) and lower intramolecular motions as compared to the BPA-based analogs. The inhibition of chain packing due to the SBI moiety yields polymers with much higher permeabilities for all the gases studied, despite the hindrance of mobility associated with the SBI structure. Simultaneous increase in selectivity was also observed for some gas pairs. Oxygen permeabilities up to 5.9-fold higher with increases of up to 13% in O2/ N2 selectivities were observed for a polyester based on SBI as compared to its analog based on BPA. Higher permeabilities of up to 4.3-fold for He and up to 4.8-fold for CO2 were observed due to the substitution of SBI for BPA. Not surprisingly, lower values of He/CH4 and CO2/CH4 selectivities were obtained for the more open SBI-containing polymers. The changes in FFV and inhibition of small scale mobility for some materials caused by the SBI moiety were measured and used in the interpretation of the gas-transport properties. The individual contributions of diffusivity and solubility to the overall transport behavior of the polymers are discussed and correlated to the structural alterations caused by the SBI substitution for BPA monomer.

K-94-16 PUBLISHED
Accelerated Physical Aging of Thin Glassy-Polymer Films: Evidence from Gas Transport Measurements
Pfromm, P.H. and W.J. Koros
Polymer 36(12):2379-87 (1995)
Single gas permeabilities, selectivities, and activation energies of permeation of thin (~0.5 µm), intermediate and thick (~25 µm) amorphous glassy-polymer films (polysulfone [Udel 1700, Amoco, Ridgefield, CT] and polyimide 6FDA-IPDA) were investigated. The films had identical thermal histories and were solvent free. Evidence of strongly thickness-dependent physical aging was discovered. Thin films showed decreasing permeabilities and increasing selectivities that surpassed intermediate and thick films. Thin films showed increased activation energies of permeation. These results provide evidence for an accelerated approach of thin films to the densified equilibrium state.

K-94-17 PUBLISHED
Membrane-Assisted Dehydrogenation of Normal Butane
Rezac, M.E.; W.J. Koros; S.J. Miller
Increases of up to 1.5 times the traditional equilibrium limit are reported for a membrane-assisted reactor system with the dehydrogenation of butane as a model system. The use of thermally stable polymer-ceramic composite membranes to remove product hydrogen from the dehydrogenation reaction system has been evaluated as a function of the reaction temperature from 480 to 540°C. At low temperatures, the system was stable for run times over 550 hours with normal butane conversions increasing from 22 to 33% through the use of the membrane. The selectivity of the catalyst for the production of butanes was greater than 90% and was not markedly affected by the presence of the membrane. At equivalent conversion levels, the catalytic selectivity was equivalent with or without the membrane in the system.
**K-94-18 PUBLISHED**

**Membrane-Assisted Dehydrogenation of Normal Butane Influence of Membrane Properties on System Performance**
Rezac, M.E.; W.J. Koros; S.J. Miller

The influence of membrane operating properties on the performance of a membrane-assisted dehydrogenation system has been investigated. The dehydrogenation of normal butane has been used as a test reaction based on its industrial significance. The membrane-assisted dehydrogenation system that was evaluated consisted of two plug-flow reactors in series with the possibility of an interstage hydrogen-removal membrane. Highly productive, thermally stable polyimide-ceramic composite membranes were evaluated. The mixed-gas selectivity of the membranes was strongly influenced by the degree of hydrocarbon sorption, which in turn was controlled by the membrane temperature. At temperatures below the critical temperature of butane, the mixed-gas hydrogen-hydrocarbon selectivities of the membranes were below 20. As the temperature increased to above 180°C, the selectivity increased to above 75. Under these conditions, essentially complete hydrogen removal with less than 2% hydrocarbon losses was achieved. The removal of this amount of hydrogen resulted in an increase in normal butane dehydrogenation of about 11% with no decrease in catalytic selectivity.

**K-94-19 PUBLISHED**

**A Diffusion-Controlled Procedure to Close Pores in Ceramic Membranes**
Trocha, M. and W.J. Koros

A diffusion-controlled caulking treatment using aqueous colloidal silica to plug large pores in ceramic membranes is described. Unlike the conventional slip-casting process, this more controllable process can, in principle, be tailored by proper silica particle size selection to allow minimal deposition in the small desirable pores while enabling the elimination of large, less elective pores. The 2000Å Anodisc(r) membrane has been chosen as a model for the development of the procedure. Via the diffusion controlled process, a majority of the 2000Å pores were closed using 100 to 200Å silica with negligible deposition on external membrane surfaces. The technique, therefore, is promising for selective closure of large undesirable pores without surface fouling or closure of desirable 100Å or smaller pores. The efficiency of the procedure has been characterized by a number of independent methods. The gas and water permeability of the caulked membranes decreased one and two orders of magnitude, respectively. Pore-size analyses by a variation of the bubble point test and by rejection measurements of polyethylene glycol (MW 1500 to 12000) have found the average pore size of the dried silica treated membranes to be approximately equal to the precursor silica sol particle size used in the treatment. While this suggests less than close packing in the large pores, the low permeability of the silica-treated membrane demonstrates that the treatment is highly effective. Indeed, given the selective caulking capability of this approach, it appears to be an attractive means of healing defects in microporous ceramic membranes.

**K-94-20 PUBLISHED**

**Solubilization of Aromatic Solutes in Block Copolymer Micelles**
Gadelle, F.; W.J. Koros; R.S. Schechter

Several factors affecting solubilization of aromatic solutes in triblock copolymers (K-94-20) (PEOn-PPOm-PEOn or PPOm-PEOn-PPOm) known to form micelles have been investigated. Solubilization isotherms of toluene, benzene, chlorobenzene, and p-xylene in various aqueous polymeric solutions were determined using head space gas chromatography. The solute partition coefficient in the polymer, Ks, was shown to have a strong dependence on the solute concentration for all the polymers. The amount solubilized was at its highest for the high molecular weight, hydrophobic polymers. For the less hydrophobic or lower molecular weight polymers, it was determined that solubilization capacity was a function of the polymer concentration. Finally, comparisons between the different solute solubilization isotherms and with conventional
surfactants indicate that PPO-PEO, polymer-water and solute-polymer interactions have a strong influence on micellization and solubilization.

K-94-21
Thermo-Mechanical Stability of Polymer-Ceramic Composite Membranes
Rezac, M.E.; W.J. Koros; S.J. Miller
Accepted by Polymer Science and Engineering, in press
The mechanical stability of thin-filmed polymer-ceramic composite membranes have been evaluated in a variety of processing steps with temperatures ranging from 25°C to 350°C. Although not measured in this work, references for similar materials would indicate that the coefficient of thermal expansion for the two layers of the membrane are considerably different. Upon heating, this difference led to the development of thermally-induced stresses. These stresses could be relieved if the membrane were heated in an unrestrained manner; however, they were sufficient to cause membrane failure if not relaxed. Heating to temperatures above the glass transition of the polymer resulted in defect formation in that layer due to flow into the ceramic support. These results indicate that, if properly handled, the membranes are sufficiently stable to be used over a wide range of temperatures. However, serious consideration must be given to these issues in the design of larger-scale devices.

K-95-1
Phase Separation Instability and Manifestation of Macrovoids in Polymeric Asymmetric Membranes in Polymeric Asymmetric Membranes
McKelvey, S.A. and W.J. Koros
Submitted to Journal of Membrane Science
Nonsolvent-induced precipitation processes generate morphology from an initially single-phase homogeneous polymer solution. In these processes, mass transfer induces phase separation and subsequent vitrification eliminates further reorganization of a polymer-rich phase. Kinetics are responsible for trapping specific morphologies and can be influenced by local composition, temperature, applied stress, and pre-existing nuclei. Focusing only on the influence of composition changes, the growth of a preformed hypothetical nucleus in a metastable region is considered during a rapid-phase separation induced by an advancing front that is rich in nonsolvent for the dissolved polymer. Expansion of the preformed nucleus can be promoted by osmotically-generated forces arising from more rapid ingress of nonsolvent compared to egress of solvent from the local region contiguous to the nucleus. Growth of the nucleus is opposed by the vitrification of the polymer-rich matrix surrounding the nucleus. The process described is a form of instability and produces structures, typically referred to as macrovoids, which are an undesirable feature that tend to weaken the membrane's mechanical strength. Thus, the balance between the local rate of solvent-nonsolvent exchange compared to the vitrification rate are key factors in the growth or suppression of macrovoids. This process may be controlled by altering initial dope compositions, the nature of the various additives, applied stress, and the rate of exchange across the nucleus wall-for instance-by temperature, or external quench bath composition.

K-95-2 $20.00
Removal of Volatile Organic Compounds from Aqueous and Vapor Streams Using Polymeric Sorbents: Friedel-Crafts Modified Polystyrene
Simpson, E.J.
PhD dissertation
Friedel-Crafts Modified Polystyrenes (FCMPS) were synthesized and characterized as potential activated carbon replacements in water and air pollution control applications for volatile organic compounds (VOCs). The effect of FCMPS synthesis conditions on VOC removal effectiveness was the fundamental area of focus. Other commercially available polymeric sorbents, including FCMPS beads and macroreticular resins, and an activated carbon were also studied. Highly accurate aqueous-and vapor-phase sorption equilibrium isotherms were measured for a variety of priority pollutants-namely, benzene, toluene, chlorobenzene, and several others. The equilibrium sorption isotherm results demonstrate the FCMPS polymers have competitive VOC sorption capacities at all aqueous-phase concentrations when compared with activated carbon. In the vapor
phase, activated carbon has a higher capacity in highly dilute streams. However, unlike activated carbon, FCMPS is not affected by high humidity in dilute vapor streams. In both the aqueous and vapor phases, FCMPS shows remarkably higher capacities in concentrated streams, with ultimate capacities of 150 to 300% by weight. The results of the study clearly support the theory that FCMPS polymers operate by combined adsorptive and absorptive mechanisms. The equilibrium isotherm results were analyzed by Polanyi potential theory. The Polanyi characteristic curves for each sorbent allow prediction of sorption capacity for a wide range of pollutants over a range of temperatures. From the Polanyi parameter fits, isosteric heats of sorption were calculated for each sorbent at different sorption levels. The calculations showed activated carbon has significantly higher heats of sorption versus each of the polymeric sorbents. Comparative regeneration experiments, in conjunction with the heats of sorption calculations, demonstrated the FCMPS and other polymeric sorbents are significantly easier to regenerate than activated carbon. This ease of regeneration, combined with competitive or superior sorption capacity, suggests FCMPS may be an attractive activated carbon replacement in selected applications.

**K-95-3**

**Phase Separation, Vitrification, and the Manifestation of Macrovoids in Polymeric Asymmetric Membranes**

McKelvey, S.A. and W.J. Koros
Submitted to Journal of Membrane Science

Nonsolvent-induced precipitation processes may generate an asymmetric morphology from an initially single-phase homogeneous polymer solution. In these processes, mass transfer induces phase separation and subsequent vitrification eliminates further reorganization of a polymer-rich phase. Kinetics is responsible for trapping specific morphologies and can be influenced by local composition, temperature, applied stress, and preexisting nuclei. Focusing only on the influence of composition changes, the growth of a preformed hypothetical nucleus in a metastable region is considered during rapid phase separation induced by an advancing front that is rich in nonsolvent for the dissolved polymer. Expansion of the preformed nucleus can be promoted by osmotically-generated forces arising from a net volumetric accumulation of fluid in the nucleus. Growth of the nucleus is opposed by the vitrification of the polymer-rich matrix surrounding the nucleus. The process described produces structures, typically referred to as macrovoids, which are undesirable features and tend to reduce the mechanical strength of the membrane. Thus, the balance between the local volumetric rate of solvent-nonsolvent exchange compared to the vitrification rate are key factors in the growth or suppression of macrovoids. This process may be controlled by altering the initial dope composition, the nature of the various additives, and the rates of mass transfer (specifically across the nucleus wall), by imposing temperature gradients or by altering the external quench bath composition.

**K-95-4**

**Effects of Colloidal Silica Incorporation on Oxygen/Nitrogen Separation Properties of Ceramic-Supported 6FDA-IPDA Thin Films**

Moaddeb, M. and W.J. Koros
Submitted to Journal of Membrane Science

The effect of silicon dioxide particles on the gas transport properties of 6FDA-IPDA thin films was investigated in this work by casting the films on silica impregnated ceramic substrates. The pore structure of the Anopore TM ceramic support provides an ideal environment for bringing the silica particles into intimate contact with the polymer chains. Overall the properties of the resulting membranes for separation of oxygen from nitrogen are significantly improved compared to the properties of homogeneous film 6FDA-IPDA.

**K-95-5**  **PUBLISHED**

**A Free Volume Distribution Model of Gas Sorption and Dilation in Glassy Polymers**

Jordan, S.S. and W.J. Koros

A new approach is employed to model the sorption of gases in glassy polymers. The dual-mode concept that sorption occurs in both "equilibrium" (Henry's law) sites and "nonequilibrium"
(Langmuir) sites is used to separate the two contributions. The Sanchez-Lacombe equation of state is applied to predict the sorption in the Henry's law region of the polymer matrix. Characteristic parameters for the polymer liquid are used at glassy temperatures to provide a description of sorption in a hypothetical "equilibrium" state. The additional contribution provided by sorption into the regions of excess free volume that arise from the glassy state is addressed using a modified version of an approach first proposed by Kirchheim. The excess free volume is presumed to exist in a distribution of sizes, which in turn gives rise to a distribution of sorption energies. Positron annihilation lifetime spectroscopy data are used in conjunction with PVT data to characterize the glassy polymer. This independent description of the glassy state is then used to calculate the Langmuir-type sorption. The resulting model uses only one adjustable parameter to provide excellent descriptions of the sorption of several gases in three polycarbonates, as well as the volume dilation caused by the sorbed gas.

**K-95-6** PUBLISHED

**Membranes: Learning a Lesson from Nature**
Koros, W.J.
Chemical Engineering Progress, pp. 68-81 (October 1995)
Membranes occupy a special place in the separations' spectrum. They combine thermodynamically based partitioning and kinetically based mobility discrimination in an integrated separation unit. Because two distinct mechanisms contribute to selectivity, properly balancing their relative roles can produce devices for solving an unparalleled, wide range of complex problems. This dual character also defines membranes' strengths and weaknesses. To give a sense of the current role and future prospects of this interesting separation technique, this article describes industrially significant membrane processes and discusses the relative importance of partitioning and mobility discrimination for each process type. Viewing membrane processes from this perspective helps to understand their potential capabilities and limitations within a general framework.

**K-95-7**

**Dehydrogenation Using Dehydrogenation Catalyst and Polymer-Porous Solid Composite Membrane**
Miller, S.J.; M.E. Rezac; W.J. Koros
United States Patent 5,430,218 (July 1995)
Light paraffinic hydrocarbons are catalytically dehydrogenated using a dehydrogenation catalyst and a polymer-porous solid composite membrane capable of separating hydrogen from the effluent of the dehydrogenation reaction. The polymer-porous solid composite membrane may be, e.g., a porous ceramic material coated with a fluorinated dianhydride-diamine, a fluorinated polycarbonate or fluorinated polysulfone.

**K-95-8**

**An Emerging Class of VOC Sorbents: Friedel-Crafts Modified Polystyrenes. I. Synthesis, Characterization and Performance in Aqueous and Vapor Phase Applications**
Simpson, E.J.; W.J. Koros; R.S. Schechter
Submitted to Industrial and Engineering Chemistry Research
In the first of a two part series on Friedel-Crafts Modified Polystyrene (FCMPS), custom synthesis and characterization of FCMPS are described, including aqueous and vapor phase sorption equilibrium isotherms. The effect of synthesis variables on the final polymer properties was studied, including the choice of the crosslinking agent, % DVB in the PSDVB starting polymer % total crosslinking, and polymer concentration. The most effective VOC sorbent is formed when the FCMPS is synthesized at 100% "theoretical" crosslinking with CMME or CMEE using a lightly crosslinked starting PSDVB (<2.5% DVB). Both the anomalous swelling behavior and significant absorption contributions to VOC sorption were verified for FCMPS. Part II of the series compares custom synthesized FCMPS and commercial sorbents, including detailed isotherm analysis.
Activated carbon and macroporous resins are commercially available materials useful for removal of trace volatile organic compounds (VOCs) from aqueous process streams. While activated carbon adsorption beds are commonly used for this application, the process can be inconvenient and costly in that (1) energy intensive reactivation is very often not done on site, typically requiring the user to return the carbon to the manufacturer, and (2) it is not a continuous process. The reactivation step is the main energy consumer, requiring kiln furnaces operated at temperatures in excess of 1000°C, thus destroying the adsorbates and precluding recovery for reuse. While macroporous resins are also used in batch columns, regeneration is often achieved by a solvent wash, creating another difficult separation. In this project, a new alternative is under consideration: a continuous, membrane-based recovery process using polymeric sorbents with on-site regeneration via spray drying.

Commercial polymeric gas separation membranes exhibit a trade-off between productivity and selectivity. However, on this same trade-off curve molecular sieving materials like zeolites and carbon molecular sieves (CMS) lie above the upper bound for polymers. A comparison of the gas transport properties of these three different classes of materials highlights the importance of "entropic selectivity" which has hitherto not been recognized for membrane-based separation of gases. A whole new generation of polymeric membrane materials may result from enhancement of entropic selectivity of polymeric membrane materials.

This research investigated the feasibility and influence of a two-step modification technique on mass-transfer properties of commercial gamma-alumina ultrafiltration membranes. The rather coarse (40Å) minimum pore size available in typical commercial ceramic membranes renders them useless for micromolecular sieving separations. Moreover, the presence of a small but significant fraction of large defects, i.e. pores much larger than the nominal 40Å, complicates the pore size reduction. The first modification step was aimed at selectively caulking the defects in native membranes via the deposition of colloidal silica inside of these defects. After caulking, the membranes underwent a reaction with trichloro-organosilanes employing a vapor deposition technique. The feasibility and effect of the silica treatment was studied employing chemically similar flat disc γ-alumina membranes, i.e. Anodisc™ membranes. The well-defined morphology of Anodisc™ membranes, almost straight and relatively cylindrical 2000 Å pores, makes them an ideal medium for fundamental transport studies. The deposition of silica inside of porous media was monitored by evaluating weight gain, scanning electron micrographs, and pure gas and liquid permeation, by comparing solute rejection experiments with the hindered transport theory, and with a bubble point technique involving two immiscible liquids. Scanning electron micrographs showed that colloid silica was able to penetrate the pores and was deposited towards the membrane center. Gas and liquid permeances through the modified Anodisc™ membranes were reduced by one to two orders of magnitude. Rejection and bubble point tests showed a reduction of the average pore size by a factor of 15 to 30. Experience gained with Anodiscs™ was applied to the modification of tubular membranes. The effect of each modification step was evaluated by characterizing membranes in the native, partially modified and final states, giving insight into fundamental transport properties. The silica treatment of tubular membranes was quite successful in increasing the flow resistance through non-selective defects without forming a significant surface deposit.
Permeances of silica-treated and silanated membranes were radically reduced by 2 to 3 orders of magnitude, which could largely be attributed to the pore size reduction and the inevitable loss of porosity. After the silanation, the viscous flow contribution appeared to vanish and the solute rejection significantly enhanced. Our physical model of a final effective pore size somewhat larger than 10Å was corroborated by rejection and gas permeation results. It was possible to reduce the flux decrease by introducing a so-called pore-mouth-modification without compromising the improved sieving abilities.

K-96-2

Effects of Polyimide Pyrolysis Conditions on Carbon Molecular Sieve Membrane Properties
Geiszler, V.C. and W.J. Koros

In previous research, carbon molecular sieve (CMS) membranes for gas separations have been produced using either a vacuum pyrolysis or an inert purge pyrolysis technique on a precursor which is often polymeric. This study compares both techniques using the same polyimide precursor material. Additional pyrolysis variables included the type of "inert" purge gas (argon, helium, and carbon dioxide), purge flow rate, and temperature. Vacuum pyrolysis produced more selective but less productive CMS membranes than the inert purge pyrolyzed membranes. "High" purge gas flow rates (i.e., 200 standard cubic centimeters per minute or cm³(STP)/min) produced a much higher permeability, but lower selectivity membrane compared to those produced in a "low" purge flow rate (20 cm³(STP)/min). By raising the pyrolysis temperature from 550 to 800°C, the effective pore size was reduced, thereby making the CMS membranes more selective but less productive. Mixed gas tests using oxygen/nitrogen and hydrogen/nitrogen mixtures were used to evaluate membrane performance.

K-96-3 PUBLISHED
Gas Transport Properties of Thin Polymeric Membranes in the Presence of Silicon Dioxide Particles
Moaddeb, M. and W.J. Koros

The fundamental gas transport properties of thin films of six high performance polymers were evaluated in the presence of silicon dioxide particles. The silica particles were brought in close contact with the polymer inside the 200Å (DIA) pores of Anopore® aluminum oxide membranes. This unique environment allows intimate contact between the polymer and the silica particles. The presence of silica improves the gas separation properties of the permselective layer, particularly for oxygen and nitrogen. The increase in O2/N2 selectivity for some membranes is accompanied by an increase in oxygen permeability. The oxygen/nitrogen separation properties of the polymers in the presence of silica falls above the so-called "upper limit" of performance reported for polymeric materials. The observed significant increases in the glass transition temperature suggest restriction of chain segmental mobility possibly due to adsorption of polymer to silica surface. The increase in the activation energy of permeation points to increases in energetics of diffusion as the reason for the improved selective permeation. The observed behavior was not limited to oxygen and nitrogen as demonstrated by the results for other gas pairs tested.

K-96-4 PUBLISHED
A Rapid Feedback Characterization Technique for Polymeric Hollow Fiber Membranes Using Disperse Dyes
Clausi, D.T. and W.J. Koros

The long time lag between fiber spinning and the availability of characteristic data for process evaluation currently complicates research in hollow fiber membrane formation. This lag time is due to the downstream processing required before traditional gas based permeation measurements can be made on the spun fiber. A rapid feedback characterization technique based on commercially available disperse dyes is described here for polymeric hollow fiber membrane spinning applications. This technique involves dyeing wet hollow fibers immediately after spinning in an aqueous dye bath. In the present work, polysulfone fibers are shown to be
characterizable using this method before lengthy downstream processing (i.e. solvent exchange, drying, and post-treatment). Dye uptake in the hollow fibers is a function of skin porosity, thereby allowing quick evaluation of permeation characteristics. Dye uptake was measured using UV-visible spectrophotometry. Examples of fibers characterized using this technique and relationships between dye uptake and post-treated permeability are shown and discussed.

K-96-5 PUBLISHED
Mathematical Modeling of Gas Separation Permeators for Radial Crossflow, Countercurrent, and Cocurrent Hollow Fiber Membrane Modules
Thundiyil, M.J. and W.J. Koros
A new approach to solve the mass transfer problem posed by the permeation process in a hollow fiber permeator is presented and analyzed. The algorithm models the separation offered for a membrane module, for given gas conditions, simulating the permeate and residue compositions and the stage cut. The advantage of the "succession of states" approach utilized here is the option of retroactive incorporation of more complex interactions such as permeate pressure buildup, a pressure, composition and temperature dependent permeability. The two dimensional mass transfer in a radial crossflow permeator has been qualitatively discussed in the past, but it has not been modeled in the literature. The countercurrent, cocurrent and crossflow configurations (all single dimensional mass transfer cases) for gas separation have been modeled in literature primarily by numerical integration of the differential equations over the relevant boundary conditions. Incorporation of non-linearities such as pressure and permeability variations complicate the mathematics considerably for a single dimension, and make their solution almost impossible in two dimensions. This paper proposes an algorithm that simplifies the understanding of the problem posed, in terms of practical parameters (such as stage cut), and analyses the three flow patterns (radial crossflow, countercurrent, and cocurrent) in detail.

K-96-6 PUBLISHED
Ceramic Membrane Characterization via the Bubble Point Technique
Jakobs, E. and W.J. Koros
Porous membranes having nanometer and smaller pores challenge existing characterization methods. An easy, fast and inexpensive method to determine the maximum pore size and the pore size distribution is offered by the bubble point technique. Several methods based on similar principles have been presented in the literature. Here the original bubble point test and a liquid-liquid variation are considered. Two types of ceramic membranes with very different morphologies have been characterized with these methods in our lab. Results obtained for Anodisc® flat disc membranes with straight, non-intersecting pores using binary and ternary probing liquid systems are in very good agreement with each other, the manufacturers characteristics, and SEM micrographs. On the other hand, analysis of tubular γ-alumina membranes, i.e. Membralox®, resulted in two phase flow within the pores, and hence information about the pore size distribution could not be extracted from these tests.

K-96-7
Effects of Colloidal Silica Incorporation on Oxygen/Nitrogen Separation Properties of Ceramic-Supported 6FDA-IPDA Thin Films
Moaddeb, M. and W.J. Koros
The effect of silicon dioxide particles on the gas transport properties of 6FDA-IPDA thin films was investigated in this work by casting the films on silica impregnated ceramic substrates. The pore structure of the Anopore® ceramic support provided an ideal environment for bringing the silica particles into intimate contact with the polymer chains. Overall the properties of the resulting membranes for separation of oxygen from nitrogen are significantly improved compared to the properties of a homogeneous film of 6FDA-IPDA.
K-96-8
Phase Separation, Vitrification, and the Manifestation of Macrovoids in Polymeric Asymmetric Membranes
McKelvey, S.A. and W.J. Koros

Nonsolvent-induced precipitation processes may generate an asymmetric morphology from an initially single-phase homogeneous polymer solution. In these processes, mass transfer induces phase separation and subsequent vitrification eliminates further reorganization of a polymer-rich phase. Kinetics is responsible for trapping specific morphologies and can be influenced by local composition, temperature, applied stress, and preexisting nuclei. Focusing only on the influence of composition changes, the growth of a preformed hypothetical nucleus in a metastable region is considered during rapid phase separation induced by an advancing front that is rich in nonsolvent for the dissolved polymer. Expansion of the preformed nucleus can be promoted by osmotically-generated forces arising from a net volumetric accumulation of fluid in the nucleus. Growth of the nucleus is opposed by the vitrification of the polymer-rich matrix surrounding the nucleus. The process described produces structures, typically referred to as macrovoids, which are undesirable features and tend to reduce the mechanical strength of the membrane. Thus, the balance between the local volumetric rate of solvent-nonsolvent exchange compared to the vitrification rate are key factors in the growth or suppression of macrovoids. This process may be controlled by altering the initial dope composition, the nature of the various additives, and the rates of mass transfer (specifically across the nucleus wall), by imposing temperature gradients or by altering the external quench bath composition.

K-96-9
Gas Sorption-Induced Dilation of Poly(4-methyl-1-pentene)
Pope, D.S. and W.J. Koros

Sorption and volume dilation isotherms of semicrystalline poly(4-methyl-1-pentene) (PMP) were measured using CO2 and C3H8 as penetrants, which have sieving diameters of 3.3 and 4.3 Å, respectively. On the other hand, the PMP crystal has a void width of approximately 4 Å as estimated by X-ray diffraction, so it was anticipated that CO2 would be able to sorb into the PMP crystal while C3H8 would not. The data show that C3H8 has a constant partial molar volume of approximately 87 cc/mol, just above the value reported in other rubbery polymers, and are consistent with the hypothesis that the C3H8 molecules are too large to sorb into the PMP crystals. The partial molar volume of CO2 was found to be 39 cc/mol for CO2 weight fractions of up to 0.03. Since the typical partial molar volume of CO2 in rubbery materials is 46 cc/mol, the lower values in this study were attributed to CO2 sorption into crystalline regions of the polymer, which provided no dilation. Application of a two-phase model using the assumption of Henry's law sorption showed that apparently all C3H8 sorption was occurring in the amorphous region but approximately 16% of CO2 sorption occurred in the crystalline regions.

K-96-10
An Emerging Class of Volatile Organic Compound Sorbents: Friedel-Crafts Modified Polystyrenes. 2. Performance Comparison with Commercially-Available Sorbents and Isotherm Analysis
Simpson, E.J.; W.J. Koros; R.S. Schechter

The performance of Friedel-Crafts modified polystyrene (FCMPS) as a volatile organic compound (VOC) sorbent is compared with commercially available polymers and activated carbon. Detailed analyses of the equilibrium isotherms are presented, including vapor phase isotherm temperature dependence and isosteric heats of sorption. Although significant absorption contributions are observed for the polymeric sorbents of this study, the data are mathematically well represented by Polanyi potential analysis. FCMPS can be synthesized with desirable performance qualities such as ultimate VOC sorption capacity of ~2 mL/g, competitively high capacity in dilute streams versus activated carbon, insensitivity to humidity in vapor phase applications, and comparative ease of regeneration.
A Guide to Establishing Hollow Fiber Macroscopic Properties for Membrane Applications
McKelvey, S.A.; D.T. Clausi; W.J. Koros
Production of advanced hollow fiber membranes involves optimizing permeation and mechanical properties. If mechanical properties are insufficient, time dependent losses in permeation performance will occur. Practically speaking, numerous hollow fiber properties are considered and established concurrently; however, such a discussion would be quite complex for a single manuscript. Therefore, this work focuses on the specification and establishment of large-scale macroscopic properties such as those identified in Table 1. With optimal macroscopic properties specified, a basic understanding of fiber spinning couples process variables and macroscopic properties. This paper focuses on dry-jet wet spinning and associated processing complications, since these complications represent the first practical hurdles that must be overcome to produce useful continuous fiber suitable for membrane applications.

Tailoring Mixed Matrix Composite Membranes for Gas Separations
Zimmerman, C.; Singh, A.; Koros, W.
Polymeric gas separation membrane materials have improved significantly over the past two decades due to systematic optimization in backbone structures. Recent evidence suggests, however, that advantages of purely polymer-based approach are reaching diminishing returns for important separations such as O2 and N2. Zeolites, carbon molecular sieves (CMS), and rigid rod polymers offer attractive transport properties but are difficult and expensive to process. Mixed matrix composite (MMC) membranes, incorporating molecular sieving materials within polymeric substrates, may provide economical, high performance gas separation membranes if defects at the molecular sieve/polymer interface can be eliminated.

Pyrolytic Carbon Membranes for Air Separations
Singh, A. and W.J. Koros
Membrane Journal Vol. 7, No.1, April 1997, 15-21
Carbon molecular sieve (CMS) membranes were synthesized by the pyrolysis of polymeric precursors. The CMS materials had oxygen-nitrogen selectivities much higher than those observed for the polymeric precursors. Typically molecular sieving materials have diffusion selectivities much higher than polymeric materials. This has been identified as a result of higher entropic selectivity of the molecular sieving materials. A study of the development of molecular sieving properties as the polymeric precursor is pyrolyzed into a CMS material will offer us an insight into polymeric molecular structures needed for enhanced entropic selectivity membrane materials.

Characterization, Analysis and Modeling of Non-ideal Effects in Polymeric Membrane Based Natural Gas Processing
Thundyil, M.J. and W.J. Koros
PhD dissertation
Polymeric membrane-based carbon dioxide removal from natural gas steams is an important industrial unit operation. Membrane performance (i.e., flux and selectivity) is strongly dependent on process conditions. Natural gas steams contain hundreds of components. The compositions, temperatures and pressures of these steams vary between gas wells and over time. Consequently, it is important to understand how process conditions affect membrane performance. The most important factors affecting membrane performance are carbon dioxide content, temperature and temperature variation in the module, presence of moisture and heavier hydrocarbons. This understanding is important for design of membrane permeators and development of better materials for this separation. A glassy polyimide was experimentally studied over a range of conditions of industrial relevance-feed pressure (50-1000 psia), composition (pure CO2, 50/50
CO2/CH4, 10/90 CO2/CH4, pure CH4), temperature (30-70°C) and permeate pressure (vacuum, 25 psia). The experimental observations were analyzed from the dual-mode sorption and transport standpoint. It was demonstrated, both theoretically and experimentally, that permeate pressure has the effect of reducing the selectivity of the membrane significantly. The cooling observed in process streams as a result of permeation was modeled. The membrane separation process can be considered as an isenthalpic process. It is also necessary to consider heat transfer between the feed and the permeate stream. The cooling of the process streams increases with increasing carbon dioxide content in the feed, and with increasing stage cut (i.e., fraction of feed permeated). The countercurrent and cocurrent permeators will experience the greatest and least cooling, respectively. Mathematical model for design of membrane systems were developed. The radial crossflow configuration was modeled for the first time. The model framework enabled the incorporation of permeabilities and selectivities as functions of the process conditions in the permeator. The constant permeability models over predict the performance of the various modules. The model was also extended to incorporate cooling of process streams. It was shown that the radial crossflow permeator outperforms the countercurrent permeator in terms of carbon dioxide removal under non-isothermal conditions.

K-98-2 $20.00
Advanced Gas Separation Membrane Materials: Hyper Rigid Polymers and Molecular Sieve-Polymer Mixed Matrices
Zimmerman, C.M. and W.J. Koros
PhD dissertation
Despite efforts by the membrane community to develop polymeric materials with improved O2/N2 separation performance, limited progress has occurred for almost a decade. Molecular sieving media, which can exhibit gas separation properties superior to polymers, tend to be brittle and difficult to produce for large scale membrane separation processes. Considering this, the hyper rigid polymer structures investigated in this work were designed to mimic aspects of the structure of molecular sieving media such as zeolites and carbon molecular sieves while maintaining the process ability associated with polymers. In addition, a fundamental analysis of mixed matrix membrane, incorporating molecular sieving materials within a polymeric matrix, was performed. This analysis indicates that high performance membranes can potentially be achieved with careful materials section and defect elimination.

K-98-3 PUBLISHED
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques
Zimmerman, C.; Singh, A.; Koros, William J.
Typically, materials with high-performance transport properties such as zeolites, carbon molecular sieves, or hyper rigid polymers are inherently difficult or impossible to characterize by steady-state membrane permeation experiments used for conventional polymers.

K-99-1 PUBLISHED
Energetic and Entropic Contributions to Mobility Selectivity in Glassy Polymers for Gas Separation Membranes
Singh-Ghosal, A. and Koros, W.J.
Gas transport and separation properties of a series of glassy polymers from different families are studied, and energetic and entropic contributions to diffusivity selectivity are estimated for the oxygen/nitrogen gas pair.
**K-00-1 PUBLISHED**

**Formation of Defect-Free Polyimide Hollow Fiber Membranes for Gas Separations**  
Koros, W.J. and D.T. Clausi  

Ultra-thin and defect-free polyimide hollow fiber membranes were formed using a dry-jet, wet quench process with spin dopes both with and without volatile solvents. Fibers were spun from the commercially available polyimide, Matrimid 5218, were precipitated in an aqueous quench bath. Spin dopes comprised volatile and non-volatile solvents, polymer, and non-solvent. The influences of dope composition, spinning parameters, and dehydration procedures on the membrane morphology and performance were investigated. Without post-treatment (i.e., defect repair), the fibers exhibited skin thicknesses on the order of 1000 Å and O₂/N₂ selectivities ranging from 90 to 100% of those determined for dense, solution-cast films. The 25 um OD/125Um ID fibers were spun at take-up rates comparable to those used in commercial processes (i.e., 50m/min) and had macrovoid-free morphologies.

**K-00-2 PUBLISHED**

**Olefin/paraffin Gas Separations with 6FDA-based Polyimide Membranes**  
Koros, W.J. and C. Staudt-Bickel  

Pure gas permeation and sorption experiments were carried out for the gases ethylene, ethane, propylene and propane using polyimides based on 4,4’-(hexafluoroisopropyliden) diphthalic anhydride (6FDA). Composite membranes and free films were used. Experiments were performed at 308 K and feed pressures up to 17 atm for theylene and ethane and 9atm for propylene and propane. Mixed gas permeation experiments were carried out with 5:50 olefin/paraffin feed mixtures. For all investigated polyimides, the ideal ethylene/ethane separation factor ranged between 3.3 and 4.4 and the ideal propylene/propane separation factor ranged between 10 and 16 at a feed pressure of 3.8 atm and 308K. In mixed gas permeation experiments, up to 20% lower selectivity was found for the ethylene/ethane separation and up to 50% reduced selectivity for the propylene/propane separation compared to the ideal selectivity. The influence of feed temperature on separation and permeation properties will be discussed based on pure gas permeability data at 298 and 308 K.

**K-00-3 PUBLISHED**

**Pushing the Limits on Possibilities for Large Scale Gas Separation: Which Strategies?**  
Koros, W.J. and R. Mahajan  

Opportunities abound to extend membrane markets for gas and vapor separations; however, the existing membrane materials, membrane structures and formation processes are inadequate to fully exploit these opportunities. The requirements for viability of membranes vary somewhat with each application. Nevertheless, the key requirements of durability, productivity and separation efficiency must be balanced against cost in all cases. The various 'contender' technologies for large scale gas separation membrane applications and the gas transport mechanisms are considered. The current spectrum of applications of gas separation membranes include: nitrogen enrichment, oxygen enrichment hydrogen recovery, acid gas (CO₂, H₂S) removal from natural gas and dehydration or air and natural gas. The current status and the limitations faced by the available membrane materials for each of these applications are discussed. Two key technical challenges exist. Achieving higher permeability for the relevant application with at least equivalent productivity is the first of these challenges. Maintaining these properties in the presence of complex and aggressive feeds is the second challenge. Attractive avenues to overcome these challenges for each application with be presented. Finally, several new membrane applications with immense potential (e.g. fuel cells and olefin-paraffin separations) are discussed.
Air Separation Properties for Flat Sheet Homogeneous Pyrolytic Carbon Membranes
Koros, W.J. and A. Singh-Ghosal
Journal of Membrane Science 174: 177-188, 2000
Carbon molecular sieve (CMS) membranes with attractive separation properties were formed by pyrolysis of a polymeric precursor. Defect-free membranes with oxygen/nitrogen permselectivities three times greater than the polymer precursor were obtained. Gas separation properties were also measured at intermediate stages during the pyrolysis protocol to study the evolution of entropic selectivity, which distinguished molecular sieving materials from typical polymeric materials. Initially, permeabilities increase dramatically during the pyrolysis process due to an increase in overall sorption coefficients. In the finally pyrolyzed membrane, however, permeabilities are three times lower than in the polymer precursor due to significantly lower oxygen diffusion coefficients. Nevertheless, the separation properties of the pyrolyzed membranes are well above the so-called property 'upper-bound trade-off curve' offer used to compare conventional polymeric materials. The increase in permselectivity is entirely due to an increase in mobility selectivity. Entropic selectivity increases are responsible for the higher mobility selectivity in the finally pyrolyzed membranes; however, energetic contributions were more significant for materials at the intermediates stage. Significant conclusions about the structure of the evolving molecular matrix can be drawn from the gas separation results.

Separation of Gas Mixtures with Polymer Membranes: A Brief Overview
Stern, S.A. and Koros, W.J.
Chimi Nouvelle 18 (72) 3201-3215, 2000.

Experimental Procedure Utilizing Head-Space Analytical Method of Obtaining Methanol/MTBE Mixed-Liquid Sorption Isotherms in a Glassy Polymer
Kamaruddin, H.D. and Koros, W.J.

Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide
Karmaruddin, H. D. and Koros, W.J.

Elevated Temperature Application of Polymer Hollow-Fiber Membranes
Woods, D. and Koros, W.J.
Three asymmetric hollow-fiber polymer membrane systems were studied for application in elevated temperature, low feed pressure systems: (1) a single component polyaramide, (2) a single component polyimide, and (3) a composite polyimide on a polyimide/polyetherimide blend support. Permeation driving force was increased for the 2.2 psig feed pressure by sweeping an inert gas along the downstream side of the membrane. Both cocurrent and countercurrent sweep flow patterns were examined with only minimal differences found. The polyaramide membrane was stable in the entire range of temperatures tested (23-220°C). After utilizing a silicone rubber post-treatment, the membrane exhibited a hydrogen permeance of approximately 300 GPU at 175°C with a hydrogen to n-butane selectivity of 700. The polyimide-containing membranes had superior room-temperature properties; however, the thin skins aged at elevated temperatures. This aging effect decreased the permeance of the membranes approximately 40% at 175°C and slightly increased the permselectivity; however, the effects of aging leveled out over 200-250 h at 175°C and the membrane properties became constant. At this level, the polyimide membranes exhibited approximately 400 GPU of hydrogen permeance with a 660 selectivity to n-butane.
Pervaporative Introduction of Organic Vapors into High-Pressure Gas Feeds
Djoekita, G.; Vu, D.Q.; Koros, W.J.

Factors Controlling Successful Formation of Mixed-Matrix Gas Separation Materials
Mahajan, R. and Koros, W.J.

Diffusion in Polymer Glasses
Koros, W.J. and Punsalan, D.

Membranes, Synthetic, Application
Lee, E.K. and Koros, W.J.

High Pressure Co2/CH4 Separation Using Carbon Molecular Sieve Hollow Fiber Membranes
Vu, D.Q.; Miller, S.J.; Koros, W.K.
Carbon molecular sieve (CMS) hollow fiber membranes have been investigated for CO2/CH4 separation. High-pressure (up to 1000 psia), mixed-gas feeds of 10% CO2/90% CH4 on the shell side were examined for three different temperatures (24, 35, and 50°C). The mechanical, permeance, and selectivity stabilities of the CMS membranes under high pressure were encouraging and could be industrially relevant for many high-pressure applications, such as CO2 removal from natural gas. Two asymmetric polyimide precursor fibers, 6FDA/BPDA-DAM and Matrimid 5218, were pyrolyzed under vacuum to form the CMS membrane fibers. When pyrolyzed under identical protocols, the two types of CMS fibers had different permeation properties and physical characteristics. Modifications of the pyrolysis protocol and conditions were explored. Increasing the final pyrolysis temperature was shown to dramatically increase the CO2/CH4 selectivity (>600) of the CMS membranes but was detrimental to the CO2 permeance. On the other hand, using a helium purge gas instead of a vacuum environment during pyrolysis did increase CO2 permeance but resulted in a significant loss of CO2/CH4 selectivity. Shortening the thermal soak time at the final pyrolysis temperature was the most effective approach to increasing the CO2 permeance while maintaining the CO2/CH4 selectivity.

An Investigation of the Effects of Pyrolysis Parameters on Gas Separation Properties of Carbon Materials
Steel, K. and Koros, W.J.
Carbon, in press
A significant extension of an earlier analysis of molecular sieving carbons formed from polymeric precursors is reported for separation of important gas pairs including O2/N2, CO2/CH4, and C3H6/C3H8. Previously, it was shown that changing the time or temperature of the pyrolysis protocol for a commercially available polyimide (Matrimid) altered the final properties of the carbons produced. Changing the precursor material is shown in this study to also affect the final carbon material obtained for a given final pyrolysis temperature.
The separation of olefins from paraffins is energy intensive, and consequently polymer membrane based separations have been considered as an attractive alternative. Although much research has been conducted on polymer membranes for the C3H6/C3H8 separation in recent years, no comprehensive review exists that considers and evaluates all of the available literature data. A review is necessary in order to define the challenges that must be overcome to achieve adequate separation performance using polymer membranes. The goal of this paper is to present the experimentally observed C3H6/C3H8 upper bound based on available literature data, as well as C3H6/C3H8 permeation measurements reported herein. A mathematical prediction of the C3H6/C3H8 upper bound curve was also developed, and it compares very well to the most credible experimentally observed C3H6/C3H8 upper bound.

Mixed Matrix Membrane Materials: An Answer to the Challenges Faced by Membrane Based Gas Separation Today?
J. Chin. Inst. Chem. Engrs., 33(1) 77-86
The current status and the limitations faced by available membrane materials used for gas separations are reviewed. One of the biggest challenges that emerges from this survey is the need for materials with enhanced permselectivity with at least equivalent productivity compared to current materials. So called "mixed matrix" materials comprising molecular sieving entities such as zeolites dispersed in conventional polymer materials are possibly attractive solutions to this challenge.

An Investigation of Porosity of Carbon Materials and Related Effects on Gas Separation Properties
Steel, K. and Koros, W
Manuscript
Carbon molecular sieving membranes are chemically robust materials with tailorable gas transport properties of O2/N2, CO2/CH4 and C3H6/C3H8 separations. Such carbon materials were formed in this study by the pyrolysis of polyimide precursors. The final pyrolysis temperature was varied to alter the carbon structure, which changed the average pore size. Characterization of the porosity of these materials and how this feature changes when pyrolysis conditions are varied could guide the systematic control of these materials.

Challenges in Forming Successful Mixed Matrix Membranes with Rigid Polymeric Materials
Mahajan, R.; Burns, R.; Schaeffer, M.; Koros, W.J.
Mixed matrix materials comprised of molecular sieve domains embedded in processable polymer matrices have the potential to provide membranes with higher permselectivity and equivalent productivity compared to existing membrane materials. It has been shown that successful mixed matrix materials can be formed using relatively low glass transition (Tg) polymers that have a favorable interaction with the sieves. This article extends this earlier work to include the use of more practical rigid matrix polymers with high Tgs that can ultimately be used in forming high-performance mixed matrix layers for composite membranes.

Mixed Matrix Membrane Materials with Glassy Polymers. Part 1
Mahajan, R. and Koros, W.J.
Mixed matrix materials comprising molecular sieve entities embedded in a polymer matrix can economically increase membrane permeability, thereby addressing a key challenge hindering the
widespread use of membrane-based gas separations. Prior work has clarified the importance of proper selection of the dispersed sieve phase and the continuous matrix phase based on their intrinsic transport properties. Proper material selection for the two components, while necessary, is not sufficient since the interfacial contact zone appears to be equally important to achieve optimum transport properties. Specifically, it was found that chemical coupling of the sieve to the polymer can lead to better macroscopic adhesion but to even poorer transport properties than in the absence of the adhesion promoter. This counterintuitive behavior may be attributed to a nanometric region of disturbed packing at the polymer sieve interphase. The poor properties are believed to result from “leakage” of gas molecules along this nanometric interface. The Maxwell model was modified to take into account these complexities and to provide a first order quantification of the nanometric interphase. The analysis indicates that optimization of the transport properties of the interfacial region is key to the formation of ideal mixed matrix materials. This approach is used in the second part of this paper to form successful mixed membrane materials.

K-02-9 PUBLISHED
Mixed Matrix Membrane Materials with Glassy Polymers. Part 2
Mahajan, R. and Koros, W.J.
Analysis presented in Part 1 of this paper indicated the importance of optimization of the transport properties of the interfacial region to achieve ideal mixed matrix materials. This insight is used in this paper to guide mixed matrix material formation with more conventional gas separation polymers. Conventional gas separation materials are rigid, and, as seen earlier, lead to the formation of an undesirable interphase under conventional casting techniques. We show in this study that if flexibility can be maintained during membrane formation with a polymer that interacts favorably with the sieve, successful mixed matrix materials result, even with rigid polymeric materials. Flexibility during membrane formation can be achieved by formation of films at temperatures close to the glass transition temperature of the polymer. Moreover, combination of chemical coupling and flexibility during membrane formation produces even more significant improvements in membrane performance. This approach leads to the formation of mixed matrix material with transport properties exceeding the upper bound currently achieved by conventional membrane materials. Another approach to form successful mixed matrix materials involves tailoring the interface by use of integral chemical linkages that are intrinsically part of the chain backbone. Such linkages appear to tighten the interface sufficiently to prevent “nonselective leakage” along the interface. This approach is demonstrated by directly bonding a reactive polymer onto the sieve surface under proper processing conditions.

K-02-10 PUBLISHED
Strategies for Purging the Pellicle Space for 157 nm Lithography
Mahajan, R.; Vu, D.Q.; Koros, W.J.

K-02-11 PUBLISHED
The Effects of Crosslinking Chemistry on CO₂ Plasticization of Polyimide Gas Separation Membranes
Wind, J.D.; Staudt-Bickel, C.; Paul, D.R.; Koros, W.J.

K-03-1 PUBLISHED
Mixed Matrix Membranes using Carbon Molecular Sieves I. Preparation and Experimental Results
Vu, De Q.; Koros, W.J.; Miller, S.J.
Carbon molecular sieves (CMSs) have been incorporated into two different polymer matrices to form mixed matrix membrane films for gas separations. The CMSs were formed by pyrolysis of a polyimide (Matrimid®) precursor to a final temperature of 800°C. The CMS membrane films have an intrinsic CO₂/CH₄ selectivity of 200 with a CO₂ permeability of 44 Barrers and an O₂/N₂
selectivity of 13.3 with an O$_2$ permeability of 24 Barrers at 35°C. The pyrolyzed CMS materials were ball-milled into fine particles, ranging in size from submicron to 2µm, prior to dispersal in casting solvent. Mixed matrix films comprising high CMS particle loadings (up to 35 wt.%) dispersed within two polymer matrices (Matrimid® 5218 and Ultem® 1000) were successfully formed from flat-sheet solution casting. For Ultem®-CMS mixed matrix membrane films, pure gas permeation tests showed enhancements by as much as 40% in CO$_2$/CH$_4$ selectivity over the intrinsic CO$_2$/CH$_4$ selectivity of the pure Ultem® polymer matrix. Likewise, for Matrimid®-CMS mixed matrix films, enhancements by as much as 45% in CO$_2$/CH$_4$ selectivity were observed. Similar enhancements were observed when these mixed matrix membrane films were examined for the O$_2$/N$_2$ separation (8 and 20% for the Ultem®-CMS and Matrimid®-CMS mixed matrix films, respectively). Effective permeabilities of the fast-gas penetrants (O$_2$ and CO$_2$) through the mixed matrix membranes were also significantly enhanced over the intrinsic permeabilities of the Ultem® and Matrimid® polymer matrices. These encouraging selectivity and permeability enhancements confirm that mixed matrix membrane behavior is achievable with CMS particles.

**K-03-2** PUBLISHED

**Mixed Matrix Membranes using Carbon Molecular Sieves II. Modeling Permeation Behavior**

Vu, De Q.; Koros, W.J.; Miller, S.J.

Journal of Membrane Science 211 (2003) 335-348

Mixed matrix membranes have been formed from flat-sheet solution casting of carbon molecular sieves (CMS) dispersed within two different polymer matrices. In a preceding paper (Part I), the performance of these mixed matrix membrane films has been demonstrated for gas separations. It was shown that the CMS particles produced a mixed matrix or heterogeneous membrane having significantly enhanced effective permselectivities (CO$_2$/CH$_4$ and O$_2$/N$_2$) and fast-gas permeabilities (CO$_2$ and O$_2$) over the intrinsic properties of the pure polymer matrix phase alone. For the CO$_2$/CH$_4$ separation, enhancements by as much as 45% in CO$_2$/CH$_4$ permselectivity and 200% in CO$_2$ permeability over the corresponding intrinsic permeation properties of the pure polymer matrix phases were observed. These performance enhancements increased incrementally as the loading CMS particles (up to 35% by weight) being dispersed within the two polymer matrices (Matrimid® 5218 and Ultem® 1000) increased. In this paper, these experimental findings are compared with two theoretical mixed matrix models, the Maxwell and the Bruggeman Models. In general, the Bruggeman Model was observed to consistently predict both higher permeabilities and permselectivities than the Maxwell Model. For the Ultem®-CMS mixed matrix films, the Bruggeman Model reasonably predicted the experimental permeability data, while the Maxwell Model underpredicted the gas permeabilities. Both models, however, gave permselectivity predictions that compared reasonably well with experimental values for the Ultem®-CMS mixed matrix films. For the Matrimid®-CMS mixed matrix films, both models significantly overpredicted the observed gas permeabilities and permselectivities. A matrix rigidification phenomenon in Matrimid® was postulated to be occurring in the region or zone near the CMS surface. An ad hoc adaptation to the Maxwell Model was employed to account for this phenomenon. Predictions from this modified approach gave better agreement with experimental values for the Matrimid®-CMS mixed matrix films.

**K-03-3** PUBLISHED

**Effect of Condensable Impurities in CO$_2$/CH$_4$ Gas Feeds on Carbon Molecular Sieve Hollow-Fiber Membranes**

Vu, De Q.; Koros, W.J.; Miller, S.J.


The presence of vapor impurities in gas streams presents problems for both polymeric and carbon materials. For natural gas processing applications, it is suspected that condensable hydrocarbons can cause significant performance declines for polymer membranes. This paper investigates the effect of these condensable vapor impurities on the performance of carbon molecular sieve (CMS) hollow-fiber membranes. Toluene and n-heptane were separately used as representative aromatic and paraffinic impurities, respectively, in 10% CO$_2$/90% CH$_4$ gas feed streams. Shell-side feed pressures of up to 900 psia and temperatures of 35 and 50°C were used. Experimental results
reveal that the CMS membranes maintained CO₂/CH₄ selectivity with a maximum of 20% reduction in CO₂ permeance during exposure to gas feeds containing these impurities, in comparison to “clean” gas feeds without these impurities. Furthermore, a simple in situ regeneration procedure of moderate heating (70-90°C) with dry N₂ purge gas resulted in almost complete recovery of CO₂ permeance without loss of CO₂/CH₄ selectivity. Comparisons with polyimide membrane performance in similar adverse environments are also presented. The robustness and regeneration capabilities of the CMS fibers offer noteworthy advantages over polyimide fibers, which can display significant losses in membrane performance under similar conditions.

K-04-1
An Investigation of the Effects of Pyrolysis Parameters on Gas Separation Properties of Carbon Materials
Steel, K.M. and Koros, W.J.
A significant extension of an earlier analysis of molecular sieving carbons formed from polymeric precursors is reported for separation of important gas pairs including O₂/N₂, CO₂/CH₄ and C₃H₆/C₃H₈. Previously, it was shown that changing the time or temperature of the pyrolysis protocol for a commercially available polyimide (Matrimid®) altered the final properties of the carbons produced. Changing the precursor material is shown in this study to also affect the final carbon material obtained for a given final pyrolysis temperature. Analysis of low temperature carbon dioxide adsorption isotherms using density functional theory was employed to characterize the microporosity of the materials. Results are given here for a different packing-inhibited polyimide precursor (6FDA/BPDA-DAM). Sorption, permeation and diffusion data are compared with those obtained using the more densely packed commercial polyimide precursor Matrimid® studied earlier. Thermal soak was also investigated and the effect on permeation properties determined for carbons using both precursors. The results indicate that carbons from both precursors have size-selective ultramicropores as well as larger nonselective micropores that provide high capacity sorption sites for penetrants. High permselectivities, combined with high permeabilities are found for some of the samples when compared with conventional polymer materials. A hypothetical ultramicropore size distribution is shown to be useful to relate transport data to results from more commonly used characterization techniques such as pore size distribution analysis.

K-04-2
Characterization of Integral-Skin Layers in Hollow Fiber Gas Separation Membranes
Carruthers, S.B.; Ramos, G.; Koros, W.J.
Polym. Engr. & Sci., submitted

L-82-1 PUBLISHED
Cyclic Hydrocarbon-Water Separations Using a Pressure-Driven Membrane Separation Process
Lloyd, D.R.; M. Babai-Pirouz; J.M. Dickson
This project is concerned with the factors affecting the removal of cyclic hydrocarbons from water by a pressure-driven membrane separation (L-82-1). Reverse osmosis separation (L-82-1) of single-solute aqueous solutions is reported. Results are explained in terms of the magnitude and direction of solute-membrane interactions.

L-82-2 $10.00
The Enhancement of Albumin Binding by Alkyl Derivitization of Cellulose Acetate Membranes
Frautschi, J.R.
Master's thesis
In-depth study of the use of surface passivation by albumin adsorption as a method for improving the thromboresistance of polymeric materials. Portions of this thesis were published in L-83-6.
Mixed Polymer-Solvent Thermodynamics by Gel Permeation Chromatography
Robledo-Muniz, J.G.
Master's thesis
Equilibrium studies of the partially miscible system PS-polybutadiene-chloroform were made using gel permeation chromatography to analyze the conjugate solutions. A summary of the research done for this thesis appears in L-84-13.

Characterization of Dense Sulfonated Polysulfone Membranes
Dinno, M.A.; Y. Kang; D.R. Lloyd; J.E. McGrath; J.P. Wightman
An extensive study of dense membranes made from sulfonated polysulfones having six different degrees of sulfonation. The effect of the degree of the sulfonation and the counter ion on the properties of the membrane were examined.

Asymmetric Membrane Preparation from Nonsolvent Casting Systems
Kinzer, K.E.; D.R. Lloyd; J.P. Wightman; J.E. McGrath
Desalination 46:327-34 (1983)
The use of two nonsolvents serving as a cosolvent system in the formation of asymmetric phase inversion membranes (L-83-2) was investigated. The structure of each membrane was evaluated using SEM; the performance was evaluated for use in pressure-driven membrane separation (L-83-2) processes.

Physicochemical Interactions in Pressure-Driven Membrane Separation of Glucose, Ascorbic Acid, Citric Acid, and Mannitol from Single Solute Aqueous Solutions
Theil, S.W. and D.R. Lloyd
Desalination 46:399-406 (1983)
The pressure-driven membrane separation of dilute single-solute aqueous solutions of glucose, ascorbic acid, citric acid, and mannitol was studied at low pressure using an asymmetric cellulose acetate membrane in a batch stirred cell. The observed results are explained on the basis of significant physicochemical interactions (L-83-3) between solute, solvent, and membrane.

Ion-Containing Polymers. III: Synthesis and Characterization of Sulfonated Poly(arylene Ether Sulfoes)
Johnson, B.C.; C. Tran, I. Yilgor; M. Iqbal; J.P. Wightman, D.R. Lloyd; J.E. McGrath
Polymer Preprints, American Chemical Society Division of Polymer Chemistry 21(2):31-34 (1983)
This paper presents results of recent work that deals with synthesis details, important aspects of purification, and continued efforts at improved analytical methods. One particular aspect of the work concerns the investigation of soxhlet extractions on the sulfonated PSF, with emphasis on the characterististics and quality of the resultant hydrophilic films.

Aromatic Hydrocarbon-Water Separations by a Pressure-Driven Membrane Separation Process
Dickson, J.M.; Babai-Pirouz, M.; D.R. Lloyd
This project is concerned with the removal of aromatic hydrocarbons from water by a pressure-driven membrane separation process. Reverse osmosis separation (L-83-5) of single-solute aqueous solutions is reported. Results are explained in terms of the direction and magnitude of solute-membrane interactions.
Alkyl Derivatized Cellulose Acetate Membranes with Enhanced Albumin Affinity
Frautschi, J.R.; M.S. Munro; D.R. Lloyd; R.C. Eberhart

The technique of surface passivation by albumin adsorption as a way to improve the thromboresistance of polymeric materials is reported. Emphasis is on the use of this technique for cellulose acetate membranes (L-83-6).

Preparation and Characterization of Asymmetric Sulfonated Polysulfone Membranes
Kinzer, K.E.
Master's thesis
The use of two nonsolvents in the formation of asymmetric phase inversion membranes was investigated. The performance of the membranes for use in pressure-driven membrane separation (L-83-7) processes was evaluated.

Removal of Cyclic Hydrocarbons
Babai-Pirouz, M.
Master's thesis
Factors affecting the removal of cyclic hydrocarbons from water by a pressure-driven membrane separation process were studied. Results are explained in terms of magnitude and direction of solute-solvent-membrane interactions. Results of this thesis research are summarized in L-82-1, L-83-5, and L-84-6.

Characterization of Membranes for Use in Pressure-Driven Membrane Separation Processes
Thiel, S.W.
Master's thesis
A mathematical analysis of a steady-state pressure-driven membrane separation process was developed and used as the basis for a method for characterizing membranes using flux and solute rejection data. Summary information about this thesis research can be found in L-82-1, L-83-3, and L-84-6.

Synthesis and Characterization of Sulfonated Poly(arylene ether sulfones)
Johnson, B.C.; I. Yilgor; C. Tran; M. Iqbal; J.P. Wigthman; D.R. Lloyd; J.E. McGrath

The synthesis and physical characterization of sulfonated PSF are addressed. A detailed synthesis route is provided and methods that yield determinable levels of sulfonation are described.

Material Selection and Evaluation for Liquid Separation Membranes
Lloyd, D.R.; T.B. Meluch; K.E. Kinzer

This paper presents one possible approach to membrane material selection for pressure-driven separation processes. Methods for evaluating potential membrane materials are also discussed.

Asymmetric Membrane Preparation from Solventless Casting Systems
Lloyd, D.R.; T. Prado; K.E. Kinzer; J.P. Wigthman; J.E. McGrath

This paper reports on a number of concepts that should allow for the preparation of asymmetric membranes from a wider variety of polymers than previously believed possible.
L-84-4 PUBLISHED
Influence of Polymer Molecular Weight on Selected Thermodynamic Properties of Polymer/Solvent Systems and the Application of the UNIFAC Theory
Tseng, H.S. and D.R. Lloyd
Original and modified UNIFAC methods were used to determine solvent activity, clustering function of the solvent, and the interaction parameters; these were compared with experimental data. Results indicate that the influence of molecular weight on these three solvent properties is insignificant.

L-84-5 PUBLISHED
The Use of Gel Permeation Chromatography for the Determination of Polymer-Polymer Interaction Parameters
Narasimhan, V.; C.M. Burns; R.Y.M. Huang; D.R. Lloyd
The use of gel permeation chromatography for the quantitative analysis of composition in mixed polymer systems is presented. Also includes equations developed for the determination of polymer-polymer interaction parameters for monodisperse and polydisperse polymers.

L-84-6 PUBLISHED
The Effect of Solute-Membrane Affinity on Cyclic Hydrocarbon-Water Transport in Pressure-Driven Membrane Separation Processes
Babai-Pirouz, M.; S.W. Theil; D.R. Lloyd; J.M. Dickson
Experimental results for the pressure-driven membrane separation of cyclic hydrocarbons from dilute binary aqueous solution using asymmetric cellulose acetate membranes (L-84-6) are reported in this article.

L-84-7 PUBLISHED
Correlation of Low-Concentration Organic Solubility in Polymers Using the Principle of Corresponding States
Tseng, H.S.; P. Wong; T.C. Ward; J.W. Barlow; D.R. Lloyd
Correlation equations based on the principle of corresponding states were developed by using solubility data available in the literature and from the results of this study. These equations are useful in estimating thermodynamic properties when no data other than critical pressure and temperature are available.

L-84-8 PUBLISHED
Use of the Three-Component Solubility Parameter in Asymmetric Phase-Inversion Membrane Preparation
Ventoza, T.P.; S.A. Gouye; D.R. Lloyd
Explains why Hansen's solubility parameter is a logical choice for selection of solvents for the preparation of asymmetric membranes.

L-84-9 PUBLISHED
Membrane Materials Science: An Overview
Lloyd, D.R.
An overview of membrane materials science. Includes material selection, characterization, and evaluation, and membrane preparation, characterization, and evaluation.
Selection and Evaluation of Membrane Materials for Liquid Separations
Lloyd, D.R. and T.B. Meluch
Physicochemical interactions between permeating molecules and the macromolecules that comprise the membrane structure are considered. Dispersive, polar, and H2-bonding interactions are used to establish an index which is useful for selecting membrane material.

Correlation of Organic Solubility in Poly(vinyl acetate)
Tseng, H.; D.R. Lloyd; T.C. Ward
Polymer Communications 25(9):262-65 (1984)
This paper reports empirical correlations for prediction of the solubility of polar, nonpolar, aromatic, and nonaromatic solutes in poly(vinyl acetate). The usefulness of these equations in predicting solution thermodynamic properties is illustrated.

Correlation of Solubility in Polydimethylsiloxane and Polyisobutylene Systems in Polydimethylsiloxane and Polyisobutylene Systems
Tseng, H.S.; D.R. Lloyd; T.C. Ward
This paper presents empirical correlations for the estimation of solubilities and other thermodynamic properties of nonpolar and slightly polar probe molecules in polydimethylsiloxane and polyisobutylene.

Phase Behavior Studies of the System Polystyrene-Polybutadiene-Chloroform. I: Application of the Flory-Huggins Theory
Robledo-Muniz, J.G.; H.S. Tseng; D.R. Lloyd; T.C. Ward
Study of the equilibrium phase behavior of the partially miscible system PS-polybutadiene-chloroform. The Flory-Huggins theory was used to determine the polymer-polymer interaction parameter (L-84-13).

Phase Inversion Sulfonated Polysulfone Membranes
Kinzer, K.E.; D.R. Lloyd; M.S. Gay; J.P. Wigthman; B.C. Johnson; J.E. McGrath
Introduces a number of concepts that should enable the preparation of asymmetric membranes from a wider variety of polymers than previously believed possible. Hansen's three-component solubility parameter is used to select casting solution components and compositions.

Solubility of Nonpolar and Slightly Polar Organic Compounds in Low-Density Polyethylene by Inverse Gas Chromatography with Open Tubular Column
Tseng, H.S.; D.R. Lloyd; T.C. Ward
Inverse gas chromatography with an open tubular column was used to determine low-pressure solubilities of thirteen organic solutes in low-density polyethylene.
Use of Solubility Parameters in Asymmetric Phase-Inversion Membrane Preparation
Prado, T.
Master's thesis
The use of partial solubility parameters in membrane preparation is demonstrated. The selection of solution components and solution composition is facilitated by their use. In addition, the membrane formation steps are easily explained in terms of these parameters. In addition to, other publications from this thesis are forthcoming.

Analysis of Transport in a Pressure-Driven Membrane Separation Process
Thiel, S.W.; D.R. Lloyd; J.M. Dickson
A theoretical analysis was developed to model and predict membrane performance. The model is independent of any proposed transport mechanisms, but the final result is similar to Merten's finely porous model.

Physicochemical Interpretation of the Behavior of a Pressure-Driven Membrane Separation Process
Thiel, S.W.; D.R. Lloyd; J.M. Dickson
The model developed in L-85-1 was applied to systems in which the solute-membrane affinity dominates transport. The equation coefficients were interpreted in terms of the strength of physicochemical interactions (L-85-2).

Inverse gas chromatography was used to characterize the physicochemical interactions between low molecular weight compounds and polymers. Compounds of varying polarity were investigated. A number of specially made polymers were studied. The results are to be used to develop filters for removing chemical warfare agents from air.

The thermodynamics and phase behavior of PS-polyisoprene-toluene and PS-polybutadiene-chloroform were studied. The original Flory-Huggins theory was modified to explain results. Publications from this dissertation are forthcoming.

The ability of various models to adequately describe membrane performance in the presence of strong solute-membrane affinity was investigated. A version of the finely porous model appears to work best in these situations. The following papers had their origin in this dissertation: L-83-5 and L-84-6.
Synthesis, Analysis, and Albumin Adsorption Properties of Alkylated Poly-4-Vinyl-Pyridine Grafted Polyethylene Terephthalate
Tingey, K.G.
Master's thesis
The albumin adsorption properties of PET were modified as a means of increasing blood-compatibility. The modification involved the grafting of poly-4-vinyl-pyridine to the PET, then alkylating the product. Proprietary research funded by industrial concern.

Poly(ether sulfone) Membranes for Desalination: Membrane Preparation and Characterization
Ventoza, T.P. and D.R. Lloyd
Desalination 56:381-94 (1985)
Desalination membranes were prepared from PES by casting from a ternary system comprised of the polymer, a nonsolvent, and a swelling agent. Phase inversion was induced by a combination of evaporation and gelatin in a second nonsolvent. Membrane performance was related to the composition of the initial casting solution, the composition of the cast film at the time of gelatin, and the solution history. Partial solubility parameters were used to quantify the compositions and to facilitate a visualization of the membrane preparation process.

The Effect of N-Pentanol on the Transport of Salt in Reverse Osmosis
Chumley, L.J.
Master's thesis
The separation of NaCl from water via cellulose acetate membranes was monitored in the presence and absence of the solute 1-pentanol. This solute has a strong affinity for the membrane and thus alters the membrane performance in desalination. These experiments represent our initial studies in the area of fouling.

Solute-Membrane Interactions in Dilute Aqueous Alcohol Solutions
Costain, C.T.
Master's thesis
A series of three-carbon and six-carbon alcohols were studied to investigate the role of solute structure in alcohol-water separations via pressure-driven membrane processes (L-86-2). Performance differences were related to differences in the effective size of the solutes and differences in solute-membrane chemical affinities. The latter was particularly influential in the partitioning step of permeation.

Interaction Between Organo-Phosphorus Ester and Poly(styrene-co-vinyl benzyl hexafluorodimethyl carbinol)
Lim, G.
Master's thesis
Inverse gas chromatography was used to investigate the nature of the chemical interactions between organophosphorus esters and poly(styrene-co-vinyl benzyl hexafluorodimethyl carbinol). This polymer had been used in earlier studies (L-85-3) for the removal of simulated chemical warfare agents from air (L-86-3).
Transport of Multicomponent Liquid Solutions of Nonelectrolytes in Pressure-Driven Membrane Separation Processes
Thiel, S.W.
PhD dissertation

The transport behavior of a number of ternary solutions through cellulose acetate membranes was studied. A model to describe the observed behavior was developed using the Stefan-Maxwell equations as a starting point. The coefficients were discussed in terms of frictional interactions.

Polymer Sorbents for Phosphorus Esters: I. Selection of Polymers by Analog Calorimetry
Chang, Y.; J. Noriyan; D. R. Lloyd; J. W. Barlow
Heats of mixing of a variety of solvents with dimethyl methyl phosphonate (DMMP) are presented. A qualitative correlation between the exothermicity of the heat of mixing of DMMP with a particular solvent and sorption of DMMP by polymers containing structural units analogous to the solvent is observed. By this approach, poly (styrene-co-vinyl benzyl hexafluoro-dimethyl carbinol) was identified as a good sorbent for DMMP.

Polymer Sorbents for Phosphorus Esters: II. Hydrogen Bond Driven Sorption in Fluoro-Carbinol Substituted Polystyrene
Barlow, J.W.; P.E. Cassidy; D.R. Lloyd; C.J. You; Y. Chang; P.C. Wong; J. Noriyan
A series of copolymers containing styrene and vinyl benzyl hexafluorodimethyl carbinol were prepared by substitution of hexafluoroacetone on PS followed by hydrolysis and by copolymerization of styrene and substituted styrene monomers. Sorption of DMMP vapor in the copolymers was examined at 135°C by the piezoelectric sorption method (L-86-6) and at 135°C and 165°C by inverse gas chromatography. The results were analyzed by the Flory-Huggins equation. A simplified thermodynamic analysis, based on experimental studies of the H2 bond formed between DMMP and hexafluoro-isopropanol, an analog of the fluorocarbinol, is shown to predict the Chi dependency on copolymer composition.

Interaction Parameters of Polystyrene-Polyisoprene-Toluene Systems at 45°C via Gel Permeation Chromatography
Tseng, H. S.; D. R. Lloyd; T. C. Ward
The equilibrium phase diagrams of narrow molecular weight distribution samples of PS and permeation chromatography. The polymer-polymer interaction parameter was evaluated based on the Flory-Huggins approach. The influence of the polymer molecular weight and polymer-solvent interaction parameters on the shape and location of the binodal curve, the location of the critical point, and the polymer-polymer interaction parameter (L-86-7) was investigated.

Application of the Stefan-Maxwell Equations to the Pressure-Driven Membrane Separation of Dilute Multicomponent Solutions of Nonelectrolytes
Thiel, S.W. and D.R. Lloyd
The Stefan-Maxwell equations are applied to the steady-state pressure-driven membrane separation of dilute multicomponent liquid solutions of nonelectrolytes. An analytical solution to the Stefan-Maxwell equations is obtained in which permeation is described using parameters with unambiguous physical interpretations. These results indicate that at a given total flux through the membrane, the rejection of a given solute can be written as the rejection of that solute from binary solution plus multicomponent corrections that are proportional to the permeation mole fractions of...
the other solutes in the system. It is proposed that multicomponent effects arise due to differences
in the physicochemical natures of the permeants.

L-87-2 PUBLISHED
Thermodynamic Interaction in Polybutadiene/Solute Systems by Inverse Gas Chromatography
Tseng, H.S.; P.C. Wong; D.R. Lloyd; J.W. Barlow
The dependence of polymer-solute interactions on temperatures in the range from 66°C to 96°C
was studied by inverse gas chromatography (IGC). A correlation equation was developed for
estimation of the specific retention volume of nonpolar and slightly polar solutes in polybutadiene.
Using equation-of-state solution theory, thermodynamic interaction was discussed in terms of
contact energy and equation-of-state contributions in polybutadiene/solute systems. It is found that
equation-of-state theory serves better than the Flory-Huggins theory as a comprehensive model to
describe the temperature dependence of thermodynamic interaction.

L-87-3
Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Warzel and Wang for the Liquid Separations Using
Membranes Study Group Meeting.

L-87-4 PUBLISHED
Phase Behavior Studies of the System Polystyrene-Polybutadiene-Chloroform. II. Modification of the
Flory Huggins Theory
Tseng, H.S.; D.R. Lloyd; T.C. Ward
Polymer Engineering and Science 27(22):1688-92 (1987)
Phase behavior of polymer-polymer-solvent systems can be determined using gel permeation
chromatography. This technique enables one to generate the binodal curve and tie lines relating
equilibrium phases, to locate the critical point, and through the use of an appropriate solution
theory, to calculate interaction parameters. Previous studies of the incompatible PS-polybutadiene-
chloroform system indicated that the classical Flory-Huggins theory yields an anomalous behavior
of negative interaction parameters. Probable causes are specific interactions due to the polar nature
of chloroform plus failure to account for the concentration dependence of the PS-chloroform
interaction. A modified version of the Flory-Huggins theory incorporating concentration
dependence of polymer-solvent interactions was used to re-evaluate the PS-polybutadiene-
chloroform systems. This approach yields positive interaction parameters for the incompatible
system PS and polybutadiene.

L-87-5 PUBLISHED
Phase Behavior of Polystyrene-Polyisoprene-Toluene Systems in the Temperature Range 15 to 45°C
Tseng, H.S.; D.R. Lloyd; T.C. Ward
The phase behavior of narrow molecular weight distribution samples of PS and polyisoprene in
the presence of toluene was investigated by means of gel permeation chromatography.
Equilibrium phase diagrams, tie lines, and critical points for a number of partially miscible PS-
polyisoprene-toluene systems were generated at 15°C and 30°C and 1 atm pressure. The data was
combined with previously reported results at 45°C. With the experimentally determined phases
compositions along with literature values of the polymer-solvent interaction parameters, the
polymer-polymer interaction parameter was evaluated using the Flory-Huggins theory. The
influence of temperature, polymer molecular weight, and polymer-solvent interaction parameters
on the size, shape, and location of the equilibrium phase curve, the location of the critical point,
and the polymer-polymer interaction parameter (L-87-5) was studied.

L-87-6
Membranes for Liquid Separations: Overview, Review, and Preview
Handout for SRP Membrane Study Group Meeting, October 1987
Review of research results and future directions for research.
**L-88-1 PUBLISHED**  
Multicomponent Effects in the Pressure-Driven Membrane Separation of Dilute Multicomponent Solutions of Nonelectrolytes  
Thiel, S.W. and D.R. Lloyd  
The rejection of mannitol, 1,6-hexanediol, and 1-pentanol from dilute binary and ternary aqueous solutions was measured using asymmetric cellulose acetate membranes (L-88-1). For the binary systems, mannitol rejection was greater than 1,6-hexanediol rejection, which was in turn greater than 1-pentanol rejection. The presence of either 1,6-hexanediol or 1-pentanol caused an increase in mannitol rejection; the presence of mannitol caused a decrease in 1-pentanol rejection. 1-Pentanol rejection is independent of the presence of 1,6-hexanediol. 1,6-Hexanediol rejection is independent of the presence of either mannitol or 1-pentanol. The observed multicomponent effects are not caused by frictional coupling of solute fluxes; a physical model for the membrane that is consistent with the observed multicomponent effects is proposed.

**L-88-2 PUBLISHED**  
Microporous Membrane Formation via Thermally Induced Phase Separation  
Lloyd, D.R.; J.W. Barlow; K.E. Kinzer  
Microporous membranes have been prepared via thermally induced phase separation (TIPS) of polymer-diluent mixtures. The process is discussed in terms of the thermodynamics of the binary mixture and the phase separation mechanism. It is demonstrated that membranes can be produced by liquid-liquid phase separation followed by solidification of the polymer, or by solid-liquid phase separation. Liquid-liquid phase separation can proceed via nucleation and growth of the polymer-lean phase or via spinodal decomposition, depending on the cooling rate. The former results in a polymer matrix containing spherical cells connected by circular pores; the latter results in a lacy structure of co-continuous polymer and void phases. Solid-liquid phase separation proceeds via nucleation and growth of polymer crystals to produce a variety of structures, depending on crystallization kinetics. Polypropylene and high density polyethylene membranes are presented as examples.

**L-88-3 $10.00**  
Effect of Solute Structure on Solute Distribution in Water-Alcohol-Cellulose Acetate Systems  
Meluch, T.B.  
PhD dissertation  
The intermolecular interactions influencing equilibrium solute distribution between dilute, aqueous alcohol solutions, and cellulose acetate are examined. Distribution coefficients for several isomeric alcohols and glycols were determined using liquid chromatography. The Flory-Huggins theory, using concentration independent interaction parameters, was used to estimate the difference in solute chemical potential from the standard state in the polymer phase for various solute concentrations. Solvent-solute interaction parameters (L-88-3) were estimated using vapor-liquid equilibrium data. Solvent-polymer and solute-polymer interaction parameters were determined from equilibrium vapor sorption data. Equilibrium volume fractions were calculated from the equilibrium distribution coefficients determined using liquid phase sorption. The solute chemical potential difference in the dilute, binary solution was estimated from the Wilson equation. The estimates of the two models did not show good agreement unless solvent-solute-polymer interactions (L-88-3) in the polymer phase were taken into account by a ternary interaction parameter, cT.

**L-88-4**  
Handout for the Separations Research Program Spring Conference, April 1988  
Includes transparencies used by Costain for the Membranes Study Group Meeting.
L-89-1
Handouts for the Separations Research Program Fall Conference, September 1988
Includes copies of transparencies used by Lloyd, Kim, Lim, and Alwattari for the Membranes for Liquid Separations Study Group (L-89-1) Meeting.

L-89-2
Membrane Distillation
Handouts for the Separations Research Program Spring Conference, April 1989
Includes copies of transparencies used by Betts for the Membrane Technology Study Group Meeting.

L-89-3
Handouts from the Separations Research Program Fall Conference, September 1989
Includes copies of handouts used by Ye, Lim, Wallace, and Betts for the Membrane Technology Study Group Meeting.

L-89-4 PUBLISHED
Frictional and Osmotic Effects in the Pressure-Driven Membrane Separation of Dilute Solutions
Thiel, S.W. and D.R. Lloyd
A mathematical relationship was developed to describe flux reduction in the pressure-driven membrane separation of a dilute binary solution of a solute strongly rejected from the membrane. When the concentration reduction factor across the membrane changes linearly with flux, the relative flux reduction is a linear function of the solute concentration in the permeate. This result is consistent with data obtained for the pressure-driven membrane separation of dilute aqueous mannitol solutions using asymmetric cellulose acetate membranes. The flux reduction due to frictional effects is related to membrane structure; structures closer to equilibrium have greater frictional effects than those farther from equilibrium. In the systems studied, frictional effects play a central role in determining membrane performance (L-89-5).

L-90-1 $10.00
Crystallization of Isotactic Polypropylene and Dotriacontane: A Study of Kinetics and Morphology
Wang, Y.F.
PhD dissertation
The isothermal crystallization kinetics of isotactic polypropylene (iPP) and dotriacontane (C32H66) mixtures have been studied using DSC and optical microscopy. The half times were compared at equal super cooling for different polymer concentrations and a maxima was observed in the neighborhood of 70 wt.% iPP. The addition of diluent (C32H66) may have promoted the polymer mobility, thus enhancing the crystallization rate. Regime III-to-II transition was observed in all iPP/ C32H66 systems. The regime III growth rate data correlated well with the LH theory. Regime II growth rate data showed anomalous behavior and cannot be fully explained by the LH theory. The iPP crystalline lamellae morphology has been thoroughly examined by transmission and SEM. More diluent in the system provides slower crystallization kinetics and a freer environment for the lamellae to bend and extend. Molecular nucleation has been observed to affect the lamellar morphology by (1) including the rejected molecules in the crystalline region at fast crystallization rates; (2) forming thinner lamellae between thicker lamellae or lamellae clusters at moderate crystallization rates; and (3) forming uniform lamellar thickness at extremely low super cooling. The spherulite growth has been modeled by a moving boundary problem using the kinetics and diffusion data obtained by optical microscopy and microdensitometry. The moving coordinate system and the computation algorithm have proven effective in solving the ISP for the case studied. The mathematical model has been shown to correlate the spherulite growth quantitatively and qualitatively. The spherulite growth is not only controlled by nucleation but is also a function of mutual diffusion coefficients.
Effect of Solute Structure on Solute Distribution in Water-Alcohol-Cellulose Acetate Systems
Meluch, T.B. and D.R. Lloyd
Intermolecular interactions influencing equilibrium solute distribution between dilute aqueous alcohol solutions and cellulose acetate are examined. Distribution coefficients for several isomeric alcohols and glycols were determined using liquid chromatography. Distribution coefficients increased with increasing solute aliphatic chain length and decreased with increasing solute hydroxyl substitution or increased solute branching. These effects are attributed to changes in the hydrophobic effect, solute-polymer dispersive interactions, and solute-polymer hydrogen bonding.

Microporous Membrane Formation via Thermally Induced Phase Separation. I. Solid-Liquid Phase Separation
Lloyd, D.R.; K.E. Kinzer; H.S. Tseng
Microporous membranes have been prepared via thermally induced solid-liquid phase separation of polymer-diluent mixtures. The thermally induced solid-liquid phase separation process is discussed in terms of the solution thermodynamics of the binary mixture and the crystallization kinetics. Solid-liquid phase separation proceeds via nucleation and growth of polymer crystals to produce a variety of structures. Polypropylene, high-density polyethylene, polychlorotrifluoroethylene, PMP and PVDF membranes are presented as examples.

Handouts from the Separations Research Program Spring Conference, April 1990
Includes copies of transparencies used by Lloyd, Betts, and Kim for the Membrane Technology Study Group Meeting.

Thermodynamics and Structural Study of Thermally Induced Phase Separation Membranes
Kim, S.S.
PhD dissertation
Flory's equation-of-state analysis was performed for several polypropylene [PP]/diluent systems undergoing TIPS. Model systems were chosen to represent several phase separation behaviors. Interaction parameters and phase diagrams were estimated and confirmed by comparison with experimental data from melting temperature depression and cloud point measurements. A simple, reliable methodology to provide the equation-of-state parameters was developed. The free volume effect was significant due to the dissimilarity of equation-of-state properties between polymer and diluent. The enthalpic interaction increased with increasing diluent end group polarity. Increased diluent chain length decreased the free volume effect within each class of diluent. The interaction parameters for the PP/n-alkane systems, PP/n-fatty acid systems, and PP/tallowamine system were studied as a function of temperature. The PP/n-alkane systems underwent solid-liquid phase separation; PP/n-fatty acid systems underwent solid-liquid phase separation (L-90-5) when slowly cooled and liquid-liquid phase separation (L-90-5) when quenched; and the PP/n,n-bis(2-hydroxyethyl) tallowamine system underwent liquid-liquid phase separation or solid-liquid phase separation, depending on the initial composition. The influence of thermodynamic and kinetic parameters on TIPS membrane structure was investigated. The parameters studied were thermodynamic interaction parameter, diluent size, composition, cooling condition, and the diluent crystallization temperature. The membranes formed via TIPS usually have a dual structure with inter- and intraspherulitic pores. The coarsening of phase separated domains after spinodal decomposition was experimentally confirmed. Procedures detailed in this work facilitate polymer and diluent selection and provide guidelines for continuing cooling conditions.
Thermally induced phase separation is perhaps the most versatile and simplest technique to form microporous polymeric membranes from a variety of semicrystalline and thermoplastic polymers. The primary objective of this work was to investigate how the addition of nucleating agent affected the crystallization kinetics of polymer-diluent mixtures undergoing solid-liquid TIPS (that is, the rate at which the membrane is formed) and how this influenced membrane structure. The work focused on the model system iPP/C32H66, with adipic acid as the nucleating agent. Differential scanning calorimetry was used to study the overall crystallization kinetics, and thermal optical microscopy was used to determine the spherulitic growth rates. This study used isothermal and nonisothermal modes of crystallization to characterize the crystallization kinetics of non-nucleated and nucleated iPP/C32H66 system. A method was developed to determine growth rates from non-isothermal crystallization data. The L&H equation was modified to approximate nonisothermal growth rate and to predict isothermal growth rate. Thermally induced phase separation membranes were prepared under various thermal conditions. Cross-sections of the membranes were examined using SEM. The largest pore size was obtained by bubble-point method, and porosity was obtained by ASTM Method D 792-66. Wide-angle x-ray scattering was used to characterize the different iPP polymorphs and to determine the presence of the smectic phase in TIPS membranes. Knowledge of the polymorphs aided in the interpretation of the internal structure of the membranes.

Microporous membranes prepared from crystallizable polymers via the TIPS process are of particular interest for their potential ability to withstand chemically and thermally hostile environments. A variety of applications exists for the membranes prepared using the techniques such as microfiltration and ultrafiltration separation processes (L-90-7). This research project investigated the influence of the processing parameters of cooling rate and polymer/diluent weight ratio on membrane morphologic, thermal, and physical properties for the iPP/C32H66 polymer/diluent system. A simple and reproducible compression molded film fabrication method was used to prepare microporous membranes on a laboratory scale. The method was used to prepare films with polymer concentration of 20 to 100 wt. % in intervals of 10 wt.%. Four average cooling rates, 7, 46, 760, and 1100 K/min, were realized by the method. The effect of the processing parameters on the membranes was investigated experimentally by measuring the morphology, the crystalline form, and the crystalline fraction of the membrane samples. The effect of the processing parameters on the crystallization peak temperature and melting temperature of the polymer in the iPP/C32H66 system were investigated using DSC. In the experimental conditions exploited in this research, spherulitic morphology and α-crystalline form were found for all samples. The spherulite size generally decreased with increasing cooling rate and decreasing polymer concentration. The crystalline fraction was decreased by increasing cooling rate or increasing diluent concentration. The crystallization peak temperature was observed shifting to a lower temperature range as the cooling rate and the diluent concentration were increased.

Includes copies of transparencies used by Alwattari, Laxminarayan, and Ondaatjie for the Membrane Technology Study Group (L-90-8) Meeting.
Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation. I. Determination of Equation of State Parameters
Kim, S.S. and D.R. Lloyd
Polymer 33:1026-35 (1992)

The parameters for Flory's equation of state adapted to polymer/oligomer systems were determined to estimate the thermodynamic properties of iPP-diluent systems undergoing TIPS. Three kinds of diluents were covered: n-alkanes, n-fatty acids, and n,n-bis(2-hydroxyethyl) tallowamine. Reduced volumes and temperatures were determined by measuring the volumetric properties; characteristic pressures were determined by measuring the vapor pressures; and exchange interaction parameters were determined by measuring the heat of mixing for analogue systems of small molecules. The exchange interactional parameters obtained from analogue systems were extrapolated to polymeric systems by using a series of analogue molecules for iPP. The equation-of-state parameters determined in this study were proved reliable for the thermodynamic analyses covered in other papers in this series.

Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation. II. Solid-Liquid Phase Separation Systems
Kim, S.S. and D.R. Lloyd
Polymer 33:1036-46 (1992)

Thermodynamic analysis of solid-liquid phase separation was performed using Flory's equation-of-state theory adapted to polymer/oligomer system. Interaction parameters were estimated for iPP/n-alkane and iPP/n-fatty acid systems using parameters determined in the previous paper in this series. The adapted Flory's equation-of-state theory and parameters proved reliable by comparing the estimated interaction parameters with the experimental ones obtained from melting temperature depression measurements. Isotactic polypropylene/n-alkane systems have dominant free-volume effects. Isotactic polypropylene/n-fatty acid systems have greater enthalpic interactions than iPP/n-alkane systems due to the functional end group of the n-fatty acid. The free volume effect decreased with increasing chain length. Isotactic polypropylene/n-alkane systems were stable within the temperature range of interest, and iPP/n-fatty acid systems were expected to be unstable at temperatures below the iPP crystallization curves.

Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation: III. Liquid-Liquid Phase Separation Systems
Kim, S.S. and D.R. Lloyd
Polymer 33:1047-57 (1992)

Thermodynamic analysis of the system iPP/n,n-bis(2-hydroxyethyl) tallowamine was performed using Flory's equation-of-state theory adapted to the polymer/oligomer system using parameters determined in the first paper in this series. The estimated results were in good agreement with those from melting temperature depression and cloud point measurements. The equilibrium phase diagram was estimated even in the experimentally unavailable region. When the estimated phase diagram could be compared to the experimental data, the agreement was good. The interaction parameter for this system greatly increased with temperature resulting in upper critical solution temperature behavior. The increased end-group polarity of n,n-bis(2-hydroxyethyl) tallowamine resulted in much greater enthalpic interactions than the n-alkane and n-fatty acid systems covered in the second paper in this series.

Microporous Membrane Formation via Thermally Induced Phase Separation. II. Liquid-Liquid Phase Separation
Lloyd, D.R.; S.S. Kim; K.E. Kinzer

Microporous membranes have been prepared via thermally induced liquid-liquid phase separation of polymer-diluent mixtures. The TIPS process is discussed in terms of the thermodynamics of the
binary mixture and the phase separation mechanism. It is demonstrated that membranes can be produced by liquid-liquid phase separation followed by solidification of the polymer or by solid-liquid phase separation. Liquid-liquid phase separation can proceed via nucleation and growth of the polymer-lean phase or via rapid spinodal decomposition, depending on the cooling rate and the initial composition of the mixture. The former results in a polymer matrix containing cells connected by pores; the latter results in a lacy structure of co-continuous polymer and void phases. Coarsening in the later stages of spinodal decomposition may produce a structure similar to that resulting from nucleation and growth. Solid-liquid phase separation after the liquid-liquid phase separation proceeds via nucleation and growth of polymer crystals to produce a variety of structures. Isotactic polypropylene, PMMA, and Nylon 11 membranes are presented as examples.

**L-91-5 PUBLISHED**

**Microporous Membrane Formation via Thermally Induced Phase Separation. III. Effect of Thermodynamic Interactions on the Structure of Isotactic Polypropylene Membranes**

Kim, S.S. and D.R. Lloyd


Isotactic polypropylene membranes were prepared via TIPS using three iPP-diluent systems, at three concentrations, and two thermal histories. The three diluents had similar structure and molar volume but differed in end-group structure, and therefore differed in interactions with the iPP. The two thermal histories represented isothermal and non-isothermal TIPS processes. Membrane structure as determined by SEM depended on the phase separation mechanism (liquid-liquid versus solid-liquid), which depended on the concentration-dependent iPP-diluent interactions and the thermal history.

**L-91-6 PUBLISHED**

**Microporous Membrane Formation via Thermally Induced Phase Separation. IV. Effect of Isotactic Polypropylene Crystallization Kinetics on Membrane Structure**

Lim, G.B.A.; S.S. Kim; Q. Ye; Y.F. Wang; D.R. Lloyd


Non-nucleated and nucleated iPP microporous membranes have been prepared via thermally induced solid-liquid phase separation of polymer-diluent mixtures. Three linear alkanes were used as the diluents and adipic acid was used as the nucleating agent. The membranes were formed under isothermal and non-isothermal crystallizing conditions. Membrane structures as determined by SEM depended on polymer concentration, cooling rate, and the addition of a nucleating agent.

**L-91-7 PUBLISHED**

**Microporous Membrane Formation via Thermally Induced Phase Separation. V. Effect of Diluent Mobility and Crystallization on the Structure of Isotactic Polypropylene Membranes**

Kim, S.S.; G.B.A. Lim; A.A. Alwattari; Y.F. Wang; D.R. Lloyd


The role of diluent in the TIPS membrane was examined for solid-liquid phase separation systems in terms of the diluent mobility and crystallization temperature. The inter- and intra-spherulitic voids were formed for iPP/n-alkane and iPP/n-fatty acid systems. The diluent mobility played an important role in determining those structures. The diffusivities of some diluents through the iPP melt were measured by microdensitometry to support the explanation of structure in terms of diluent mobility. The diluents with high crystallization temperatures affected the structure due to the diluent crystallization prior to the polymer crystallization.

**L-91-8 PUBLISHED**

**Microporous Membrane Formation via Thermally Induced Phase Separation. VI. Effect of Diluent Crystallization Kinetics and Morphology on the Structure of iPP Membranes**

Alwattari, A.A. and D.R. Lloyd


Microporous membranes were prepared via TIPS of iPP blended with hexamethylbenzene. The effects of melt composition and isothermal crystallization temperature on the microstructure of the
resulting membranes were determined via SEM. The structures formed were interpreted in terms of the sequence and mechanism of phase transformations in the super cooled melt.

**L-91-9 $15.00**

**Thermally Induced Phase Separation of Isotactic Polypropylene and Hexamethylbenzene**

Alwattari, A.A.

PhD dissertation

The thermodynamics, polymer crystallization kinetics, sequence of crystallization events, and microstructure of the eutectic class of TIPS were studied as a function of melt composition, Wp, and isothermal crystallization temperature, Tc, using the model system iPP and hexamethylbenzene. Differential scanning calorimetry was used to test iPP crystallization kinetics via the crystallization theories of Avrami and Hoffman-Lauritzen to determine the sequence of phase transitions during crystallization, and combined with a modified Flory lattice model to generate an equilibrium phase diagram. Electron microscopy combined with solvent extraction and permanganic etching permitted characterization of iPP crystal structure and voids formed by removal of HMB. Lamellar structures coincided with pure iPP lamellae. Spherulitic structures were deformed for compositions to the left of the eutectic as a result of primary diluent crystals. Diluent crystallization prior to polymer crystallization (L-91-9) was predicted by DSC studies and resulted in a random distribution of rectangular-shaped voids. Both the dimensions of these voids and iPP spherulite radii decreased as Tc was decreased. Below 383K, a secondary void microstructure appeared in between the larger voids. This structure consisted of tiny needle-like voids and was attributed to diluent crystallizing simultaneously with polymer. Above 383K, all the diluent was consumed prior to polymer crystallization; below 383K, polymer crystallization rate and the viscosity of the super cooled melt both increase, as predicted by the kinetic theories, reducing the transport rate of diluent remaining in the eutectic fraction and preventing random diluent crystal distribution within the eutectic. To the right of the eutectic, primary iPP spherulites dominated structure, restricting voids to interspherulite regions. Spherulite size decreased as Tc was decreased. Both solid and void size, shape, and relative distribution were controlled by Tc and Wp. Trends were interpreted in terms of the mechanism, sequence, and type of phase transitions in the super cooled melt.

**L-91-10**

**Handouts for the Separations Research Program Spring Conference, April 1991**

Copies of transparencies used by Ondaatji and Betts for the Membrane Technology Study Group Meeting.

**L-91-11 $5.00**

**Removal of Volatile Organics from Water by Membrane Distillation**

Betts, D.S.

Masters thesis

1,1,2-Trichloroethane and 1,2-dichloroethane were removed from aqueous solution by membrane distillation. Eight experiments involved 1,1,2-trichlorethane as the feed solute. Experiments were also carried out with pure water as the feed. These experiments quantified the dependence of permeate flux on both feed vapor pressure and trans-membrane vapor pressure difference. At a fixed feed concentration, the activity coefficient increases with increasing temperature, resulting in a higher concentration factor. At a fixed temperature, the activity coefficient does not vary significantly with solute concentration for the concentrations of interest. The concentration factor is unaffected by feed concentration. The dependence of permeate flux on feed vapor pressure and trans-membrane vapor pressure difference is demonstrated. Also, the dependence of concentration factor on feed temperature and trans-membrane temperature difference is shown. Finally, the independence of concentration factor from feed concentration at low feed concentrations is demonstrated.
L-91-12 PUBLISHED
Isothermal Crystallization of iPP in Dotriacontane. I. Effect of Nucleating Agent Addition on Overall Crystallization Kinetics
Lim, G.B.A. and D.R. Lloyd
Polymer Engineering and Science 33(9):513-21 (1993)

The overall isothermal crystallization kinetics for the nucleated and non-nucleated iPP-dotriacontane systems was investigated. Adipic acid was used as the nucleating agent. Half-time was determined via DSC as a function of the experimentally controlled variables dilution, crystallization temperature, and the addition of nucleating agent. The influence of these variables on crystallization mechanism and spherulitic structure, as implied by the Avrami analysis, was determined. The influence of these variables on fold surface energy was examined by the Lauritzen and Hoffman analysis.

L-91-13 PUBLISHED
Isothermal Crystallization of iPP in Dotriacontane. II. Effect of Nucleating Agent Addition on Growth Rate
Lim, G.B.A. and D.R. Lloyd

Isothermal crystallization growth rates of nucleated and non-nucleated iPP-dotriacontane systems were determined experimentally by thermal optical microscopy (TOM). Adipic acid was used as the nucleating agent. The Lauritzen and Hoffman analysis was used to determine the fold surface energy of the nucleated and non-nucleated mixtures.

L-92-1 $5.00
Asymmetric Nylon Membrane Formation via Phase Inversion
Ondaatjie, A.M.
Masters thesis

Aromatic and aliphatic polyamides are common materials for reverse osmosis, ultrafiltration, and microfiltration membranes. They are particularly useful because a hydrophilic/hydrophobic balance can be achieved via minor modifications of the polymer chemistry, and because they can withstand modest operating temperatures, high operating pressures, and strong chemical environments. Unfortunately, their chemical stability is both an advantage and a disadvantage. From a membrane formation standpoint the chemical stability of polyamides is an undesirable feature; that is, the formation of integrally skinned polyamide membranes requires severe conditions of temperature and strong organic solvents (i.e., hot formic acid). The objective of this project was to develop an alternate solvent system for the formation of integrally skinned polyamide membranes. The thermodynamics of polymer dissolution and the kinetics of the phase separation were investigated. Asymmetric membranes were prepared by casting and coagulating solutions of polymer in different gelatin baths. The effect of polymer and salt concentration in the casting solution and gelatin bath composition on membrane structure and kinetics were investigated. Membranes were characterized by SEM and DSC. The kinetics of the phase separation and membrane formation were experimentally determined using an optical microscope with video recording equipment. The advance of the precipitation front as a function of time does not follow Fickian diffusion kinetics, contrary to what is suggested in the literature. The apparent break points on the rate curve are related to structural transitions of the asymmetric membrane. The correlations between resulting membrane characteristics and the properties of both polymer-solvent and solvent-nonsolvent systems are discussed.

L-92-2 PUBLISHED
Microporous Membrane Formation via Thermally Induced Phase Separation. VII. Effect of Dilution, Cooling Rate, and Nucleating Agent Addition on Morphology
McGuire, K.S.; D.R. Lloyd; G.B.A. Lim

Microporous polypropylene films were produced from nucleated and non-nucleated melt-blends of iPP and dotriacontane using nonisothermal thermally induced phase separation. Adipic acid was
used as the nucleating agent. The morphology of these microporous iPP films as determined by TOM and SEM is reported. The effect on film structure of diluent crystallization is also shown.

**L-92-3 PUBLISHED**

**A Comparative Study of Partition Coefficients Determined by Sorption and by Liquid Chromatography in Alcohol-Water-Cellulose Acetate Systems**

Meluch, T.B. and D.R. Lloyd  
Polymer 34(9):1984-87 (1993)

Partition coefficients obtained from liquid chromatography are compared to those obtained from equilibrium sorption experiments for various alcohol-water-cellulose acetate systems. In the liquid chromatography experiments, cellulose acetate powder was used as the stationary phase with water as the mobile phase and alcohols injected into the mobile phase. In the equilibrium sorption experiments, cellulose acetate powder was equilibrated with an alcohol-water solution.

**L-92-4 PUBLISHED**

**Nonisothermal Crystallization of iPP in Dotriacontane iPP in Dotriacontane. I. Effects of the Dilution, Cooling Rate, and Nucleating Agent Addition on Overall Crystallization Kinetics**

Lim, G.B.A. and D.R. Lloyd  
Polymer Engineering and Science 33(9):529-36 (1993)

The overall nonisothermal crystallization kinetics for nucleated and non-nucleated iPP in dotriacontane systems were investigated. Adipic acid was used as the nucleating agent. Crystallization peak temperature was determined via DSC as a function of the experimentally controlled variables iPP concentration, cooling rate, and nucleating agent concentration. The influence of these variables on crystallization mechanism and spherulitic structure as implied by the Ozawa and Ziabicki analyses was determined. The nonisothermal crystallization kinetics presented here are the first for iPP-diluent systems with and without nucleating agent.

**L-92-5 PUBLISHED**

**Nonisothermal Crystallization of iPP in Dotriacontane iPP in Dotriacontane. II. Effect of Dilution, Cooling Rate, and Nucleating Agent Addition on Growth Rate**

Lim, G.B.A.; K.S. McGuire; D.R. Lloyd  
Polymer Engineering and Science 33(9):537-42 (1993)

Nonisothermal crystallization growth rates of nucleated and nonnucleated iPP in dotriacontane were determined experimentally by TOM. Adipic acid was used as the nucleating agent. The nonisothermal growth rates of the nucleated and non-nucleated systems were compared with experimentally determined isothermal growth rates. The Lauritzen and Hoffman growth rate equation, originally developed for isothermal crystallization, was modified to describe the nonisothermal growth. The modified Lauritzen-Hoffman equation was used to predict isothermal growth rates from nonisothermal crystallization for the nucleated and non-nucleated polymer-diluent mixtures. This study is the first to deal with polymer-diluent-nucleating agent systems vital to membrane production.

**L-92-6 PUBLISHED**

**Spherulitic Crystallization: An Analysis of Inverse Stefan Problems in Cartesian, Cylindrical, and Spherical Coordinate Systems**

Wang, Y.F. and D.R. Lloyd  
Polymer Engineering and Science 34(6):477-84 (1994)

Spherulitic crystallization presents an inverse Stefan problem, which is solved by numerical methods using the DuFort-Frankel scheme and Lagrangian coordinate systems. The numerical solution shows excellent agreement with the analytical solution in the Cartesian coordinate system. A systematic error in the numerical solution for the spherical and cylindrical coordinate systems is examined by a material balance for the system. The systematic error was found to decrease rapidly as the dimensionless time increased and the grid spacing decreased.

**L-93-1 REPLACED BY L-93-4**
Electrodialysis of Electrolyte Mixtures on Modified Ion Exchange Membranes (Ion-selective Electrodialysis)
Starov, V.M.; A.N. Filippov; D.R. Lloyd; V.D. Grebenjuk; R.D. Chebotareva

Water to be purified often contains a mixture of salts, for example, NaCl + CaCl2 or NaCl + Na2SO4. In these cases the electrolyte mixture includes uni- and divalent ions; that is, either Na+, Cl-, and Ca++ or Na+, Cl-, and SO4--. Usually divalent ions are preferentially transported through membranes in electrodialysis; however, in a number of industrial applications it is required to remove just univalent ions. In this paper, two different approaches to increase the transfer number of univalent ions are described: (i) adding to the feed solution polyvalent ions with the same charge sign as the divalent ions; (ii) modification of the ion-exchange membrane (L-93-3) on the feed side to create a layer, either inside the membrane or on its surface, with the same charge sign as the divalent ion. Consequently, the electric field is changed either in front of the membrane or inside the modified layer in such a way that the transfer number of divalent ions decreases and the transfer number of univalent ions increases.

Isothermal Crystallization of Isotactic Polypropylene in Dotriacontane. III. Effect of Dilution and Crystallization Temperature on Growth Rate
Wang, Y.F. and D.R. Lloyd
Polymer 34(11):2324-29 (1992)
The sperulitic growth rate of isotactic polypropylene in dotriacontane was studied using optical microscopy. Polymer concentration was varied from 100 to 10 wt% iPP in 10 wt% intervals. Crystallization temperature was varied from 372 to 429 K in 1 K intervals. The influence of these variable on polymer spherulitic growth rate and regime transitions was analyzed using the Lauritzen-Hoffman and Toda nucleation theories. Replaces L-93-1

Isothermal Crystallization of Isotactic Polypropylene in Dotriacontane. IV. Effect of Dilution and Crystallization Temperature on Overall Crystallization Kinetics
Wang, Y.F. and D.R. Lloyd
The overall isothermal crystallization kinetics for isotactic polypropylene (iPP) in dotriacontane was investigated. Half-time was determined via differential scanning calorimetry as a function of the experimentally-controlled variables dilution and crystallization temperature. Polymer concentration was varied from 100 to 10 wt% in 10 wt% intervals. Crystallization temperature was varied from 415 to 380 K in 1 K intervals. The influence of these variables on crystallization mechanism and spherulitic structure, as implied by the Avrami analysis, was determined. The influence of these variables on fold surface energy was examined by the Lauritzen and Hoffman analysis. Replaces L-93-2

Sieve Mechanism of Microfiltration
Filippov, A.N.; V.M. Starov; D.R. Lloyd; S. Chakravarti; S. Glaser
Submitted to Journal of Membrane Science
A mathematical model for dead-end microfiltration (MF) of dilute suspensions is suggested. The model is based on a sieve mechanism and takes into account the probability of membrane pore blocking during the MF of dilute colloid suspensions. An integro-differential equation (IDE) that includes both the membrane pore size and particle size probability distribution functions is deduced. According to the suggested model a similarity property is deduced, which allows one to predict flux through the MF membrane as a function of time for any pressure and dilute concentration based on one experiment at a single pressure and concentration. The model enables...
one to calculate all the necessary physico-chemical parameters that are relevant for determination of the dependency of flux on time. For a narrow pore size distribution in which one pore diameter predominates (track etched membranes) the IDE is solved analytically and the derived equation is in a good agreement with measurements on four different track etched membranes. A condition is found for which the MF membrane transforms into an ultrafiltration membrane. A simple approximate solution of the IDE is deduced and that approximate solution as well as the similarity property of MF processes is in good agreement with measurement with measurements on a commercial Teflon MF membrane.

**L-93-7 REPLACED BY L-95-7**

**L-95-1 PUBLISHED**

**Isothermal Crystallization of Isotactic Polypropylene-Hexamethylbenzene Blends: Crystal Morphology**

Alwattari, A.A., and D.R. Lloyd


Lamellar crystal organization and spherulite formation were investigated as functions of melt polymer concentration and isothermal crystallization temperature for the model eutectic-forming system isotactic polypropylene (iPP) and hexamethylbenzene (L-95-1). Permanganic etching and scanning electron microscopy were used to reveal iPP crystal features. The results were interpreted in terms of the kinetics of crystallization events during thermally induced phase separation of this system.

**L-95-2 PUBLISHED**

**Compaction of Microporous Membranes Used in Membrane Distillation. I. Effect on Gas Permeability**

Lawson, K.W.; M.S. Hall; D.R. Lloyd


Membrane compaction effects are well documented in reverse osmosis (RO), ultrafiltration (UF), and gas separation, but little attention is paid to compaction effects in microporous membrane processes. This paper examines the effects of compaction on the gas permeability of microporous membranes to be used in membrane distillation (MD). Contrary to what is observed in RO and UF systems where membrane permeability is reduced by compaction, limited compaction of microporous membranes can result in enhanced permeability. This enhancement is the result of decreased membrane thickness, which increases the pressure gradient across the membrane. An experimental method is devised to determine the effects of membrane compaction on permeability, and a theory for modifying flux equations to include a parameter for membrane compaction is introduced.

**L-95-3 PUBLISHED**

**Effect of Initial Composition Phase Separation Temperature and Polymer Crystallization on the Formation of Microcellular Structures via Thermally Induced Phase Separation**

Laxminarayan, A.; K.S. McGuire; S.S. Kim; D.R. Lloyd


Microcellular polypropylene structures were obtained through liquid-liquid thermally induced phase separation followed by polymer crystallization using the model system isotactic polypropylene (iPP)-diphenyl ether (DPE) (L-95-3). The effect of the phase separation temperature and initial polymer concentration on the final morphology has been investigated. The observed morphological characteristics have been explained on the basis of the kinetics of liquid-liquid phase separation and polymer crystallization using a phase diagram developed for the iPP-DPE system, optical microscopy and scanning electron microscopy. Movement of the diluent-rich droplets (formed via liquid-liquid phase separation) due to spherulitic growth has been observed and the effect of this displacement on the final morphology has been assessed.
The kinetics of microcellular membrane formation via the Thermally Induced Phase Separation (TIPS) process has been investigated. The membranes were formed by inducing liquid-liquid phase separation (through a drop in temperature) in an initially homogeneous polymer solution. Liquid-liquid phase separation resulted in a diluent-rich phase being dispersed within the polymer-rich matrix. The diluent-rich phase upon extraction leaves behind empty spaces that form the cells and pores of the resulting microporous membrane. When a sample undergoing liquid-liquid phase separation is held at the phase separating temperature for an extended period of time the droplets of the diluent-rich phase grow in size and decrease in number. This phenomena, known as coarsening, may be used to control the cell size of a microcellular structure formed via liquid-liquid TIPS. A thorough understanding of the kinetics of coarsening enables better control of cell size and size distribution. In the present study, existing domain growth models have been evaluated for a polymer-diluent system and a new model based on a unique mechanism of domain growth is presented. After establishing the equilibrium phase diagram for the model system isotactic polypropylene (iPP)-diphenyl ether (DPE), kinetic experiments were carried out at different temperatures and polymer concentrations. The growth of the diluent-rich phase droplets was monitored through a microscope, and analyzed using digital image analysis. The domain growth rate was dependent on the initial polymer concentration and temperature of phase separation. It has been demonstrated that volume fraction of the droplet phase has a profound influence on the growth rate exponent. It is quantitatively shown that existing models do not adequately describe domain growth in the late stages of liquid-liquid phase separation in a polymer-diluent system. A unique mechanism of domain growth, which considers the influence of the coalescence of two drops on a neighboring drop has been proposed. An approximate model based on this mechanism has been derived to describe the kinetics of domain growth in the late stages of liquid-liquid phase separation. The new model provides reasonable agreement with experimental data. The influence of the relative rates of liquid-liquid phase separation and polymer crystallization, the effect of spherulitic growth, and a two-step quench in temperature on the final morphology of the membrane was evaluated using scanning electron microscopy.

In forming microporous membranes via Thermally using digital image analysis. It was found that the drop growth rate was strongly dependent upon the quench condition. In fact, it was shown that the droplet phase volume fraction has a profound influence upon the drop growth rate, and this influence is nearly independent of temperature. No existing kinetic model could describe the droplet growth kinetics measured in this study. The droplet phase volume fraction was determined using a tie-line construction on the equilibrium phase diagram. The interfacial tension between the two phases was measured using a spinning drop tensiometer and was Induced Phase Separation (TIPS), phase separation can be initiated by solid-liquid, liquid-solid, or liquid-liquid phase separation. In this study, the liquid-liquid phase separation (L-95-5) mechanism was used. Membranes were made from an initially homogeneous polymer-diluent mixture by inducing phase separation through a temperature drop. Upon phase separation, droplets rich in diluent formed within a continuous matrix phase rich in polymer. Through a process known as coarsening, these droplets grew in size and decreased in number in an effort to minimize the interfacial area of the phase separated mixture. At any point in time, if the temperature of the mixture were dropped further to solidify the polymer, then upon removal of the diluent, the drops in the phase separated mixture became the cells in the resulting membrane. The overall objective of this research was to understand the influence of the independent variables phase separation temperature and initial weight fraction of polymer on the phase separation kinetics of liquid-liquid TIPS in an effort to control the resulting cell sizes, pore sizes, and porosities of membranes made via liquid-liquid TIPS. The model system chosen for study in this work consisted of isotactic poly(propylene) (iPP)
dissolved in diphenyl ether (DPE). Once the equilibrium phase diagram for the model system was determined, kinetic experiments were carried out with a variety of temperatures and mixture compositions within the liquid-liquid phase separation region. The droplet growth was monitored under an optical microscope and was measured found to increase with decreasing temperature. The viscosity of the polymer-rich matrix phase was measured in a cup and bob viscometer and was found to increase with decreasing temperature and increasing polymer concentration. The van der Waals Hamaker constant was estimated and found to increase with decreasing temperature. A new model was derived to account for the influence of two coalescing drops upon neighboring drops. Excellent qualitative and quantitative agreement was found to exist between the model predictions and the experimental observations. A method was developed to measure the pure size distributions using a liquid permeation technique. It was found that the average pore size was approximately one-tenth the average cell size for the experimental conditions studied.

L-95-6 PUBLISHED
Pore Size Distribution Determination from Liquid Permeation through Microporous Membranes
McGuire, K.S.; K.W. Lawson; D.R. Lloyd
Knowledge of the pore size distribution of a microfiltration or ultrafiltration membrane is necessary in order to accurately predict membrane performance in any given application. The liquid permeation technique presented in this paper has been used to obtain data for determining pore size distribution for nearly sixty years. However, the mathematical technique presented in this paper to interpret the experimental data has not been used since its conception in the early nineteen-thirties. This paper examines the merits of this mathematical technique which, when coupled with modern computing capabilities and precise data acquisition, can be used to effectively determine accurate, continuous pore size distributions of hydrophobic membranes.

L-95-7 PUBLISHED
A Simple Method of Extrapolating the Coexistence Curve and Predicting the Melting Point Depression Curve from Cloud Point Data for Polymer-Diluent Systems
McGuire, K.S.; A. Laxminarayan; D.R. Lloyd
Polymer 35(20):4404-7 (1994)
This paper presents a quick, useful method for obtaining an equilibrium phase diagram (including the melting point depression curve) for a semicrystalline polymer-diluent mixture from cloud point data. Good agreement was obtained between the theoretically predicted and experimentally generated equilibrium crystallization curves in spite of simplifying assumptions. An accurate extrapolation of the coexistence curve to regions in the phase diagram where experimental generation of cloud point data is not possible was also obtained. Flory's original polymer swelling theory was used to determine the complete phase diagram. In the system studied (isotactic polypropylene in diphenyl ether), the interaction parameter was assumed to be a function of temperature only. Cloud points were generated experimentally, and an interaction parameter was determined at each temperature. A melting point depression curve was calculated from the temperature dependent interaction parameter and compared with experimentally determined equilibrium melting points. The resulting phase diagram was used to interpret the morphology of microporous structures prepared by the thermally induced phase separation mechanism. Replaces L-93-7

L-95-8
Starov, V.M.; J. Smart; D.R. Lloyd
Journal of Membrane Science, in press
Overall performance of hollow fiber membranes can be engineered based upon the interplay of fiber productivity and fiber selectivity. Fiber length and diameter can be optimized to render the desired balance of fiber performance. Fundamental analytical models are developed for feed outside (concurrent and countercurrent flow configurations) and feed inside. Part 2. of this series
of papers will evaluate the sensitivity of fiber performance to such operating conditions as pressure, packing density, and fiber diameter.

**L-95-9 $10.00**

**Membrane Distillation**
Lawson, K.W.

A new general model for membrane distillation (MD) based on the dusty-gas model was developed and tested in a variety of MD applications. The model includes three parameters, which characterize the Knudsen, viscous, and molecular diffusion permeabilities of the microporous MD membranes. The Knudsen and viscous permeabilities of each membrane were measured by permeating nitrogen through the membrane. During these permeation experiments it was discovered that compaction of the membrane affects its permeability. In most cases, membrane compaction results in a decreased permeability, but the permeabilities of the membranes used in this work increased with compaction. A theory was developed to explain this phenomenon, and the MD flux equations were modified to include a compaction parameter. Vacuum MD experiments were then performed to evaluate the heat and mass transfer boundary layer resistances of the membrane module. The membrane module designed for use in this work is unique in that it can use flat-sheet membranes without a support. Additionally, the membrane module and associated apparatus were designed to achieve relatively high feed and permeate Reynolds numbers within the module. These two factors led to a dramatic reduction in the boundary layer resistances; therefore, the MD fluxes reported in this work were two to three times higher than those reported in the literature. The molecular diffusion permeability of each membrane was then determined with direct contact MD experiments using pure water. The new MD model was used to predict the performance of MD with ethanol-water and NaCl-water solutions, and the predictions were compared to experimental results. The model was also used to predict the performance of a special case of direct contact MD in which the flux is limited by molecular diffusion resistance (MDLMD). For any given feed temperature, MDLMD has an optimum permeate temperature that corresponds to a trans-membrane temperature drop of approximately 60°C. Additionally, when properly normalized, the individual MDLMD performance curves can be unified to give a single universal performance curve. Both of these phenomena were also examined experimentally with direct contact MD using pure water.

**L-97-1 PUBLISHED**

**Effects of Process Conditions on the Formation of Microporous Membranes via Solid-Liquid Thermally Induced Phase Separation**
Chiang, Chung-Yuan and D.R. Lloyd

Poly(phenylene sulfide)(PPS) membranes were formed via solid-liquid thermally induced phase separation. The effects of nucleation density (N) on final membrane structure were investigated. N was varied by changing dissolution temperature (T_d, the temperature at which the melt-blend is formed) and polymer concentration in the initial polymer-diluent mixture.

**L-97-2 PUBLISHED**

**Kinetics of Droplet Growth in Liquid-Liquid Phase Separation of Polymer-Diluent Systems: Model Development**
McGuire, Kenneth S.; A. Laxminarayan; D.S. Martula; D.R. Lloyd

A new model is presented for describing the increase in average droplet size as a function of time for systems composed of diluent droplets in a polymer-diluent matrix phase. The new model describes the merging of any two droplets and accounts for the effect that two coalescing drops has on neighboring drops. In particular, as two drops coalesce, fluid is expelled from between them. This expelled fluid causes the movement of neighboring drops, which leads to further coalescence of drops. The model predicts a strong influence of the droplet growth rate on the volume fraction of the droplet phase, which corresponds with experimental observations. The
model was found to be sensitive to the matrix phase viscosity and the single fitting parameter, and
less sensitive to the interfacial tension and Hamaker constant. (1996 Academic Press, Inc.

L-97-3 PUBLISHED
Performance Optimization of Hollow Fiber Reverse Osmosis Membranes. Part II. Comparative
Study of Flow Configurations
Smart, Jim; V.M. Starov; D.R. Lloyd
Sensitivity evaluation of overall performance of hollow fiber membranes was preformed to study
the effects of such operating parameter as pressure, packing density, and giver diameter. It is
shown that in a wide range of operating conditions, fiber productivity and selectivity as dependent
upon hollow fiber length exhibit a similarity property. This is demonstrated in all three flow
configurations of concurrent, countercurrent, and flow inside hollow fibers.

L-97-4 PUBLISHED
Membrane Distillation. I. Module Design and Performance Evaluation Using Vacuum Membrane
Distillation
Lawson, Kevin W.; D.R. Lloyd
Journal of Membrane Science 120:111-121 (1996)
Pure water vacuum membrane distillation (VMD) experiments were performed to evaluate the
heat and mass transfer boundary layer resistances in a new laboratory-scale membrane module.
The membrane module designed for this work is unique in that it can use flat-sheet membranes
without a support. Additionally, the membrane module and associated apparatus were designed to
achieve relatively high feed and permeate Reynolds numbers within the module. These two
factors led to a dramatic reduction in boundary layer resistances, which resulted in improved
VMD fluxes. This paper also examines a new complete VMD model based on the dusty-gas
model, which accounts for both Knudsen and viscous mass transport across the membrane. The
new model was used to predict the performance of VMD with pure water and ethanol-water
solutions.

L-97-5 PUBLISHED
Membrane Distillation. II. Direct Contact MD
Lawson, Kevin W. and D.R. Lloyd
Pure water direct contact membrane distillation (DCMD) experiments were used to measure the
permeability parameter associated with the molecular diffusion in membrane distillation (MD).
The fluxes given by a recently reported MD model, which Is based on the dusty-gas model of gas
transport through porous media, showed good agreement with the experimental results over the
entire range of feed temperatures studied. The model was also capable of predicting flux as a
function of the difference between bulk feed and permeate temperatures for the limiting case in
which only molecular diffusion contributes to flow. The DCMD experiments were performed in
this work with a new laboratory-scale module that does not require a support for flat-sheet
membranes. The resulting DCMD fluxes were two to three times higher than those reported in the
literature for either DCMD or reverse osmosis. The MD model was also used to predict the
performance of DCMD desalination, and the results were compared to those of reverse osmosis, in
terms of both water production rates and NaCl rejection.

L-97-6 PUBLISHED
Membrane Distillation
Lawson, Kevin W. and D.R. Lloyd
This paper provides a state-of-the-art review of the separation process known as membrane
distillation, MD. An introduction to the terminology and fundamental concepts associated with
MD as well as a historical review of the developments in MD are presented. Membrane
properties, transport phenomena, and module design are discussed in detail. A critical evaluation
of the MD literature is incorporated throughout this review.
**L-97-7 PUBLISHED**

Crystallization Kinetics of Polymer Diluent Systems. II. Experimental Verification of Model  
Chiang, C.Y.; V.M. Starov; D.R. Lloyd  
Colloid Journal of Russian Academy of Science (English) 59:236-247 (1997)

**L-97-8 PUBLISHED**

Reverse Osmosis of Multicomponent Electrolyte Solutions Part I. Theoretical Development  
Hall, Matthew S.; V.M. Starov; D.R. Lloyd  

A model is developed to treat reverse osmotic separations of electrolyte solutions. Transport in the model is based on the Extended Nernst-Planck equation, which includes diffusion, convection, and electromigration. Boundary conditions include a distribution coefficient that is due to a specific interaction potential representing repulsion of ions from the membrane material. Boundary conditions also include potential jumps known as Donnan Potentials. The model incorporates a mechanism for varying-membrane-fixed-charge as a function of ion concentrations and pH inside the membrane. In addition to salt ions, hydrogen and hydroxide ions are also considered, as pH changes indicate they take part in the transport. A high Peclet approximation is developed which simplifies calculations.

**L-97-9 PUBLISHED**

Reverse Osmosis of Multicomponent Electrolyte Solutions Part II. Experimental Verification  
Hall, Matthew S.; V.M. Starov; D.R. Lloyd  

A variety of single salt experiments were performed over a wide range of concentration and pH using NaCl and CaCl2, to test the model developed in Part I. The model was shown to be effective in producing the same type of separation behaviors as was experimentally observed. Using the parameters obtained from single salt experiments, separations of mixtures of NaCl and CaCl2 were predicted and experimentally confirmed. Agreement between the predictions and experimental data was quite good, and confirms that the model is useful for prediction of multicomponent separations using data from single salt experiments.

**L-97-10 PUBLISHED**

Formation of Microporous Teflon (PFA) Membranes via Thermally Induced Phase Separation  
Caplan, Michael R.; C. Chiang; D.R. Lloyd; L.Y. Yen  

Poly(tetrafluoroethylene-co-perfluoro-(propyl vinyl ether)) (Teflon( PFA) membranes of a variety of structures have been produced through thermally induced phase separation of Teflon( PFA-chlorotrifluoroethylene melt-blends of different compositions. A phase diagram of the two component was constructed, and electron microscopy was used to characterize the structures of membranes produced. The morphological characteristics of the Teflon( PFA membranes have been explained on the basis of equilibrium driving forces for liquid-liquid and solid-liquid phase separations.

**L-97-11 PUBLISHED**

Isothermal Crystallization of Isotactic Polypropylene-Hexamethylbenzene Blends: Kinetics Analysis  
Alwattari, Ali A. and D.R. Lloyd  

This paper analyses the polymer crystallization kinetics (obtained via differential scanning calorimetry) for a model eutectic-forming polymer-diluent system, isotactic polypropylene (iPP)-hexamethylbenzene(HMB). The Avrami and Hoffman-Lauritzen crystallization theories were applied to iPP crystallization in the presence of HMB. In addition, an experimental-computational method of obtaining the phase diagram for an eutectic-forming system is presented along with a technique for determining the sequence of phase separation events. (1997 Elsevier Science LTD. All rights reserved.
L-97-12
Formation of Anisotropic Membranes via Thermally Induced Phase Separation
Matsuyama, Hideto; S. Berghmans; D.R. Lloyd
Manuscript on file, Separations Research Program
The applicability of the thermally induced phase separation (TIPS) process to the production of anisotropic membranes was investigated. To induce an anisotropic structure, diluent was evaporated from one side of the polymer-diluent melt-blended, thereby creating a concentration gradient in the nascent membrane prior to inducing phase separation. The system used to prepare these membranes was isotactic polypropylene (iPP) in diphenyl ether. The resulting membrane structures showed that this evaporation process was useful in producing anisotropic structures. The effects of evaporation time and initial polymer concentration on the anisotropic membrane structure were investigated. The evaporation process was analyzed by solving appropriate mass transfer and heat transfer equations. The agreement between the calculated results and the experimental data on the membrane weight loss and the membrane thickness was satisfactory. The membrane structures are discussed in detail based on the calculated polymer volume fraction profiles in the membranes.

L-97-13
Effects of Thermal History on Anisotropic and Asymmetric Membranes Formed by Thermally Induced Phase Separation
Matsuyama, Hideto; S. Berghmans; M.T. Batarseh; D.R. Lloyd
Manuscript on file, Separations Research Program
The effects of thermal history, such as cooling rate and quench temperature, on membrane structure were investigated in the formation of anisotropic and asymmetric membranes via thermally induced phase separation. A polymer concentration gradient was produced by evaporating diluent from the top surface of an isotactic polypropylene-diphenyl ether melt-blend before cooling to induce phase separation. The quench temperature and the quench medium (that is, air or water) were used to influence the cell size and the diameter of crystallized spherulites. The membrane structures are discussed in terms of the calculated polymer volume fraction as a function of position from the top to bottom surfaces. To superimpose a cooling rate gradient on the polymer concentration gradient, one side of the sample was immersed in ice water after the evaporation. This combined use of a thermal gradient and concentration gradient produced pronounced asymmetric structures with a skin layer at the top surface.

L-97-14
Formation of Hydrophilic Microporous Membranes via Thermally Induced Phase Separation
Matsuyama, Hideto; S. Berghmans; D.R. Lloyd
Manuscript on file, Separations Research Program
Hydrophilic microporous membranes were produced via the TIPS process using two hydrophilic ethylene-acrylic acid copolymers (zinc salt) with different co-unit contents. These copolymers were confirmed to be hydrophilic by the contact angle measurements. Low density polyethylene homopolymer was also used in the work as a reference to investigate the effect of polymer properties on membrane structures. First, dynamic phase diagrams for these three polymer systems were determined. The cloud point curves shifted to higher temperatures and the crystallization temperature curves shifted to lower temperatures as the acrylic acid content of the copolymer increased. The membrane structures were investigated and related to the initial polymer concentration and cooling rate. Increasing either the polymer concentration or the cooling rate decreased the pore size. Furthermore, structures with smaller pores and a skin layer at the top surface were obtained by introducing an evaporation process before the cooling to generate a polymer concentration gradient in the melted polymer solution.
Pervaporative Extraction of Volatile Organic Compounds from Aqueous Systems with Use of a Tubular Transverse Flow Module. Part I. Composite Membrane Study
Smart, Jim; R.C. Schucker; D.R. Lloyd
Manuscript on file, Separations Research Program

The effect of a woven fiberglass support layer in a composite silicone rubber membrane is examined. Flux reduction during the pervaporation process is attributed to the additional resistance offered by the support layer in both flat sheet and hollow fiber configurations. A 40% reduction (from that of the bare silicone rubber membrane) in toluene flux from a toluene-water feed solution is estimated to occur in 0.9 mm outer diameter hollow fibers. These fibers are later used in the construction of tubular transverse flow module to be discussed in part II of this series.

Pervaporative Extraction of Volatile Organic Compounds from Aqueous Systems with Use of a Tubular Transverse Flow Module. Part II. Experimental Results
Smart, Jim; V.M. Starov; R.C. Schucker; D.R. Lloyd
Manuscript on file, Separations Research Program

Experimental flux and selectivity results are shown for the toluene-water-silicone rubber system in a tubular transverse flow module. These results are compared to predictions offered from nonlinear pervaporation models based upon modified Flory Huggins and Lattice Fluid thermodynamics. A comparison of experimental with model results show good predictions of solute flux for both thermodynamic theories. However, the model was discovered to be very sensitive to calculations of infinite dilution diffusion coefficients and a priori predictions of experimental membrane selectivities were underestimated.

Formation of Anisotropic and Asymmetric Membranes via Thermally Induced Phase Separation
Matsuyama, H.; S. Berghmans; M.T. Batarseh; D.R. Lloyd
ACS Symposium Series, in press

Anisotropic Flat Sheet Membrane Formation via TIPS. I. Thermal Effects.
Atkinson, P.M. and Lloyd, D.R.

Anisotropic Flat Sheet Membrane Formation via TIPS. II. Forced Convection and Molecular Weight Effects
Atkinson, P.M. and Lloyd, D.R.

Coalescence-induced Coalescence of Inviscid Droplets in a Viscous Fluid

Formation of Anisotropic and Asymmetric Membranes via Thermally Induced Phase Separation
Matsuyama, H; Berghmans, S.; Batarseh, M.T.; Lloyd, D.R.
Structure Control of Anisotropic and Asymmetric Polypropylene Membrane Prepared by Thermally Induced Phase Separation
Matsuyama, H.; M. Yuasa; Y. Kitamura; M. Teramoto; D.R. Lloyd
Journal of Membrane Science 179 (2000) 91-100

Anisotropic (gradation in pore size) and asymmetric (dense surface skin) polypropylene membranes were produced by the thermally induced phase separation (TIPS) process and solute rejection by these membranes was investigated. Anisotropic membranes were obtained by inducing a polymer concentration gradient in the polymer-diluent solution prior to phase separation. The concentration gradient was established by controlled evaporation of diluent from one side of the solution. The anisotropic membranes showed much higher rejection coefficients for latex particles with diameter of 100 nm than an isotropic polypropylene membrane prepared by TIPS method without evaporation. Asymmetric structures were achieved by imposing a cooling rate gradient across the membrane. The membrane had a skin layer of about 1 µm thickness at the surface that was rapidly cooled. The solute rejection coefficient reached more than 0.95 for lysozyme of molecular weight of 14600. This result shows that ultrafiltration polypropylene membranes can be produced by the TIPS process if asymmetry is induced during the membrane formation process.

Coalescence-Induced Coalescence in Polymeric Membrane Formation
Martula, D.S. and Lloyd, D.R.

Formation of Anisotropic and Asymmetric Membranes via Thermally-Induced Phase Separation
Matsuyama, H.; S. Berghmans; M.T. Batarseh; D.R. Lloyd
American Chemical Society, 2000, Chapter 2

Anisotropic (gradient in pore size) and asymmetric (integrally-skinned) membranes were formed by the thermally-induced phase separation (TIPS) process. To form such structures, evaporation of diluent was allowed from one side of an isotactic polypropylene (iPP)-diphenyl ether melt-blend, thereby creating a polymer concentration gradient in the sample before cooling and phase separation. The quench temperature was used to influence the cell size. The combined use of temperature gradient and polymer concentration gradient produced pronounced asymmetric structures with a skin layer at the top surface. The evaporation process was analyzed by solving appropriate mass transfer and heat transfer equations. The membrane structures are discussed in detail based on the calculated polymer volume fraction profiles in the membranes.

Anisotropic Flat Sheet Membrane Formation via TIPS: Thermal Effects
Atkinson, P.M. and D.R. Lloyd

The use of liquid-liquid thermally induced phase separation (TIPS) to produce cellular flat sheet membranes with an anisotropic nature was investigated theoretically and experimentally for the model system isotactic polypropylene (iPP) and diphenyl ether (DPE). Anisotropic structures were obtained experimentally by evaporating diluent from one surface of a polymer-diluent solution prior to phase separation. The effects of initial sample temperature, atmospheric temperature, and applied cooling rate on membrane cell size and the cell size profile across the membrane thickness were studied using scanning electron microscopy (SEM). The effect of an applied cooling rate was studied for the cases of simultaneous heat and mass transfer aspects of the evaporation process were modeled up to the point of phase separation. Two measures were used to evaluate the model: the extent of anisotropy in the polymer concentration predicted by the model was compared to the extent of anisotropy observed in the cell size using SEM, and the theoretical and experimental weight loss during evaporation were compared.
The use of liquid-liquid thermally induced phase separation (TIPS) to produce anisotropic cellular flat sheet membranes was investigated for the model system isotactic polypropylene (iPP) and diphenyl ether (DPE). Anisotropic structures were obtained experimentally by evaporating diluent from one surface of a polymer diluent solution prior to phase separation. The effects of convective air flow above the exposed surface were studied. The effects on membrane cell size and extent of anisotropy were studied using scanning electron microscopy (SEM); the effects on the iPP concentration profile within the nascent membrane at the time of phase separation were predicted using a model developed in this work. The extent of anisotropy in the membrane and the predicted concentration profile were compared as one measure of the validity of the model. The theoretical and experimental weight loss during evaporation were also compared as a further measure of the validity of the model. The effects of polymer molecular weight on membrane cell size and cell size profile as well as weight loss were also studied.

A comprehensive simulation of the coarsening mechanism coalescence-induced coalescence (CIC) is developed to predict the growth rate of inviscid droplets in a viscous matrix fluid. In CIC, the shape relaxations of coalescing droplets establish flow fields that drive other droplets into contact, thus creating a cascade of coalescence events. It is believed that CIC is responsible for droplet growth in some demixed polymer solutions, such as isotactic polypropylene (iPP) and diphenyl ether (DPE). A cascade of coalescence events is simulated using a three-dimensional molecular dynamics-like simulation of a dispersed two-phase isopycnic fluid system. The coalescence-induced flow is driven mostly by the strong gradients in curvature at the neck of a coalescing pair of droplets, and the flow is modeled analytically by approximating it as due to a ring of point forces. The resultant velocity of each droplet in the suspension is calculated by superimposing all of the coalescence-induced flow fields and applying Faxen’s Law. The mean droplet size (a) grows like \( t^{\xi} \), where \( t \) is the coarsening time and \( \xi \) a growth exponent that increases with increasing minority phase volume fraction \( \phi \). Good agreement with experimental values of \( \xi \) (0.22 < \( \xi \) < 0.47) is obtained for a phase-separated iPP-DPE solution for \( \phi \geq 0.23 \). It is also shown that the droplet size distribution broadens for semidilute suspensions (\( \phi \geq 0.42 \)) but remains relatively narrow for highly concentrated suspensions (\( \phi \geq 0.54 \)). A phenomenological kinetic theory of coalescence is proposed. It is believed that in nondilute emulsions, CIC can account for coarsening that has been attributed previously to more traditional coalescence mechanisms.

Liquid-liquid thermally induced phase separation of the polymer-diluent system of poly(ethylene-co-vinyl alcohol) (EVOH)-glycerol was examined under light scattering. For EVOH with an ethylene content of 38 mol % (EVOH38), maxima of the scattered light intensity were observed that indicated that phase separation occurred by the spinodal decomposition (SD). The growth of
the structures formed by the general liquid-liquid phase separation obeyed a power-law scaling relationship in SD. For EVOH with an ethylene content of 32 mol % (EVOH32), the liquid-liquid phase separation resulted from the polymer crystallization. In this case, the structure growth showed the characteristic behavior in which the crystalline particles were initially formed, and then the droplets formed by the liquid—liquid phase separation induced by the crystallization grew rapidly. Furthermore, the growth of the droplet by the phase separation was followed by an optical microscopic measurement at a constant cooling rate. The phase-separated structure formed after the crystallization can grow faster than that formed by the normal liquid-liquid phase separation.

**L-03-2 PUBLISHED**

**Preparation and Characterization of Poly(ethylene-co-vinyl alcohol) Membranes via Thermally Induced Liquid-Liquid Phase Separation**

Shang, M.; H. Matsuyama; T. Maki; M. Teramoto; D.R. Lloyd


Porous membranes were prepared through the thermally induced phase separation of poly(ethylene-co-vinyl alcohol) (EVOH)/glycerol mixtures. The binodal temperature and dynamic crystallization temperature were determined by optical microscopy and differential scanning calorimetry measurements, respectively. It was determined experimentally that the liquid-liquid phase boundaries were shifted to higher temperatures when the ethylene content in EVOH increased. For EVOHs with ethylene contents of 32-44 mol %, liquid-liquid phase separation occurred before crystallization. Cellular pores were formed in these membranes. However, only polymer crystallization (solid-liquid phase separation) occurred for EVOH with a 27 mol % ethylene content, and the membrane morphology was the particulate structure. Scanning electron microscopy showed that the sizes of the cellular pores and crystalline particles in the membranes depended on the ethylene content in EVOH, the polymer concentration, and the cooling rate. Furthermore, the tendency of the pore and particle sizes was examined in terms of the solution thermodynamics of the binary mixture and the crystallization kinetics.

**L-05-1**

**Effect of the Polypropylene Type on Polymer-Diluent Phase Diagrams and Membrane Structure in Membranes Formed via the TIPS Process. Part 1: Metalloocene and Ziegler-Natta Polypropylenes**

Yave, W., Quijada, R., Serafine, D., and Lloyd, D. R.


**L-05-2**

**Effect of the Polypropylene Type on Polymer Diluent Phase Diagrams and Membrane Structure in Membranes Formed via the TIPS Process. Part 2: Syndiotactic and Isotactic Polypropylenes Produced Using Metalloocene Catalysis**

Yave, W., Quijada, R., Serafine, D., and Lloyd, D. R.


**L-06-1**

**Propylene/1-hexene Copolymer as a Tailor-Made Polypropylene for Membrane Preparation via the Thermally Induced Phase Separation (TIPS) Process**

Yave, W., Quijada, R., Lloyd, D.R., Cerrada, R.B., and Ulbricht, M.


**L-06-2**

**The Effect of Uni-Axial Orientation on Macroporous Membrane Structure**


*Journal of Porous Materials*, in press

**L06-3**

**The Effect of Uni-Axial Stretching on the Roughness of Microfiltration Membranes**


*J. Membr. Sci.*, in press

240
L-06-4
Theoretical Observations of Recirculation Regions in the Bore Fluid during Hollow Fiber Spinning
AIChE J., in press

L-06-5
Microfiltration Membrane of Polymer Blend of Poly(L-lactic acid) and Poly(A-caprolactone)
Tanaka, T., Tsuchiya, T., Takahashi, H., Taniguchi, M., and Lloyd, D.R.
Desalination, 193, 367 C374 (2006)

L-06-6
Formation of Biodegradable Polyesters Membranes via Thermally Induced Phase Separation
Tanaka, T., Tsuchiya, T., Takahashi, H., O’hara, H., and Lloyd, D.R.

P-84-1 PUBLISHED
Effect of Crystallinity on Gas Permeation in Miscible Polycarbonate-Copolyester Blends
Preston, W.E.; J.W. Barlow; D.R. Paul
A paper showing the effect on permeability and separation factors of blending these two polymers when the mixture is amorphous and when the copolyester component is allowed to crystallize via an annealing procedure.

P-84-2 PUBLISHED
Gas Transport in Homogeneous Multicomponent Polymers
Paul, D.R.
Develops theoretical relationships for gas sorption and transport in random copolymers and miscible polymer blends. Specifically concerned with "mixing rules" for the permeability coefficient.

P-84-3 PUBLISHED
Transport Properties of Polymers
Paul, D.R.
A basic review of transport behavior of polymers with references to a variety of applications including, but not limited to, membranes. Intended to be an introduction and not a literature review.

P-84-4 PUBLISHED
Sorption and Transport of Gases in Miscible Poly(methyl acrylate)/Poly(epichlorohydrin) Blends
Chiou, J.S.; J.W. Barlow; D.R. Paul
Discusses sorption and permeation data for He, Ar, N2, CH4, and CO2 in this series of amorphous rubbery miscible blends. Comparison of data with theoretical mixing rules is made.

P-84-5
Selected Reports on Gas Sorption/Transport
Research-Handout for SRP Membrane Study Group Meeting, May 1984
A review of student research results obtained from NSF and ARO projects under the supervision of D. R. Paul. Includes copies of all transparencies used in talks by Paul, Chiou, and Maeda.
P-84-6 Published
Solute Release from Membrane-Membrane-Matrix Composites
Paul, D.R.
Develops mathematical analysis for controlled release of solutes from polymers in which diffusion rates in the matrix and in the membrane covering the matrix are comparable in magnitude.

P-84-7
Selected Reports on Gas Sorption/Transport
Research Handout for SRP Membrane Study Group Meeting, October 1984
A review of student research results. Includes copies of all transparencies used in talks by Muruganandam, El-Hibri, and Story.

P-85-1
Effect of Orientation on Gas Sorption and Transport in Polymers
Paul, D.R.
Extended abstract of a talk given at the IUPAC Symposium on Noncrystalline Order in Polymers, Naples, Italy, May 1985
Results of sorption and transport of gases in polymer films which have molecular orientation resulting from drawing are used to speculate about behavior of liquid crystalline polymers (P-85-1) (LCPs).

P-85-2 Published
Plasticization of Glassy Polymers by CO2
Chiou, J.S.; J.W. Barlow; D.R. Paul
Describes a differential scanning calorimetry (DSC) technique for measuring the Tg of polymers containing dissolved CO2. Technique will be of value in assessing effects of high CO2 partial pressures on membranes.

P-85-3 Published
Polymer Crystallization Induced by Sorption of CO2 Gas
Results show that because dissolved CO2 plasticizes glassy polymers, the presence of CO2 can sometimes induce certain polymers to crystallize just as liquid and vapor sorption are known to do.

P-85-4 Published
Gas and Vapor Sorption in Polymers Just Below Tg
Chiou, J.S.; Y. Maeda; D.R. Paul
Sorption isotherm shape is dependent on whether the polymer is above or below Tg. For gases that plasticize, Tg may be above the observation temperature at low pressures but below it at high pressures. This results in a transition from a curved isotherm at low pressures to a linear isotherm at high pressures.

P-85-5 Published
Effects of Uniaxial Drawing and Heat-Treatment on Gas Sorption and Transport in PVC
El-Hibri, M.J. and D.R. Paul
An extensive study of the drawing behavior of poly(vinyl chloride)(PVC) and its effects on birefringence, density, thermal characteristics, gas sorption, and gas permeation. The study is unique in that it separates the changes caused by thermal treatment from those caused by molecular orientation.
Selective Gas Transport in Miscible PPO-PS Blends
Maeda, Y. and D.R. Paul
Polymer 26:2055 (1985)
Permeation rates of He, CO2, and CH4 through PS and poly(phenylene oxide) (PPO) blends are reported as a function of pressure. Estimated separation factors are higher for some blends than for either pure polymer.

Modeling of Solute Release from Laminated Matrices
Paul, D.R.
The Higuchi model for diffusion-controlled release of a solute from a matrix whose initial loading of solute is greater than the solubility limit was used to analyze the temporal release pattern from laminated sheets having different levels of initial solute loading. The solute release rate of such laminates is more constant than simple single-layer matrix structures.

Sorption Equilibria and Kinetics of Ethanol in Miscible Poly(vinylidene fluoride)/Poly(methyl methacrylate) Blends
Chiou, J.S. and D.R. Paul
Polymer Engineering and Science 26:1218-27 (1986)
This study shows that the equilibrium sorption and kinetics of ethanol are affected by blend composition and polymer film history.

Effects of Uniaxial Drawing and Processing Temperature on Gas Transport in Poly(vinylidene fluoride)
El-Hibri, M.J. and D.R. Paul
Sorption and transport behavior of various gases in PVDF were studied prior to and following uniaxial drawing and heat treatment operations. The results have been interpreted in terms of existing theories on morphology and microstructure in semicrystalline polymers (P-85-9).

Sorption and Transport of Inert Gases in PVF2/PMMA Blends
Chiou, J.S. and D.R. Paul
Sorption and transport of several inert gases (He, Ar, N2, and CH4) in miscible blends of PMMA and PVDF are reported as a function of pressure at 35°C. The data are analyzed using appropriate models for sorption and transport, and the parameters are correlated in terms of blend composition and molecular characteristics of the gases.

Sorption and Transport of CO2 in PVF2/PMMA Blends
Chiou, J.S. and D.R. Paul
Sorption and transport of CO2 in miscible PVDF/ PMMA blends are reported at 35°C as a function of pressure from 1 to 25 atm. Significant plasticization by CO2 is evident for all blend compositions. Modified sorption and transport models that account for plasticization are used to analyze the data.
Homogeneous, Multicomponent Glassy Polymers as Membranes for Gas Separations
Maeda, Y.
PhD dissertation
A study of the sorption and transport of various gases in miscible PS/PPO blends and in PS, polysulfone (PSF), and PPO containing low molecular weight additives. In some cases, antiplasticization was observed. A manuscript describing the PPO/PS blend results is available (P-85-6); the plasticization cases have not been summarized into a separate manuscript.

Sorption and Transport Behavior of Miscible Polymer Blends
Chiou, J.S.
PhD dissertation
A report on the sorption and transport behavior in two miscible blend systems: poly(epichlorohydrin)/PMMA blends and PVDF/PMMA blends. The former are rubbery and amorphous, but the latter are both rubbery and glassy with various levels of crystallinity. Solubilities, diffusion coefficients, and permeabilities of five gases in all blends and sorption kinetics of ethanol in PVDF/PMMA blends were measured at 35°C and correlated with the blend composition to compare with ideal mixing rules. Results of this dissertation appear in P-85-8, P-85-10, and P-85-11.

Selected Reports on Gas Sorption/Transport
Research-Handout for the SRP Membrane Study Group Meeting, October 1985
A review of student research results and plans for future research. Includes a copy of all transparencies used by Barbari, Muruganandam, Chiou, Raymond, and Puleo.

Effects of Mechanical Drawing on Gas Transport in an Emulsion Acrylic Multipolymer
El-Hibri, M.J. and D.R. Paul
A study was conducted on the gas sorption and transport properties of a multiphase commercial acrylic polymer before and after subjecting the polymer to mechanical drawing. The drawing technique greatly increased the permeability to several gases. These changes are interpreted in terms of a morphological transformation in the phases of the drawn polymer, which causes the originally dispersed rubber particles to assume a more continuous character.

Gas Transport in Partially Fluorinated Low-Density Polyethylene
Kiplinger, C.L.; D.F. Persico; R.J. Lagow; D.R. Paul
Low density polyethylene film was subjected to direct fluorination by exposure to a dilute fluorine gas stream for various periods of time. Permeability coefficients for He, CO2, and CH4 were measured at 35°C. The permeability of He was not changed by fluorination, but the values for CO2 and CO4 were decreased by as much as two orders of magnitude. The selectivity of transport (P-85-16) for gas pairs of different molecular size was greatly improved, suggesting applications of this technique for membrane separation processes.

Water Extraction of Polyethyloxazoline from Miscible and Immiscible Polymer Blends
Pfenning, J.L.G.; H. Keskkula; D.R. Paul
Recent studies suggest that it is surprisingly difficult to extract a hydrophilic polymer from a miscible blend with a hydrophobic polymer by water. These authors' research confirms this conclusion through the use of blends of water soluble polyethyloxazoline with a series of styrene/acrylonitrile copolymers of different acrylonitrile contents.
P-85-18 PUBLISHED
Plasticization of Glassy Polymers by CO₂
Chiou, J.S.; J.W. Barlow; D.R. Paul
A technique is described which uses DSC to estimate the glass transition of polymers containing a dissolved gas. The effects of CO₂ sorption at pressures up to 25 atm were examined in detail for PMMA and its blends with PVDF. Less extensive results for PS, polycarbonate (PC), PVC, and poly(ethylene terephthalate) are also given. Reductions in Tg of up to 50°C are observed. A theoretical relation by Chow predicts results in reasonable agreement with the experimental data. These findings are relevant to various applications such as membrane separation processes for gases.

P-85-19 PUBLISHED
Sorption and Transport of Gases in Miscible Poly(methyl acrylate)/Poly(epichlorohydrin) Blends
Chiou, J.S.; J.W. Barlow; D.R. Paul
The sorption and the transport of He, Ar, N₂, CH₄, and CO₂ in miscible poly(methylacrylate)/poly (epichlorohydrin) blends from 1 to 20 atm at 35°C are reported. For He, Ar, N₂, and CH₄, the permeabilities and the diffusion time lags are independent of the upstream pressure. The permeability of CO₂ increases with upstream pressure but solubility follows a simple Henry's law behavior. For all five gases, the dependence of solubility, diffusion coefficient, and permeability on blend composition are compared with theoretical mixing rules with the conclusion that both the interaction energy density and the excess activation energy for gas diffusion in the blends are near zero.

P-86-1
Selected Reports on Gas Sorption/Transport; Research-Handout for the SRP Membrane Study Group Meeting, April 1986
Includes a copy of all transparencies used by Barbari, Chiou, and Muruganandam for presentation of their research results.

P-86-2 PUBLISHED
Gas Permeation in Polyethersulfone
Maeda, Y. and D.R. Paul
The permeability of He, methane, and CO₂ in polyethersulfone (PES) are reported and compared to polycarbonate and PSF. The latter have comparable gas permeabilities which are about an order of magnitude greater than permeabilities for PES, which does not have the bulky bisphenol-A unit as part of its structure. The activation energy for CO₂ permeation in PES is about twice that for PSF. The effects of solution versus melt fabrication for PSF are shown.

P-86-3 PUBLISHED
Effect of Antiplasticization on Gas Sorption and Transport. Part I: Polysulfone
Maeda, Y. and D.R. Paul
The addition of tricresyl phosphate, N-phenyl-2-naphthylamine, and 4,4'-dichlorodiphenyl sulfone to PSF causes changes in thermal and mechanical properties of the glassy mixtures associated with antiplasticization, i.e., reduction in glass transition temperature and increase in stiffness. These changes are also found to be accompanied by reductions in sorption of CO₂ and the permeability coefficients for He, CO₂, and methane at low diluent concentrations with reversal of these trends at higher levels as also occurs for the mechanical properties.
Effect of Antiplasticization on Gas Sorption and Transport. Part II: Poly(phenylene oxide)
Maeda, Y. and D.R. Paul
The propensity for various diluents to cause antiplasticization of PPO was examined and compared to similar responses for PSF. Of the diluents used, none resulted in significant stiffening of PPO at 35°C relative to what was observed for PSF in an earlier study. However, these diluents did cause substantial reduction in gas sorption levels and permeability coefficients. The latter is consequently a more sensitive indicator of changes in molecular motions of glassy polymers caused by diluents. The permeability response of adding low molecular weight diluents is compared to that of adding a high molecular weight polymer, PS, to PPO.

Effect of Antiplasticization on Gas Sorption and Transport. Part III: Free Volume Interpretation
Maeda, Y. and D.R. Paul
The antiplasticization of PSF and PPO by low molecular weight diluents is accompanied by substantial reductions in permeability to gases like He, CO2, and methane because of reduced mobility in the glass. These effects are not explained even qualitatively by the extent of volume contraction on mixing for these mixtures. However, a simple free volume treatment provides an excellent correlation of these effects. Free volume was computed from measured specific volume and an estimate of the volume at the absolute zero of temperature of the material from a group contribution method.

Effect of Antiplasticization on Selectivity and Productivity of Gas Separation Membranes
Maeda, Y. and D.R. Paul
Addition of certain low molecular weight diluents cause glassy polymers to become stiffer owing to reduced rates of segmental motions. This antiplasticization response is accompanied by a decrease in permeability to gases and may be accompanied by either an increase or a decrease in the selectivity of transport for any two gases. When compared with the trade-off between selectivity and productivity of gas separation membranes made from a variety of polymer structures, antiplasticization does not offer any advantageous combination of these traits for either PSF or PPO. However, this approach may have value when increased selectivity at the expense of productivity is justified and the development of membranes from another polymer is not desirable.

Effects of Molecular Orientation and Processing Conditions on Gas Sorption and Transport in Various Polymers
El-Hibri, M.J.
PhD dissertation
Gas sorption and transport properties were examined for various polymers prior to and following mechanical drawing and heat-treatment operations. The materials studied were PVC, PVDF, bisphenol-A polycarbonate, and a rubber-modified emulsion acrylic polymer (trade name Korad(r) ACV). Sorption and transport data were obtained and correlated for five gases: He, Ar, N2, CH4, and CO2. Orientation and heat-treatment effects on transport; were investigated over a wide range of processing temperatures for each polymer. Drawing was performed in both the glassy and rubbery state temperature regimes for the amorphous polymers (PVC, polycarbonate, and Korad(r) ACV). For the semicrystalline PVDF, processing temperatures in the solid state and the melt state were employed. Drawing was primarily restricted to the uniaxial mode, but some biaxial samples were also examined.
Gas Permeation in Miscible Blends of Poly(methyl methacrylate) with Bisphenol Chloral Polycarbonate
Chiou, J.S. and D.R. Paul

Blends of PMMA, with bisphenol chloral polycarbonate (BCPC) are miscible over the whole composition range. Single composition dependent Tg and LCST behavior have been observed for each blend. The specific volumes of the blends follow closely the simple additivity rule indicating the interaction between PMMA and BCPC is weak. Gas permeability coefficients for He, H2, O2, Ar, N2, CH4, and CO2 measured at 35°C under 1 to 2 atm upstream pressure are lower than those calculated from the semi-logarithmic additivity rule. The difference between this calculated permeability and the measured one increases with gas molecular size. As a result, the ideal gas separation factors for He/CH4, CO2/CH4, and O2/N2 gas pairs estimated from the ratio of pure gas permeabilities are higher than predicted from the semilogarithmic additivity rule. These permeation results were interpreted in terms of free volume theory and the activated state theory.

Selected Reports on Gas Sorption/Transport
Research-Handout for SRP Membrane Study Group Meeting, October 1986

A review of student research projects including all transparencies used by Paul, Barbari, Raymond, and Puleo in their presentations.

Mixed Gas Transport in Multicomponent Polymers
Paul, D.R. and W.J. Koros
Proposal approved by the Petroleum Research Fund
Complete technical text of a proposal submitted to the PRF (administered by the American Chemical Society), which resulted in a three-year grant to Drs. Paul and Koros for the study of controlled plasticization of polymer membranes by gases like CO2 and their effects on mixed gas transport.

Gas Sorption and Transport in Substituted Polycarbonates in Substituted Polycarbonates
Muruganandam, N.; W.J. Koros; D.R. Paul
The effects on sorption and transport of various gases were studied using tetramethyl, tetrachloro, and tetrabromo substitutions onto the aromatic rings of bisphenol-A polycarbonate. Solubility and permeability measurements were made at 35°C over the pressure range of 1-20 atm for a variety of gases, namely CO2, CH4, O2, N2, and He. A two- to threefold increase in permeability was caused by the tetramethyl substitution whereas the tetrachloro and tetrabromo substitutions reduced the permeability relative to the tetramethyl substitution.

Gas Transport in a Thermotropic Liquid Crystalline Polyester
Chiou, J.S. and D.R. Paul
Gas permeation in a commercially available LCP (Vectra® from Celanese) has been studied. This polymer appears to be comparable or better than polyacrylonitrile (PAN) as a barrier material; however, selectivity of transport is exceptional. The low gas permeabilities appear to stem from abnormally low solubility coefficients rather than low mobility. This is a preliminary report and more work is planned.
Effects of CO₂ Exposure on Gas Transport Properties of Glassy Polymers
Chiou, J.S. and D.R. Paul
The effects of CO₂ driving pressure and CO₂ exposure history on transport properties for two polycarbonates and two acrylic polymers are described. For the polycarbonates, the CO₂ permeability decreases with increased driving pressure, while exposure to CO₂ causes (in subsequent measurements) a decrease in permeability and an increase in the diffusion time lag. For the acrylics, each response is exactly the opposite. The effects may be important for membrane separation processes involving CO₂ at high pressures.

Gas Permeation in Miscible Homopolymer-Copolymer Blends: I. Poly(methyl methacrylate) and Styrene/Acrylonitrile Copolymers
Chiou, J.S. and D.R. Paul
Gas transport properties in homogeneous blends of PMMA with each of two styrene with acrylonitrile (SAN) random copolymers, containing 13.5% and 28% by weight of acrylonitrile respectively, have been measured at 35°C for He, H₂, O₂, N₂, Ar, CH₄, and CO₂. For all cases, the permeability and diffusion coefficients are higher than those expected from the semilogarithmic additivity rule. On the other hand, the solubility coefficients and the ideal gas separation factors follow this rule well. These results for PMMA/SAN blends differ from those observed recently for other miscible blend systems; however, they agree well with recent theories proposed to describe gas sorption and permeation behavior in polymer mixtures.

Gas Permeation in Miscible Homopolymer-Copolymer Blends: II. Tetramethyl Bisphenol-A Polycarbonate and a Styrene/Acrylonitrile Copolymer
Chiou, J.S. and D.R. Paul
Gas sorption and transport properties are reported for miscible blends of TMPC and a random copolymer of SAN containing 9.5% by weight of acrylonitrile. All gas permeability, diffusion, and solubility coefficients obtained are lower than that calculated from the semilogarithmic additivity rule. For He/CH₄ and H₂/CH₄ pairs, the permselectivities for the blends are higher than that for either pure tetramethyl bisphenol-A polycarbonate (TMPC) or SAN. The deviation from additivity for gas transport properties of TMPC/SAN blends is opposite of that observed for PMMA/SAN blends because of the stronger interactions in the former.

Evaluation of Substituted Polycarbonates and a Blend with Polystyrene as Gas Separation Membranes
Muruganandam, N. and D.R. Paul
The balance between the rate and the selectivity of transport has been examined for various gas pairs in a series of polycarbonates where the four available positions on the aromatic rings of the bisphenol-A unit were H₂, CH₃, C₁, or Br. CH₃ substitution increases the permeability to O₂ by nearly a factor of four with no loss in O₂/N₂ selectivity compared to polycarbonate while using Br substitution increases O₂/N₂ selectivity by 50% without any loss in O₂ permeability compared to polycarbonate. The TMPC forms miscible blends with PS. These blends show absolute permeability coefficients which are lower than additivity while the selectivity of transport is greater.
Gas Sorption and Transport in Miscible Blends of Tetramethyl Bisphenol-A Polycarbonate and Polystyrene
Muruganandam, N. and D.R. Paul
Permeability coefficients for He, O2, N2, CH4, and CO2 in miscible blends of PS and TMPC are reported along with sorption isotherms for CO2 and CH4. For each gas, the permeability was found to go through a minimum when plotted against blend composition because of the volume change on mixing observed for this system. The attractive interaction between TMPC and PS is relatively strong based on density and solubility data.

Sorption and transport of various gases in polycarbonates having tetramethyl, tetrachloro, and tetrabromo substitutions onto the aromatic rings of the bisphenol-A units are reported. Similar results are reported for a miscible blend system containing TMPC and PS. Methyl substitution causes a three- to fourfold increase in permeability while chlorine and bromine substitutions reduce the permeability relative to the methyl-substituted polymer. The substituted polymers and the blend were evaluated as gas separation membranes for CO2/CH4, O2/N2, and He/CH4 separations. Substitutions were found to improve the productivity-selectivity relation in these separations, but no definite advantages were seen in the case of blending.

Gas sorption and permeation measurements for CO2, CH4, and N2 were made with three polymers based on bisphenol-A-a polyhydroxyether, a polyetherimide, and a polyarylate. These data, plus previous data on two other bisphenol-A polymers-polycarbonate and PSF-were analyzed using the dual mode/partial immobilization model and the more recent gas-polymer-matrix model. These models were compared on the basis of physical interpretations of the resulting parameters. Permeation measurements for O2 and He were also made with the three above-mentioned polymers. Parameters from the dual mode/partial immobilization model were related to various gas and polymer properties. The Langmuir saturation capacity was related to the unrelaxed volume of the glassy polymer. The Henry's law coefficient was related to the internal pressure of the polymer and its tensile stress at yield. The infinite dilution diffusion coefficient was related to the free volume of the polymer. The work suggests a means for estimation of gas sorption levels from thermal and mechanical properties of the polymer. The work also suggests a means for order-of-magnitude estimation of diffusion coefficients from the density and molecular structure of the polymer. Permeation measurements were also made for a mixture of CO2 and CH4 with PSF, polyarylate, polyetherimide, and polyhydroxyether. The experimental permeabilities were compared to values predicted with a mixed gas extension of the dual mode/partial immobilization model. Actual separation factors were determined and compared to predicted and ideal values. No general conclusions could be drawn regarding the ability of the mixed gas model to predict the actual data. Proper membrane conditioning and a more extensive data base are recommended for future mixed gas work.

Selected Reports on Gas Sorption/Transport Research-
Handouts for the Separations Research Program Spring Conference, April 1987
Includes copies of transparencies used by Paul, McHattie, and Min for the Gas Separations Using Membranes Study Group (P-87-6) Meeting.
Gas Sorption in Polymers Based on Bisphenol-A
Barbari, T.A.; W.J. Koros; D.R. Paul
Equilibrium gas sorption measurements for CO2, CH4, and N2 were made with three polymers based on bisphenol-A, viz. a polyhydroxyether, a polyetherimide, and a polyarylate. These data, plus previous results for two other bisphenol-A polymers, polycarbonate and PSF, were analyzed using the dual mode sorption model and the more recent gas-polymer-matrix model. The models were compared on the basis of physical interpretations of the resulting parameters. The Langmuir capacity from the dual mode model was related to the unrelaxed volume of the glassy polymer. The Henry's law sorption parameter from the dual mode model was related to the internal pressure of the polymer and to its tensile stress at yield. The work suggests a means for estimation of gas sorption levels from thermal and mechanical properties of the polymer.

Gas Transport in Polymers Based on Bisphenol-A
Barbari, T.A.; W.J. Koros; D.R. Paul
Permeation measurements for CO2, CH4, O2, N2, and He were made with three polymers based on bisphenol-A, viz. a polyhydroxyether, a polyetherimide, and a polyarylate. Measurements were also made for CO2 and CH4 in PSF. The data for CO2, CH4, and N2, plus previous data for these gases in polycarbonate and PSF, were combined with equilibrium gas sorption data and analyzed with the dual mode/partial immobilization model and the more recent gas-polymer-matrix model. A comparison of the two models was done on the basis of physical interpretations of the resulting parameters. The diffusion coefficient for the Henry's law population was related to the kinetic diameter of the gas. The infinite dilution, Henry's law, and Langmuir diffusion coefficients were related to the free volume of the polymer. The work suggests a means for order-of-magnitude estimation of diffusion coefficients from polymer density and molecular structure.

Effect of Tacticity on Permeation Properties of Poly(methyl methacrylate)
Min, K.E. and D.R. Paul
The effect of stereo regularity on gas permeation properties of PMMA was investigated for He, H2, O2, N2, Ar, CH4, and CO2 at 35°C. The permeability, solubility, and diffusion coefficients increase as the content of syndiotactic sequences increase. These observations are consistent with more dense packing of the isotactic form in the glassy state that stems in part from its lower glass transition temperature. The transport behavior for a 50/50 isotactic/syndiotactic blend was also studied. These so-called stereo complexes exhibit permeation behavior comparable to other weakly interacting miscible blend systems. Separation factors are presented.
Polymeric Membranes Based on Bisphenol-A for Gas Separations
Barbari, T.A.; W.J. Koros; D.R. Paul
Five commercially available bisphenol-A based polymers were used to examine the effect of the connecting group between bisphenol-A units on the gas separation characteristics of membranes formed from these polymers. An unusually high He/CH4 selectivity was noted for one of the members in the series of polymers. Permeability coefficients and separation factors for a mixture of CO2 and methane were measured and compared to predicted values from pure gas permeability coefficients.

Gas Permeation in a Dry Nafion Membrane
Chiou, J.S. and D.R. Paul
A perfluorosulfonic acid polymer membrane; (Nafion 117) was extensively dried in vacuum after which gas transport properties were measured at 35°C for He, H2, O2, Ar, N2, CH4, and CO2. In the dry state, this membrane has high separation factors for He/CH4, He/H2, and N2/CH4 relative to other polymeric membranes; however, this material is no better than many other polymers for CO2/CH4 or O2/N2 separations. The transport properties are compared with other information in the literature and discussed in terms of the complex phase structure of the ionomeric material.

Gas Sorption and Transport in Semicrystalline Poly(4-methyl-1-pentene)
Puleo, A.C.; D.R. Paul; P.K. Wong
Polymer 30:1357 (1989)
The solubility of CO2 and CH4, plus permeability coefficients for these and other gases, were measured for a series of PMP polymers with crystallinity levels ranging from 20% to 75%. The crystallinity was varied through thermal treatment and by addition of a comonomer that permitted thermally induced crosslinking. An extrapolation, assuming a two-phase model, of the sorption results to 100% crystallinity indicates a finite solubility for CO2 and CH4 in the crystal (about 25% to 30% of the solubility for the amorphous phase). Regression analysis of the permeation data using a two-phase transport model indicated that diffusion occurs at finite rates in the crystal. This is contrary to the usual situation for polymers like polyethylene but is consistent with the unusual fact that the density of the PMP crystal is slightly less than that of the amorphous phase. The diffusion rate in the crystal appears to become nil as the dimensions of the gas molecules exceed the estimated gap sizes between chains in the crystal.

Response to Comments by Vrentas, Duda and Ling
Paul, D.R. and Y. Maeda
A rebuttal to comments criticizing the use of a simple free-volume correlation for diffusion coefficients of gases in polymers.

The Effects of Pendant Groups on Gas Sorption and Transport in Polymers
Puleo, A.C.
PhD dissertation
The relationship between the chemical structure of a polymer and gas sorption and transport was examined by focusing on the effects of pendant groups. Three aspects were considered: (1) a semicrystalline polymer with large pendant groups that interfere with chain packing in the crystal; (2) a commercial membrane material with strong interactions between pendant groups; and (3) a systematic variation of pendant groups to isolate the individual effect of each functionality.
P-89-3
Selected Reports on Gas Sorption/Transport Research
Handouts for the Separations Research Program Fall Conference, September 1988
Includes copies of transparencies used by Mohr, Raymond, and Puleo for the Gas Separations Using Membranes Study Group (P-89-3) Meeting.

P-89-4 PUBLISHED
Gas Sorption and Permeation in Poly(ethyl methacrylate)
Chiou, J.S. and D.R. Paul
Gas sorption isotherms for N2, Ar, CH4, and CO2 have been measured at various temperatures for poly(ethyl methacrylate) (PEMA) below its Tg. For the three low solubility gases, N2, Ar, and CH4, the sorption isotherms are concave as predicted for glassy polymers (P-89-4), but the amount of sorption in PEMA is much lower than that in high Tg polymers. For the higher solubility gas CO2, however, the amount of sorption is the same as that in high Tg polymers. Gas permeability coefficients for PEMA to He, H2, O2, Ar, N2, and CH4 measured at 35°C are independent of pressure, but those for CO2 increase with pressure. Appropriate models are used to describe the transport behavior. Evidence from gas sorption and DSC thermograms show that PEMA can sub-Tg anneal under CO2 plasticization. However, when the Tg is depressed by plasticization below the observation temperature, the annealing effect is erased.

P-89-5
Advanced Polycarbonate and Polysulfone Materials for Membrane-Based Gas Separation Applications
Hellums, M.W.; J.S. McHattie; W.J. Koros; D.R. Paul
A program to develop advanced polymeric membranes for gas separation applications is described. The work focuses on the interpretation of high-pressure gas permeation, sorption, and diffusion data for a series of novel polymers.

P-89-6
Gas Sorption and Diffusion within Polymer Crystallites
Puleo, A.C. and D.R. Paul
Poster presented at the North American Membrane Society Meeting, Syracuse, New York, June 1988
Short discussion on the effect of crystallinity on gas sorption in polyethylene and PMP.

P-89-7 PUBLISHED
Gas Sorption and Transport in Substituted Polystyrenes
Puleo, A.C.; N. Muruganadam; D.R. Paul
The effects of pendant groups on gas transport; were investigated using a series of substituted polystyrenes. Permeability coefficients were measured at 35°C and 1 atm for He, N2, O2, CH4, and CO2, and diffusion coefficients were calculated from time lag data. The absolute permeabilities for the polystyrenes are correlated reasonably well using a free volume model. All pendant group substitutions resulted in a reduction of the mobility selectivity for CO2/CH4 separation relative to PS, although there was very little effect on the O2/N2 selectivity. The effects of the various substitutions were analyzed in terms of size, rigidity, and polarity.

P-89-8 PUBLISHED
The Effect of Degree of Acetylation on Gas Sorption and Transport Behavior in Cellulose Acetate
Puleo, A.C.; D.R. Paul; S.S. Kelley
Journal of Membrane Science 47:301 (1989)
Cellulose acetate films with degrees of substitution of 1.75, 2.45, and 2.84 were characterized in terms of chemical composition, acetyl group distribution, glass transition, crystallinity, and dynamic mechanical properties. Permeability coefficients for a series of gases, at 1 atm and 35°C,
were found to increase with degree of acetylation. Sorption isotherms for CO2 and CH4 at 35°C were analyzed in terms of the dual mode sorption model. The permeability of CO2 was found to increase with pressure above 10 atm due to plasticization. Highly sorbing CO2 swells the polymer such that interchain interactions are disrupted and segmental mobility increases.

**P-89-9**

**Selected Reports on Gas Sorption/Transport Research**

Handouts for the Separations Research Program Spring Conference, April 1989

Includes copies of transparencies used by Paul, Weinkauf, and Aitken for the Membrane Technology Study Group (P-89-9) Meeting.

**P-89-10 NO LONGER AVAILABLE**

**P-89-11**

**Selected Reports on Gas Sorption/Transport Research**

Handouts from the Separations Research Program Fall Conference, September 1989

Includes copies of handouts used by Paul, Mohr, McHattie, Weinkauf, Aitken, and Aguilar-Vega for the Membrane Technology Study Group (P-89-11 Meeting).

**P-89-12 PUBLISHED**

**Sorption and Transport of Pure CO2 Polycarbonate/Poly(methyl methacrylate) Blends and CH4 in Miscible Bisphenol Chloral**

Raymond, P.C. and D.R. Paul


Sorption and permeation behavior of CO2 and CH4 was examined in detail for a series of miscible blends based on BCPC and PMMA. The former pure polymer exhibits decreases in the permeability coefficients for both CO2 and CH4 as the upstream driving pressure increased, as predicted by the dual mode sorption model. On the other hand, PMMA shows a decrease for CH4 but an increase for CO2. The latter is attributed to plasticization by this more soluble gas. The blends show intermediate behavior. CO2 permeation was examined on pressurization, at constant pressure for two weeks, and then on depressurization. The pattern of behavior progressively changed between that of BCPC and PMMA as the MMA content of the blends was varied. These trends were contrasted with that found for a series of styrene methyl methacrylate (SMMA) copolymers described previously. Some differences in behavior between the blends and the copolymers were noted when compared at constant MMA content. These results have important ramifications for the design and selection of polymers for membranes to separate the CO2/CH4 gas pair.

**P-89-13 $20.00**

**Controlled CO2 Plasticization of Random Copolymers and Miscible Polymer Blends**

Raymond, P.C.

PhD dissertation

The sorption and transport behavior of several gases in a series of random SMMA copolymers and miscible bisphenol chloral polycarbonate/PMMA blends (PCMMMA) was investigated. The solubility of CO2 was high and increased with methyl(methacrylate) (MMA) content. The CO2 permeability change in isobaric (20 atm) experiments ranged from -6% (PS) to 57% (PMMA) showing that MMA content could control plasticization. An isoconcentration (C2i = C2PS at 20 atm) study yielded a larger (11%) increase in CO2 permeability for PMMA than PS, confirming that CO2 concentration was not the only factor controlling plasticization. Long-term, high-pressure CO2 experiments investigated the effects of gas conditioning. The rates of conditioning for SMMA copolymers were similar for isoconcentration conditions and appeared to be determined by CO2 concentration. Conversely, isoconcentration rates for the blends were different, PMMA being the highest, reflecting the varied response of these polymers to CO2 concentration.
The Effects of Structural Order on Barrier Properties
Weinkauf, D.H. and D.R. Paul
In Barrier Polymers and Barrier Structures, W. J. Koros (ed.), ACS Symposium Series, No. 423.
Washington, D.C.: American Chemical Society

The effects of molecular order on the gas transport mechanism in polymers are examined. Generally, orientation and crystallization of polymers improve the barrier properties of the material as a result of the increased packing efficiency of the polymer chains. Liquid crystal polymers have a unique morphology with a high degree of molecular order. These relatively new materials have been found to exhibit excellent barrier properties. An overview of the solution and diffusion processes of small penetrants in oriented amorphous and semicrystalline polymers is followed by a closer examination of the transport properties of LCPs.

Sorption and Transport of Pure Gases in Random Styrene/Methyl Methacrylate Copolymers
Raymond, P.C. and D.R. Paul

Previous work has shown that permeability coefficients for CO2 can increase with pressure for PMMA; whereas, those for PS decrease slightly as found for many glassy polymers. This response is attributed to a greater propensity for PMMA to be plasticized by CO2. This issue is considered in detail here by examining the behavior of a series of random SMMA copolymers in order to learn how the plasticization response varies with MMA content. At low pressure, the sorption and transport of CO2 and other gases in these copolymers depend on copolymer composition in ways expected from simple theories for multicomponent polymers. The change in CO2 permeability coefficient on pressurization from 1 to 20 atm ranged from -6% for PS to +57% for PMMA. In addition, upon holding at 20 atm of CO2 driving pressure, the CO2 permeability coefficient significantly increased with time for PMMA; whereas, this conditioning effect was much smaller for PS. Conditioning and plasticization effects seem to be related to the same molecular causes. The responses change progressively for the copolymers but not directly proportional to MMA content. The greater effects of CO2 for PMMA are to a significant extent, but not entirely, due to its much higher level of CO2 sorption compared to PS. The results are discussed in terms of relevant theories.

Kinetics of CO2 Conditioning of Copolymers and Blends Containing MMA Units
Raymond, P.C. and D.R. Paul

Long-term, high-pressure CO2 permeation experiments were conducted for SMMA random copolymers and BCPC/PMMA miscible blends to investigate the effects of gas conditioning. The extent and rate of CO2 permeability changes with time increased dramatically with content of MMA units in both series when compared at a constant upstream CO2 pressure of 20 atm. The higher solubility of CO2 in PMMA than PS or the polycarbonate was found to be responsible for a part but not all of this response, as shown by isobaric versus isoconcentration experiments. The rate of conditioning cannot be described by a single relaxation time. The conditioning process discussed here seems to be intimately connected to the plasticization process reported earlier for these same systems.

Effect of Structural Modifications on the Gas Transport Properties of Polysulfones and Polycarbonates
McHattie, J.S.
PhD dissertation

The gas sorption and transport properties of a number of structurally modified polysulfones and polycarbonates are reported. Two types of substitutions have been investigated, replacement of the isopropylidene unit of the bisphenol-A monomer or substitution for phenylene hydrogens with methyl groups. The polysulfones were synthesized from commercially available monomers, while...
the polycarbonates were obtained from industrial sources. Permeability measurements were made for He, H2, O2, N2, CH4, and CO2 at 35°C over a range of pressures up to 20 atm. Sorption experiments were also done for N2, CH4, and CO2 under the same conditions. The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and DSC were used to judge chain mobility, while x-ray diffraction and free volume calculations provide information about chain packings. The independent effects of chain packing and chain stiffness allow for some deviation from the usual trade-off between permeability and selectivity. Therefore, structural modifications that purposefully affect these two factors can be used to tailor new materials for gas separation applications. The size, placement, flexibility, and polarity of the substituent groups are critical issues in determining the effects on gas transport properties. Bulky, immobile substituents, including symmetric ring replacements, generally result in more rigid and open structures that are highly permeable and maintain relatively high selectivity. Asymmetric dimethyl ring replacement results in tightly packed structures that are highly selective, but less permeable than the unsubstituted materials. Flexible substituents or groups that are easily polarized also tend to increase packing efficiency, yielding low permeability.

**P-90-2 PUBLISHED**

**Gas Transport Properties of Polysulfones. Part I: Role of Symmetry of Methyl Group Placement on Bisphenol Rings**

McHattie, J.S.; W.J. Koros; D.R. Paul

Polymer 32:840 (1991)

Gas sorption and transport properties are reported for a series of polysulfones having either two or four phenylene hydrogens per repeat unit replaced with methyl groups. The results for tetramethyl bisphenol-A PSF (TMPSF), dimethyl bisphenol-A polysulfone (DMPSF), and dimethyl bisphenol-Z polysulfone (DMPSF-Z) are compared to unsubstituted bisphenol-A PSF. The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and DSC were used to judge chain mobility, while x-ray diffraction and free volume calculations give information about chain packing to 20 atm. Sorption experiments were also done for N2, CH4 and CO2 under the same conditions. The permeability coefficients of these polymers rank in the order of TMPSF>>PSF>>DMPSF>DMPSF-Z for all the gases. This order correlates well with free volume as well as with the g transition temperature. The symmetric methyl substitution of TMPSF yields a relatively open structure with improved separation characteristics over PSF. The asymmetric substitution results in tightly packed structures for the dimethyl materials, which are highly selective but less permeable than PSF or TMPSF. The flexible cyclohexane substituent of DMPSF-Z further reduces the gas permeability and improves the selectivity.

**P-90-3 $15.00**

**Surface Fluorination of Gas Separation Membranes**

Mohr, J.M.

PhD dissertation

The potential use of surface fluorination to improve the gas separation properties of polymer membranes was investigated using PMP and PSF. Fluorination was found to lead to a reduction in flux accompanied by a very significant increase in selectivity. The series resistance model was used to illustrate the relationship between the total membrane thickness and the fraction that the fluorinated polymer layer contributes to the total. This relationship was demonstrated experimentally by fluorinating PMP membranes of varying thicknesses. The transport of six gases was measured and the transport properties of the fluorinated polymer layer are estimated to be two orders of magnitude lower than that of the original PMP. Upon exposure to molecular fluorine, some of the H2 atoms in the polymer are replaced with larger and more polar fluorine atoms. The transport properties of two polymer series were investigated to understand the effect this substitution has on solubility and diffusivity. Gas sorption and permeation measurements were made for a series of poly(ether ketone) (PEK) polymers where the isopropylene [-C(CH3)2-] groups in the backbone are systematically replaced with hexafluoro-isopropylidene [-C(CF3)2-] units. The gas transport properties of some vinyl and vinylidene polymers were compared to
examine the effect of pendant group type (H, CH3, F, and Cl) and symmetry of placement. An investigation of the effect of casting solvent on the permeability of PMP was done. Permeability coefficients were measured on films of PMP cast from six solvents and they can differ by a factor of nearly six for some films. X-ray diffraction patterns and thermal analysis were used to show that the casting solvent influences which crystalline modification is formed and the spatial arrangement of the crystallites within the film.

P-90-4 PUBLISHED
Surface Fluorination of Composite Membranes. Part I. Transport Properties
Mohr, J.M.; D.R. Paul; T.E. Mlnsa; R.J. Lagow
The potential use of surface fluorination to improve the gas separation properties of a polymer membrane was investigated using PMP. Fluorination was found to lead to a reduction in flux accompanied by a very significant increase in selectivity, and after this initial change, these trends continue to a lesser degree for up to one year after fluorination. An idealized composite structure consisting of a fluorinated layer with unfluorinated material comprising the rest of the thickness is used to visualize the structure of these membranes. The series resistance model is used to illustrate the relationship between the total membrane thickness and the fraction that the fluorinated polymer layer contributes to the total. This relationship was demonstrated experimentally by fluorinating composite membranes (P-90-4) with a permselective PMP layer ranging in thickness from 0.2 to 20 µm. The transport of six gases was measured. The series resistance model was used to estimate the transport properties of the fluorinated polymer layer.

P-90-5 PUBLISHED
Surface Fluorination of Composite Membranes. Part II. Characterization of the Fluorinated Layer
Mohr, J.M.; D.R. Paul; Y. Taru; T.E. Mlnsa; R.J. Lagow
The fluorinated layer of membranes exposed to a dilute stream of fluorine gas has been characterized. X-ray photoelectron spectroscopy (XPS) and Fourier Transform infrared spectroscopy/attenuated total reflection (FTIR/ATR) were used to determine the concentration and profile of reacted fluorine in PMP membranes after exposure to fluorine. The thickness of the fluorinated layer as a function of reaction time was calculated using the results of bulk elemental analysis and of XPS. The permeability of this layer was determined using the calculated thickness and the (P_/l_) values reported previously. It is shown that the permeability of the fluorinated material is two orders of magnitude lower than that of the original PMP. A simple diffusion limited reaction model is able to give a good estimate of the thickness of the fluorinated layer as a function of fluorine reaction time.

P-90-6 PUBLISHED
Surface Fluorination of Polysulfone Asymmetric Membrane and Films
Mohr, J.M.; D.R. Paul; I. Pinnau; W.J. Koros
Asymmetric PSF membranes were surface fluorinated using a fixed set of treatment conditions and the transport of six gases was measured. After 2 and 5 minutes of fluorination, the membranes show a significantly reduced (P/l) and an improved selectivity for certain gas pairs like H2, He, and CO2 relative to methane. There is some variability in the H2/CH4 selectivity improvement observed, but, in general, it increases two to three fold for membranes fluorinated for 5 minutes and two to five fold for those fluorinated for 2 minutes. In order to gain insight about the fraction of the asymmetric membrane thickness that is being fluorinated and to determine the chemical nature of the fluorinated layer, thick (76 µm) isotropic films of PSF were fluorinated from one side only for a wide range of times. The chemical composition and structure of the fluorinated layer were determined from bulk elemental analysis and FTIR/ATR. X-Ray photoelectron spectroscopy was also used to determine the chemical composition at the surface of asymmetric membranes and the thick films. The fluorinated surface of selected membranes was examined by scanning electron microscopy (SEM).
XPS Characterization of Surface Fluorinated Poly(4-methyl-1-pentene)
Mohr, J.M.; D.R. Paul; Y. Taru; T.E. Mlnsa; R.J. Lagow

The fluorinated surface layer of PMP membranes exposed to a dilute stream of fluorine gas has been characterized with XPS. The concentration and profile of reacted fluorine as a function of exposure time were determined. A computer routine was employed to deconvolute the poorly resolved carbon spectra after various fluorine exposure times. The concentrations of mono-, di-, and tri-fluorocarbon groups thus determined were used to propose specific structures of PMP at the surface after 1 and 15 minutes of fluorination. The carbon spectra collected at electron take-off angles of 15°, 30°, and 90° were also deconvoluted giving insight into the placement of fluorine as a function of depth. Oxygen is incorporated into the polymer during the fluorination reaction and the O1s spectra was deconvoluted to determine how the O2 is bound.

Effect of Casting Solvent on the Permeability of Poly (4-methyl-1-pentene)
Mohr, J.M. and D.R. Paul
Polymer 32:1236 (1991)

The permeability of gases in PMP films cast from solution depends strongly on the casting solvent used. Permeability coefficients for several gases were measured for PMP films cast from six solvents and for a film prepared from the melt. Sorption isotherms were measured for selected gas-film pairs. Films cast from decalin, xylene, and chloroform have lower permeation rates relative to the melt prepared film. Films cast from cyclopentane, cyclohexane, and carbon tetrachloride have permeability coefficients similar to that for the melt processed film. The differences may be as great as six fold. X-ray diffraction and thermal analysis were used to characterize the films. The casting solvent is shown to influence which crystalline modification is formed and the spatial arrangement of the crystallites within the film. The films with very low gas permeability coefficients have a strong preferential orientation of the crystallites with the chain axis normal to the film surface. It is suggested that in these cases, some single crystals were formed during casting which aligned preferentially in the film to give a long tortuous path for permeation of gas molecules. The relative rate of gas transport in the unusually open crystals of PMP is discussed.

Comparison of Gas Permeation in Vinyl and Vinylidene Polymers
Mohr, J.M. and D.R. Paul

The gas transport properties of several simple vinyl and vinylidene polymers are compared to examine the effect of pendant group type (H, CH3, F, Cl) and symmetry of placement. The gas transport data available for many of these polymers are quite variable because of differences in additives, thermal history, and crystallinity. The values used here are from studies where the physical properties of the film were reported along with the transport data. The appropriate data were not available for poly(vinyl fluoride) or poly(vinylidene chloride). For poly(vinyl fluoride), permeability measurements and thermal analysis were done to supply this information. Results for poly(vinylidene chloride) were obtained by extrapolation of copolymer permeation properties. Estimates of the permeability of O2 in the amorphous phase of each polymer are discussed in terms of the estimated fractional free volume (FFV) of that phase. In this way, the intrinsic effects of molecular structure on gas permeation exclusive of crystallinity effects have been evaluated.

Gas Transport Properties of a Series of Poly(ether ketone) Polymers
Mohr, J.M.; D.R. Paul; G.L. Tullos; P.E. Cassidy
Polymer 32:2387 (1991)

The gas sorption and transport properties of a series of poly(aryl ether ketone) materials are reported. In this series, the isopropylidene groups [-C(CH3)2-] in the backbone are systematically replaced with a hexafluoroisopropylidene group [-C(CF3)2-]. Dynamic mechanical analysis and DSC were used to show that the substitution of [-C(CF3)2-] for [-C(CH3)2-] units results in a
stiffer polymer chain. Free volume calculations show that the substitution opens up the polymer structure and leads to an increase in diffusion coefficients. Methane and CO2 sorption measurements were made to examine the solubility and diffusivity contributions to the permeability. The permeability increases as [-C(CF3)2-] units replace the [-C(CH3)2-] groups, and, in general, the increase in diffusivity accounts for the permeability increase. Along with the increase in permeability is an increase in the selectivity for gas pairs like He/CH4 and CO2/CH4. This simultaneous increase in permselectivity and permeability when [-C(CF3)2-] units replace [-C(CH3)2-] units seems to be a general trend as it has been observed for polycarbonate and PSF materials as well.

P-90-11 PUBLISHED

Gas Transport Properties of Liquid Crystalline Poly(ethylene terephthalate-co-p-oxybenzoate)
Weinkauf, D.H. and D.R. Paul

Gas transport properties are reported for a series of films prepared from thermotropic poly(ethylene terephthalate-co-p-oxybenzoate), or PET/PHB, having compositions of 60 and 80 mol% PHB. The mesomorphic and crystalline morphology of the copolyester films was examined by cross polarized light microscopy, DSC, and x-ray diffraction. Melt processed films of both compositions appeared to exhibit an entirely anisotropic morphology with low levels of conventional crystallinity. Solution cast films prepared from the 60 mol% material were found to contain a large fraction of isotropic regions, which become ordered upon annealing above the glass transition. Permeability measurements were made for He, H2, O2, N2, and CO2 at 35°C and the diffusivities were computed from time-lag data. The largely anisotropic films exhibit good barrier properties resulting from very low solubility coefficients. The partially isotropic 60 mol% films show much higher permeability coefficients driven primarily by increased solubility coefficients, while diffusivity is affected to a lesser extent. These results appear in contrast with what is observed in semicrystalline systems where increased crystalline order results in more dramatic reductions in penetrant mobility.

P-90-12 PUBLISHED

Effect of Isopropylidene Replacement on Gas Transport Properties of Polycarbonates
McHattie, J.S.; W.J. Koros; D.R. Paul

The gas sorption and transport properties of a series of polycarbonates in which the isopropylidene unit of bisphenol-A polycarbonate has been replaced with another molecular group are presented. Two new materials, bisphenol of norbornane polycarbonate (NBPC) and bisphenol-Z polycarbonate (PCZ), are compared to several polymers which have been studied previously in this laboratory, including polycarbonate, hexafluoro bisphenol-A polycarbonate (HFPC), and BCPC. The effect of molecular structure on chain mobility and chain packing is related to gas transport properties. Dynamic mechanical thermal analysis and DSC are used to judge chain mobility, while x-ray diffraction and free volume calculations give information about chain packing. Permeability measurements were made for He, H2, O2, N2, CH4, and CO2 at 35°C over a range of pressures up to 20 atm. Sorption experiments were also done for N2, CH4, and CO2 under the same conditions. The permeability coefficients of these polymers rank in the order of HFPC >> NBPC > PC > BCPC >> PCZ for all of the gases. With the exception of BCPC, this order correlates well with FFV. The low gas permeability (P-90-12) for BCPC is attributed to a polarity effect. In general, bulky and relatively immobile substituents, as in HFPC and NBPC, can yield improved separation characteristics. The polar group of BCPC and the flexible cyclohexyl substituent PCZ result in relatively low gas permeability.

P-90-13

Selected Reports on Gas Sorption/Transport Research-
Handouts from the Separations Research Program Spring Conference, April 1990
Includes copies of transparencies used by Paul, Aitken, Mohr, and Aguilar-Vega for the Membrane Technology Study Group (P-90-13) Meeting.
Gas Transport Properties of Polysulfones. Part II. Effect of Bisphenol Connector Groups
McHattie, J.S.; W.J. Koros; D.R. Paul
Polymer 32:2618 (1991)

The gas sorption and transport properties of a series of polysulfones in which the isopropylidene unit of bisphenol-A PSF has been replaced with another molecular group are reported. Bisphenol-A PSF is compared to several newly synthesized materials, including hexafluorobisphenol-A polysulfone (HFPSF), bisphenol-F polysulfone (PSF-F), and bisphenol-O polysulfone PSF-O. These polymers are also compared to Victrex® PES. The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and DSC were used to judge chain mobility, while x-ray diffraction and free volume calculations give information about chain packing. Permeability measurements were made for He, H2, O2, N2, CH4, and CO2 at 35°C over a range of pressures up to 20 atm. Sorption experiments were also done for N2, CH4, and CO2 under the same conditions. The permeability coefficients for all gases rank in the order: HFPSF > PSF > PSF-F @ PSF-O > PES. With the exception of PES, these permeability trends are in good agreement with the FFV. Possible reasons for this are discussed.

Gas Transport Properties of Polysulfones. Part III. Comparison of Tetramethyl Substituted Bisphenols
McHattie, J.S.; W.J Koros; D.R. Paul
Polymer 33:1701 (1992)

The gas sorption and transport properties of a series of polysulfones with tetramethyl ring substitution are reported. The results for tetramethyl hexafluorobisphenol-A polysulfone (TMHFPSF) and tetramethyl bisphenol-F PSF (TMPSF-F) are compared to TMPSF and bisphenol-A PSF. The effect of the substituents on chain mobility and chain packing has been related to the gas transport properties. Dynamic mechanical thermal analysis and DSC were used to judge chain mobility, while x-ray diffraction and free volume calculations give information about chain packing. Permeability measurements were made for He, H2, O2, N2, CH4, and CO2 at 35°C over a range of pressures up to 20 atm. Sorption experiments were also done for N2, CH4, and CO2 under the same conditions. The permeability coefficients of the methyl substituted polymers rank in the order: TMHFPSF >> TMPSF > TMPSF-F for all the gases. This is the same order as the unsubstituted materials, HFPSF, PSF, and PSF-F, which suggests that the effects of tetramethyl substitution are somewhat additive with other structural modifications. Relative gas permeability values are in agreement with relative FFV values as well as with g transition temperatures.

Gas Transport Properties of Liquid Crystalline Polymers
Weinkauf, D.H.
PhD dissertation

Gas transport properties are reported for several main-chain LCPs, including thermotropic copolyester and lyotropic polyamide systems, and the potential use of these materials in
membrane and barrier material applications is explored. The report focuses on the unique morphology of LCPs and its relationship to gas transport.

**P-91-5 PUBLISHED**

Gas Transport Properties of Thermotropic Liquid Crystalline Copolyesters: I. The Effects of Orientation and Annealing
Weinkauf, D.H. and D.R. Paul

The objective of this investigation was to provide some assessment of the effects of morphological features on the gas transport in one particular LCP with the hope of achieving a better understanding of transport in this general class of materials. Gas transport measurements are reported for two series of films prepared from copolyesters of hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA), which systematically vary the degree of orientation and annealing time. A more detailed description of LCP morphology and the general effects of orientation and annealing is followed by a review of pertinent issues of gas transport in semicrystalline polymers. The paper concludes with an attempt to assess the relative permeability of the nematic mesophase by analysis of the observed behavior in terms of a simple two-phase model.

**P-91-6 PUBLISHED**

Gas Transport Properties of Thermotropic Liquid Crystalline Copolyesters: II. The Effects of Copolymer Composition
Weinkauf, D.H. and D.R. Paul

Transient gas transport measurements were made on a series of LCP films with varying HBA/HNA composition. The effects of skin-core structure, polydomain texture, and crystallinity studied previously were effectively normalized by standardization of the film processing conditions. Some characterization of chain dynamics and film morphology precedes a detailed discussion of the transport properties of these materials. The paper concludes with an analysis of the transport properties of LCPs using a FFV approach.

**P-91-7 PUBLISHED**

Dynamic Mechanical and Gas Transport Properties of Blends and Random Copolymers of Bisphenol-A Polycarbonate and Tetramethyl Bisphenol-A Polycarbonate
Kim, C.K.; M. Aguilar-Vega; D.R. Paul

Dynamic mechanic and gas transport properties for homogeneous homopolymer blends and random copolymers of bisphenol-A and tetramethyl bisphenol-A polycarbonates were determined. The gas transport measurements were performed at 35°C for the gases He, H2, O2, Ar, N2, CH4, and CO2. The results show that the copolymers have lower permeability, apparent diffusion, and solubility coefficients than the blends. Permeability coefficients for blends follow a semilogarithmic ideal mixing rule while copolymers exhibit negative deviations from this. Specific volume measurements show that the free volume available for gas transport is slightly larger in copolymers than in blends of the same composition. These apparently contradictory results may relate to the differences in local mode chain motions observed for the copolymer and blend series. The g relaxation processes in PC and TMPC seem to operate independently in the blends (no intermolecular coupling) while there is clear evidence for intermolecular coupling in the copolymers.

**P-91-8 PUBLISHED**

Gas Transport Properties of Liquid Crystalline Poly(p-phenyleneterephthalamide)
Weinkauf, D.H.; H.D. Kim; D.R. Paul

A series of films was prepared from anisotropic poly(p-phenyleneterephthalamide) (PPT) solutions and annealed at 100°C, 200°C, and 300°C. By using cross-polarized light microscopy, the PPT films appeared to exhibit a completely anisotropic morphology. From x-ray diffraction
analysis, each film appeared to contain a fixed level of modification II crystallites with the level of
modification I crystallites increasing with annealing temperature. Amorphous films were also
prepared from a structural isomer of PPT that contains a large fraction of meta linkages along the
polymer main chain. Permeability measurements were made for He, H2, O2, N2, and CO2 at
35°C, and the diffusivities of the larger gases were computed from time-lag data. In general the
permeability coefficients of the PPT films are very low and approach those reported for PAN and
liquid crystalline copolyesters. The O2 permeability coefficients of the amorphous PPT-isomer are
over an order of magnitude larger than those for the anisotropic PPT materials. The solubility
coefficients for the noncrystalline regions of the PPT and PPT-isomer, however, are very close. In
contrast to the well-documented effect of meta- versus para-linked moieties on transport in
amorphous, glassy polymers (P-91-8), the mesomorphic para-linked PPT materials exhibit O2
diffusion coefficients that are nearly an order of magnitude lower than those of the meta-linked
PPT-isomer. Among the PPT films, the permeability coefficients of the samples annealed at 100°C
and 200°C are nearly the same, while annealing at 300°C results in significant reduction in both
permeability and diffusivity.

P-92-1  PUBLISHED
Gas Transport Properties of Biphenol Polysulfones
Aitken, C.L.; W.J. Koros; D.R. Paul
Macromolecules 25:3651 (1992)
Gas sorption and transport properties at 35°C are reported for the polysulfone based on 4,4'-
biphenol (BIPSF) and corresponding polysulfones with methyl ring substitutions, tetramethyl
biphenol polysulfone and hexamethyl biphenol polysulfone. Comparisons are made to PSF and
TMPSF. 4,4'-Biphenol polysulfone and PSF have very similar transport characteristics. This is
attributed to the similar packing behavior of these polymers. Tetramethyl substitution on the
biphenyl rings increases permeability, while hexamethyl substitution does not lead to a
comparable further increase, but does enhance selectivity characteristics for certain gas pairs.
Permeability values are discussed in terms of chain packing, FFV, and sub-Tg relaxation behavior.

P-92-2  PUBLISHED
Effect of Structural Symmetry on Gas Transport Properties of Polysulfones
Aitken, C.L.; W.J. Koros; D.R. Paul
Macromolecules 25:3424 (1992)
The effects of structural symmetry of phenylene linkages and methyl group placement on the
properties of polysulfones have been investigated. Polysulfones with unsymmetric structures have
lower gas permeability and higher selectivity coefficients than their symmetric counterparts. The
polysulfones with meta phenylene linkages or dimethyl substitutions to the bisphenol unit have
lower Tg temperatures, lower FFV's, and higher sub-Tg relaxation temperatures. The chains of the
unsymmetric polymers are generally more efficiently packed and appear to have greater mobility
constraints, stemming from both intramolecular and intermolecular origins, than their symmetric
counterparts, all of which influence properties and especially permeation (P-92-2) behavior.

P-92-3  PUBLISHED
Dynamic Mechanical Behavior of Polysulfones
Aitken, C.L.; J.S. McHattie; D.R. Paul
The dynamic mechanical properties of a series of polysulfones made from a wide range of
bisphenols have been analyzed. The structural variations include zero, one, two, or three methyl
groups per phenyl ring and a wide range of groups connecting the phenyl rings in the bisphenol
while the diphenyl sulfone unit was not changed. The symmetry and placement of these
modifications and the resulting rigidity affect the Tg and the sub-Tg spectra. Both intramolecular
and intermolecular factors contribute to these changes. For these polysulfones, the glass transitions
ranged from 150°C to 298°C and the sub-Tg relaxation temperatures ranged from -100°C to
200°C. Substitutions that directly hinder phenylene mobility increase the temperature at which the
g relaxation occurs. The appearance of more than one g peak for some structures has been
interpreted to mean that the extended intramolecular coupling of monomer units proposed for
polycarbonates is apparently not a necessary component of the sub-Tg relaxation in these polymers. Differences in the molecular motions of polysulfones and polycarbonates were briefly addressed by molecular modeling. A comparison of selected polysulfones and polyetherketones shows that whatever contribution the sulfone unit makes to the sub-Tg mechanical spectra, carbonyl units make a similar contribution. Intermolecular chain packing or free volume strongly affects the temperature location of the g relaxation attributed to motions of diphenyl sulfone units.

**P-92-4 PUBLISHED**

**Gas Transport Properties of Polysulfones Based on Dihydroxynaphthalene Isomers**

Aitken, C.L. and D.R. Paul  
Polysulfones based on dihydroxynaphthalene isomers have been synthesized and their gas transport properties have been characterized at 35°C. The naphthalene polysulfones have lower gas permeability coefficients but higher Tg temperatures and selectivity coefficients than the polysulfone based on bisphenol-A. The position of the dihydroxynaphthalene linkage does not have a large effect on gas permeability. This is probably due to the inherent lack of symmetry of the naphthalene unit regardless of the linkage location.

**P-92-5**

**Preparation of Composite Membranes by a Spin-Coating Process**

Le Roux, J.D. and D.R. Paul  
The formation of composite membranes on a laboratory scale by spin coating a selective layer of PMP onto a microporous polysulfone support is described. In most cases the support had been precoated with an intermediate layer of poly(dimethyl siloxane) (PDMS). The thickness of the PMP layer, determined indirectly from gas flux measurements on the composite membrane, can be controlled within certain limits by varying the spinning speed, the coating solution concentration, or the number of selective layers coated onto the substrate. Coated skin thickness varies approximately with the inverse of the square root of spin speed and with the second power of the coating solution concentration. The model coefficients compare well with those of models proposed for the production of photo resists in which polymer films are spin coated onto impermeable substrates. Gas permeation characteristics of the composite membranes were adequately described by a series resistance model. Composite membranes made without a PDMS intermediate layer required more than one layer of the selective polymer to bridge the larger pores and ensure a defect-free skin. For thin selective layers, these membranes have selectivities somewhat higher than that of PMP, since the PSF matrix of the substrate participates in the separation. Thus, multilayer composite membranes formed directly on microporous PSF substrates can be superior to composites with a PDMS intermediate layer.

**P-92-6 PUBLISHED**

**Gas Transport Properties of Poly(arylether bissulfone)s and Poly(arylether bisketone)s**

Aitken, C.L.; D.R. Paul; D.K. Mohanty  
The transport properties of the poly(arylether bissulfone) based on bisphenol-A (PBSF) and the poly(arylether bisketones) based on bisphenol-A (PKB) and bisphenol-S (PBK-S) are reported at 35°C. Comparisons are made to the polysulfone and the polycarbonate also based on bisphenol-A to determine the effect of the long, rigid bisketone and bissulfone groups on polymer properties. A direct comparison also is made between PKB and PBSF, which differ only by their ketone and sulfone groups. The bulkier sulfone group increases free volume and Tg more than the ketone group. This results in higher solubility and diffusivity coefficients for the bissulfone versus the bisketone polymer, both of which contribute to higher permeability coefficients (P-92-6).
P-92-7 Published
Gas Permeation in a Fluorine Containing Polynorbornene
Teplyakov, V.V.; D.R. Paul; N.B. Bespalova; E.S. Finkelshtein

Recently there has been considerable interest in the relationship between the repeat unit molecular structure of polymers and the gas permeability characteristics of these materials driven by the need for improved membranes for separation processes. Structures that lead to both high permeability and high selectivity for certain gas pairs like O2/N2, He/CH4, and CO2/CH4 are sought. The most promising membrane (P-92-7) candidates tend to have rigid backbones to suppress chain motion and substitutions that prohibit dense packing, i.e., high FFV. Polymers made by metathesis polymerization of norbornene and its derivatives have been described recently, but investigations of their gas permeation behavior are quite limited. The purpose here is to report the gas transport properties of poly[4,4-difluoro-5,5-bis (trifluoromethyl) norbornene], or DFHFPNB, and compare them with other pertinent polymers. In addition, comparisons are made with modifications to PSF. Finally, DFHFPNB is compared to unsubstituted polynorbornene, which unlike all the other polymers considered here is in the rubbery state at 35°C, the temperature where permeability measurements were made.

P-92-8 Published
Gas Transport Properties of Poly(3-hydroxyoxetane)
Aguilar-Vega, M.; D.R. Paul; E.J. Vandenberg; J.C. Mullis

Gas transport properties for poly(3-hydroxyoxetane), PHO, were measured for five gases at 35°C. While PHO has very low gas permeability coefficients, they are larger than those reported for PAN, poly(vinyl alcohol) (PVAI), and copolymers of ethylene/vinyl alcohol (EVAL) for all gases tested except He. The permeability coefficients for PHO and EVAL are well correlated with the density of hydroxyl groups along the chain. Extrapolations to PVAI give values that agree well with those estimated by others using the "Permachor" method. It is suggested that some of the reported experimental values for PVAI are in error.

P-92-9 Published
Gas Transport Properties of Poly(2,2,4,4-Tetramethyl Cyclobutane Carbonate)
Aguilar-Vega, M. and D.R. Paul

Gas transport properties of semicrystalline films of poly(2,2,4,4-tetramethyl cyclobutane carbonate), (TMCBPC) were studied. Permeability coefficients for He, O2, N2, CH4, and CO2 at 35°C for pressures between 1 and 20 atm are reported as well as sorption isotherms for N2, CH4, and CO2 at the same conditions. The permeability coefficients for TMCBPC are larger than corresponding values for the aromatic bisphenol-A polycarbonate, and TMPC, even though the TMCBPC films are semicrystalline. These results are explained on the basis of the larger free volume available for permeation in this polymer. Significant TMCBPC plasticization by CO2 was also observed and this causes typical time-dependent behavior. The plasticization process starts at very low pressures compared to the aromatic polycarbonates PC and TMPC. This early onset of plasticization seems to be related to the larger free volume in the amorphous phase of TMCBPC, which favors high gas sorption. The diffusion coefficients (P-92-9) for TMCBPC are also larger than those reported for the aromatic polycarbonates PC and TMPC. Ideal gas separation factors were found to follow the usual trend; that is, as permeability increases the ideal separation factor decreases.

P-92-10 Published
Comparison of Mixed and Pure Gas Permeation Characteristics for CO2 and CH4 in Copolymers and Blends Containing Methyl Methacrylate Units
Raymond, P.C.; W.J. Koros; D.R. Paul

Permeation of pure CO2 and CH4 and their 50/50 mixtures (at 5 and 20 atm partial pressures) were measured at 35°C in a series of SMMA and a series of miscible blends of BCPC and PMMA.
Poly(methyl methacrylate) is significantly plasticized by CO2 at 20 atm, whereas BCPC and to a lesser extent polystyrene are not. Thus by incorporating MMA units into the copolymer or into the blend, a varying extent of plasticization response was built in. Mixed gas separation factors were found to be well-predicted by pure gas measurements for CO2 and CH4 at 5 atm partial pressure for all copolymers and all blends. However, at 20 atm partial pressure of CO2, the actual mixed gas separation factors (P-92-10) are much lower than that predicted by pure gas measurement as the MMA content of the copolymers or the blends increased. Significant history or conditioning effects accompany plasticization in glassy polymers (P-92-10) so the results obtained depend on the measurement protocol. For this reason, no attempt was made to fit these data to current models since they do not allow for this fact.

P-93-1 REPLACED BY P-93-9

P-93-2 PUBLISHED

Gas-Transport Properties of Polyphenylene Ethers
Aguilar-Vega, M. and D.R. Paul
Gas transport properties of the polyphenylene ethers poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) and poly(2,6-diphenyl-1,4-phenylene oxide) (PDPPO) and the thioether poly(1,4-phenylene sulfide) (PPS) have been measured as a function of pressure and temperature. The PPS material and free volume correlations were used to estimate the behavior of the unavailable poly(1,4-phenylene oxide) (PPO). The results show that symmetrical substitution of phenyl groups on the backbone of polyphenylene ether (PDPPO) increases the gas transport properties by one order of magnitude relative to the unsubstantiated material (PPO). Symmetrical methyl substitution (PDMPO) however, increases the permeability, apparent diffusion, and sorption coefficients even further. The gas transport coefficients correlate with the FFV of the polymers. PDMPO has the largest FFV and gas transport coefficients followed by PDPPO and then PPS. The results show that substitution of phenyl groups, which leads to polymers that have better thermal and oxidative stability than methyl substituted ones, can be a useful means for increasing free volume and gas-permeability coefficients. While methyl groups appear to be more effective for the latter, the enhanced chemical stability of phenyl rings may be useful when gas separation membranes are to be used in harsh environments.

P-93-3 PUBLISHED

Modification of Asymmetric Polysulfone Membranes by Mild Surface Fluorination. Part I. Transport Properties
Le Roux, J.D.; D.R. Paul; J. Kampa; R.J. Lagow
Flat sheet integral asymmetric polysulfone membranes were subjected to gas-phase surface fluorination in a well-mixed reactor. Short residence times ensured a constant fluorine concentration in the reactor (i.e., at the membrane surface) after one minute of operation, so that the fluorination time and the fluorine feed concentration could be investigated independently. Fluorination conditions were optimized to yield an improvement in the selectivity of the gas pairs O2/N2, H2/N2, H2/CH4, He/N2, He/CH4 and CO2/CH4 with a varying decrease in the permeability of all gases. For example, at 0.02% F2, the O2/N2 selectivity was improved up to 50% at fluorination times of two minutes. However, five minutes of fluorination produced the optimum (more than ten-fold) increase in the He/CH4 selectivity with an average decrease in He permeance (P/l) of only 27%. Low F2 feed concentrations of 0.02%-0.04% gave optimum results, and higher concentrations resulted in a sharp decline in the selectivity of all gas pairs. Good transport properties were also obtained by subjecting membranes to successive fluorination cycles of short duration at 0.02% F2. Two cycles of one minute each produced optimum results. Membranes coated with highly permeable silicone rubber (PDMS) after fluorination invariably showed an increase in selectivity with a relatively small additional loss of permeability.
Modification of Asymmetric Polysulfone Membranes by Mild Surface Fluorination. Part II. Characterization of the Fluorinated Surface
Le Roux, J.D.; D.R. Paul; M.F. Arendt; Y. Yuan

Integrally-skinned asymmetric polysulfone membranes (PSF) membranes were surface fluorinated under mild treatment conditions, according to one of two strategies: at fluorination times of one to ten minutes with a constant fluorine feed concentration of 0.02% F2 (by volume), or at concentrations ranging from 0.02% to 0.15% F2 for a fixed treatment time of two minutes. The fluorinated region was characterized using dynamic contact angle analysis (DCA) and X-ray photoelectron spectroscopy (XPS). It was shown that increasing fluorination times from one to five minutes resulted in increased F/C and O/C ratios in the fluorinated subsurface region and also increased the polar surface energy contribution (gsr) at the surface. Longer fluorination times resulted in an apparent decrease in polarity, possibly due to surface damage. For increasing fluorine concentrations at a constant treatment time, the F/C and O/C atomic ratios in the subsurface region increased up to 0.04% F2 and effectively leveled off at higher feed concentrations. At the surface, gsr decreased after reaching a maximum at 0.06% F2. For both treatment strategies the ideal selectivities for certain gas pairs (He or H2 with N2 or CH4) follow trends similar to that of gsr. Decreases in selectivity appear to be associated with fluorination damage (surface roughness and damage to the polymer structure), rather than with a change in the chemical nature of the fluorinated skin region.

Surface Fluorination of Composite Membranes Poly(phenylene oxide). Part I. Transport Properties
Le Roux, J.D.; D.R. Paul; J. Kampa; R.J. Lagow

The effect of surface fluorination treatment on the gas transport properties of composite membranes comprising an inert porous ceramic support and a selective layer consisting of PPO, was examined. A small reactor volume permitted the treatment time and the fluorine feed concentration to be investigated independently. The gas transport properties of the treated membranes were evaluated for six gases (N2, O2, CH4, H2, and CO2), in terms of permeance (P/l or pressure normalized flux) and the ideal selectivity for eight pairs of these gases. It was found generally that fluorination at different fluorine feed concentrations and reaction times reduced the permeance of all of the gases. The permeance of the lighter gases (He and H2) was reduced by a smaller factor than that of the heavier gases (N2 and CH4). Fluorination increased the selectivity of He and H2 relative to N2 or CH4 by a small factor, but reduced the selectivity of O2 and CO2 relative to N2 or CH4. When the membranes were coated with a layer of poly(dimethyl siloxane) subsequent to fluorination, the permeance decreased, considerably more for N2 and CH4 than for the other gases. Surface coating also substantially increased the selectivities of all the gas pairs. The highest gains in selectivity after fluorination and coating were found at the higher concentration (0.1% F2) and intermediate treatment times of 3 to 5 minutes. Based on these results, surface coating with PDMS is recommended as a post-treatment step in the fluorination process.

Surface Fluorination of Composite Membranes Poly(phenylene oxide). Part II. Characterization of the Fluorinated Layer
Le Roux, J.D.; D.R. Paul; M.F. Arendt; Y. Yuan; I. Cabasso

Composite membranes comprising a selective layer of poly (2,6-dimethyl-1,4phenylene oxide) (PPO) on a microporous ceramic support, were surface fluorinated under mild fluorination conditions. The treatment parameters, fluorine feed concentration and treatment time, were each varied independently while the other parameter was kept constant. The fluorinated region was characterized using dynamic contact angle analysis (DCA) and x-ray photoelectron spectroscopy (XPS). The fluorine to carbon (F/C) ratio increased as a function of treatment time, but showed little variation when the feed concentration was varied. A relatively high oxygen to carbon ratio
was observed which showed little change over the range of fluorination conditions. Angle dependent XPS showed the concentration of fluorine species to be higher at greater depths below the surface. Fluorination times of 5 to 7 minutes minimized the water contact angle and maximized the total and polar surface free energies. Water contact angles decreased after fluorination but showed no definite trend as a function of feed concentration. The composition of the fluorinated region is discussed in relation to the gas transport properties of membranes fluorinated at similar conditions (Part I of this study).

**P-93-7 PUBLISHED**

**Gas-Transport Properties of Surface Fluorinated Poly(vinyltrimethylsilane Films and Composite Membranes**

Le Roux, J.D.; V.V. Teplyakov; D.R. Paul


The surface fluorination of both thick isotropic films and composite membranes formed from poly(vinyl trimethyl silane) (PVTMS), is described. For films ranging in thickness from 23 to 200 µm, fluorination treatment reduced the permeability coefficients for the gases N2, O2, CH4, CO2, Kr and Xe while the permeability of He was not affected. The ideal selectivities for He, CO2, Kr and Xe relative to N2 or CH4 were increased, but the ratio for the O2/N2 pair remained unchanged. Repeated fluorination at increasingly harsh fluorination conditions progressively lowered the permeability and increased the selectivities still further. Effective diffusivity coefficients for the entire treated film were found to be more responsive to fluorination than the solubility coefficients. For composite membranes, comprising a thin (~0.5 µm) selective layer of PVTMS, two sets of fluorination conditions were considered: variable treatment time at a constant fluorine feed concentration of 0.02% and different feed concentrations at a constant treatment time of 2 minutes. In the absence of fluorination damage, the selectivity generally increased as a function of treatment time while the permeance (P/1 ) was reduced. Fluorination damage to some membranes caused a decrease in both selectivity and permeance, but these defects could be caulked by applying a surface layer of poly(dimethyl siloxane).

**P-93-8 PUBLISHED**

**Gas Transport Properties of Polyphenylene Ethers**

Aguilar-Vega, M. and D.R. Paul


Gas transport properties of the polyphenylene ethers poly (2,6-dimethyl-1,4-phenylene oxide), PDMPO, and poly(2,6-diphenyl-1,4-phenylene oxide), PDPPO, and the thioether poly(1,4-phenylene sulfide ), PPS, have been measured as a function of pressure and temperature. The PPS material and free volume correlations were used to estimate the behavior of the unavailable poly(1,4-phenylene oxide), PPO. The results show that symmetrical substitution of phenyl groups on the backbone of polyphenylene ether, PDPPO, increases the gas transport properties by one order of magnitude relative to the unsubstituted material, PPO. Symmetrical methyl substitution, PDMPO, however, increase the permeability, apparent diffusion and sorption coefficients even further. The gas transport coefficients correlate with the fractional free volume of the polymers. PDMPO has the largest fractional free volume and gas transport coefficients followed by PDPPO and then PPS. The results show that substitution of phenyl groups, which leads to polymers that have better thermal and oxidative stability than methyl substituted ones, can be a useful means for increasing free volume and gas permeability coefficients. While methyl groups appear to be more effective for the latter, the enhanced chemical stability of phenyl rings may be useful when gas separation membranes are to be used in harsh environments.
The effect that substitution of aromatic groups on the bisphenol connector unit of bisphenol-A based polycarbonate and polysulfone materials has on their gas transport properties was assessed. Replacement of a methyl group by a phenyl ring (bisphenol acetophenone polycarbonate, PC-AP, and bisphenol acetophenone polysulfone, PSF-AP) gives a small increase in permeability coefficients with similar or slightly higher selectivity for all gases compared to bisphenol-A polycarbonate, PC, or polysulfone, PSF. Substitution of two locked phenyl rings (fluorene bisphenol polycarbonate, FBPC, and fluorene bisphenol polysulfone, FBPSF) in place of the methyl groups in the connector unit leads to permeability and solubility coefficients that are about twice those observed for PC or PSF. Increases in permeability for the polycarbonate and polysulfone materials with aromatic substitutions are related to their larger fractional free volume. FBPC and FBPSF have the largest fractional free volume and the largest permeability coefficients. Thermal measurements show that the fluorene based polycarbonate and polysulfone materials have the highest thermal and oxidative stability. Such aromatic substitutions can be useful for developing gas separation membranes to be used in harsh thermal or oxidative environments.

Replaces P-93-1

The gas-transport properties for a series of polysulfones made from a wide range of bisphenols have been analyzed. Polysulfones with high glass-transition (Tg) temperatures, e.g., those based on biphenol and dihydroxynaphthalene, were synthesized and characterized. In addition, the role of structural symmetry on polymer properties was studied. Because molecular mobility is an important facet of the permeation process, the Tg and sub-Tg spectra of polysulfones were analyzed in depth. Differences in molecular flexibility of polysulfones and polycarbonates were also addressed. The polymers were synthesized from commercially available and custom synthesized monomers. In addition, several poly(aryl ether bisketone)s and poly(aryl ethyl bissulfone)s were obtained from outside sources. Permeability measurements for He, H2, O2, N2, CH4, and CO2 as well as sorption measurements for N2, CH4, and CO2 were taken at 35°C and pressures up to 20 atm. The effects of interchain packing and chain mobility on the transport properties of these materials were explored using x-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, dilatometry, dynamic mechanical analysis, and molecular modeling. The effects of structural symmetry of phenylene linkages and methyl-group placement on the properties of polysulfones were investigated. The polysulfones with meta phenylene linkages or dimethyl substitutions to the bisphenol unit have lower glass-transition temperatures, lower fractional free volumes (FFVs), and higher sub-Tg relaxation temperatures than their symmetric counterparts. This results in lower gas permeability and higher selectivity coefficients. In general, both unsymmetric polymers and simple liquid molecules packed more efficiently. In addition, the unsymmetric polymers have higher mobility constraints than the materials with symmetric structures. Thus, both intramolecular intermolecular factors appear to influence polymer properties, especially permeation behavior. The gas sorption and transport properties were evaluated for the polysulfone based on 4,4'-biphenol and corresponding polysulfones with methyl ring substitutions. Bisphenol polysulfone has a much higher Tg than bisphenol-A polysulfone, however, these two polymers have very similar transport characteristics. Tetramethyl substitution on the biphenyl rings increases permeability, while hexamethyl substitution does not lead to a comparable additional increase but does enhance selectivity characteristics. The permeability coefficients are related to polymer packing behavior.
The gas transport characteristics of main chain liquid crystalline polymers have been examined in order to understand the nature of the mesophase and what opportunities these materials offer for useful membranes or barriers. Is the liquid crystalline state more like a liquid (or amorphous glass) or a crystal? Experimental investigations of commercial aromatic polyamide and polyester liquid crystalline materials are reviewed. All of these materials prove to be exceptional barriers to permeation. For the polyesters, this is largely due to an extraordinarily low gas solubility. Analyses in terms of two-phase and free volume models suggest that most of the transport may be occurring in a small volume fraction of a less dense boundary phase. The polyamides do not show the unusually low solubility; thus, a different physical model must be imagined for these materials.

Gas transport of helium hydrogen, oxygen, nitrogen, methane and carbon dioxide gases in a series of polyarylates based on isophthalic acid has been examined. These polyarylates were prepared from bisphenol-A, hexafluorobisphenol-A, phenolphthalein and fluorene bisphenol monomers to study the effects of varying the bisphenol connector group size and shape. Substitution of a tertiary butyl group at position five on the isophthalate ring increases polymer permeability. The incorporation of a large, bulky connector group increases gas permeability and maintains permselectivity while the substitution of t-butyl groups increases gas permeability by two- to four-fold but lowers permselectivity. Most of the increases in permeability can be related to increases in the diffusion coefficients of all the gases. All the polyarylates have high glass transition temperatures and may be suitable for high temperature gas separation applications.

The gas transport properties of a series of polyarylates based on isophthalic acid have been examined. The polyarylates were synthesized from the following bisphenol monomers with and without tetrabromo substitution: bisphenol-A, hexafluorobisphenol A, phenolphthalein and fluorene bisphenol, to study the effects of tetrabromination in combination with varying the bisphenol connector group size and shape. Substitution of a tertiary butyl group at position five on the isophthalate ring was used to increase polymer permeability. Tetrabromination (P-94-4) of the bisphenol maintains or increases gas permeability and significantly increases permselectivity particularly for the O2/N2 gas pair as compared with the non-brominated analog. The substitution of t-butyl groups increases gas permeability by two- to four-fold but lowers permselectivity. Most of the increase in permeability can be related to an increase in the diffusion coefficient for each gas. All the brominated polyarylates have gas transport properties superior to most known glassy materials for O2/N2 separation with several materials close to a proposed empirical "upper bound" between permeability and selectivity.

Gas transport of helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide gases in 2,2-(4-hydroxyphenyl)adamantane polysulfone and 1,3-(4-hydroxyphenyl)adamantane polysulfone has been measured. The adamantane containing polymers have higher gas permeabilities in all cases and higher permselectivities in some cases compared with bisphenol A based polysulfone (PSF).
Oxygen solubility is higher for both adamantane-based polysulfones, particularly for the 2,2-isomer. And the high oxygen solubility coefficients are entirely responsible for the higher oxygen permeabilities compared with PSF. The physical properties of these materials are similar to fluorene bisphenol polysulfone; however, the Tg of the 2,2-isomer is higher while that of the 1,3-isomer is lower.

**P-95-2 $30.00**

Gas Transport Properties of Aromatic Polyester and Polysulfone Materials  
Pixton, M.R.  
PhD dissertation  
The effects of polymer structure on the physical and gas transport properties of a series of highly aromatic isophthalates were analyzed. Three types of modifications were investigated: symmetric and asymmetric replacement of the bisphenol phenylene hydrogens by bromine or alkyl groups, replacement of the bisphenol A isopropylidene connector unit by a bulky or aromatic cross-planar connector group, and substitution of a tertiary butyl (t-butyl) group at position five of the isophthalate unit. Pure gas permeability coefficients for He, H2, O2, N2, CH4, and CO2 gases were measured in a pressure-rise type permeation cell at 35°C and pressure up to 20 atm. Pure gas sorption of O2 at pressures up to 6 atm, and N2, CH4, and CO2 at pressures up to 35 atm were measured in a two volume pressure decay type sorption cell at 35°C. Polymer physical properties were assessed using differential scanning calorimetry, thermal gravimetric analysis, dynamic mechanical analysis, wide angle x-ray diffraction, and densitometry. The introduction of packing disruptive t-butyl and large cross-planar bisphenol connector groups in combination with selectivity enhancing meta linkages optimizes polymer gas-transport properties. Substitution of bromine at all positions ortho to the bisphenol hydroxyl function improves selectivity while maintaining adequate levels of permeability, particularly for the O2/N2 gas pair. Dibromodimethylbisphenol A isophthalate has properties very similar to tetrabromobisphenol A isophthalate. The selectivity enhancing ability of the bromine substitution appears to result from both size and polarity considerations. Interchain polar attractions stiffen the polymer backbone, increasing permselectivity, while packing constraints prevent a collapse of free volume and concomitant loss of permeability. Dimethyl substitution of each of the bisphenol phenyl rings increases polymer permeability while lowering permselectivity as compared with the BPA-based analogs. Monomethyl substitution of each of the bisphenol-phenyl-rings gives materials that are more selective, but less permeable than the BPA-based analogs, while monoisopropyl substitution of both bisphenol phenyl rings gives materials that have similar permeabilities, but lower selectivities.

**P-95-3 PUBLISHED**

Gas Transport Properties of Polyarylates Based on 9,9-Bis(4-hydroxyphenyl)anthrone  
Pixton, M.R. and D.R. Paul  
Gas transport of helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide gases in two polyarylates based on 9,9-bis(4-hydroxyphenyl)anthrone and isophthalic acid or t-butyl isophthalic acid has been examined. Substitution of a t-butyl group on the isophthalate ring increases polymer permeability by 2 to 3 fold, primarily due to higher diffusion coefficients. The physical properties of these materials are very similar to their fluorene bisphenol-based analogs; however, the former are more permselective but less permeable than the latter. The favorable interaction of CO2 with the anthronylidene carbonyl unit and the higher degree of polarity in the repeat unit apparently contribute to these differences.

**P-95-4**

Gas Transport Properties of Polyarylates Part I: Connector and Pendant Group Effects  
Pixton, M.R., and D.R. Paul  
Manuscript on file, Separations Research Program  
Gas transport of helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide gases in a series of polyarylates based on isophthalic acid has been examined. These polyarylates were prepared from bisphenol A, hexafluorobisphenol A, phenolphthalein, and fluorene-bisphenol
monomers to study the effects of varying the bisphenol connector group's size and shape. Substitution of a tertiary butyl group at position five on the isophthalate ring increases polymer permeability. The incorporation of a large, bulky connector group increases gas permeability and maintains permselectivity while the substitution of t-butyl group increases gas permeability by two- to four-fold, but lowers permselectivity. Most of the increases in permeability can be related to increases in the diffusion coefficients of all the gases. All the polyarylates have high- glass-transition temperatures and may be suitable for high-temperature gas-separation applications.

P-95-5
Gas Transport Properties of Polyarylates Part II: Tetrabromination of the Bisphenol
Pixton, M.R. and D.R. Paul
Manuscript on file, Separations Research Program

The gas transport properties of a series of polyarylates based on isophthalic acid have been examined. The polyarylates were synthesized from the following bisphenol monomers with and without tetrabromo substitution: bisphenol A, hexafluorobisphenol A, phenolphthalein and fluorene bisphenol, to study the effects of tetrabromination in combination with varying the bisphenol connector-group's size and shape. Substitution of a tertiary butyl-group at position five on the isophthalate ring was used to increase polymer permeability. Tetrabromination of the bisphenol maintains or increases gas permeability and significantly increases permselectivity, particularly for the O2/N2 gas pair as compared with the non-brominated analog. The substitution of t-butyl groups increases gas permeability by two- to four-fold, but lowers permselectivity. Most of the increase in permeability can be related to an increase in the diffusion coefficient for each gas. All the brominated polyarylates have gas transport properties superior to most known glassy materials for O2/N2 separation with several materials close to a proposed empirical "upper bound" between permeability and selectivity.

P-95-6
Gas Transport Properties of Polyarylates Substituent Size and Symmetry Effects
Pixton, M.R. and D.R. Paul
Manuscript on file, Separations Research Program

Gas transport of helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide gases in a series of polyarylates based on isophthalic acid has been examined. These polyarylates were prepared from dimethylbisphenol A, tetramethylbisphenol A, diisopropylbisphenol A, and dibromodimethylbisphenol A monomers to study the effects of varying bisphenol substituent group size, symmetry, and polarity. Symmetrical placement of substituent groups increases permeability while asymmetrical placement lowers permeability. Substitution of a tertiary butyl group at position five on the isophthalate ring increases polymer permeability. Most of the increases in permeability can be related to increases in the diffusion coefficients of all the gases. The isophthalate of dibromodimethylbisphenol A has gas separation properties very similar to those of the tetrabrominated analog.

P-95-7
Techniques for Measurement of Water Vapor, Water Sorption and Permeation in Polymer Films
Schult, K.A. and D.R. Paul
Manuscript on file, Separations Research Program

The accurate measurement of water vapor sorption and permeation in polymers is complicated because water has a tendency to adsorb on high energy surfaces, a relatively high heat of vaporization, and a high solubility in most polymers. These issues and the difficulties they cause in the design of sorption and permeation equipment are reviewed. Some new approaches to circumvent these problems are described. Data for bisphenol A polysulfone films are used to illustrate these approaches.
Current literature results suggest that crosslinking may be a useful route to balance the productivity/selectivity tradeoff of polymeric gas separation membranes. This study explores the use of benzylocyclobutene chemistry to thermally crosslink polyarylate membranes based on 1,2-dihydroxybenzobenzene-3,6-dicarbonyl dichloride (XTA-Cl), fluorene bisphenol (FBP) and 5-tertiary-butyl isophthalic acid dichloride (tBIA). Very high temperatures were required to produce significant crosslinking which also caused significant degradation of the polymers. The result of this heat treatment was small increases in gas permeability coefficients and small decreases in permselectivity; this is opposite what is typically observed for simple crosslinking. It is concluded that the thermal treatment required for crosslinking is too severe to utilize this approach successfully for polyarylate gas separation membranes.

Water sorption and transport properties for a series of polysulfones are presented and interpreted in terms of the changes in the structure of the repeat unit compared to that of bisphenol A polysulfone. The differences between the sorption and diffusion of water and of permanent gases in these materials are also discussed. Water has the ability to interact with the polymer and with itself through hydrogen bonding in a way that permanent gases cannot. The equilibrium solubility of water in the polymer, unlike permanent gases, does not have a simple dependence on free volume but correlates more strongly with the frequency of hydrogen bonding sites on the polymer. Analysis of the sorption isotherms using the method of Zimm and Lundberg suggests that water molecules cluster in these polysulfones to various extents. For each polysulfone except polyethersulfone, the water diffusion coefficient decreases with increasing activity, which also suggests water clustering. For most of these materials, the water diffusion coefficient is larger than that of bisphenol A polysulfone and is directly related to the polymer free volume. Water permeability in these materials broadly correlates with the polymer free volume, but a favorable water-polymer interaction can be an overriding factor.

The accurate measurement of water vapor sorption and permeation in polymers is complicated because water has a tendency to adsorb on high energy surfaces, a relatively high heat of vaporization, and a high solubility in most polymers. These issues and the difficulties they cause in the design of sorption and permeation equipment are reviewed. Some new approaches to circumvent these problems are described. Data for bisphenol A polysulfone films are used to illustrate these approaches.

Gas sorption and transport properties at 35°C are reported for a series of ultraviolet irradiated polyarylates prepared from tetramethyl bisphenol-A (TMBPA), 4,4-dihydroxybenzophenone (DHB), and 5-tertiary-butyl isophthalic acid dichloride (tBIA). UV irradiation induces crosslinking and photo-Fries rearrangements in these polymers. The gas permeability of the polyarylates decreases with UV irradiation due to reductions in the diffusion coefficient; however,
the ideal selectivity for all gas pairs increases with UV irradiation. The effect of UV irradiation on the gas transport properties of the polyarylates is compared with that reported in the literature for similar polyimide materials. The polyimides show much greater improvement in selectivity than do the current polyarylate materials. The photo-Fries rearrangements limit the amount of crosslinking achievable in these polyarylate materials in spite of the fact that additional benzophenone units are formed.

P-96-5 PUBLISHED
Correlation and Prediction of Gas Permeability in Glassy Polymer Membrane Materials via a Modified Free Volume Based Group Contribution Method
Park, J.Y. and D.R. Paul
Over the past decade or more an extensive amount of data on the permeation of gases like helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide in a wide array of glassy polymers has been published. Much of this work has been motivated by the search for materials with high permeability and high selectivity for potential use as gas separation membranes. This paper attempts to develop a method for correlating these data in a way that permits prediction of permselectivity behavior of other polymer structures. The method used involves an empirical modification of a free volume scheme that has been used in the past with some success. The previous method requires an experimental density of the polymer and an estimate of occupied volume from a group contribution method developed by Bondi. The present method actually predicts the density and uses a refined estimate of occupied volume specific to each gas. The parameters in the model were deduced from a database including over one hundred polymers. The new method significantly improves the accuracy of correlation and of prediction.

P-96-6 PUBLISHED
Water Sorption and Transport in Blends of Poly(vinyl pyrrolidone) and Polysulfone
Schult, K.A. and D.R. Paul
Water sorption and transport properties for a series of miscible blends of hydrophobic bisphenol A polysulfone and hydrophilic poly (vinyl pyrrolidone) are reported. Study was restricted to blends that remained homogeneous after exposure to liquid water. The solubility of water in the blend films increased with increasing hydrophilic polymer content. Equilibrium sorption isotherms show dual-mode behavior at low activities and swelling behavior at high activities. The sorption kinetics are generally Fickian for blends containing 20% poly (vinyl pyrrolidone) or less, but exhibit two-stage behavior in blends containing 40% poly (vinyl pyrrolidone). Diffusion coefficients extrapolated to zero concentration decrease with increasing poly (vinyl pyrrolidone) content, owing to a decrease in the fractional free volume. However, the diffusion coefficient becomes a greater function of activity as the composition of hydrophilic polymer in the blend is increased, due to plasticization of the material by large levels of sorbed water. Permeability coefficients generally decrease with increasing poly (vinyl pyrrolidone) content for blends containing 20% poly (vinyl pyrrolidone) or less because the decrease in the diffusion coefficient is greater than the increase in the solubility coefficient. Blends containing 40% poly (vinyl Pyrrolidon) have permeability coefficients greater than those of polysulfone due to high water solubility. The permeability coefficients depend on water concentration in approximately the same way for all blends.

P-96-7 PUBLISHED
Polyarylate Gas Separation Membranes
Paul, D.R. and M.R. Pixton
The molecular design of polymers for membrane separation of gases is illustrated for the oxygen/nitrogen pair by a series of polyarylates. The use of tetrabromo ring substitutions combined with a fluorene connector group on the bisphenol with or without a t-butyl group on the isophthalic acid monomer leads to state-of-the-art productivity-selectivity combinations.
Water Sorption and Transport in Blends of Polyethyloxazoline and Polyethersulfone
Schult, K.A. and D.R. Paul
Water sorption and transport properties for a series of homogeneous blends of hydrophobic polyethersulfone and hydrophilic polyethyloxazoline are reported. Only blends that remained homogeneous after exposure to liquid water were studied in detail. Equilibrium solubility of water in the blend films increases with increasing hydrophilic polymer content. For all materials, equilibrium sorption isotherms show dual-mode behavior at low activities and swelling behavior at high activities. The sorption/desorption kinetics for PES are generally Fickian, but two-stage behavior is evident in blends containing 10 and 20% polyethyloxazoline. Diffusion coefficients decrease with increasing polyethyloxazoline content, owing to a decrease in the fractional free volume. For all materials, the diffusion coefficient show a positive dependence on activity or concentration due to plasticization of the material by high levels of sorbed water, but it becomes a greater function of activity as the composition of hydrophilic polymer in the blend is increased. Since the decrease in the diffusion coefficient is greater than the increase in the solubility coefficient, the permeability coefficient decreases with increasing hydrophilic polymer content.

Water Vapor Sorption and Transport in Polysulfones and Their Blends
Schult, K.A.
Ph. D. Dissertation
Water sorption and transport properties of homogeneous blends of a water soluble polymer with a relatively hydrophobic polymer were investigated. Specifically, a series of miscible blends of hydrophobic bisphenol A polysulfone and water soluble poly (vinyl pyrrolidone), as well as hydrophobic polyethersulfone and water soluble polyethyloxazoline, were studied. The effects of polymer repeat unit structure on the water sorption and transport properties of a series of polysulfones based on bisphenol A polysulfone were also analyzed. The accurate measurement of water vapor sorption and permeation in polymers is complicated because water has a tendency to adsorb on high energy surfaces, a relatively high heat of vaporization, and a high solubility in most polymers. These issues and the difficulties they cause in the design or sorption and permeation equipment are reviewed, and some new approaches to circumvent these problems are described and employed in the design of the equipment used in this study. The equilibrium solubility of water in a polymer, unlike permanent gases, does not have a simple dependence on free volume but correlates more strongly with the frequency of hydrogen bonding sites on the polymer. Thus, the solubility of water in the polymer blend films increases with increasing water soluble polymer content. Structural modifications to the repeat unit of bisphenol A polysulfone which enhance the ability of the polymer to hydrogen bond also generally increase the solubility of water in the polymer. For all systems studied, water diffusivity is directly dependent on polymer fractional free volume. For the blend systems studied, the addition of the water soluble polymer decreases the fractional free volume of the polymer blend, resulting in a diffusion coefficient that generally decreases with increasing water soluble polymer content in the blend. Structural modifications to bisphenol A polysulfone that increase the polymer fractional free volume tend to increase the diffusion coefficient of water in the polymer. Water permeability is equal to the product of the solubility and the diffusivity. Thus, in all of the systems studied, water permeability broadly correlates with the polymer free volume, but a favorable water-polymer interaction can be an overriding factor.

Gas Sorption and Transport in Poly(tertiary-butyl methacrylate)
Wright, C.T. and D.R. Paul
Polymer 38(8):1871-1878 (1997)
Gas sorption and transport properties of poly(tertiary-butyl methacrylate) (PtBMA) have been measured at 35°C and are compared with prior results for poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(ethyl methacrylate) (PEMA). The t-butyl substitution increases the gas permeability as a result of increases in both diffusivity and solubility.
coefficients; however, the ideal selectivity for a given gas pair may increase or decrease depending upon the methacrylate polymer to which it is compared. Poly(t-butyl methacrylate) does not show plasticization by CO² up to 10 atm of CO². The effect of t-butyl substitution on gas permeability observed here for the methacrylate polymer is compared to that reported in the literature for other polymer types. This substitution causes a larger increase in permeability the smaller the repeat unit of the base polymer since this results in a greater modification in structure and subsequent greater decrease in efficiency of chain packing.

P-97-2  PUBLISHED
Modification of Polysulfone Gas Separation Membranes by Additives
F.A. Ruiz-Trevino and D.R. Paul
The incorporation of additives into polymers like bisphenol A polysulfone (PSF) can provide an attractive alternative for modifying their permselective properties for gas separation, provided the additive is appropriately selected. In this work, three series of additives based on naphthalene, bisphenol A, and fluorene structures were incorporated into PSF and their effect on gas transport properties was measured. The results show that these additives increase selectivity and reduce permeability of PSF when incorporated at low concentrations. The largest increases in selectivity for the gas pairs He/CH₄, H₂/CH₄, and O₂/N₂ are caused by those additives that cause the largest reductions in the glass transition temperature and fractional free volume, and typically, they are made up of planar molecules containing polar or small asymmetric protuberances. The productivity-selectivity balance response of the modified PSF membranes reveals that the naphthalene-based additives containing asymmetric groups of atoms lead to membranes with higher selectivity and with only small losses in permeability relative to the unmodified PSF membranes. The addition of 20 wt % of the glassy additive Kenflex A into PSF causes a fourfold increase in the selectivity of PSF to He/CH₄ at the expense of a 37% reduction in the permeability of helium. Copyright 1997 John Wiley & Sons, Inc.

P-97-3  PUBLISHED
Gas Permselextivity Properties of High Free Volume Polymers Modified by a Low Molecular Weight Additive
F.A. Ruiz-Trevino and D.R. Paul
Submitted to Journal of Applied Polymer Science
The permselectivity properties of mixtures of the highly substituted polymers tetramethylhexafluoro polysulfone, TMHFPFS, and tetramethylhexafluoro bisphenol A t-butyl isophthalate, TMHFBPAtBIA, with a low molecular weight glassy additive Kenflex A (denoted here as KXA) were measured for different gases and compared to the permselectivity properties shown by the base, unsubstituted polymers polysulfone, PSF, and bisphenol A t-butyl isophthalate, BPA-tBIA. The results show that the selectivity - permeability balance of polymer membranes may be appropriately tailored by a combination of chemical and physical alterations of the base polymer. The addition of modest amounts of KXA (ca 20 wt%) into TMHFPFS or TMHFBPAtBIA, leads to materials whose permeability / selectivity combination is better than that of the unsubstituted materials, PSF or BPA-tBIA. The polymer TMHFPFS responds more beneficially to the incorporation of KXA than TMHFBPAtBIA. At the same level of permeability, mixtures based on TMHFPFS have higher selectivity factors for H₂/CH₄ and CO₂/CH₄ than those based on TMHFBPAtBIA.

P-97-4
A Quantitative Model for the Specific Volume of Polymer - Diluent Mixtures in the Glassy State
Ruiz-Trevino, F.A. and D.R. Paul
Manuscript on file, Separations Research Program
A mathematical model to describe the specific volume of glassy mixtures of a polymer and a low molecular weight diluent or additive is presented. The model is based on understanding physical assumptions and relies on parameters that can be determined experimentally or estimated from methods available in the literature. The predictions of the model show good agreement with the experimental data for mixtures of four polymer with diluents which in the pure state are liquid,
glassy, or crystalline. The observed negative departure from volume additivity, as defined by simple additivity of the specific volume of the pure glassy polymer and the pure amorphous diluent, is the result of the relaxation of the excess volume of the glassy mixture relative to the equilibrium state caused by mixing two components with different glass transition temperatures.

P-97-5 PUBLISHED
Gas Sorption and Transport in UV-Irradiated Poly (2,6-dimethyl-1,4-phenylene oxide) Films
Wright, C.T. and D.R. Paul
Gas sorption and transport properties at 35°C have been reported for a series of UV-irradiated films of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). UV-irradiation induced crosslinking in all films. The gas permeability was reduced upon crosslinking while significant increases in gas permeability were observed. The addition of benzophenone to the PPO films did not result in marked improvements in crosslinking or the resulting gas transport properties of the film.

P-98-1
Effects of Bromine Substitution on the Physical and Gas Transport Properties of Five Series of Glassy Polymers
McCaig, M.S.; E.D. Seo; D.R. Paul
Manuscript on file, Separations Research Program
The effects of bromine substitution on the physical and gas transport properties was examined for five families of tetra-substituted glassy polymers: bisphenol A polycarbonates (PC), hexafluoropolycarbonates (HFPC), hexafluorobisphenol-tertiary butyl isophthalates (HFBP-tBIA), fluorenebisphenol-t-butyl isophthalates (FBP-tBIA) and bisphenol A-t-butyl isophthalates (BPA-tBIA). Additionally, the thermal response of the substituted PBA-tBIA polymers was explored to elucidate the effects of bromine substitution on the activation energies of permeation and diffusion and on the heat of gas sorption. Compared to its methyl substituted analog, each bromine substituted polymer had a higher cohesive energy density, a higher glass transition temperature and a lower oxygen specific fractional free volume. Bromine substitution significantly reduced O₂ and CO₂ permeability and substantially increased both O₂/N₂ and CO₂/CH₄ selectivity. An increase in the activation energy of diffusion for N₂ compared to O₂, and for CH₄ compared to CO₂ may be credited for the majority of the selectivity gain. A new method for evaluating penetrant dependent fractional free volume proved to be a valuable tool in determining the effects of structural changes on gas transport behavior.

P-98-2 PUBLISHED
Effect of Film Thickness on the Changes in Gas Permeability of a Glassy Polyarylate Due to Physical Aging: Part I. Experimental Observations
McCaig, M.S. and D.R. Paul
Polymer 41:629-637, 2000
The effects of thickness (0.25 to 33 μm) and aging time on the gas permeation properties of films formed from a glassy polyarylate made from bisphenol-A benzophenone dicarboxylic acid were examined. Evidence is presented which shows that physical aging is responsible for a significant decrease in gas permeability with time following quenching the polymer from above its glass transition temperature; the rate of change is greater for the thinner films. Two methods of determining accurate film thicknesses were used to obtain absolute permeability coefficients. The importance of the permeation protocol on the aging rate was examined, and a reversal of the aging process was demonstrated by annealing the aged film above the Tg. These results indicate that physical aging occurs by two distinct simultaneous mechanisms; one that is thickness dependent and another that is not.
Effect of Film Thickness on the Changes in Gas Permeability of a Glassy Polyarylate Due to Physical Aging: Part II. Mathematical Model.
McCaug, M.S.; D.R. Paul; J.W. Barlow
Polymer 41:639-648, 2000

Part I of this series documented a substantial loss in gas permeability over time for thin films of glassy polyarylate made from bisphenol-A benzophenone dicarboxylic acid. The rate of permeability loss, and, thus, again was found to be dependent on film thickness in a way that suggested that physical again occurs by two mechanisms. In this paper, a mathematical model was developed to quantitatively describe the physical again process in terms of the free volume (permeability) loss observed using reasonable physical parameters. The model describes two simultaneous mechanisms of free volume loss: free volume diffusion to the film surface (thickness dependent) and lattice contraction (thickness independent). A step-wise model development is described with comparison to the data and optimization of the model parameters at each step. The final dual-mechanism model describes the experimental data presented in Part I remarkably well. Flue Gas Desulfurization/ Acid Gas Treatment.

Effect of UV Crosslinking and Physical Aging on the Gas Permeability of Thin Glassy Polyarylate Films
McCaug, M.S. and D.R. Paul
Polymer 40:7209-7225, 1999

The effect of crosslinking by UV irradiation on the gas permeation properties of thin films (thickness < 1 um) made from two benzophenone-based polyarylates were examined. In addition to the permeation response to UV crosslinking in these two polymers, the effects of crosslinking on the rate of physical aging was also explored. The sequence of physical aging and crosslinking, as well as reversal of the aging process was studied in order to separate the similar effects of again and crosslinking. The results show that crosslinking very thin films can greatly improve the long-term performance of membranes when compared to non crosslinked films of similar thickness.

Membrane Formation Techniques for Gas Permeation Measurement for Side-Chain Crystalline Polymers
Mogri, Z. and D.R. Paul
Journal of Membrane Science 175:253-265, 2000

Modifications of traditional membrane support assemblies are described that permit accurate measurement of gas permeability coefficients for side-chain crystalline poly(n-alkyl acrylate)s or poly(n-alkyl methacrylate)s above and below the melting point. These modification address the problems associated with the very brittle nature of these materials below the melting point and their fluid-like nature above the melting point. An Anopore(TM) porous ceramic disc coated with poly(w2,6-dimethyl-1, 4 phenylene oxide) (PPO) masked with aluminum tape on the downstream surface was the support ultimately chose to perform these measurements. The problems and concerns leading to the choice of this assembly are described. Crystallite orientation in solvent cast films of the side-chain crystalline polymers is demonstrated by wide-angle X-ray diffraction. Melting the film and recrystallization on cooling effectively eliminates such orientation.

Water Vapor Transport in a Series of Polyarylates
Kelkar, A.I. and Paul, D.R.
Manuscript on File

Water vapor sorption and transport properties are presented for a series of polyarylates. The effect of making various structural changes in the polymer backbone has been studied, by comparing the transport properties to those of the base polymer bisphenol A isophthalate. All the polymers exhibit an upturn in the sorption isotherm at moderate to high activities, which in most cases is caused by plasticization of the polymer by water vapor. the response of water vapor to the structural changes is compared to that of the permanent gases. A good correlation is established.
between the diffusion and permeability coefficients and the fractional free volume. A similar behavior is seen in gases. However, the solubility coefficient, which decreases with increase in the fractional free volume, shows an opposite effect. Water vapor has the ability to hydrogen bond with itself and interact strongly with the polymer. In the case of solubility, the water vapor-polymer interaction plays an important role and overrides the effect of the increase in fractional free volume. The structural changes described here have similar effects on the permeation of water in a series of polysulfones reported earlier, as seen here for the polyarylates.

P-00-3 PUBLISHED
Pervaporation Separation of Aromatic/Aliphatic Hydrocarbons by Crosslinked (Methyl Acrylate-co-acrylic Acid) Membranes
Matsui, S. and Paul, D.R.
Copolymers of methyl acrylate and acrylic acid were synthesized to fabricate membranes ionically crosslinked using aluminum acetylacetonate for the separation of toluene/i-octane mixtures by pervaporation at high temperatures. The formation of the ionic crosslinking via bare aluminum cations was characterized by UV-visible spectroscopy and solubility tests. Reproducibility and reliability of the methodology for membrane formation and crosslinking were confirmed. The effects of acrylic acid content, crosslinking conditions, pervaporation temperature, and feed composition on the normalized flux and the selectivity for toluene/i-octane mixtures were determined.

P-01-1 PUBLISHED
Gas Sorption and Transport in Side-Chain Crystalline and Molten Poly(octyldecyl acrylate)
Mogri, Z. and Paul, D.R.
The gas sorption and transport properties of poly(octadecyl acrylate) are described for the semi-crystalline and molten states. The change in permeability upon traversing the melting point, or permeation switch, was observed to be as high as two orders of magnitude depending on the penetrant. Analysis of gas transport is explained using the Michaels and Bixler model for semicrystalline polyethylene. This analysis shows chain immobilization of the amorphous phase by surrounding crystals to play a significant role in describing the penetrant-dependent permeation switch in this side-chain crystalline polymer. Traditional two-phase models describing crystallites as impenetrable barriers with no effect on amorphous phase properties may explain solubility in this system but do not describe diffusion. The dependence of transport parameters on polymer composition, e.g. side-chain length, is also discussed.

P-01-2 PUBLISHED
Water Vapor Transport in a Series of Polyarylates
Kelkar, A.J. and Paul, D.R.

P-01-3 PUBLISHED
Gas Separation Performance of Poly(4-vinylpyridine)/Polyetherimide Composite Hollow Fibers
Shieh, J.J.; Shung, T.S.; Wang, R.; Srinivasan, M.P.; Paul, D.R.
J. Membrane Sci., 182, 111, 2001

P-01-4 PUBLISHED
Water-Vapor Permeation in Semicrystalline and Molten Poly(octadecyl acrylate)
Mogri, Z. and Paul, D.R.
The water-vapor permeability of poly(octadecyl acrylate)(PA-18) was measured as a function of temperature in the region traversing its melting point (50 degrees C). The molten-state permeability of PA-18 is comparable to that of shorter side-chain methacrylate polymers Water permeability in the semicrystalline state of PA-18 is similar to that of polyethylene at comparable crystallinity levels. The permeation switch, or change in permeability with the traversing of the
melting point, for water is discussed in the context of previous results for other penetrants in this and other side-chain crystalline polymers.

**P-01-5** **PUBLISHED**  
Gas Sorption and Transport in Poly(alkyl(meth)acrylates). Part I. Permeation Properties  
Mogri, Z. and Paul, D.R.  

The gas permeability of poly(alkyl acrylate)s was measured as a function of temperature in both the amorphous and crystalline states. Penetrant permeability in the amorphous state increases as the side-chain length becomes longer but shows mixed trends in the crystalline state. A decrease in permeability was observed in the amorphous state when the backbone was stiffened, i.e. polymethylacrylate versus polyacrylate. The influence of side-chain length and backbone stiffness on the magnitude of the change in permeability upon traversing the melting point, or permeability switch, is discussed. The effect of main versus side-chain crystallinity on the permeation switch is analyzed. The influence of a compositional change in the amorphous phase upon melting on the gas permeability of side-chain crystalline polymers is addressed.

**P-01-6** **PUBLISHED**  
Gas Sorption and Transport in Poly(alkyl(meth) acrylate)s. Part II. Sorption and Diffusion Properties  
Mogri, Z. and Paul, D.R.  

Gas sorption in amorphous ethyl and decyl acrylate polymers and semi-crystalline and molten octadecyl and behenyl acrylate polymers were measured as a function of temperature of CH4 and CO2. Diffusion coefficients, calculated based on permeability data for these polymers, are found to increase with increasing side-chain length. The large differences in permeability observed between poly(methyl acrylate) and poly(ethyl acrylate) are described in terms of the diffusion and solubility of gases in these polymers. Anomalous permeation switch behavior of poly(behenyl acrylate) is further analyzed using diffusion switch data. The solubility coefficients for CH4 and CO2 in amorphous poly(alkyl acrylate)s are correlated with alkyl content and extrapolated to the long side-chain limit. The extrapolated values are larger than those for amorphous polyethylene found by extrapolation to zero crystallinity using the traditional two-phase mode.

**P-04-1** **PUBLISHED**  
Natural Gas Permeation in Polyimide Membranes  
Wind, J.D.; Paul, D.R.; Koros, W.J.  

**P-04-2** **PUBLISHED**  
A Simple Model for Pervaporative Transport of Binary Mixtures through Rubbery Polymeric Membranes  
Matsui, S. and Paul, D.R.  

**P-04-3** **PUBLISHED**  
Reformulation of the Solution-Diffusion Theory of Reverse Osmosis  
Paul, D.R.  

**P-04-4** **PUBLISHED**  
Copolymers of Poly(-alkyl Acrylates): Synthesis, Characterization, and Monomer Reactivity Ratios  
O'Leary, K. and Paul, D.R.  
*Polymer*, 45, 6575 (2004)
Experimental Methods for Tracking Physical Aging of Thin Glassy Polymer Films by Gas Permeation
Huang, Y. and Paul, D.R.

Nanocomposites Formed from Linear Low Density Polyethylene and Organoclays
Hotta, S. and Paul, D.R.

Physical Aging of Thin Glassy Polymer Films Monitored by Gas Permeability

Effect of Temperature on Physical Aging of Thin Glassy Polymer Films
Huang, Y. and Paul, D.R.

Physical Properties of Poly(n-alkyl acrylate) Copolymers. Part I. Crystalline/Crystalline Combinations
O’Leary, K.A. and Paul, D.R.
*Polymer*, 47, 1226 (2006)

Physical Properties of Poly(n-alkyl acrylate) Copolymers. Part II. Crystalline/Crystalline Combinations
O’Leary, K.A. and Paul, D.R.
*Polymer*, 47, 1245 (2006)

Novel Separations

Olefin/Paraffin Separations by Reactive Absorption: A Review
Safarik, D.J. and R.B. Eldridge

Light olefins and paraffins are commonly separated by cryogenic distillation. A process based upon reversible chemical complexation, which employs a mass-separating agent rather than an energy-separating agent, presents an attractive alternative to distillation. Use of such a facilitated-transport-assisted process could substantially reduce the capital costs and energy requirements of olefin/paraffin separations. Copper(I) and silver(I) have long been known to form electron donor/acceptor complexes with olefins. Several chemical systems using these transition metals as the selective separating agent have been studied. A review of copper- and silver-based complexing solutions for olefin/paraffin separations via gas/liquid contacting is presented.

Sieve-Tray Extractor Continuous-Phase Mixing
Eldridge, R. Bruce and James R. Fair

The continuous-phase-mixing characteristics of a sieve-tray extractor were studied in a specially designed single-stage experimental apparatus. Two chemical systems were studied: toluene-water
and n-butanol-water. The degree of continuous-phase axial mixing was determined for various tray geometries and phase flow rates. A predictive model was developed and combined with a point efficiency correlation to yield an overall tray efficiency. The results indicate that the level of continuous-phase mixing does not significantly affect the overall mass-transfer efficiency of an extractor sieve tray.

RB-99-2

**General Heuristics for the Design of Catalytic Distillation Columns**

Schell, John; Amanda Whaley; R.B. Eldridge

Presented at the 1998 Annual AIChE Meeting, Miami, FL, Nov. 15-21, 1998

A growing interest is seen in reactive distillation. In the past decades, industrial application of catalytic distillation (CD) to MTBE and other ether production has become common place. However, the literature is remarkably devoid of experimental results. Much of this is due to the proprietary environment surrounding the development of catalytic distillation systems. However, several authors have proposed guidelines and heuristics of the design of CD columns. The present authors approach the design of columns for two reactive systems using existing heuristics and suggest modifications to extend applicability. Specifically, the study of the production of TAME and of the alkylation of benzene to form long chain linear alkylbenzene is addressed.

RB-99-3 **S10.00**

**Investigation of Local Scale Phenomena in Vapor Liquid Contactors Using X-Ray Tomography**

Cartmel, Dwight Bradley

Master's Thesis

The existing mass transfer and hydraulic models for predicting distillation column performance are based upon macroscopic experimental data. These models are limited by the ranges of the data and are semi-empirical. The current research applies X-ray tomography to non-invasively obtain images of the vapor-liquid interface. The key goal is to use X-ray computed tomography to obtain quantitative information on factors such as fluid hold-up, and fluid distribution for packed columns. The information obtained will be used to further understanding and to provide insights into mass transfer.

RB-99-4 **PUBLISHED**

**HETP and Pressure Drop Prediction for Structured Packing Distillation Columns Using a Neural Network Model**

Whaley, Amanda K.; Christopher A. Bode; Joydeep Ghosh; R. Bruce Eldridge


A neural net framework was used to predict the mass-transfer and hydraulic performance of a commercial structured packing operating in distillation service. The results indicated that the approach produced a more accurate prediction than a traditional semiempirical model. The neural net methodology was also used to yield a detailed sensitivity analysis of the operating variables.

RB-99-5 **PUBLISHED**

**Olefin/Paraffin Separation Technology: A Review**

Eldridge, R. Bruce


A review of traditional and nontraditional technologies for the separation of light olefins and paraffins is presented. The technologies addressed range from conventional low-temperature distillation to chemical complexion using copper and silver ions.

RB-00-1 **PUBLISHED**

**Process Tomography: An Option for the Enhancement of Packed Vapor-Liquid Contactor Model Development**

Eldridge, R.B.; Carolyn E. Schmidt; Dwight Cartmel


A multitude of packed vapor-liquid contactor mass-transfer and hydraulic models exist in the literature. With few exceptions, the development of these models has been based on a very limited
understanding of the microscale hydraulic phenomena inside the contacting column. Recently, the use of X-ray tomography has been shown to be an effective technique for imaging flow patterns in multiphase contactors. This paper describes the potential benefits that X-ray tomography analysis can bring to the understanding and modeling of the vapor-liquid contacting process. The technology has significant potential for enhancing the prediction of both mass-transfer efficiency and packing pressure drop of commercial packed columns.

**RB-00-2 PUBLISHED**

**Neural Network Modeling of Structured Packing Height Equivalent to a Theoretical Plate**
Eldridge, R. B. and Gregory S. Pollock

The height equivalent to a theoretical plate (HETP) of nine types of structured packing was successfully modeled using a neural network. The network was trained on data similar to that used to develop semiempirical mass-transfer models. The HETP was then predicted using the trained network. The neural network model yields a very accurate prediction of experimentally determined HETP values, and it is more accurate than a traditional semiempirical model. Using the neural network, it is also possible to rank the relative importance of input variables in determining the HETP. In particular, this work shows that the roughness of the structured packing surface is a very important input parameter.

**RB-00-3 PUBLISHED**

**The Experimental Application of X-ray Tomography to a Vapor-Liquid Contactor**
Eldridge, R.B.; Cartmel, Dwight B.; Schmit, Carolyn E.

Initial results obtained from the application of X-ray tomography to an operating vapor-liquid contactor indicate that the technology has the potential to provide insight into the underlying hydraulic behavior of a packed column. Experiments were performed with counter-current air-water flows in a six-inch-diameter contactor packed with random packing. Liquid and gas velocities typical of a commercial column were tested. Liquid distribution patterns and holdup values were obtained for a series of tower elevations. The holdup values obtained from the tomography experiments were typically within 30 percent of experimental values obtained from traditional techniques. The experimental flow patterns for random packing showed a preference for the liquid stream to flow in rivulets.

**RB-01-4 PUBLISHED**

**The Prediction of Trayed Distillation Column Mass Transfer Performance by Neural Networks**
Olivier, E. and Eldridge, R.B.

**RB-02-1 NEW $20.00**

**Evaluation of X-Ray Imaging to Investigate Hydraulic Performance of Vapor-Liquid Contactors**
Schmit, C.E.
PhD dissertation

Vapor-liquid contacting applications, such as distillation, absorption, and stripping, require contact between the two phases to accomplish the desired separation. The current models to predict the efficiency of the operation of columns rely upon measurements representative of the column average, and thus, do not predict detrimental behavior caused by variations in properties throughout the column. In this work, x-ray imaging techniques are investigated to determine the feasibility of measuring vapor-liquid contacting behavior at a local scale within packed columns. X-ray computed tomography (CT) was used to obtain images of three experimental systems, and x-ray transmission measurements were used to quantify and measure the variability of the liquid present. The experimental studies were focused on characterizing the materials present in an air-water contactor, measuring the thickness of a liquid film on a steel surface, and observing the hydraulic behavior of an air-water contactor containing structured packing.
A Comparison of Steady-State Equilibrium and Rate-Based Models for Packed Reactive Distillation Columns

Peng, J.; Lextrait, S.; Edgar, T.F.; Eldridge, R.B.

A steady-state equilibrium model and a rate-based model were developed and compared for packed reactive distillation columns for the production of tert-amyl methyl ether (TAME) and methyl acetate. For the methyl acetate system, both models yield good agreement with experimental data. The results predicted by the equilibrium and rate-based models are similar with very few differences found under all simulation conditions.

Investigation of X-Ray Imaging of Vapor-Liquid Contactors. 1. Studies Involving Stationary Objects and a Simple Flow System

Schmit, C. and Eldridge, R. B.
Manuscript on file

X-ray computed tomography was used to image two experimental systems containing vapor, liquid, and stainless steel. The first system consisted of a set of test objects designed to incorporate interfaces between the phases at multiple angles. The second system was film-flow apparatus designed to operate with a film of water in the range of 0.2 to 0.4 mm thick. The amount of liquid present at selected elevations of both experimental systems was measured from the x-ray transmission data. Less than 10 percent variation from expected values was measured for both the stationary objects and film-flow apparatus. The tomography systems used included a high-energy scanner and a low-energy scanner. The size of a pixel in the reconstructed image ranged from 0.15 to 0.40 mm. The measurement noise was identified as an important factor of the imaging system. The second article in this series will include experimental x-ray CT results of a vapor-liquid contactor and results of the analysis of images produced from simulations of x-ray CT.

Dynamic Rate-based and Equilibrium Models for a Packed Reactive Distillation Column

Peng, J.J.; Edgar, T.F.; Eldridge, R.B.


Schmit, C.; Perkins, J.; Eldridge, R.B. Manuscript on File

Experimental studies and computer simulations were performed to evaluate the potential of x-ray imaging to quantify the hydraulic characteristics of a vapor-liquid contactor. Cross-sectional images of a 6-inch-diameter air-water contactor containing Mellapak 500Y structured packing were obtained at various elevations, air flow rates, and liquid flow rates. In addition, stationary transmission measurements were obtained to provide an indication of the variability of flow in the contactor over the duration required to acquire an image. Computer simulations of the imaging technique were performed to validate the cause of ring-like artifacts observed in the images obtained from the experiments. It was concluded that the subpositions required for the pseudo-third generation scan geometry are a primary cause of the artifacts.

Steady-State Rate-Based Simulation of Packed Reactive Distillation: Spatial Discretization

Lextrait, Sebastian; Eldridge, R.B.; Edgar, T.F

This paper investigates issues related to the numerical simulation of rate-based models for catalytic distillation processes. Special emphasis is placed on spatial discretization in the solution of steady-state models describing packed reactive distillation columns. A general rate-based model for packed reactive distillation is briefly presented, along with its underlying assumptions. This
mathematical model is then discretized along its spatial dimensions using different finite-difference schemes. In this paper, steady-state simulations are considered to assess various properties of the different discretization methods. Using a tert-amyl methyl ether (TAME) packed reactive distillation as a case study, we show that a cell-based approach, similarly to a first order finite-difference approximation, is inefficient in converging to the solution of the mathematical model. To address this problem, a higher-order discretization scheme is used, and its advantages are illustrated. This latter method is of interest for reducing computation time and might permit model-based control strategies, which require steady-state and dynamic models of tractable sizes.

**Supercritical Fluid Technology**

**F-86-8 PUBLISHED**

Phase Equilibria for Supercritical Extraction of Lemon Flavors and Palm Oils with Carbon Dioxide
Mathias, P.M.; T.W. Copeman; J.M. Prausnitz (from Air Products and Chemicals, Inc.)
Fluid Phase Equilibria 29:545-54 (1986)

A correlation is presented for solubility data in high-pressure CO2 of lemon oil and of a triglyceride mixture of palm oil. These data are compared with calculations based on the Peng-Robinson equation and on an equation of state containing a theoretically realistic repulsive term. The correlated data are useful for the design of processes to upgrade agricultural products.

**J-82-1 PUBLISHED**

Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented vander Waals Treatment
Johnston, K.P.; D.H. Ziger; C.A. Eckert

Numerous solubility data in ethylene, ethane, and CO2 are presented along with a predictive model.

**J-83-1 PUBLISHED**

The Use of Partial Molal Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures
Eckert, C.A.; D.H. Ziger; K.P. Johnston; T.K. Ellison
Fluid Phase Equilibria 14:167-75 (1983)

A new approach for understanding the phase behavior in supercritical systems.

**J-84-1 PUBLISHED**

Thermodynamic Models for Nonrandom and Strongly Nonideal Liquid Mixtures
Wong, J.M. and K.P. Johnston

Not yet applied to supercritical fluids, but it will be useful for our future models.

**J-84-2 PUBLISHED**

Supercritical Fluids
Johnston, K.P.

Introduction to and review of supercritical fluid behavior, data, models, and applications.

**J-84-3 PUBLISHED**

Supercritical Fluid Extraction
Johnston, K.P. and W.M. Flarsheim II

This is a tutorial on supercritical fluid technology.
Since supercritical mixtures are far removed from an ideal reference state, previous theories have been unsuccessful for the prediction of solubility isotherms. Such a goal has been accomplished quantitatively by calculating the interaction energy based on the molecular volume.

Supercritical-fluid extraction is based on the extreme sensitivity of solubility with respect to pressure. The universal aspects of this pressure effect are identified and characterized quantitatively.

To study chemistry in supercritical water (Tc = 374°C, Pc = 221 bar), we have developed an electrochemical cell of novel design.

For supercritical CF3H, a modest change in pressure or temperature causes a large change in reaction rate constants.

An experimental technique was developed to study the effects of cosolvents on the solubility of benzoic acid in CO2. The data are correlated using the Peng-Robinson equation of state.

Cosolvents can have a pronounced impact on the economics of supercritical fluid processes. This paper includes numerous data and an engineering model to correlate the data. This is our final and most comprehensive paper on partial molal volumes in supercritical fluids. Our modeling efforts for supercritical fluid phase behavior were aided by this study.
J-85-9 PUBLISHED
Nonpolar Cosolvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide
Dobbs, J.M.; J.M. Wong; K.P. Johnston
Journal of Chemical Engineering Data 31:303 (1985)
A new microsampling experimental technique is described for measuring the solubility of solids in supercritical fluid CO2 with liquid cosolvents. Since the polarizability of CO2 is relatively low, the solubility of hydrocarbons increases significantly with the addition of small amounts of alkane cosolvents. In many cases, the sensitivity of the solubility with respect to pressure actually increases with the addition of the cosolvent. The data are predicted to within an average of 15.5% using solubility parameters to calculate the interaction constants in a modified van der Waals equation of state.

J-85-10 PUBLISHED
Effects of Supercritical Solvents on the Rates of Homogeneous Chemical Reactions
Kim, S. and K.P. Johnston
Solvatochromatic shift data have been obtained for phenol blue in supercritical fluid CO2, with and without a cosolvent, over a wide range of temperature and pressure. At 45°C, supercritical fluid CO2 must be compressed to a pressure of more than 2k bar in order to obtain transition energy, ET, and a polarizability per unit volume which is comparable to that of liquid n-hexane. The ET data can be used to predict that the solvent effect on rate constants of certain reactions is extremely pronounced in the near-critical region where the magnitude of the activation volume approaches several liters/mole.

J-85-11 PUBLISHED
Selectivities in Pure and Mixed Supercritical Fluid Solvents
Dobbs, J.M. and K.P. Johnston
Supercritical fluid CO2 offers several advantages over organic liquid solvents for separations and reaction processes of thermally labile biomolecules. A major limitation is that even the moderately polar biomolecules are only slightly soluble. Experimental solubility and vapor pressure data were obtained for cholesterol, stigmasterol, and ergosterol in supercritical CO2 with and without cosolvents over a pressure range of 100 to 300 bar. Small concentrations of certain cosolvents can increase solubilities of particular sterols by one or two orders of magnitude due to complexes found in the solid phase. The experimental data were correlated using component solubility parameters to obtain the unlike-pair attraction constant used in a modified van der Waals equation of state.

J-85-12 PUBLISHED
Solubilization of Biomolecules in Carbon Dioxide Based Supercritical Fluids
Wong, J.M. and K.P. Johnston
Biotechnology Progress 2:29 (1986)
Moderately polar biomolecules are only slightly soluble in supercritical CO2. Small concentrations of certain cosolvents can increase solubilities of particular sterols by one to two orders of magnitude but have little effect on other sterols due to complexes formed in the solid phase. This demonstrates a new concept for supercritical fluid separations of certain classes of solids in which the cosolvent improves the selectivity dramatically due to interactions in both phases.
J-86-1  $15.00
Modification of Supercritical Fluids Equilibrium and Selectivity Using Polar and Nonpolar Cosolvents
Dobbs, J.M.
Ph.D. dissertation
Experimental and modeling results are presented for the effects of cosolvents on solubilities and selectivities of solids in supercritical fluids. Most of the dissertation is summarized in J-85-6, J-85-9, and J-85-11.

J-86-2  PUBLISHED
Extreme Solvent Effects on Reaction Rate Constants at Supercritical Fluid Conditions
Johnston, K.P. and C. Haynes
The reaction rate constant was adjusted over several orders of magnitude for the unimolecular decomposition of a-chlorobenzyl methyl ether using the supercritical fluid solvent 1,1-difluoroethane. Activation volumes were observed as low as -6,000 cc/mol, which is about an order of magnitude more negative than those of others reported previously in the literature for a homogeneous reaction. Spectral shift (solvatochromic) data were measured for phenol blue in the same fluid in order to interpret the rate data. A method is presented to predict solvent effects on rate constants at supercritical fluid conditions.

J-86-3  PUBLISHED
Local Composition Models for Fluid Mixtures Over a Wide Density Range
Johnston, K.P.; S. Kim; J.M. Wong
Fluid Phase Equilibria 38:39 (1987)
A local composition model has been developed to correlate phase equilibria rate of both nonpolar and polar systems over a wide range in density. The model has been tested using a large data base consisting of solubilities of solids in supercritical fluids.

J-86-4
Report on Supercritical Fluid Research
Handout for SRP Extraction Study Group Meeting, October 1986
Review of student research results. Includes copies of handouts by Wong, Lemert, and Flarsheim.

J-86-5  $10.00
Molecular Thermodynamics of Steroids and Polyfunctional Organic Solids in Supercritical Fluid Mixtures
Wong, J.M.
Ph.D. dissertation
Supercritical fluid CO2 offers several advantages compared with organic liquid solvents for separations and reaction processes involving thermally labile biomolecules. A disadvantage is that moderately polar biomolecules such as sterols are only slightly soluble in pure supercritical fluid CO2. Experimental solubility and vapor pressure data were obtained for steroid and sterols including cholesterol, stigmasterol, ergosterol, cholestenone, and pregnenolone in supercritical fluid CO2 with and without cosolvents, and over a pressure range of 100 to 350 bar. Small concentrations of certain cosolvents can increase solubilities of particular sterols by one or two orders of magnitude but have little effect on other sterols due to complexes formed in the solid phase. To gain a better understanding of how the chemical nature of solvent, cosolvent, and solute molecules affect the phase behavior of supercritical fluid systems, a fundamental thermodynamic model based on the density-dependent local composition concept was developed. The model was developed and tested using computer simulation data and was applied successfully to predict the phase behavior of binary and ternary supercritical fluid mixtures containing polar solvents and cosolvents and polyfunctional organic solids.
Molecular Thermodynamics at Supercritical Fluid Conditions: Solvent Effects on Reaction Kinetics and Separation Processes
Kim, S.
Ph.D. dissertation
A large part of this dissertation is described in papers J-85-2, J-85-7, J-85-10, and J-86-3.

Separation of Isomers Using Retrograde Crystallization from Supercritical Fluids
Johnston, K.P.; S.E. Barry; N.K. Read; T.R. Holcomb
Solubilities have been measured for a mixture of 2,3- and 2,6-dimethylnaphthalene in supercritical fluid CO2 to identify retrograde regions that have an inverse solubility versus temperature relationship. A retrograde crystallization process has been designed and tested for the separation of the two isomers at supercritical conditions. A thermodynamic framework has been developed which may be used to locate retrograde regions in order to evaluate the feasibility of retrograde crystallization processes.

Review of Supercritical Fluid Technology at The University of Texas at Austin
Handouts for the Separations Research Program Error! Bookmark not defined. Spring Conference, April 1987
Includes copies of transparencies used by Johnston, Lemert, and Flarsheim for the Supercritical Extraction Technology Study Group Meeting.

Adjustment of the Selectivity of a Diels-Alder Reaction Network Using Supercritical Fluids
Kim, S. and K.P. Johnston
Chemical Engineering Communications 63:49 (1988)
The thermodynamic pressure effect on rate constants is reported in supercritical fluid CO2 for a homogeneous reaction network over a wide density range. The selectivity, or ratio of rate constants, has been controlled over a continuum for the parallel Diels-Alder additions of methyl acrylate and cyclopentadiene by adjusting the pressure. The selectivity for the more polar product, the endo-adduct, increases as the pressure or density increases, which indicates that it has a more negative partial molar volume in the transition state. The data may be correlated quantitatively with solvatochromic transition energies for phenol blue in CO2.

Clustering in Supercritical Fluid Mixtures
Kim, S. and K.P. Johnston
The local compositions of supercritical fluid CO2 and a cosolvent about a solute at infinite dilution have been estimated for the first time using spectroscopic measurements. The solute was phenol blue, the bulk concentrations of the cosolvents n-octane, acetone, ethanol, and methanol ranged from 0 mol% to 100 mol%, and the pressure ranged from 80 bar to 300 bar. In each case, the clusters of solvents about the solute are enriched in cosolvent. Solubility data have been measured for phenol blue in CO2, with and without the cosolvent acetone, and regressed using an augmented van der Waals-density dependent local composition model to determine the relevant binary interaction energies. The local compositions, which were calculated from the model, agree with those which were estimated spectroscopically. The model was used to predict solubilities of solids in supercritical fluid CO2 with various cosolvents.
**J-87-6 PUBLISHED**

Molecular Interactions in Dilute Supercritical Fluid Solutions
Kim, S. and K.P. Johnston
An indicator dye, phenol blue, has been used to probe dispersion, induction, and dipole-dipole (orientation) and acid-base interactions in supercritical fluid ethylene, chlorotrifluoromethane, and fluoroform. Spectral shifts are compared for the dye in these supercritical fluid solvents vs. in conventional liquid solvents. The data are used to predict the thermodynamic solvent effect on reaction rate constants and also to determine the local solvent density around the dye, which is described theoretically.

**J-87-7 PUBLISHED**

High-Pressure Electrochemical Oxidation of Benzene at a Lead Dioxide Electrode in Aqueous Bisulfate Solutions at 25°C to 250°C
Flarsheim II, W.M.; K.P. Johnston; A.J. Bard
The oxidation of benzene at a lead dioxide electrode, which produces predominantly benzoquinone, maleic acid, and CO₂, has been investigated in aqueous NaHSO₄ solutions as a function of temperature up to 250°C. An increase in the benzene concentration does not increase the concentration of benzoquinone formed at high temperature, which is different from the behavior at 25°C. The formation of biphenyl at high temperature was also discovered. A novel type of single-pass flow reactor for studying high-temperature electrochemistry is described.

**J-87-8 PUBLISHED**

Modeling the Solubility of Solids in Supercritical Fluids with Density as the Independent Variable
Kumar, S.K. and K.P. Johnston
Journal of Supercritical Fluids 1:15-22 (1988)
An alternate thermodynamic formalism was developed to correlate the solubility of a nonvolatile solute in a supercritical fluid (SCF) as a function of the density of the fluid phase. It is shown that this solubility varies approximately in a linear fashion with the solvent density when examined in either log-log or log-linear coordinates, depending on the system under consideration. The slope of this plot is related to the solvent isothermal compressibility and the partial molar volume of the solute present at infinite dilution in the SCF phase. From literature solubility data, we obtain estimates for the partial molar volumes for some infinitely dilute mixtures of solutes in SCF which are in agreement with independently measured experimental values.

**J-87-9**

Handout for SRP Extraction Study Group Meeting, October 1987
Review of student research results. Includes copies of handouts by Little, Lemert, Mehta, Shim, and Johnston.

**J-88-1**

Handout for the SRP Supercritical Fluid Technology Study Group Meeting, April 1988
Includes copies of transparencies used by Flarsheim, Lemert, McFann, Shim, and Mehta for the Supercritical Fluid Technology Study Group Meeting.

**J-88-2 PUBLISHED**

Solid-Liquid-Gas Equilibria in Multicomponent Supercritical Fluid Systems
Lemert, R.M. and K.P. Johnston
Pressure versus temperature solid-liquid-gas (S-L-G) lines were determined visually for naphthalene in CO₂, with and without the cosolvent n-pentane, and for 2-naphthol, with and without methanol. In the nonpolar system, the addition of a small amount of cosolvent causes small changes in the melting point depression but large changes in the pressure for the upper critical end point. In the polar system, the increase in the melting point depression is pronounced. An equation of state and Regular Solution Theory are used in a synergistic manner to correlate the
S-L-G behavior over a wide range of pressure and to interpret the results as a function of the calculated compositions in the liquid phase. The implications of this behavior on supercritical fluid separation processes are discussed.

**J-88-3** $10.00
**Electrochemistry in High Temperature and Supercritical Water**
Flarsheim II, W.M.

Ph.D. dissertation
The density, viscosity, and dielectric constant of water decrease greatly at temperatures near the critical point. These changes lead to chemical effects that have been studied electrochemically. A new type of apparatus was constructed for carrying out electrochemistry in near-critical and supercritical aqueous. The high-temperature electrochemistry of the following systems was surveyed: O2/H2O, I2/I-, Br2/Br and benzoquinone/hydroquinone. A large reduction in the potential required for the electrolysis of water was observed. The diffusion coefficient of iodide ions and hydroquinone was also measured. General agreement with the Stokes-Einstein model was observed in the temperature range from 25°C to 375°C. The oxidation of benzene at a lead dioxide electrode, which produces predominantly benzoquinone, maleic acid, and CO2, was investigated in aqueous NaHSO4 solutions as a function of temperature up to 250°C. A theoretical model for the which uses no fitted parameters, was developed and compared to the experimental data.

**J-88-4** PUBLISHED
**Solvent Effect on Chemical Reactions at Supercritical Fluid Conditions**
Johnston, K.P.; W.M. Flarsheim II; B.J. Hrnjez; A.J. Mehta; M.A. Fox; A.J. Bard

In their regions of high compressibility, supercritical fluids are powerful tools for probing solvent effects in a wide variety of chemical systems. To understand the behavior of supercritical fluids on a molecular level, and the fundamental nature of solvent effects in general, we examined the photochemical behavior of cyclic enone, isophorone 1. This photochemical study complements our recent investigations of a thermal unimolecular reaction, parallel Diels-Alder reactions, an electrochemical reversible redox reaction, and a reversible tautomeric reaction, each at supercritical conditions. In most cases, extreme pressure effects were discovered corresponding to activation volumes or volume changes on reaction with a magnitude of a thousand to thousands of cm3/mol. A major goal is to identify new possibilities for the manipulation and control of selectivities in reacting systems. It should become possible to integrate a variety of reaction processes with supercritical fluid separation processes for additional benefit, as has been done for other reactions.

**J-88-5** PUBLISHED
**Pronounced Pressure Effects on Reversible Electrode Reactions in Supercritical Water**
Flarsheim II, W.M.; A.J. Bard; K.P. Johnston

An alumina electrochemical cell containing an ultra-microelectrode was used to make precise voltametric measurements in supercritical water. The effect of pressure on the redox potential of the I2/I- couple was measured from 230 and 300 bar at 385°C. The partial molar volume change for the reduction of I2 to I-, _o(v,-)rxn, is pronounced, mostly because of the interplay between strong electrostatic forces and the large isothermal compressibility of the fluid. A modified Born model, together with a perturbed hard sphere equation of state, predict the data accurately above 265 bar with no adjustable parameters. At lower pressures, ion pairing is thought to reduce the magnitude of _o(v,-)rxn. These large pressure effects on solvation free energies may be used to manipulate reaction equilibria and reaction mechanisms in supercritical water.
J-88-6  PUBLISHED
Pressure Tuning of Chemical Reaction Equilibria in Supercritical Fluids
Peck, D.G.; A.J. Mehta; K.P. Johnston
Supercritical fluid solvent effects were studied for the tautomeric equilibria of 2-hydroxypyridine and 2-pyridone at infinite dilution, both experimentally and theoretically. The fluids were propane at 393K and 1,1-difluoroethane at 403K, and pressures ranged from 21 to 206 bar. The equilibrium constant, measured by in-situ UV spectroscopy, increased four fold for a pressure increase 40 bar in 1,1-difluoroethane, with a partial molar volume change on reaction reaching -1400 cm3/mole. A thermodynamic model was developed to increase the range of pressures studied and to explore temperature effects. Not only is the experimental technique convenient, but the data and theory explain the key advantage of supercritical solvents-their flexibility in manipulating chemical potentials.

J-88-7  $10.00
Solvent Effects on Reactions in Supercritical Fluids
Mehta, A.J.
Master's thesis
This paper examines the characteristics of pressure effects on a reversible reaction, both experimentally and theoretically. There are two major ways to use these large pressure effects in supercritical solvents: (1) the equilibrium position in a reversible reaction may be adjusted and controlled over a continuum by varying pressure, without the need for a harsh chemical change, for example in pH; (2) the nature of transition states and reaction mechanisms may be explored in a fundamental manner by perturbing the system using variations in pressure. This presents a unique opportunity to investigate solvent effects in a single phase, without the complications that arise from studying a reaction in a variety of solvents of different chemical structure. Both a polar and a nonpolar supercritical fluid solvent will be investigated to achieve a fundamental understanding of the pronounced pressure effects in terms of the relevant physical and chemical properties. This study complements a recent investigation of the reversible redox reaction of the I2/I- couple in supercritical water. Together these studies explore reactants that are nonpolar, polar, and ionic, and supercritical solvents that are nonpolar (propane) and polar (1,1-difluoroethane and water) in order to obtain a broad understanding of the pressure effects.

J-88-8  PUBLISHED
The Photodimerization of Isophorone in Supercritical Trifluoromethane and Carbon Dioxide
Hrnjez, B.J.; A.J. Mehta; M.A. Fox; K.P. Johnston
An examination of the regio- and stereoselectivity for the photodimerization of isophorone in both supercritical CHF3 and CO2 as a function of pressure is presented. This selectivity is discussed in terms of solvent polarity and differential solvent reorganization. The stereoselectivity is influenced mostly by solvent reorganization, and the regioselectivity is influenced by both solvent polarity and solvent reorganization. Differential solvent reorganization is shown to exert the dominant effect on the selectivity, and the viability of a supercritical medium as a mechanistic probe is thereby demonstrated.

J-89-1
Handouts for the Separations Research Program Fall Conference, September 1988
Includes copies of transparencies used by Lemert, McFann, Shim, Peck, Little, Gloyna, and Li for the Supercritical Fluid Technology Study Group Meeting (J-89-1)

J-89-2
Handouts for the Separations Research Program Spring Conference, April 1989
Includes copies of transparencies used by Lemert, McFann, Combes, and Shim for the Supercritical Fluid Technology Study Group Meeting (J-89-2).
J-89-3
Handouts from the Separations Research Program Fall Conference, September 1989
Includes copies of handouts used by McFann, Lemert, Peck, and Shim for the Supercritical Fluid Technology Study Group Meeting (J-89-3).

J-89-4 PUBLISHED
Solubilities and Selectivities in Supercritical Fluid Mixtures Near Critical End Points
Lemert, R.M. and K.P. Johnston
Fluid Phase Equilibria 59:31 (1990)
Solubilities and selectivities were measured for hydrocarbon solids in pure and mixed supercritical fluids (J-89-4) near multicomponent upper critical end points (UCEPs). Densities of both the mixed solvents and saturated solutions were also measured in order to interpret the results. Selectivities do not change significantly with pressure or temperature, even in the vicinity of the UCEP, for the naphthalene-2,6-dimethylnaphthalene-CO2 system. In solid-cosolvent-CO2 systems, solubilities are enhanced and highly adjustable with small changes in pressure near the UCEP. The logarithm of the solubility is fairly linear in density, even in the complex UCEP region, which provides a means for data correlation. The cosolvent offers a potential benefit in that the UCEP pressure is reduced 50%, for example, with the addition of 8 mol% n-pentane to the naphthalene-CO2 system. At moderate pressures, the slopes of solubility versus pressure isotherms can be increased in some cases with a cosolvent due to this pressure reduction in the UCEP. This increase is explained in terms of the measured values of the apparent solute molar volume. In the quaternary 2-naphthol-phenanthrene-methanol-CO2 system, the selectivity varies by 50% as the pressure changes by 2000 bar, whereas this variation is much smaller for systems that are further away from the UCEP. The operation of a separation process in the UCEP region leads to higher yields at lower pressures, and for particular systems may lead to more selective extraction or product recovery as well. Future work is needed to develop a method to locate multicomponent UCEPs more efficiently.

J-89-5 PUBLISHED
Reverse Micelles in Supercritical Fluids. 2. Fluorescence and Absorption Spectral Probes of Adjustable Aggregation in the Two-Phase Region
Yazdi, P.T.; G.J. McFann; M.A. Fox; K.P. Johnston
The properties of bis-2-ethylhexyl sodium sulfosuccinate (AOT) reverse micelles and microemulsions in supercritical fluid ethane, liquid propane, and other alkanes are reported. The microscopic environment inside the reverse micelles was investigated with the absorption probe pyridine-N-oxide and the fluorescent probe 8-anilino-1-naphthalenesulfonic acid (ANS). The microscopic behavior is related directly to a macroscopic property, the water-to-surfactant ratio Wo. In the one-phase region, a reverse micelle in a supercritical fluid is much like that in a liquid solvent. However, in the two-phase region, both the microscopic and macroscopic properties may be adjusted with pressure in ethane and propane because of changes in the partitioning of the components between the phases. The large effect of pressure on Wo at saturation, Wosat, and likewise on the micelle radius, is explained in terms of the repulsive solvent penetration of the surfactant tails and the attractive tail-solvent interactions.

J-89-6 PUBLISHED
Design and Characterization of the Molecular Environment in Supercritical Fluids
Johnston, K.P.; G.J. McFann; D.G. Peck; R.M. Lemert
Fluid Phase Equilibria 52:337 (1989)
Spectroscopic studies can be combined synergistically with phase equilibria data and molecular thermodynamic models to provide a better understanding of supercritical solutions to aid process design. Highly compressible supercritical fluids condense about solutes to form large physical clusters. This clustering phenomenon has been characterized in terms of solubilities, partial molar volumes, solvatochromic shifts in UV-visible and fluorescence spectroscopy, Dvrxn for reversible reactions, Kirkwood-Buff solution theory, and computer simulation. In most cases, the clustering or the effect of clustering scales as the isothermal compressibility. The addition of a cosolvent,
complexing agent, or surfactant to a fluid such as CO2 can have large beneficial effects on solubilities and selectivities. Preferential solvation by cosolvents has been measured spectroscopically to develop and test advanced mixing rules. The complexing agent tributylphosphate increases the solubility of hydroquinone (HQ) by a factor of 300. The anionic surfactant AOT forms aggregates and reverse micelles in supercritical ethane, which can solubilize ionic substances such as tryptophan at levels of 0.4 wt%. Using complexing agents and surfactants can help extend supercritical technology to hydrophilic substances such as biomolecules.

**J-89-7 PUBLISHED**

**Adjustable Solute Distribution Between Polymers and Supercritical Fluids**

Shim, J.J. and K.P. Johnston


The sorption of toluene, dilute in CO2, and likewise the distribution coefficient of toluene between silicone rubber and CO2 have been explored from gaseous to supercritical fluid conditions. Sorption and desorption isotherms were determined by frontal analysis using a new inverse supercritical fluid chromatography (SFC) technique at 35°C and 70°C up to 250 bar. Complementary swelling data are presented for pure CO2 in silicone rubber up to 315 bar. A new result is that the sorption of toluene goes through a maximum and is highly adjustable over a continuum in the highly compressible region of CO2. The behavior is explained physically and predicted quantitatively with the Flory equation and the Peng-Robinson equation of state using only information from binary systems. These results are useful for a wide variety of applications including impregnation of polymers with pharmaceuticals, fragrances and other additives, and polymer purification.

**J-89-8 PUBLISHED**

**Transfer Fluorescence Emission Dependence on Excitation Wavelength for Ethyl p(Dimethylamino)benzoate in Supercritical Trifluoromethane**

Hrnjez, B.J.; P.T. Yazdi; M.A. Fox; K.P. Johnston


Supercritical fluids have been recognized only recently for probing solvent effects on photophysical phenomena. The alluring feature of a supercritical fluid is that a minor perturbation, such as a small change in pressure in the vicinity of the critical point, affords a large change in the density-dependent bulk solvent properties such as dielectric constant and viscosity. Uniquely then, solvent effects can be probed without change of solvent. We report here the use of supercritical media to examine the highly polarity-dependent formation of the twisted-intramolecular-charge-transfer (TICT) state of ethyl p-(dimethylamino) benzoate.

**J-89-9 PUBLISHED**

**Modeling Supercritical Mixtures: How Predictive Is It?**

Johnston, K.P.; D.G. Peck; S. Kim


In the last decade, major advances have been made in modeling solubilities and phase behavior in SCF mixtures. It is possible to predict the solubility of a solid in pure and mixed SCFs semi quantitatively with perturbed hard-sphere equations of state, but it is necessary to know the vapor pressure. For liquid-fluid and multiphase systems, cubic equations of state and lattice models have been used to correlate complex phase behavior, but enormous challenges remain to make these models predictive.

**J-89-10 PUBLISHED**

**New Directions in Supercritical Fluid Science and Technology**

Johnston, K.P.


An overview of new research directions is presented. The domain of this field has grown significantly with advances in separations, reactions, and materials processing of complex substances such as polymers, surfactants, and biomolecules. The field has encompassed a large
number of areas in engineering and the chemical, physical, and biological sciences, which will be discussed. In the US, new commercial processes include coffee decaffeination, hops extraction, catalyst regeneration, extraction of organic wastes from water, and supercritical fluid chromatography. These applications complement older technologies such as residuum oil supercritical extraction, CO2-enhanced oil recovery, and reaction processes for the production of polyethylene and primary alcohols in supercritical fluid ethylene. The interest in environmental applications is increasing rapidly. Given the experience gained in developing commercial plants in Europe, the US, and now Japan and Korea, it would be expected that the time lag between research and commercialization will diminish.

**J-89-11 PUBLISHED**

Spectroscopic Determination of Solvent Strength and Structure in Supercritical Fluid Mixtures: A Review

Johnston, K.P.; S. Kim; J.R. Combes


Ultraviolet-visible, fluorescence, and infrared spectroscopy have been used to characterize the solvent strength of pure and mixed supercritical fluid solvents and to study solute-solvent interactions. The use of spectroscopic probes for the determination of clustering of pure and binary supercritical fluids about solutes is discussed. Spectroscopic studies of solvent strength and solute-solvent interactions are valuable for the development of molecular thermodynamic theory, engineering models, and for the molecular design of separation and reaction processes.

**J-89-12 PUBLISHED**

Pressure Tuning of Reverse Micelles for Adjustable Solvation of Hydrophiles in Supercritical Fluids

Johnston, K.P.; G.J. McFann; R.M. Lemert


The spectroscopic probe pyridine-N-oxide was used to characterize polar microdomains in reverse micelles in supercritical ethane from 50 to 300 bar. For both anionic and nonionic surfactants, the polarities of these microdomains were adjusted continuously over a wide range using modest pressure changes. The solubilization of water in the micelles increases significantly with the addition of the cosolvent octane or the cosurfactant octanol. Quantitative solubilities are reported for the first time for hydrophiles in reverse micelles in supercritical fluids. The amino acid tryptophan has been solubilized in ethane at the 0.1 wt % level with the use of the anionic surfactant AOT. The existence of polar microdomains in aggregates in supercritical fluids at relatively low pressures, along with the adjustability of these domains with pressure, presents new possibilities for separation and reaction processes involving hydrophilic substances.

**J-90-1 PUBLISHED**

Reverse Micelles in Supercritical Fluids. 3. Amino Acid Solubilization in Ethane and Propane

Lemert, R.M.; R.A. Fuller; K.P. Johnston


The solubilization of the amino acids tryptophan and proline in AOT reverse micelles and microemulsions is described for the solvents supercritical fluid ethane and liquid propane. Two different types of condensed phases, a solid crystalline amino acid phase and an aqueous phase, were investigated at 37°C from 22 to 325 bar. The concentration of surfactant in both the aqueous and dense fluid phases is reported for the first time, giving insight into the natural curvature of the micelles. In regions where pressure has little effect on the water-to-surfactant ratio, Wo, solubilization in the micelles is relatively constant. At lower pressures, there is a pronounced effect of pressure on the partitioning of surfactant and water, and thus on solubilization. The partitioning of an amino acid between the water pool inside the micelles and the micelle interfacial region is described by a surface monolayer model. This partitioning is influenced by pressure in regions where Wo and thus the curvature and rigidity of the interface are variable. The model explains the experimental result that the micelles are highly selective for proline versus tryptophan. Based on the measured concentrations of AOT and tryptophan in both the fluid and
aqueous phases, a process is presented for separating hydrophilic substances from water with supercritical fluid reverse micelle solutions.

**J-90-2  PUBLISHED**

**Phase Equilibria, Partial Molar Enthalpies, and Partial Molar Volumes by Supercritical Fluid Chromatography**

Shim, J.J. and K.P. Johnston


A variety of types of thermodynamic properties has been determined at infinite dilution by SFC. A key challenge is to identify clearly the retention mechanism. An experimental technique is presented for the measurement of retention due to absorption into a bulk C18 liquid (stationary) phase, independently of the adsorption on the support. The important effect of the swelling of the liquid phase by the fluid phase is included. Distribution coefficients are presented for naphthalene and phenanthrene between CO2 and the C18 liquid phase, and used to determine Henry's constants in the liquid phase and solute partial molar volumes and enthalpies in the fluid phase. In the highly compressible region of CO2 at 35°C, solute partial molar enthalpies have been found to reach negative values of hundreds of kJ/mole, indicating strongly exothermic solute-solvent clustering.

**J-90-3**

**Handouts from the Separations Research Program Spring Conference, April 1990**

Includes copies of transparencies used by Johnston, Dixon, Condo, Shim, McFann, Peck, and Combes for the Supercritical Fluid Technology Study Group (J-90-3) Meeting.

**J-90-4  $20.00**

**Solubility Enhancements in Dense Gas Extraction Produced by Critical End Points, Chemical Complexation, and Reverse Micelles**

Lemert, R.M.

Ph.D. dissertation

Liquid cosolvents such as methanol or acetone are often added to nonpolar near-critical and supercritical solvents (J-90-4) to increase the solubilities of polar solutes. These two cosolvents are shown to also influence the behavior of the three-phase solid-liquid-gas equilibrium line. The solute's melting point is depressed from 50°C to over 70°C in these systems, depending on the solute, the cosolvent, and the cosolvent's concentration. A 50% decrease in the pressure of the UCEP, where the liquid and gas phases become identical in the presence of the solid phase, is also noted. Solubilities are large and highly adjustable with pressure near the UCEP, demonstrating that extractions can be carried out at lower pressures than are currently required. The Peng-Robinson equation of state is combined with Regular Solution Theory to explain the melting point depressions, while measured densities of the solvent mixtures and saturated solutions provide insights into the solubilities. The solubilization of hydrophiles in nonpolar near-critical and supercritical solvents (J-90-4) requires new additives to produce greater solubility enhancements than are currently available. Two such additives are identified in this report. The complexation reagent tri-n-butyl phosphate increases the solubility of 1,4-dihydroxybenzene in CO2 by a factor of 250, an order-of-magnitude improvement over the cosolvents described above. Chemical equilibrium is combined with the Peng-Robinson equation to help interpret the results. The surfactant AOT forms water-in-oil reverse micelle microemulsions in supercritical ethane and near-critical propane, which can dissolve amino acids. Both crystalline amino acid and aqueous condensed phases are investigated. Pressure can have either a very small or a very large effect on the solubilization. The partitioning of the amino acid between the micelle interface and the water pool in the micelle is described by a surface monolayer model that also explains the observed selectivity of the micelle solution.
J-90-5  PUBLISHED
Chemical Complexing Agents for Enhanced Solubilities in Supercritical Fluid Carbon Dioxide
Lemert, R.M. and K.P. Johnston

The effect of the strong Lewis base tributyl phosphate (TBP) on the solubility of benzoic acid and
HQ in supercritical fluid CO2 (J-90-5) is reported. Tributyl phosphate is shown to be a much
stronger cosolvent for these solutes than methanol. The principles of chemical reaction equilibria
are combined with the Peng-Robinson equation of state in order to model these results. The
behavior of the HQ-CO2-TBP system is shown to be attributable to the formation of an HQ  TBP2
complex having an enthalpy of formation of -18.9 kcal/gmole. The performance of this chemical
model is compared to that of a recently developed density-dependent local composition model.

J-90-6
Handouts from the Separation Research Program Fall Conference, September 1990
Includes copies of transparencies used by Peck, Combes, Dixon, and Williams for the
Supercritical Fluid Technology Study Group (J-90-6) Meeting.

J-91-1
Handouts for the Separations Research Program Spring Conference, April 1991
Copies of transparencies used by Peck, Combes, Dixon, Condo, and Gupta for the Supercritical
Fluid Technology Study Group Meeting (J-91-1).

J-91-2  PUBLISHED
Polar and Hydrogen-Bonding Interactions in Supercritical Fluids. Effects on the Tautomeric
Equilibrium of 4-(Phenylazo)-1-naphthol
O'Shea, K.E.; K.M. Kirmse; M.A. Fox; K.P. Johnston

The azo-hydrazone tautomeric equilibrium of 4-(phenylazo)-1-naphthol is compared in various
liquid and supercritical fluid solvents (J-91-2). The less polar azo tautomer is dominant in the
dilute gas phase, compressed ethane, and liquid alkanes. In liquid and supercritical CO2, the
equilibrium shifts toward the more polar hydrazone to yield similar amounts of the two tautomers.
This shift is attributed to the Lewis acidity and large quadruple moment of CO2. The dominance
of the hydrazone tautomer in fluoroform (>90%) can be attributed to that solvent's large dipole
moment and ability to act as a strong electron acceptor (H2 bond donor). Since acid-base
interactions are prevalent at the lowest pressure studied (1000 psia), changes in the equilibrium
constant as a function of pressure have been assigned primarily to increases in the nonspecific
polar interactions. The large differences in the polarities, acidities, and basicities of these fluids,
despite their similar polarizabilities per volume, are of interest for manipulating chemical
processes and for practical applications of supercritical fluid science and technology.

J-91-3  PUBLISHED
Theory of the Pressure Effect on the Curvature and Phase Behavior of Di-2-Ethylhexyl Sodium
Sulfosuccinate Water-in-Oil Microemulsions in a Compressible Solvent
Peck, D.G. and K.P. Johnston

Pressure effects (J-91-3) on both the curvature and phase behavior of water-in-oil microemulsions
(swollen reverse micelles) in propane are predicted with a unified classical and molecular
thermodynamic theory. The theory is used to identify quantitatively the roles of the intramicellar
interfacial interactions and micelle-micelle interactions. A supplementary molecular model is used
to calculate the strength of attractive intermicellar interactions over a wide range of conditions,
based on previous small-angle neutron scattering data. An important distinction is made between
systems with only a trace amount of excess water and those where the water-to-oil ratio is much
larger, on the order of unity. In the latter, the micelle radius is controlled primarily by interfacial
interactions, specifically the enthalpic propane-surfactant tail interactions. In the former, the
micelle radius is limited by attractive micelle-micelle interactions that cause surfactant to
precipitate. Here the radius increases with pressure, but eventually reaches a maximum governed
by the interfacial interactions. There is good agreement between the predictions and experiments over a wide range of water-to-oil ratios.

**J-91-4 PUBLISHED**

**Photolysis of Dibenzylketones in Supercritical Ethane and Carbon Dioxide**

O'Shea, K.E.; J.R. Combes; M.A. Fox; K.P. Johnston


The Norrish Type I photofragmentation of two dibenzyl ketenes [1,3-diphenyl-2-propanone and 1-(4-methylphenyl)-3-phenyl-2-propanone] in supercritical ethane and CO2 proceeds without evidence for cage recombination of the photogenerated radical pair. The statistical mixture of the dibenzyls formed by random coupling of benzyl and p-xylyl radicals and the lack of attenuation in the first order rate constant for the depletion of the reactant with pressure indicate that solvent cage effects are not operative in these low viscosity supercritical fluids even in the near-critical region where solute-solvent clustering is presumably maximal.

**J-91-5 S10.00**

**Thermodynamics and Phase Equilibria of Polymer-Solute-Supercritical Fluid Systems by Supercritical Fluid Chromatography**

Shim, J.J.

Ph.D. dissertation

New frontal analysis and elution SFC techniques were developed for fast and accurate measurement of thermodynamic properties and phase equilibria of polymer-solute-supercritical fluid systems. The frontal analysis technique was used to measure sorption of solutes at finite concentrations in polymers, while the elution method was used to determine the capacity factors at infinite dilution. Several experimental advancements were made, including a new "coating-crosslinking" method for coating polymers on silica and a timed-split fluid-injection system for injecting very dilute solutes. Major improvements were made in interpreting the chromatographic data, such as a retention correction for adsorption and a swelling correction for the stationary phase. The distribution coefficient of a solute between a polymer and a supercritical fluid is a key thermodynamic property for describing phase equilibria. It was measured for toluene, naphthalene, and phenanthrene up to 100°C and 260 bar by the above SFC with two stationary phases, polymeric-C18 and silicone rubber. A large pressure effect was observed, as predicted theoretically, on the sorption (and the distribution coefficient) of toluene in silicone rubber, resulting in a maximum near 40 bar. Thermodynamic properties of toluene, naphthalene, and phenanthrene, such as partial molar volumes and partial molar enthalpies at infinite dilution in the fluid phase, and Henry's constants and activity coefficients in the liquid phase, were determined from the distribution coefficient. The partial molar properties exhibited a minimum versus density in the highly compressible region, and were in good agreement with the literature and the Peng-Robinson equation of state. From these properties it was shown that about 100 solvent molecules cluster around each solute molecule in the highly compressible near-critical region. A model based on the Flory equation and the Peng-Robinson equation of state was proposed and successfully predicted the phase behavior of the ternary solute-supercritical fluid-polymer systems using only interaction parameters obtained from binary systems. The solute distribution coefficient at infinite dilution was used to calculate the phase equilibria at finite concentration. This understanding and prediction of the phase behavior provides a useful basis for discovering, developing, and designing applications of supercritical fluid polymer processing.

**J-91-6 PUBLISHED**

**A Unified Classical and Molecular Thermodynamic Theory of Spherical Water-in-Oil Microemulsions**

Peck, D.G.; R.S. Schechter; K.P. Johnston


A unified classical and molecular thermodynamic model was developed to predict the phase behavior and interfacial properties of spherical water-in-oil microemulsions. A modified Flory-Krigbaum theory is used to describe the interactions between the surfactant tails and solvent, while the ionic head group interactions are treated with the Poisson-Boltzman equation. The interfacial
tension and the bending moment of the interface are calculated explicitly. These values are incorporated into a classical thermodynamic framework that is forced to satisfy the Gibbs adsorption equation on the interface, guaranteeing thermodynamic consistency. Given a surfactant molecular architecture, the model predicts the size of microemulsion droplets as a function of the chain length of the alkane solvent. For AOT in the solvents propane through decane, the calculated trends agree with experiment and are explained mechanistically at the molecular level. The microemulsion radius increases for the solvents pentane through propane, an unusual behavior which is explained theoretically.

**J-91-7 PUBLISHED**

Molecular Thermodynamics of Solubilities in Gas Anti-Solvent Crystallization
Dixon, D.J. and K.P. Johnston

An expanded liquid molecular thermodynamic model was developed to predict the solubilities of pure solids in a liquid expanded with a gaseous antisolvent. Experimental data are presented for systems containing naphthalene, phenanthrene, and a mixture of both in toluene expanded with a gas antisolvent, CO2. The pressure range is 1 to 64 bar and the temperature is 25°C. The data are predicted accurately with regular solution theory up to moderate pressures, but not at the higher pressures where the liquid phase is nearly pure CO2. In contrast, the new expanded liquid equation-of-state model describes the wide range of behavior from the nearly ideal liquid solution at ambient pressure to the highly nonideal compressible fluid at higher pressures. As a result, it predicts solubilities accurately over three orders of magnitude by using only binary interaction parameters. The implications of the phase behavior on fractional crystallization with a gas antisolvent are discussed.

**J-91-8 PUBLISHED**

The Influence of Solvent-Solute and Solute-Solute Clustering on Chemical Reactions in Supercritical Fluids
Combes, J.R.; K.P. Johnston; K.E. O'Shea; M.A. Fox
ACS Symposium Series, No. 488 (1992)

The influence of solvent-solute and solute-solute clustering on three photochemical reactions is reported. Modeling studies for the photolysis of iodine suggest that solvent-solute clustering occurs near the critical point in supercritical fluid ethane inhibiting the diffusive separation of iodine radicals. This clustering causes the solvent cage effect to be larger than expected on bulk properties. No cage effects were observed for the diphenylacetone system, which indicates solvent-solute clusters do not present any unusually strong solvent cage effects compared with liquid solvents. The rate of cyclohexenone photodimerization and the regioselectivity to the more polar head-to-head versus the less polar head-to-tail dimer increase sharply as pressure is decreased to the critical point. This unusual result is attributed to solute-solute clustering, which increases the local polarity and the number of encounters between reacting species. Solute-solute clustering is shown to occur in a single-phase region just prior to the onset of nucleation and growth of a condensed phase.

**J-92-1 PUBLISHED**

Theory of Hydrogen Bonding in Supercritical Fluids
Gupta, R.B.; C.G. Panayiotou; I.C. Sanchez; K.P. Johnston

The degree of hydrogen bonding and macroscopic thermodynamic properties for pure and mixed fluids are predicted with the hydrogen bonding lattice fluid (HBLF) equation of state over a wide range in density encompassing the gas, liquid, and supercritical states. The model is successful for molecules forming complex self-associated networks, in this case pure methanol, ethanol, and water, and the mixture 1-hexanol-SF6. In supercritical water, significant hydrogen bonding is still present despite all the thermal energy and is highly pressure and temperature dependent. A fundamental description of pressure and temperature effects on hydrogen bonding is presented for a well-defined case, the formation of a complex between donor and acceptor in an inert solvent, where no self-association is present. The partial molar enthalpy and volume change on
complexation both become pronounced near the critical point, where the density is highly variable with temperature and pressure.

**J-92-2 PUBLISHED**

**Spectroscopic Studies of p-(N,N-Dimethylamino)benzonitrile and Ethyl p-(N,N-Dimethylamino)benzoate in Supercritical Trifluoromethane, Carbon Dioxide, and Ethane**

Sun, Y.P.; M.A. Fox; K.P. Johnston


Absorption and emission spectral maxima, bandwidths, and fractional contribution of twisted intramolecular charge transfer states to the observed emission of p-(N,N-dimethylamino)benzonitrile and ethyl p-(N,N-dimethylamino)benzoate in supercritical CHF3, CO2, and C2H6 are presented. By examining a wide range of reduced densities from 0.05 to 2.2, we have discovered a characteristic density dependence in the spectral shifts in all three fluids. A model for these spectral effects is proposed, differentiating intermolecular interactions in three distinct regions: gas-phase solute-solvent clustering, clustering in the near-critical region, and "liquid-like" solvation. Even below a reduced density of 0.5, clustering of solvent about solute is already prevalent.

**J-92-3 PUBLISHED**

**Phase Behavior of Di-2-Ethylhexyl Sodium Sulfosuccinate Microemulsions in Compressible Liquids**

McFann, G.J. and K.P. Johnston


The phase behavior of AOT-alkane-brine systems is described over a wide range of pressure, temperature, and salinity for alkanes from ethane to dodecane. The partitioning of AOT between the oil, middle, and brine phases is reported for propane in order to determine the natural curvature. This is important for understanding separation processes with water-in-oil microemulsions. For the lighter, more compressible alkanes, the pressure effect on the hydrophilicity of the surfactant is much larger and in the opposite direction as for the heavier, less compressible ones. In propane at constant temperature and salinity, water-in-oil microemulsions have been converted to middle phase microemulsions and then to oil-in-water microemulsions by decreasing the pressure. These phase inversions are described in terms of the immiscibility in the binary systems and the molecular interactions at the surfactant interface. Although temperature and salinity are used commonly to manipulate interactions primarily on the water side of the interface, these results show it is possible to control interactions on the oil side by adjusting the pressure. The well-established trends in the phase behavior and size of microemulsion drops for dodecane through hexane are not observed for the lighter alkanes. For butane through ethane, a new unusual behavior is identified and attributed to a significant decrease in the strength of the attractive interactions between the surfactant tails and the alkane.

**J-92-4 PUBLISHED**

**Molecular Thermodynamics of Solute-Polymer-Supercritical Fluid Systems**

Shim, J.J. and K.P. Johnston


The distribution coefficients of the solutes (toluene, naphthalene, and phenanthrene) are reported at infinite dilution between silicone rubber and supercritical fluid CO2 (J-92-4). A new technique is described in which a thin film of polymer is coated and cross-linked onto silica, and the distribution coefficient is measured rapidly by elution SFC. Because CO2 significantly enhances the solute's volatility and its diffusion coefficient in the polymer, it is possible to study solute-polymer interactions at room temperature for nonvolatile compounds that would be difficult to study by conventional techniques such as gas chromatography. These infinite dilution data are used to determine solute-polymer interaction parameters to calculate phase diagrams over a wide concentration range. The residual, combinatorial, and cross-link contributions to the solute activity coefficient in the polymer are discussed as a function of concentration. In addition, pronounced pressure and temperature effects are described in terms of experimentally measured solute partial molar volumes (to -14 L/mol) and partial molar enthalpies (to -850 kJ/mol) in the fluid phase.
**J-92-5 PUBLISHED**

Predictability and Effect of Phase Behavior of CO2/Propylene Carbonate in Supercritical Fluid Chromatography

Page, S.H.; D.E. Rayne; S.R. Goatees; M. Lee; D.J. Dixon; K.P. Johnston


The phase behavior of propylene carbonate was studied using a variable volume view cell for the regions applicable to SFC and supercritical fluid extraction. Type-5 phase behavior was observed. Phase separation was shown to significantly alter retention and selectivity in the analysis of coal extracts by capillary SFC. Propylene carbonate was found to have limited use as a modifier in capillary SFC. With 5.1 mol% propylene carbonate at 60°C, a single phase is maintained only at pressures above 250 atm. Twenty-two methods used to estimate critical pressure (Pc), twenty-seven methods used to estimate critical temperature (Tc), and thirty methods used to estimate critical volume (Vc) were evaluated for various modifiers employed in SFC. None of the methods could predict Pc, Tc, or Vc to within a 5% relative error for all the modifiers tested. However, several of the methods were successful in predicting Pc, Tc, or Vc to within 5% for select chemical classes of compounds. Four methods used to estimate the vapor-liquid critical loci of binary mixtures not only failed to accurately predict vapor-liquid separation, but failed to predict the type of phase separation occurring. None of the methods could reliably estimate the critical parameters of propylene carbonate or the critical parameters of the mixture.

**J-92-6 PUBLISHED**

Glass Transition Behavior Including Retrograde Vitrification of Polymers with Compressed Fluid Diluents

Condo, P.D.; I.C. Sanchez; C.G. Panayiotou; K.P. Johnston


A model is presented to predict the depression of the glass transition temperature (Tg) of a polymer in the presence of a liquid, gas, or supercritical fluid as a function of pressure. It is developed using lattice fluid theory and the Gibbs-DiMarzio criterion, which states that the entropy is zero at the glass transition. Four fundamental types of Tg versus pressure behavior are identified and interpreted as a function of three factors: the solubility of the compressed fluid in the polymer, the flexibility of the polymer molecule, and the critical temperature of the pure fluid. A new phenomenon is predicted where a liquid-to-glass transition occurs with increasing temperature, which we define as retrograde vitrification. This retrograde behavior is a consequence of the complex effects of temperature and pressure on sorption isopleths. For the limited data that are available for the PS-CO2 and poly(methyl methacrylate) (PMMA)-CO2, the predictions of the model are in good agreement with experiment.

**J-92-7 PUBLISHED**

Polymeric Materials Formed by Precipitation with a Compressed Fluid Antisolvent

Dixon, D.J.; R.A. Bodmeier; K.P. Johnston


Polymer microspheres and fibers are formed with a versatile new process, precipitation with a compressed fluid antisolvent (PCA) (J-92-7). By spraying a 1 wt% PS solution into CO2 through a 100 µm nozzle, microspheres are formed with diameters from 0.1 to 20 µm as the CO2 density decreases from 0.86 to 0.13 g/cc. The uniform sub-micron spheres produced at high CO2 density are due in part to the rapid atomization produced by the large inertial and low interfacial forces. Fibers, with and without microporosity, are obtained at higher polymer concentrations where viscous forces stabilize the jet. The effect of CO2 density and temperature on the size, morphology, and porosity of the resulting polymeric materials is explained in terms of the phase behavior, spray characteristics, and the depression in the Tg.
The influence of solvent-solute clustering on reactions is examined based on the photolysis of 1,3-diphenylacetone and a new interpretation of the photolysis of iodine. These studies indicate that solvent-solute clustering causes the solvent cage effect to be larger than expected on bulk properties, but smaller than in liquid solvents. The quantum yield of photodimerization of 2-cyclohexen-1-one and the regioselectivity of the photodimers were studied in near-critical; and dense supercritical fluid ethane and trifluoromethane. Experimental results indicate that the rate of photodimerization and the regioselectivity toward polar head-to-head dimer increases sharply as pressure is decreased to the mixture's critical point. The influence of the cohesive energy density of an inert solvent on hydrogen bonding of solutes was studied using Fourier Transform-Infrared (FTIR) spectroscopy to quantify the amount of methanol that exists in non-bonded form. For the methanol triethylamine complexation in supercritical SF6, decreasing density was discovered to linearly increase Kc in regions distant from the critical point. Hydrogen bonding complexation equilibria was explored in near-critical regions of supercritical CO2, ethane, and SF6. Dramatic increases in Kc were discovered as the density was lowered to the critical point. These results are indicative of solute-solute clustering, which enhances the hydrogen bonding complexation.

Solute-solvent interactions of N,N-dimethylamino-benzonitrile and ethyl N,N-dimethylaminobenzoate in mixtures of supercritical trifluoromethane and CO2 are studied using fluorescence spectroscopy. The density dependence of solvation in the mixtures is similar to that in the pure supercritical fluids. The polar component fluorofrom in the mixtures clusters preferentially with solute molecules. This clustering is also density dependent. Macroscopic and microscopic solvent effects in the mixtures in different density regions are rationalized based on the Onsager reaction field model and on the concepts of local density and composition.

Glass transition pressures are determined for PMMA equilibrated with a compressed CO2 phase from creep compliance measurements at various temperatures. The results confirm our theoretical prediction of a new phenomenon, retrograde vitrification, whereby a polymer undergoes a liquid-to-glass transition with increasing temperature. The retrograde behavior is manifested by a decrease in the glass transition pressure from 45°C to 5°C. At 45°C, a maximum glass transition pressure is observed, and at higher temperatures conventional glass transition behavior occurs.

A pronounced solvent effect on the hydrogen bonding of methanol and triethylamine is observed throughout the gas, supercritical, and liquid states in the relatively inert solvent sulfur hexafluoride. The free energy of hydrogen bonding is stabilized by a decrease in density; i.e., the donor and acceptor are destabilized more than the complex as the solvation is reduced. Also, the hydrogen bonding energy becomes stronger. A hydrogen bonding lattice fluid model is developed to treat this density dependence, and the calculations are in reasonable agreement with experiment. Near the mixture critical point, the number of hydrogen bonding encounters between
the donor and acceptor is enhanced due to solute-solute clustering as expected based on previous experimental and computer simulation studies.

**J-92-12 $20.00**

**Molecular Thermodynamics of Solvent and Density Effects on Interfaces in Microemulsions and on Colloidal Particles**

Peck, D.G.

PhD dissertation

A unified classical and molecular thermodynamic model was developed to predict the phase behavior and interfacial properties of spherical water-in-oil microemulsions (J-92-12). The interfacial tension and the bending moment of the interface are calculated explicitly. These values are incorporated into a classical thermodynamic framework that is forced to satisfy the Gibbs adsorption equation on the interface, guaranteeing thermodynamic consistency. For AOT in the solvents propane through decane, the calculated trends in droplet size agree with experiment and are explained mechanistically at the molecular level. For AOT in propane, pressure effects on both the curvature and phase behavior of water-in-oil microemulsions (swollen reverse micelles) are also predicted with the unified classical and molecular thermodynamic theory, which is used to identify the roles of the intramicellar interfacial and micelle-micelle interactions. An important distinction is made between systems with a small water-to-oil ratio and those where the water-to-oil ratio is much larger, on the order of unity. There is good agreement between the predictions and experiments over a wide range of water-to-oil ratios. The interfacial model is improved significantly by the combination of self-consistent field and lattice fluid theories to produce a robust model of the structure and interactions of chains anchored to smooth surfaces. The inclusion of holes in the lattice provides a means to investigate the effects of bulk solvent density and temperature on the interactions between the surfaces. This behavior is explained mechanistically. A novel result is that the forces between the surfaces become attractive at a much higher density than required for phase separation in bulk systems. The general lattice fluid self-consistent field theory is applied to microemulsions. New classical thermodynamic expressions are used to calculate the interfacial tension and bending moment of spherical interfaces between oil and water. The predicted composition throughout the interface provides a means to understand the effect of density and radius on the bending moment. The natural curvature and interdroplet interactions are calculated for water-in-propane microemulsions formed with the surfactant AOT and compared with experiment.

**J-93-1 $20.00**

**Formation and Phase Behavior of Reverse Micelles and Microemulsions in Supercritical Fluid, Ethane, Propane, and Carbon Dioxide**

McFann, G.J.

PhD dissertation

The general objective of the research reported in this dissertation was to investigate the behavior of surfactants in supercritical solvents. Solvatochromic probe experiments were used to establish that ionic and nonionic surfactants form reverse micelles in supercritical fluid (J-93-1) ethane and compressed liquid propane. The reverse micelles were found to be essentially similar to those that would be formed in a liquid solvent like hexane. The size and interior polarity of the reverse micelles change very little with pressure in the one-phase region but change significantly in the two-phase region as surfactant and water partition between the two phases. Systems having bulk water and bulk oil phases exhibit large pressure effects. Both AOT/brine/propane systems and nonionic surfactant/brine/propane systems show a Winsor type I-III-II transition when pressure is increased. A complete Kahlweit "fish" plot can be generated for the nonionic surfactant/brine/propane system with pressure alone. These are the first detailed observations of Winsor transitions in systems having a compressible oil phase. The compressible nature of fluids such as ethane and propane makes them continuously adjustable solvents, which allows solvent effects on surfactant phase behavior to be studied directly. A new type of "unusual" phase behavior was found in light alkane solvents, wherein the trends in surfactant phase behavior was found in light alkane solvents, wherein the trends in surfactant phase behavior previously established for liquid solvents reverse themselves. Surfactants were screened for their solubility in supercritical CO2.
was found that most ionic surfactants are insoluble in CO2, and those nonionic surfactants that are soluble are usually dispersed in the CO2 phase as monomer. The best results were obtained with the short-chain nonionic surfactant C8EO5. A combination of phase behavior, dye solubilization, and solvatochromic probe experiments was used to show that this surfactant forms small aggregates in CO2 which are capable of solubilizing water and ionic dyes. In another project supercritical CO2 has been used successfully to extract naphthalene from the interior of ethylene oxide-propylene oxide-ethylene oxide block copolymer micelles in aqueous solution. The extraction is one part of a proposed wastewater treatment process.

**J-93-2 PUBLISHED**

In-Situ Measurement of the Glass Transition Temperature of Polymers with Compressed Fluid Diluents  
Condo, P.D. and K.P. Johnston  

In-situ measurement of the creep compliance of PMMA and poly(ethyl methacrylate) (J-93-3) (PEMA), equilibrated with a pressurized CO2 phase, is used to determine the glass transition temperature. Corrections due to dilation of the polymer by CO2 as well as the buoyancy are assessed. Both polymer systems exhibit a recently discovered phenomenon, retrograde vitrification, in which a liquid polymer becomes a glass with an increase in temperature. The experimental results are predicted semiquantitatively in terms of the temperature and pressure effects on the solubility of the compressed fluid in the polymer.

**J-93-3 PUBLISHED**

Formation of Microporous Polymer Fibers and Oriented Fibrils by Precipitation with a Compressed Fluid Antisolvent  
Dixon, D.J. and K.P. Johnston  

Polymer morphology is controlled over a continuum from microspheres to interconnected bicontinuous networks to fibers with a versatile new process, precipitation with a compressed fluid antisolvent (J-93-3). The results are explained qualitatively as a function of phase behavior, mass-transfer pathways, and the formation rates of skin on the sprayed jet. By spraying dilute polystyrene in toluene solutions into liquid carbon dioxide, extremely small 100 nm microspheres are formed. For concentrations above the critical composition, fibers are produced which are not only microcellular but in some instances even hollow. Mass-transfer pathways that cross the binodal near the critical composition produce interconnected networks, likely due to spinodal decomposition. Highly oriented fibers are produced at high shear rates. Pre-addition of CO2 influences the morphology because of dilution, in a similar manner as a liquid antisolvent, except the viscosity reduction is larger due to added free volume. Because CO2 diffuses through the glassy polystyrene skin faster than the liquid antisolvent methanol, it produces more porous fibers that are also more cylindrical. Replaces J-93-9

**J-93-4 PUBLISHED**

Carbon Dioxide Regeneration of Block Copolymer Micelles Used for Extraction and Concentration of Trace Organics  
McFann, G.J.; K.P. Johnston; P.N. Hurter; T.A. Hatton  

The phase equilibria distribution of naphthalene between CO2, water, and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer micelle phases is examined experimentally and predicted semiquantitatively using a molecular thermodynamic model. The predictions treat the poly(propylene oxide) micelle core as a "pseudophase" resembling an ether. The favorable distribution coefficients at pressures as low as 70 bar suggest that CO2 is appropriate for regenerating block copolymer micelles which have potential use in wastewater treatment.
The ability of a compressed gas to readily dissolve and expand common organic solvents has been studied and applied to systems containing organic crystals and polymers. A versatile new process, precipitation with a compressed fluid antisolvent (J-93-5) (PCA), has been developed and used to form polymer microspheres, fibers and microcellular fibers. In addition, by using the compressed gas as a nonsolvent at its vapor pressure, microcellular microspheres and microballoons have been formed. The influence of pressure has been studied as a means of controlling crystal solubilities and fractional crystallization. An expanded liquid molecular thermodynamic model has been developed to predict the solubilities of these pure solids in a liquid expanded with a gaseous antisolvent. This model accurately predicts solubilities, from the nearly ideal liquid solution at ambient pressure to the highly nonideal compressible fluid at elevated pressures, using only binary interaction parameters. Precipitation with a compressed fluid antisolvent involves spraying a polymer solution through a capillary nozzle into compressed carbon dioxide, the nonsolvent. The effect of carbon dioxide temperature and density on the size, morphology, and porosity of the resulting polymeric materials has been explained in terms of the phase behavior, spray characteristics, and the depression of polystyrene's glass transition temperature. Extremely small (100 nm) nanospheres were formed at ambient temperature and liquid-like carbon dioxide densities. It is proposed that rapid jet breakup through atomization in dense CO2, followed by rapid vitrification of the polymer, preserves these small spheres. The transition from polymer-discrete to polymer-continuous regions has been studied. Interconnected bicontinuous networks likely result through CO2's ability to quench polystyrene rapidly into the spinodal region. Increasing the polymer concentration was found to be important in control of fiber and microsphere porosity and shell thickness. Solution viscosity plays an important role in fiber formation through increased jet stabilization. Carbon dioxide has been shown to cause faster precipitation than methanol, primarily due to its higher diffusion coefficient in amorphous glassy polystyrene. The ability of sorbed CO2 to depress polymer glass transition temperatures and initiate foaming has been demonstrated.

A new version of a lattice fluid hydrogen bonding (LFHB) model is presented to improve the predictions of the thermodynamic properties of associating fluids. The model utilizes the physical contribution to the free energy in the statistical association fluid theory (SAFT). The association term is described by the local density instead of the bulk density, which was used in the original versions of the theory. With these two modifications, predictions are improved significantly for hard sphere molecules with association sites and for real molecules. Results are presented for the densities and vapor pressures of pure water and 1-alkanols, and for the phase equilibria and association of a mixture of benzophenone and water. The predicted degree of hydrogen bonding for pure supercritical water compares quite favorably with molecular dynamics simulation data. The differences in the nature of the association parameters in the new model and in SAFT are discussed.

A molecular thermodynamic model is presented for the prediction of the chemical potential of an ion in supercritical water (J-93-7), and also the standard free energy, internal energy and entropy of hydration. The reference state is ion-water clusters in the gas phase at low pressure, containing integer numbers of water molecules from one to six. We examine changes in the stability of the ion clusters as a function of van der Waals repulsive (excluded volume) and attractive forces,
The hydrogen bonding stabilizes the ion cluster to a much greater extent than it is destabilized by repulsive forces. Consequently, hydrogen bonding increases the mean hydration number and the effective Born radius.

**J-93-8 PUBLISHED**

**UV-Visible Absorbance Spectroscopy of Organic Probes in Supercritical Water**

Bennett, G.E. and K.P. Johnston


UV-visible spectra of organic solutes are reported in supercritical water (SCW) for the first time up to 440°C and 5000 psia. Solvatochromic shifts in the _-_* absorbance band of benzophenone are compared with those for the n-_* band of acetone to characterize the solvent strength of water in terms of the dipolarity and polarizability, as well as the hydrogen bond donor strength. In the near-critical region (0.5< r <1.5), physical and hydrogen bonding interactions cause SCW to cluster about each probe in excess of the bulk density. At 380°C, hydrogen bonding persists down to a density of only 0.1 g/mL, but rapidly disappears at lower densities. These spectroscopic measurements of interactions between SCW and organic solutes at the molecular level provide new insight into solvent effects on chemical reactions in SCW. Replaces J-94-2

**J-93-9 REPLACED BY J-93-3**

**J-93-10 PUBLISHED**

**Microcellular Microspheres and Microballoons by Precipitation with a Vapor-Liquid Compressed Fluid Antisolvent**

Dixon, D.J.; G. Luna-Bárcenas; K.P. Johnston

Polymer 35(18):3998-4005 (1994)

A new type of precipitation with a compressed fluid antisolvent (PCA) is demonstrated for the formation of porous polymeric microspheres and microballoons (J-93-10) (hollow microspheres). The antisolvent is composed of pure saturated vapor over saturated liquid CO2. A polystyrene (PS) in toluene solution is sprayed through a capillary into CO2 vapor to form droplets, which fall into liquid CO2 where they are rapidly dried and vitrified. Both the thickness and porosity of the microcellular shells can be controlled by changing the initial solution composition. The thickness is inversely proportional to the initial PS concentration. As the concentration is increased there is a transition from porous microballoons to porous microspheres. The cell sizes and surface areas of the microspheres are approximately 1-20 µm and 3-40 m2/g, respectively. The mass-transfer pathway may be altered by addition of CO2 to the polymer solution before spraying, resulting in greater and more uniform porosity. Compared with methanol as an antisolvent, CO2 produces more porous and spherical microspheres, with 7-14 times faster precipitation.

**J-94-1**

**Computer Simulation Study of an SN2 Reaction in Supercritical Water**

Balbuena, P.B.; K.P. Johnston; P.J. Rossky

Submitted to The Journal of Physical Chemistry

Molecular dynamics computer simulation is used to examine solvation of species of varying polarity along the reaction coordinate for the SN2 reaction of Cl- and CH3Cl in supercritical water. At reduced densities down to 0.5, the solute-solvent interactions are sufficiently strong to preserve clusters with coordination numbers nearly as high as in ambient water. Hydrogen bonding interactions are converted to less-specific polar interactions. This loss of hydrogen bonds from ambient water to supercritical water decreases as the hydrogen bond strength increases for the series of solutes from the equivalent Cl's in the transition-state complex, to Cl- in the ion-dipole complex, to free Cl- in the reactant state. Two-dimensional cylindrically and one-dimensional spherically averaged distribution functions, along with energy distribution functions, provide a clear explanation of the origins of _A, _E, and T_S along the reaction coordinate.

**J-94-2 REPLACED BY J-93-8**
Glass Transitions of Polymers with Compressed Fluid Diluents: Type II and III Behavior
Condo, P.D.; D.R. Paul; K.P. Johnston
The effect of CO2 solubility on glass transition temperature (Tg) versus CO2 partial pressure is presented for poly(methyl methacrylate) (PMMA), polystyrene (PS), and a random copolymer of the two with 60%-by-weight methyl methacrylate. Two new features of Tg versus pressure behavior have been discovered experimentally, confirming previous theoretical predictions (Condo, et al. 1992 [J-92-6]). The results for the copolymer poly(methyl methacrylate-co-styrene (SMMA60) reveal a novel "z shape" in the Tg behavior as a function of pressure, including a narrow-pressure region in which three glass transitions take place upon changing the temperature isobarically (type III behavior). In contrast, only one Tg for each pressure is present for PS, without an extremum (type II behavior). The results are modeled accurately with lattice-fluid theory and explained in terms of the combined effects of pressure and temperature on the solubility of the diluent in the polymer.

Water in Carbon Dioxide Microemulsions with a Fluorocarbon-Hydrocarbon Hybrid Surfactant
Harrison, K.; J. Goveas; K.P. Johnston; E.A. O'Rear III
A one-phase microemulsion composed of a hybrid fluorocarbon/hydrocarbon surfactant C7F15CH(OSO3-Na+)C7H15, water, and CO2 solubilizes substantial amounts of water. For example, the water-to-surfactant ratio in a single-phase microemulsion is as high as 32 at 25°C and 231 bar, compared with a value near 0 for more than 150 previously studied surfactants for temperatures up to 50°C. Also, with 1.9 up to 2 wt% surfactant, water is soluble; this is ten times the amount soluble in pure CO2. The requirements for the design of surfactants that form microemulsions in CO2 are examined.

Safer Solutions for Chemists
Johnston, K.P.
Heat a compressed gas beyond its critical point, and the gas and liquid phases will become indistinguishable, merging into one supercritical fluid (SCF) phase. Reactions in supercritical fluids (J-94-5) have been practiced for decades-the polymerization of ethylene, the reaction of ethylene and triethylaluminium to produce olefins, and hydrothermal reactions to form inorganic materials are good examples. But a new generation of reactions in such fluids has been spawned by advances in the fundamental understanding of the nature of SCFs over the past decade. The fluids now coming into their own-carbon dioxide (critical temperature Tc = 31°C) and water (Tc = 374°C)-are much more environmentally friendly than typical organic solvents. An overview is included in this paper.

How is Hydrogen Bonding Influenced by Solvent Density? The Spectroscopic Study and Modeling of the Interaction between a Proton Donor and Acceptor from the Gas Phase to Supercritical Fluid States
Kazarian, S.G.; R.B. Gupta; M.J. Clarke; K.P. Johnston; M. Poliakoff
Fourier transform infrared spectroscopy (FTIR) is used to study the effects of solvent density on the hydrogen-bonding equilibrium between perfluoro-tert-butyl alcohol (PFTB), (CF3)3COH, dimethyl ether (DME), and (CH3)2O in solution in SF6 (Tc, 45.5°C, Pc, 540 psi, rc 5.03 mol/L). The interaction of PFTB and DME is quite strong, and thus it has been possible to use rather more dilute solutions than in previous studies of hydrogen bonding in supercritical fluids. Both PFTB and DME are highly volatile so the equilibrium could be studied over the full range of densities of SF6 from the pure-gas phase (i.e., in the absence of SF6) through the supercritical region to liquid like densities (ca. 10 mol/L (1.5 gm/L), and over the temperature range 20 to 65°C. Both
qualitative and quantitative measurements have been made at constant temperature, constant pressure, and constant density. The experiments introduce a number of innovative features both in methodology and in data manipulation. The modified lattice-fluid hydrogen-bonding model (MLFHB) has been used to calculate the effects of density on the percent of free (uncomplexed) PFTB in the solution and on the value of the equilibrium constant $K_c$. Qualitative studies show explicitly and without any spectroscopic assumptions that increasing density causes an increase in the concentration of free PFTB and a concomitant decrease in the concentration of the hydrogen-bonded PFTB/DME complex. More detailed measurements have allowed these changes to be quantified and modeled; particularly interesting are (a) the variation of $K_c$ with temperature at constant pressure (4.4 MPa) where the rapid increase in solvent density near the critical temperature cancels almost completely the effects of lowering the temperature, and (b) the isothermal dependence of $K_c$ with density, including the unusual behavior at 50°C in the density range ca. 3 to 6 mol/L of SF6, behavior which is not observed at 60°C. This unusual behavior provides good evidence of enhanced solute-solute interactions toward the solvent critical temperature, as is further demonstrated with a simplified model.

**J-94-7 PUBLISHED**

**Solubilization in Nonionic Reverse Micelles in Carbon Dioxide**  
McFann, G.J.; K.P. Johnston; S.M. Howdle  

Phase-behavior data and FTIR spectra along with solubilities and solvatochromic shifts of ionic indicator dyes are reported for binary, ternary, and quaternary systems composed of pentaethylene glycol n-octyl ether (C8E5), CO2, water, and n-pentanol as a function of temperature, pressure, and composition. With the addition of n-pentanol as a cosurfactant, the water-to-surfactant ratio, $W_o$, reaches values as high as 12. As water is added further, a surfactant-rich phase precipitates due to micelle-micelle interactions. Ionic dyes are soluble at levels of 0.03 mM, far in excess of the negligible solubility in pure CO2.

**J-94-8 PUBLISHED**

**Tri-n-butylphosphate/Carbon Dioxide and Acetone/Carbon Dioxide Phase Behaviors and Utilities in Capillary Supercritical Fluid Chromatography**  
Page, S.H.; S.R. Sumpter; S.R. Goates; M.L. Lee; D.J. Dixon; K.P. Johnston  

Because the phase behavior of the mobile phase must be known before conclusions from supercritical-fluid chromatography (SFC) can be considered reliable, the phase behaviors of tri-n-butylphosphate/CO2 and acetone/CO2 were thoroughly determined in a variable-volume view cell at conditions applicable to SFC (0 to 20 mol % modifier, 25 to 140°C, and 80 to 415 atm). The chromatographic utilities of the binary fluids were determined with test compounds (condensed tannins and steroids). Although the UV-absorbance detector base-line rise was severe with acetone/CO2, chromatographic performance was not compromised. Standard base-line correction methods were used to produce conventional-looking chromatograms. The chromatographic performance with tri-n-butylphosphate/CO2 was unsatisfactory (erratic retention). Static restrictors (integral, frit, crimped Pt/Ir, linear, ant valves) produced erratic flow. Heating the restrictors to 250 to 400°C did not improve performance. Reasons for the compromise in chromatographic performance are proposed.

**J-94-9 PUBLISHED**

**Lattice-Fluid Self-Consistent Field Theory of Surfaces with Anchored Chains**  
Peck, D.G. and K.P. Johnston  

Self-consistent field theory is combined with lattice-fluid theory to produce a robust model of the structure and interactions of chains anchored to smooth surfaces. The inclusion of holes in the lattice provides a means to investigate the effects of bulk solvent density and temperature on the interfacial properties. In a good solvent at the incompressible limit, the interactions between the surfaces are repulsive but become attractive with the addition of free volume and compressibility, e.g., in alkane liquids. As density decreases, solvent is expelled from the higher-density interfacial
region to the lower-density bulk phase. The solvent expulsion raises the entropy and increases the strength of the attractive interactions between the surfaces. This behavior is analogous to phase separation of bulk mixtures at the lower critical solution temperature. A novel result is that the forces between the surfaces become attractive at a much higher density than required for phase separation in bulk systems.

**J-94-10 PUBLISHED**

**Molecular Simulation of a Chemical Reaction in Supercritical Water**
Balbuena, P.B.; K.P. Johnston; P.J. Rossky

Supercritical water (SCW) (J-94-10) is receiving a great deal of attention as a solvent in a variety of SCW technology processes, especially for the oxidation of organic wastes. However, development has been hindered by a lack of knowledge about this unusual aqueous environment at the molecular level. A key issue is whether this environment is more like ambient water, a polar organic solvent, or a gas phase, for a given value of the density and temperature. While simulations of solvation in SCW have appeared recently, here we present the first molecular simulation study of the rate of a chemical reaction in a supercritical fluid, in particular SCW. We have chosen to simulate the SN2 substitution reaction, Cl- + CH3Cl → ClCH3 + Cl-, since the solvent effect is large, i.e., the rate constant decreases 20 orders of magnitude from the gas phase to ambient water. It will be shown that the free energy barrier in SCW is more like the barrier in ambient water than that in a polar organic solvent, namely, dimethylformamide.

**J-94-11 PUBLISHED**

**Spectroscopic Probes for Hydrogen Bonding, Extraction Impregnation and Reaction in Supercritical Fluids**
Cooper, A.I.; S.M. Howdle; C. Hughes; M. Jobling; S.G. Kazarian; M. Poliakoff; K.A. Shepherd; K.P. Johnston
Analyst 18:1111-16 (1993)

Spectroscopy is used for monitoring a number of processes relevant to solution, extraction, and impregnation in supercritical CO2 (scCO2). Examples include: a combined infrared (IR) and ultraviolet study of the interaction between para-hydroquinone and tributyl phosphate in scCO2, which reveals hydrogen bonding, detected by the characteristic v(O-H) IR bands; IR measurement of the solubility of CpMn(CO)3 (Cp = η5-C5H5) in scCO2 as a function of temperature and pressure; an investigation of the uniformity of supercritical impregnation (J-94-11); of CpMn(CO)3 into 4-mm diameter pellets of polyethylene (PE) using Fourier-transform infrared (FTIR) microscopy and FTIR depth profiling by photoacoustic detection; and an IR study of the photochemical reaction of CpMn(CO)3 with N2 with PE film.

**J-94-12 PUBLISHED**

**Reverse Miocelles, Recovery of Proteins and Amino Acids from Reverse Micelles by Dehydration with Molecular Sieves**
Gupta, R.B.; C.J. Han; K.P. Johnston
Biotechnology and Bioengineering 44:830-36 (1994)

A new method is presented to precipitate proteins and amino acids from reverse micelles by dehydrating the micelles with molecular sieves. Nearly complete precipitation is demonstrated for α-chymotrypsin, cytochrome-c, and tryptophan from 2-ethylhexyl sodium sulfosuccinate (AOT)/isooctane/water reverse micelle solutions. The products precipitate as a solid powder, which is relatively free of surfactant. The method does not require any manipulation of pH, ionic strength, temperature, pressure, or solvent composition, and is applicable over a broad range of these properties. This general approach is compared with other techniques for the recovery of biomolecules from reverse micelles.
**J-94-13** PUBLISHED

**Phase Behavior (J-94-13) of Nonionic Surfactant/Oil/Water Systems Containing Light Alkanes**
McFann, G.J. and K.P. Johnston

The phase behavior of nonionic ethoxylate surfactant/light alkane/water systems is reported in detail. In compressible liquids such as propane, phase transitions which are normally induced by changing temperature or salinity can also be accomplished with pressure. A complete transition from a lower to middle to upper phase microemulsion with pressure is reported for the first time in propane. Widely accepted trends in surfactant phase behavior as a function of the alkane carbon number (ACN) (J-94-13) of the oil component reverse themselves in the light alkanes butane, propane, and ethane. This pattern occurs in both reverse micelle systems (small water-to-oil ratio) and Winsor microemulsion systems (water-to-oil ratio near unity). The observed pressure and ACN effects can be explained qualitatively in terms of the miscibility gaps of the binary phase diagrams and quantitatively in terms of enthalpic and entropic interactions between the surfactant tails and the compressible solvent.

**J-94-14** PUBLISHED

**Formation of Poly(1,1,2,2-tetrahydroperfluorodecylacrylate) Submicron Fibers and Particles from Supercritical Carbon Dioxide Solutions**
Mawson, S.; K.P. Johnston; J.R. Combes; J.M. DeSimone

Rapid expansion from supercritical solution (RESS) of a crystalline fluoropolymer, poly(1,1,2,2-tetrahydroperfluorodecylacrylate) or poly(TA-N), in carbon dioxide produces submicron to several micron sized particles and fibers. The understanding of the RESS mechanism has been clarified by careful design of experimental variables and procedures. The concentration of the solution was held constant (at 0.5 and 2.0 wt. %), the lower critical solution temperature (LCST) phase behavior was measured, the pre-expansion temperature was varied above and below the LCST, and the length to diameter (L/D) ratio of the nozzle was varied from 8.5 to 508. The morphology is explained in terms of the location of phase separation within the expansion nozzle. The L/D is the most influential variable for achieving a transition from particles to fibers. In most cases, manipulation of the solution concentration and the pre-expansion temperature did not produce this transition, but did have a large effect on the sizes of the particles and fibers. These results are an important step in demonstrating CO2 based spray processes (J-94-14) which do not require any volatile organic solvents.

**J-94-15** PUBLISHED

**Acid-Base Behavior of Organic Compounds in Supercritical Water**
Xiang, T. and K.P. Johnston

The equilibrium constant KBHA for a reaction between an organic acid (b-naphthol) and a base (OH- ion) has been measured for the first time in supercritical water (SCW) up to 400°C and 470 bar, by using UV-vis spectroscopy. Solvatochromic shifts for the b-naphtholate anion are used to determine the extent of hydrogen bonding with water and ion pairing with the series of cations Na+, K+, and Cs+. The ionization constant for b-naphthol, Ka, is determined from KBHA and previous measurements of the ionization constant for pure water, Kw. All of the results are consistent with the Born model. At constant temperature, density effects are much larger for Ka, than KBHA, since the latter reaction is iso-Coulombic. At constant water density, KBHA is exothermic due to the stronger acidity of 2-naphthol versus water, whereas Ka is endothermic due to the energy required for ionization. However, the behavior becomes much more complex at constant pressure, due to large negative values of partial molar enthalpies, entropies, and volumes of ions at high temperatures, which are a result of the large isothermal compressibility and volume expansivity of the solvent.
J-95-1
Continuum Electrostatics Model for an SN2 Reaction in Supercritical Water
Bennett, G.E.; P.J. Rossky; K.P. Johnston
Submitted to The Journal of Physical Chemistry
The electrostatic free energy of solvation $\Delta A$ for the SN2 reaction of the chloride ion with methyl chloride is calculated with a continuum model. The predictive capacity of the continuum electrostatic model is evaluated by comparing the results with simulation. This comparison provides insight into the role of clustering (electrostriction) of solvent about the reacting species. The results for $\Delta A$ are in reasonable agreement with simulation at high and low densities, but the model underpredicts $\Delta A$ significantly in the mid-density region. This behavior is consistent with earlier spectroscopic and simulation studies which demonstrated that clustering (electrostriction) is the most prevalent in the mid-density region.

J-95-2
Distribution Coefficients and Polymer-Solute Interaction Parameters by Inverse Supercritical Fluid Chromatography
Condo, P.D.; S.R. Sumpter; M.L. Lee; K.P. Johnston
Submitted to Industrial & Engineering Chemistry Research
Inverse supercritical fluid chromatography (ISFC) is used to determine polymer-solute interaction parameters between a crosslinked poly(dimethyl siloxane) (PDMS) and five polar and nonpolar nonvolatile organic solids. The thermodynamics of the system is developed using lattice fluid theory including a term to account for the degree of polymer crosslinking. Experimental results indicate that solute adsorption on the support phase, which can be severe in packed columns, is negligible with the use of capillary columns. The correlated polymer-solute interaction parameters for all solutes are consistent with those values found in the literature for PDMS. The experimentally regressed interaction parameters are correlated successfully with the heats of vaporization of the solutes. Thus the ISFC technique may be utilized to provide physically meaningful values of this interaction parameter.

J-95-3
Excited-State Deprotonation of b-Naphthol in Supercritical Water
Green, S.; T. Xiang; K.P. Johnston; M.A. Fox
Submitted to Journal of Physical Chemistry
A kinetic characterization of the excited-state deprotonation of b-naphthol in sub- and supercritical water establishes large deviations from Arrhenius behavior above 110°C. The fluorescence decay rate constant increases much less with temperature than expected and then decreases at temperatures and pressures beyond the supercritical point. The loss of solvation of water above 200°C strongly inhibits its ability to accept a proton and accelerates the reprotonation rate. Under basic conditions, where water clustering and reprotonation are much less important, the observed decay rates deviate much less significantly from the expected Arrhenius behavior. Above the critical point, the relaxation rate constants exhibit strong pressure dependence and are linearly related to the square of the solution density. In contrast with the absence of shifts in the absorption spectrum, pressure-induced shifts in the observed emission maxima near the critical region are assigned to the involvement of contact ion pairs derived from partially deprotonated molecules, and emission from the excited state of the [NapO--K+] ion pair is observed in KOH solution at 200°C.

J-95-4
Supercritical Fluid Separation Processes
Johnston, K.P. and R.M. Lemert
Submitted to Perry's Chemical Engineering Handbook
Fluids above their critical temperature and pressures, called supercritical fluids (SCFs), exhibit properties intermediate between those of gases and liquids. Consequently, each of these two boundary conditions shed insight into the nature of these fluids. Unlike gases, SCFs possess a considerable solvent strength, yet they exhibit considerably better transport properties, e.g. lower viscosities and higher diffusion coefficients than liquid solvents. In regions where a SCF is highly
compressible, its density and hence its solvent strength may be adjusted over a wide range with modest variations in temperature and pressure. This tenability may be used to control phase behavior, separation processes (e.g. SCF extraction), rates and selectivities of chemical reactions, and morphologies in materials processing. A variety of advantages of SCF separation processes are given in Table 1 of this paper; in some cases these compensate for the disadvantage of the need for elevated pressures. Despite the diversity of SCF separation processes (Table 2), an attempt will be made to identify unifying themes. The two fluids most often studied in supercritical fluid technology, carbon dioxide and water, are the two least expensive of all solvents. Carbon dioxide is non-toxic, non-flammable, and has a near-ambient critical temperature of 31.1°C. It is an environmentally friendly substitute for organic solvents including chlorocarbons and chlorofluorocarbons. Supercritical water (Tc =374°C) is of interest as a substitute for organic solvents to minimize waste in extraction and reaction processes. Also it is used for hydrothermal oxidation of hazardous organic wastes (also called supercritical water oxidation).

J-95-5
Molecular Dynamics Simulation of Electrolyte Solutions in Ambient and Supercritical Water: I. Ion Solvation
Balbuena, P.B.; K.P. Johnston; P.J. Rossky
Manuscript on file, Separations Research Program
Free energies of solvation for C1-, OH-, Na+, HCl, and H2O are calculated at ambient conditions and several supercritical water (SCW) states using molecular dynamics-free energy perturbation computer simulation. From ambient to SCW, the magnitude of reductions in the coordination number, number of hydrogen bonds and other specific interactions are in the opposite order of the solute-water interaction energies, which are, from strongest to weakest,: Na+ > OH- > C1- > H2O > HCl. This trend also applies to the magnitude of the solvation free energy, although the changes for Na+ are very small from ambient conditions all the way to 673 K and 0.087 g/cc. Bivalent cations exhibit a well defined second shell that remains at supercritical conditions. Modest discrepancies are observed between simulation and experiment both for the local density of water about Sr+2 and for the free energy of solvation of NaCl illustrating the challenges to both theory and experiment.

J-95-6
Molecular Dynamics Simulation of Electrolyte Solutions in Ambient and Supercritical Water: II. Relative Acidity of HCl
Balbuena, P.B.; K.P. Johnston; P.J. Rossky
Manuscript on file, Separations Research Program
Molecular dynamics-free energy perturbation simulations are used to study the acidity of HCl relative to water at conditions ranging from ambient density and temperature to several supercritical water states. An increase in temperature from 25°C to the critical temperature Tc (374°C) along the coexistence curve reduces the difference between the PKa of HCl and pKw by a factor of 2. However, the corresponding difference in free energies of dissociation remains constant, even in supercritical water, along isochoric and isothermal (between 0.29 and 0.087 g/cm3) paths. This new observation is explained in terms of the effect of temperature on the thermodynamic properties of solvation of the various reacting species and is verified with previous experimental data.

J-95-7
Continuum Electrostatic Model for Ion Solvation and Relative Acidity of HCl in Supercritical Water
Bennett, G.E.; P.B. Balbuena; K.P. Johnston; P.J. Rossky
Manuscript on file, Separations Research Program
The free energy of solvation of Cl-, OH-, HCl, and H2O and the relative acidity of HCl versus H2O are calculated with a continuum electrostatic model and compared with molecular dynamics free energy perturbation (MD-FEP) simulation. The water densities span gas, liquid and supercritical conditions. Compared with the simulation data, the continuum model does not predict ion solvation accurately in supercritical water, as it neglects electrostriction, which is persistent to low densities. However, for the free energy of dissociation of HCl relative to water, the errors are
found to cancel between OH- and C1- such that the continuum model is quite accurate. Because the reaction is isocoulombic and involves species of similar size, the effects of electrostriction are cancelled, corresponding entropic contributions are negligible, and the effect of density on the free energy change is small.

**J-95-8 PUBLISHED**

Polymeric Microspheres Prepared by Spraying into Compressed Carbon Dioxide

Bodmeier, R.; H. Wang; D.J. Dixon; S. Mawson; K.P. Johnston


The objective was to prepare polymeric microparticles by atomizing organic polymer solutions into a spray chamber containing compressed CO2 (PCA-process) and to study the influence of various process parameters on their morphological characteristics. The swelling of various pharmaceutically acceptable polymers [ethyl cellulose, poly(methyl methacrylate), poly(e-caprolactone), poly(dl-lactide), poly(l-lactide) and poly(dl-lactide-glycolide) copolymers] in CO2 was investigated in order to find polymers which did not agglomerate during the spraying process. Poly(l-lactide) (L-PLA) microparticles were prepared by spraying the organic polymer solution into CO2 in a specially designed spraying apparatus. The effect of various processes (pressure and temperature of the CO2 phase, flow rate) and formulation (polymer concentration) variables on the morphology and particle size of L-PLA microparticles was investigated. Polymers with low glass transition temperatures agglomerated even at low temperatures. The formation of microparticles was favored at moderate temperatures, low polymer concentrations, high pressures and high flow rates of CO2. High polymer concentrations and low flow rates resulted in the formation of polymeric fibers. Colloidal L-PLA particles could also be prepared with this technique in a surfactant-free environment. Initial studies on the microencapsulation of drugs resulted in low encapsulation efficiencies. The PCA method is a promising technique for the preparation of drug-containing microparticles. Potential advantages of this method include the flexibility of preparing microparticles of different size and morphology, the elimination of surfactants, the minimization of residual organic solvents, low to moderate processing temperatures and the potential for scale-up.

**J-95-9**

Supercritical Fluids

Dixon, D.J. and K.P. Johnston

Submitted to Kirk and Othmer Encyclopedia

Supercritical fluids (SCFs) have gained considerable attention over the past few decades for a variety of processes and technologies. This article attempts to provide an overview of supercritical fluid technology: from a basic understanding of what constitutes a supercritical fluid, to the motivation and interest in using SCFs, to phase behavior and modeling, and finally to areas of application and current research. The term compressed fluid is more general than supercritical fluid. Thus, a compressed fluid could be a supercritical fluid, a near-critical fluid, an expanded liquid, or a highly compressed gas, depending on its temperature, pressure, and composition. Figure 1 shows schematically the supercritical region of a pure fluid, which may be defined as the area that is above both the critical pressure and critical temperature. An interesting thought experiment that demonstrates a unique feature of supercritical fluids, begins with a subcritical liquid at point A on Figure 1. Depressurizing the liquid isothermally in a view cell to point E, one will observe the presence of a meniscus as the vapor pressure line is crossed. However, for the path A - B - C - D - E, the fluid will pass from a liquid phase to a gas with NO meniscus seen. Looking only inside the view cell one could not tell whether the component was in the gas, liquid, or fluid state. The latter path is actually used in supercritical drying, to avoid collapse of delicate micro-structures by the strong surface tension forces, which arise in small liquid droplets.
**J-95-10 PUBLISHED**

**Temperature and Density Effects on an SN2 Reaction in Supercritical Water**
Flanagin, L.W.; P.B. Balbuena; K.P. Johnston; P.J. Rossky

Molecular dynamics computer simulation is used to relate the thermodynamic properties along the reaction coordinate to microscopic solvation for the SN2 reaction of the chloride ion with methyl chloride as a function of temperature and density. Extreme conditions (e.g., reduced densities of 0.05 and 0.3 for reduced temperatures of 1.0 and 1.3, respectively) are found to be necessary to remove half of the water molecules in the first solvation shell about the chloride ion. As the temperature is increased and density decreased, the number of Cl- -water hydrogen bonds decays faster than the coordination number. By analogy to adsorption phenomena, augmentation in the local solvent density relative to the bulk (clustering) is interpreted in three regions corresponding to gas, near-critical, and liquid-like densities. The lifetime of a water molecule in the first coordination sphere is found to be about 4 times shorter than under ambient conditions; the lifetime of a hydrogen bond between Cl- and water decreases by a comparable factor of about 6. The values of $DA$, $DE$ and $-TDS$ associated with conversion from the reactant state to the transition state are explained in terms of the variations in the average coordination numbers and hydrogen bonding. The combined effects of changes in temperature and solvation lead to an increase in the rate constant by 9-12 orders of magnitude under supercritical conditions compared to ambient conditions.

**J-95-11**

**Supercritical Fluid Technology: Theory and Application**
Johnston, K.P and R.M. Lemert
Submitted to Encyclopedia of Chemical Processing Technology

Supercritical fluids (SCFs) may be considered either compressed gases or expanded liquids, and have properties between those of the gas and liquid states (Paulaitis et al. 1983; Stahl et al. 1988; Johnston and Penninger, 1989; Randolph, 1990; Bruno and Ely, 1991; Kiran and Brennecke, 1993; Kiran and Sengers, 1994; McHugh and Krukonis, 1994). They are most commonly defined as "any fluid at a temperature that is greater than its critical temperature and at a pressure that is greater than its critical pressure." Unlike gases, SCFs possess a considerable solvent strength, yet they exhibit considerably better transport properties, i.e., viscosities and diffusion coefficients, than liquid solvents. Provided one works in a region where the fluid remains highly compressible, the density and hence the solvent strength of a SCF may be adjusted over a wide range simply by varying the temperature and pressure. This tunability may be used to control phase behavior, separation processes such as SCF extraction, rates and selectivities of chemical reactions, and morphology development in materials processing. Supercritical fluid technology is an extremely broad field encompassing the various reaction, separation, and materials formation processes that utilize these fluids. Furthermore, it is practiced in a wide variety of applications involving foods, pharmaceuticals, polymers, petrochemical separations, petroleum refining, environmental cleanup, waste destruction, cleaning of electronic and other materials, drying, formation of advanced materials including particles and fibers, spray coatings, crystallization and others. The main factors driving the interest in this field are the gain in fundamental understanding over the last decade, the movement towards environmentally benign processing and products, the beneficial properties of water and CO2 (including their low cost), the tunability of SCF solvents to improve process or product performance, the need for high temperature and/or pressure to drive certain reactions, and the high transport rates. The two fluids most often studied in supercritical fluid technology are carbon dioxide and water. Carbon dioxide's popularity stems from the fact that it is non-toxic and non-flammable, has a near-ambient critical temperature of 31.1°C, and it is the second least expensive solvent after water. Carbon dioxide's popularity stems from the fact that it is non-toxic and non-flammable, has a near-ambient critical temperature of 31.1°C, and it is the second least expensive solvent after water. This makes it extremely attractive for applications that involve either thermally sensitive materials or materials that are destined for human consumption, and it is therefore the solvent of choice in the food and pharmaceutical industries. Furthermore, it is an environmentally friendly substitute for organic solvents including chlorocarbons and chlorofluorocarbons. Supercritical water ($T_c = 374°C$), on the other hand, is of interest as a substitute for organic solvents in chemical synthesis (for waste minimization), for hydrothermal breeding of crystals and for the thermal oxidation of hazardous organic wastes. These fluids will
appear often in the sections describing the fundamental physical properties, phase behavior and mass transfer characteristics of these fluids, as well as in the sections on their applications.

**J-95-12**  
Published  
Semicrystalline Microfibrils and Hollow Fibres by Precipitation with a Compressed-Fluid Antisolvent  
Luna-Bárcenas, G.; S.K. Kanakia; I.C. Sanchez; K.P. Johnston  
Solutions of polyacrylonitrile (PAN) in dimethylformamide (DMF) sprayed into supercritical fluid carbon dioxide form hollow fibres (J-95-12) and highly oriented microfibrils (< 1 mm diameter). In the dilute region, microfibrils are produced with diameters as low as 100 nm due to the dipole-dipole forces, in contrast with microspheres produced from solutions of polystyrene (PS) in toluene. For PAN microfibrils, orientation increases with shear, then goes through a maximum and eventually decreases at higher flow rates due to an expanding jet. The concentration for the transition from microfibrils to a single hollow fibre is in agreement with the calculated transition concentration from the dilute to semidilute region, C*. In the semidilute region, the morphology changes from hollow fibres to highly oriented fibrils with an increase in flow rate. The increase in turbulence enhances convective mass transport, leading to more uniform nucleation throughout the cross-section of the jet, favoring the highly oriented fibrils. The enhanced transport of CO2 into the jet lowers the solvent quality, raising C*, which further favors fibril formation. For both PAN-DMF and PS-toluene solutions, the transition from highly oriented microfibrils to hollow fibres occurs at about 3C* (in a good solvent), suggesting some similarities in the mass-transfer pathways in each system.

**J-96-1**  
Water-in-Carbon Dioxide Microemulsions: An Environment for Hydrophiles Including Proteins  
Johnston, K.P.; K.L. Harrison; M.J. Clarke; S.M. Howdle; M.P. Heitz; F.V. Bright; C. Carlier; T.W. Randolph  
Carbon dioxide in the liquid and supercritical fluid states is useful as a replacement for toxic organic solvents. However, nonvolatile hydrophilic substances such as proteins, ions, and most catalysts are insoluble. This limitation was overcome by the formation of aqueous microemulsion droplets in a carbon dioxide-continuous phase with a nontoxic ammonium carboxylate perfluoropolyether surfactant. Several spectroscopic techniques consistently indicated that the properties of the droplets approach those of bulk water. The protein bovine serum albumin (BSA) with a molecular weight of 67,000 is soluble in this microemulsion and experiences an environment similar to that of native BSA in buffer.

**J-96-2**  
Supercritical Microemulsions  
McFann, G.J. and K.P. Johnston  
This brief survey begins with studies of the aggregation behavior of the anionic surfactant AOT (sodium bis-2-ethylhexyl sulfosuccinate) and of nonionic poly(ethylene oxide) alkyl ethers in supercritical fluid ethane and copresed liquid propane. One- and two-phase reverse micelle systems are formed in which the volume of the oil component greatly exceeds the volume of water. We continue with investigations into three-component systems of AOT, compressed liquid propane, and water. These microemulsion systems are of the classical Winsor type which contain water and oil in relatively equal amounts. We next examine the effect of the alkane carbon number of the oil on surfactant phase behavior. "Unusual" reversals of phase behavior occur in alkanes lighter than hexane in both reverse micelle and Winsor systems. "Unusual" phase behavior, together with pressure-driven phase transitions, can be explained and modeled by a modest extension of existing theories of surfactant phase behavior. Finally, we describe efforts to create surfactants suitable for use in supercritical CO2, and applications of surfactants in supercritical fluids are covered.
J-96-3
Swelling of Polystyrene Latex Particles in Water by High Pressure Carbon Dioxide
Otake, K.; S.E. Webber; P. Munk; K.P. Johnston
Submitted to Langmuir (1996)
The swelling of a monodisperse polystyrene latex by carbon dioxide was measured by dynamic light scattering at 25°C at pressures up to 35 MPa. At the higher pressures, the PS latex swelled by up to 1.6 times as much as bulk PS. This enhanced swelling is due largely to the adsorption of CO2 into the interfacial region, which lowers the overall interfacial tension between the latex and water phases. The surface excess of CO2 causes the PS chains to swell towards the external water phase.

J-96-4
Coaxial Nozzle for Control of Particle Morphology in Precipitation with a Compressed Fluid Antisolvent
Mawson, S.; S. Kanakia; K.P. Johnston
A coaxial nozzle has been developed to achieve further control over the morphology of microparticles precipitated from solution by carbon dioxide as a compressed fluid antisolvent. The polymer solution was sprayed through the core of the nozzle and CO2 through the annulus. For the coaxial nozzle versus a standard nozzle, polystyrene and poly(L-Lactic acid) particles can be larger by a factor of 3-8 with less flocculation. A reduction in the Weber number reduces atomization and larger droplets are formed in the jet, delaying precipitation. However, because of the much higher Reynolds number for the high velocity CO2, the mass transfer in the suspension outside of the jet is faster leading to less flocculation and agglomeration. For polyacrylonitrile, the delayed precipitation produces a transition from highly oriented microfibrils to microparticles.

J-96-5
Acid-Base Behavior in Supercritical Water: §-Naphthoic Acid-Ammonia Equilibrium
Xiang, T. and K.P. Johnston
Submitted to J. Solution Chem.
Equilibrium constants for the reaction of §-naphthoic acid and ammonia, KBHA, were measured with UV-vis spectroscopy in water from 25°C to 400°C. At high density, KBHA decreases with temperature, the normal behavior for an exothermic reaction of a stronger acid and base to a weaker acid and base. At low density, the reaction becomes endothermic as the solvation of the ionic products becomes weaker. These data were combined with literature results for the dissociation of water and ammonia to determine equilibrium constants for the dissociation of §-naphthoic acid and the reaction of §-naphthoic acid and OH. Whereas the density (and dielectric constant) of water have only a modest effect on the iso-Coulombic reaction of §-naphthoic acid and OH-, they have a large effect on all of the other reactions which are ionogenic.

J-97-1
Neutralization of Acids and Bases in Subcritical and Supercritical Water: Acetic Acid and HCl
Endle, J.P. and K.P. Johnston
Submitted to Journal of Supercritical Fluids (Jan. 1997)
Acid-base titrations were performed for the KOH-acetic acid or NH3-acetic acid and NaCl-Cl- systems in water by measuring pH with the optical indicators 2-naphthoic acid and acridine up to 380 °C and 5000 psia. KOH remains a much stronger base than NH4OH at high temperature. From 298 K to the critical temperature of water, the dissociation constant for HCl decreases by 13 orders of magnitude, and thus, Cl- becomes a stronger base. Consequently, the addition of NaCl to HCl raises the pH. The pH titration curves may be predicted with reasonable accuracy from the relevant equilibrium constants and Pitzer's formulation of the Debye-Huckel equation for the activity coefficients.
J-97-2
Solubility of Block Copolymer Surfactants in Compressed CO2 Using a Lattice Fluid Hydrogen Bonding Model
Takishima, S.; M.L. O'Neill; K.P. Johnston

The solubilities of the homopolymers poly (ethylene glycol) (PEG), poly(ethylene glycol) dimethyl ether (PEGDME), and poly(propylene glycol)(PPG) in CO2 were correlated with a lattice fluid hydrogen bonding (LFHB) model, which was then used to predict solubilities of Pluronic L (PEG-PPG-PEG) and Pluronic R (PPG-PEG-PPG) triblock copolymers. Simple averaging rules were developed to evaluate the physical properties of the copolymers without introducing any adjustable parameters. For a given average molecular weight, the predictions of the model were quite reasonable, and in some cases perhaps more accurate than the data, due to the large polydispersity of the samples. The model predicts the effects of total molecular weight, PEG/PPG ratio, terminal functional groups, temperature, and density on solubility. The much higher solubility of PPG versus PEG is due primarily to steric hindrance from the methyl branch which weakens segment-segment interactions, and to a lesser extent to the stronger hydrogen bond donor strength of a primary (in the case of PEG) versus secondary (in the case of PPG) alcohol terminal group. Consequently the predicted solubilities of Pluronic L surfactants, which have stronger hydrogen bond donors on the terminal groups, are not much smaller than those of Pluronic R surfactants, for given molecular weights of the blocks.

J-97-3
Ion Solvation in Supercritical Water Based on Adsorption Analogy
Fanagin, L.W.; P.B. Balbuena; K.P. Johnston; P.J. Rossky
Manuscript on file, Separations Research Program

The solvation structure and free energy for Li+, Na+, K+, F-, Cl-, Be2+, Mg2+, and Ca2+ in supercritical aqueous solutions are described by a dielectric concentric shell model incorporating solvent adsorption analogous to a Langmuir model. The ratio of solvent bulk density to the local density in the first coordination shell of alkali and halide ions obtained from molecular dynamics simulation is shown to be linear in bulk density at supercritical temperatures, justifying the model. The model utilizes two parameters: a maximum local density, which is found to be insensitive to temperature and correlated with the surface potential, and a desorption constant, which we find may be approximated as zero in the free energy calculations. Free energies of solvation are in good agreement with values from full molecular simulation and with those from a compressible continuum model.

J-97-4
Spectroscopic Measurement of pH in Aqueous Sulfuric Acid and Ammonia from Sub- to Supercritical Conditions
Xiang, T.; K.P. Johnston; W.T. Wofford; E.F. Gloyna

The pH of aqueous sulfuric acid and sulfuric acid-ammonia mixtures was measured using the optical indicator acridine at temperatures from 200 to 400(C and pressures from 3500 (24.1) to 6000 psia (41.3 MPa). Because of large changes in the pKa of protonated acridine in supercritical water (SCW), the measurable pH range shifts from 2-4 at a density of 0.60 g/cm^3 to 4.5-7 at a density of 0.24 g/cm^3. At 3500 psia, the first dissociation constant (Ka1) of H2SO4 decreases sharply with increasing temperature above 350(C, primarily due to a reduction in density and thus the solvation of the bisulfate and hydrogen ions. The acidity of H2SO4 relative to HCl increases with increasing temperature at constant pressure up to the critical point of pure water. Based on titrations of sulfuric acid solutions with ammonia, weak acid-weak base behavior is observed at 380(C and 5000 psia (34.5 MPa). At these conditions the system H2SO4-NH4- HSO4 may be used as a buffer to maintain pH in the range 3.5 +/- 0.25.
**J-97-5**

**Solubility of Homopolymers and Copolymers in Carbon Dioxide**
O’Neill, M.L.; Q. Cao; M. Fang; K.P. Johnston
Submitted to J. Supercritical Fluids (April 1997)

The solubilities of various poly (ether), poly (acrylate), and poly (siloxane) homopolymers, and a variety of commercially available block copolymers were measured in CO2 at temperatures from 25 to 65°C and pressures of ca. 1000 to 6000 psia. Almost without exception, polymer solubility increases with a decrease in the surface tension of the polymer, a pure component property. Consequently, solubility is governed primarily by polymer-polymer interactions, while polymer-CO2 interactions play a much smaller role. New CO2 soluble polymers were discovered including poly (propylene oxide) and poly (phosphazenes). The solubility is strongly dependent upon molecular weight for the less CO2-philic polymers. The solubilities of high molecular weight poly (fluoroalkoxyphosphazenes) in CO2 were comparable to those of poly (1,1-dihyroperfluoroocylacrylate), one of the most CO2-soluble polymers known.

**J-97-6**

**Phase Behavior of Poly(1,1-dihydroperfluoroctylacrylate) in Supercritical Carbon Dioxide**
Luna-Barcenas, G.; S. Mawson; S. Takishima; J.M. Desimone; I.C. Sanchez; K.P. Johnston
Submitted to Fluid Phase Equilibria (May 1997)

Liquid-fluid phase equilibria data are reported for the poly (1,1-dihydroperfluoroctylacrylate) (poly(FOA))-CO2 system at sub- and supercritical fluid conditions and modeled with the statistical associated fluid theory (SAFT). Lower critical solution temperature (LCST) phase behavior is observed with a critical concentration between 1.0 and 2.0 wt % poly(FOA). The high solubility of poly(FOA) is consistent with its low cohesive energy density and the weak van der Waals forces of CO2. To aid this analysis, pressure-volume-temperature (PVT) data are reported for pure poly (FOA) and correlated with lattice-fluid and SAFT theory.

**J-97-7**

**Aqueous Ion Transport Properties and Water Reorientation Dynamics from Ambient to Supercritical Conditions**
Balbuena, P.B.; K.P. Johnston; P.J. Rossky; J. Hyun
Manuscript on file

Ion transport properties including the friction coefficient, Walden product (product of conductivity and viscosity), and the limiting equivalent conductance are predicted in water at elevated temperatures using a semi-continuum model. Molecular dynamics computer simulation is used to determine water rotational reorientation times in the first coordination shell compared to the bulk, and the results are incorporated into a hydrodynamic expression for the ionic friction coefficient. Along the coexistence curve of water, the effective Stokes-Einstein radius implied by the model is relatively constant, but it increases in supercritical water where the motion of the first shell water molecules is coupled more closely to that of the ion. The limiting equivalent conductance is found to increase approximately linearly with decreasing solvent density in the supercritical regime, in qualitative accord with the experimental extrapolations of Quist and Marshall1 and in contrast to the plateau with decreasing density inferred from much more recent experiments by Zimmerman et al.2

**J-97-8**

**UV-Vis Spectroscopic Determination of the Dissociation Constant of Bichromate from 160°C to 400°C**
Chlistunoff, J.B. and K.P. Johnston
Manuscript on File

On the basis of direct measurements by UV-Vis spectroscopy, the dissociation constant of bichromate was found to decrease with temperature from 160 to 400°C. For fixed Cr(VI) and KOH concentrations, the molal concentration of HCrO4- initially increases with temperature but decreases again in the vicinity of water's critical point were the density decreases substantially. The decrease in HCrO4- at high temperature and low density may be attributed to (K+)(CrO42-)
ion pairs, to a high degree of electrostriction about CrO$_4^{2-}$, which facilitates the reaction HCrO$_4^-$ + OH$^-$ = CrO$_4^{2-}$ + H$_2$O, and to ion activity coefficients.

**J-98-1**

Boric Acid Equilibria in Near-Critical and Supercritical Water

Wofford, W.T.; E.F. Gloyna; K.P. Johnston


The pH values of aqueous solutions of boric acid and KOH were measured with the optical indicator 2-naphthol at temperatures from 300 to 380°C. The equilibrium constant $K_b$ for the reaction $\text{B(OH)}_3^+ + \text{OH}^- \rightleftharpoons \text{B(OH)}_4^-$ was determined from the pH measurements and correlated with a modified Born model. The titration curve for the addition of HCl to sodium borate exhibits strong acid-strong base behavior even at 350°C and 24.1 MPa. At these conditions, aqueous solutions of sodium borate buffer the pH at 9.6 (± 0.25).

**J-00-1 PUBLISHED**

Steric Stabilization of Inorganic Suspensions in Carbon Dioxide

Calvo, L.; Holmes, J.D.; Yates, M.Z.; Johnston, K.P.

J. Supercritical Fluids, 200, 16, 247-260.

**J-00-2 PUBLISHED**

Interfacial Thermodynamics of Surfactants at the CO$_2$-Water Interface

Rocha, S.R.P. and Johnston, K.P.

Langmuir, 2000, 16, 3690-3695

**J-00-3 PUBLISHED**

Control of Thickness and Orientation of Solution-Grown Silicon Nanowires

Holmes, J.D.; Johnston, K.P; Doty, R.C.; Korgel, B.A.

Science, 2000, 287, 1471-1473.

**J-00-4 PUBLISHED**

Solution Chemistry in Supercritical Water: Spectroscopy and Simulation

Johnston, K.P. and Rossky, P.J.


**J-00-5 PUBLISHED**

Percolation in Concentrated Water-in-Carbon Dioxide Microemulsions

Lee, C.T.; Bhargava, P.; Johnston, K.P.


**J-00-6**

Formation of Water-in-Carbon Dioxide Microemulsions with a Cationic Surfactant: A Small-Angle Neutron Scattering Study


**J-00-7 PUBLISHED**

In-Situ Investigation on the Mechanism of Dispersion Polymerization in Supercritical Carbon Dioxide

Li, G.; Yates, M.Z.; Johnston, K.P.

J-00-8 PUBLISHED
Trifunctional Ambidextrous Surfactants for Latexes in Supercritical Carbon Dioxide and Water
Li, G.; Yates, M.Z.; Johnston, K.P.; Lim, K.T.

J-00-9 PUBLISHED
Theory and Simulation of Colloid and Interface Science in Supercritical Fluids
Meredith, J.C. and Johnston, K.P.
In Supercritical Fluids Fundamentals and Applications; P.D.E. Kiran, C. Peters, Ed.; Kluwer Acad:
Dordrects, 2000, 211-228

J-00-10 PUBLISHED
Microencapsulation of Proteins by Rapid Expansion of Supercritical Solution with a Nonsolvent
Mishima, K.; Matsuyama, K.; Tanabe, D.; Yamaguchi, S; Young, T.J.; Johnston, K.P.

J-00-11 PUBLISHED
Water-in-Carbon Dioxide Emulsions with PDMS-Based Block Copolymer Ionomers

J-00-12 PUBLISHED
Chemistry in Supercritical Water: Insights from Theory and Simulation
Rossky, P.J. and Johnston, K.P.
In steam, water & Hydrothermal Systems: Physics & Chemistry Meeting the Needs of Industry

J-00-13 PUBLISHED
Steric Stabilization of Nonocrystals in Supercritical Co2 Using Fluorinated Ligands
Shah, P.S.; Holmes, J.D.; Doty, R.C.

J-00-14
Latexes Formed by Rapid Expansion of Polymer/Co2 Suspensions into Water: 1. Hydrophilic
Surfactant in Supercritical Co2
Shim, J.J.; Yates, M.Z.; Johnston, K.P.
Ind. Eng Chem Res. 2000, submitted

J-00-15 PUBLISHED
Spectroscopic Ellisometry Investigation of the Swelling of Poly(dimethylsiloxand) Thin Films with
High Pressure Carbon Dioxide
Sirard, S.M.; Green, P.F.; Johnston, K.P.

J-00-16 PUBLISHED
Steric Stabilization of Colloids by Poly(dimethylsiloxane) in Carbon Dioxide: Effect of Cosolvents
Yates. M.Z.; Shah, P.S; Johnston, K.P.; Lim, K.T.; Webber, S.E.

J-00-17 PUBLISHED
Catalysis in Supercritical Co2 using Palladium Nonparticles Encapsulated in Dendrimer Nanoreactors
Yeun, L.K.; Lee, C.T.; Johnston, K.P.; Crooks. R.M.
J-00-18  PUBLISHED
Rapid Expansion from Supercritical to Aqueous Solution to Produce Submicron Suspensions of Water-Insoluble Drugs
Young, T.J.; Mawson, S.; Johnston, K.P.; Henriksen, I.B.; Pace, G. W.; Mishra, A.K.

J-00-19
Spectroscopic Studies of Chemical Equilibrium in Supercritical Water: Cr(VI) and NOx Chemistry
Ziegler, K.J.; Chlistunoff, J.; Johnston, K.P.
In Steam, Water and Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry

J-01-1  PUBLISHED
Interfacial Phenomena with CO2-Soluble Surfactants
In Green Chemistry Using Liquid and Supercritical Carbon Dioxide, J. Desimone and W. Tumas, Ed.;

J-01-2
Simulation of an SN1 Reaction in Supercritical Water
Westacott, R.E.; Johnston, K.P.; Rossky, P.J.
J. Am. Chem Soc. 2001 submitted

J-01-3
Stability of Ionic and Radical Molecular Dissociation Pathways for Reaction in Supercritical Water
Westacott, R.E.; Johnston, K.P.; Rossky, P.J.

J-01-4  PUBLISHED
Interfacial Studies of the Formation of Microemulsions of Water in Carbon Dioxide with Fluorinated Surfactants
Psathas, P.A.; Sander, E.A.; Ryoo, W.S.; Mitchell, D; Lagow, R.J.; Johnston, K.P.

J-01-5
Formation of Miniemulsions in CO2 Using the Phase Inversion Temperature Method

J-01-6  PUBLISHED
Mapping the Stability and Curvature of Emulsions of Water and Supercritical Carbon Dioxide with Interfacial Tension
Psathas, P.A.; Sander, E.A.; Lim, K.-T.; Johnston, K.P.
J. Dispersion Sci. Tech., 23(1-3), 65-30

J-01-7  PUBLISHED
Droplet Interactions in Water-in-Carbon Dioxide Microemulsions Near the Critical Point: A Small-Angle Neutron Scattering Study

J-01-8  PUBLISHED
Reactions and Synthesis in Microemulsion and Emulsions in Carbon Dioxide
J-01-9
Water-in-Carbon Dioxide Macroemulsions and Miniemulsions with a Hydrocarbon Surfactant
Johnston, K.P.; Cho, D.; Ryoo, W.; Psathas, P.A.; DaRocha, S.R.P.; Webber, S.E.; Eastoe, J.; DuPont, A.; Steytler, D.C.

J-01-10  PUBLISHED
Nanocrystal Arrested Precipitation in Supercritical Carbon Dioxide

J-01-11
Block Copolymers as Stabilizers in Supercritical Fluids
Johnston, K.P.

J-01-12  PUBLISHED
Highly Luminescent Silicon Nanocrystals with Discrete Optical Transitions
Holmes, J.D.; Ziegler, K.J.; Doty, R.C.; Pell, L.E.; Johnston, K.P.; Korgel, B.A.

J-01-13  PUBLISHED
Polymeric Surfactants at Solid-CO2 and Liquid-CO2 Interfaces
Johnston, K.P.

J-01-14  PUBLISHED
Concentrated CO2-in-Water Emulsions with Nonionic Polymeric Surfactants
DaRocha, S.R.P.; Psathas, P.A.; Klein, E.; Johnston, K.P.

J-02-1  PUBLISHED
Preparation of Cyclosporine A Nanoparticles by Evaporation Precipitation into Aqueous Solution
Chen, X.; Young, T.J.; Sarkari, M.; Williams, R.O.; Johnston, K.P.
Int. J. Pharmaceutics, 2002, 242, 3-14

J-02-2  PUBLISHED
Preparation and Characterization of Microparticles Containing Peptide Produced by a Novel Process: Spray Freezing Into Liquid
Yu, Z.; Rogers, T.L.; Hu, J.; Johnston, K.P.; Williams, R.O.
European Journal of Pharmaceutics and Biopharmaceutics, 2002, 54, 221-228

J-02-3
Formation of TiO2 Nanoparticles in Water-in-CO2 Microemulsions
Submitted to Chem. Comm. 2002

J-02-4
Growth of Single Crystal Silicon Nanowires in Supercritical Solution from Tethered Gold Particles on a Silicon Substrate
Submitted to Chem. of Materials, 2002
J-02-5
NMR Studies of Water Transport and Proton Exchange in Water-in-Carbon Dioxide Microemulsions
2002

J-02-6 PUBLISHED
Formation of Carbon Dioxide-in-Water Miniemulsions Using the Phase Inversion Temperature Method
Langmuir, 2002, 18, 3039-3046

J-02-7 PUBLISHED
A Novel Particle Engineering Technology: Spray-Freezing into Liquid
Rogers, T.L.; Hu, J.; Johnston, K.P.; Williams, R.O.

J-02-8
Enhanced Drug Dissolution Using Evaporative Precipitation into Aqueous Solution
Sarkari, M.; Brown, J.; Chen, X.; Swinnea, S.; Williams, R.O.; Johnston, K.P.
Submitted to Int. J. Pharmaceutics, 2002

J-02-9 PUBLISHED
Size-Selective Dispersion of Dodecanethiol Coated Nanocrystals in Liquid and Supercritical Ethane by Density Tuning

J-03-1 PUBLISHED
Carbon Dioxide-in-Water Microemulsions
Lee Jr., C.T.; W. Ryoo; P. G. Smith Jr.; J. Arellano; D.R. Mitchell; R.J. Lagow; S.E. Webber; K.P.
Johnston
Journal of American Chemical Society 2003, 125, 3181-3189
Liquid and supercritical carbon dioxide swell potassium carboxylate perfluoropolyether (PFPE-K) cylindrical micelles in water to produce novel CO2-in-water (C/W) microemulsions. The swelling elongates the micelles significantly from 20 to 80 nm as the molar ratio of CO2 in the micelles to surfactant (R_{co2}) reaches approximately 8. As the micelles swell to form microemulsions, the solubility of pyrene increases by a factor of ca.10. Fluorescence spectra suggest that pyrene resides primarily in the low-polarity micelle core rather than in the palisade region. The results illustrate the ability of C/W microemulsions to solubilize both lipophilic and fluorophilic substances simultaneously.

J-04-1
Welding Colloidal Crystals with Carbon Dioxide
Abramowitz, H. and Shah, P.S.

J-04-2
Investigation of Processing Parameters of Spray Freezing into Liquid to Prepare Polyethylene Glycol Polymeric Particles for Drug Delivery
Barron, M.K. and Young, T.J.
AAPS Pharm Science Tech. 4: 90-102, 2004
J-04-3
CO2-Enhanced Transport of Small Molecules in Thin Films: A Fluorescence Study
Cao, T.K. and Johnston, K.P.
Macromolecules 37 (5): 1897-1902, 2004

J-04-4
Rapid Dissolution of High Potency Danazol Particles Produced by Evaporative Precipitation into Aqueous Solution
Chen, X. and Williams, R.O.
J. Pharm. Sci. 93 (No. 7): 1867-1878, 2004

J-04-5
Critical Flocculation Density of Dilute Water-in-CO2 Emulsions Stabilized with Block Copolymers
Dickson, J.L. and Ortiz-Estradan, C.

J-04-6
Rapid Dissolving High Potency Danazol Powders Produced by Spray Freezing into Liquid Process
Hu, J. and Johnston, K.P.

J-04-7
Rapid Release Tablet Formulation of Micronized Danazol Powder Produced by Spray Freezing into Liquid (SFL)
Hu, J. and Johnston, K.P.
French UT Journal, 2004

J-04-8
Nanoparticle Engineering Processes for Enhancing the Dissolution Rates of Poorly Water Soluble Drugs
Hu, J. and Johnston, K.P.
Drug Development and Industrial Pharmacy 30 (3): 233-245, 2004

J-04-9
Colloid and Interface Science for CO2-Based Pharmaceutical Processes
Johnston, K.P. and Da Rocha, S.R.P.
Drugs and the Pharmaceutical Sciences 138 (Supercritical Fluid Technology for Drug Product Development): 213-245, 2004

J-04-10
Interfacial Phenomena with CO2-Soluble Surfactants
Johnston, K.P. and Da Rocha, S.R.P.
Green Chemistry Using Liquid and Supercritical Carbon Dioxide

J-04-11
Making Nanoscale Materials with Supercritical Fluids
Johnston, K.P. and Shah, P.S.
Science 303: 482-483, 2004

J-04-12
Uniform Encapsulation of Stable Protein Nanoparticles Produced by Spray Freezing for the Reduction of burst Release
Leach, W.T. and Simpson, D.T.
J. Pharm.Sci., 2004
J-04-13  
Synthesis of T1O2 Nanoparticles Utilizing Hydrated Reverse Micelles in CO2  
Lim, K.T. and Hwang, H.S.  

J-04-14  
Synthesis of Germanium Nanocrystals in High Temperature Supercritical Fluid Solvents  
Lu, X. and Ziegler, K.J.  

J-04-15  
Polystyrene Thin Films in CO2  
Meli, L. and Pham, J.Q.  

J-04-16  
Electrogenerated Chemiluminescence of Ge Nanocrystals  
Myung, N. and Lu, X.  
*Nano Letters* 4: 183-185, 2004

J-04-17  
Retrograde Vitrification in CO2/Polystyrene Thin Films  
Pham, J.Q. and Johnston, K.P.  

J-04-18  
Nanocrystal and Nanowire Synthesis and Dispersibility in Supercritical Fluids  
Shah, P.S. and Hanrath, T.  

J-04-19  
Steric Stabilization of Silica Colloids in Supercritical Carbon Dioxide  
Sirard, S.M. and Castellanos, H.  

J-04-20  
Low Interfacial Free Volume of Stubby Surfactants Stabilizes Water-in-Carbon Dioxide Microemulsions  
Stone, M.T. and Smith, P.G.  

J-04-21  
Spray Freezing into Liquid for Highly Stable Protein Nanostructured Microparticles  
Yu, Z. and Garcia, A.S.  
*Eur. J. Pharm. And Biopharm.*, 2004

J-04-22  
Chemical-Mechanical Photo Resist Drying in Supercritical Carbon Dioxide with Hydrocarbon Surfactants  
Zhang, X. and Pham, J.Q.  
J-05-1
CO2-Enhanced Transport of Small Molecules in Thin PMMA Films
Cao, T., Johnston, K.P. and Webber, S.E.

J-05-2
Interfacial Properties of Fluorocarbon and Hydrocarbon Phosphate Surfactants at the Water-CO2 Interface

J-05-3
Enhanced Infusion of Gold Nanocrystals into Mesoporous Silica with Supercritical Carbon Dioxide

J-05-4
Encapsulation of Protein Nanoparticles into Uniform-Sized Microspheres Formed in a Spinning Oil Film

J-05-5
Synthesis of Germanium Nanocrystals in High Temperature Supercritical CO2
Lu, X., Korgel, B.A. and Johnston, K.P.

J-05-6
High Yield of Germanium Nanocrystals Synthesized from Germanium Diiodide in Solution
Lu, X., Korgel, B.A., and Johnston, K.P.

J-05-7
Electrostatic Stabilization of Colloids in Carbon Dioxide: Electrophoresis and Dielectrophoresis
Ryoo, W., Dickson, J.L., Dhanuka, V.V., Webber, S.E., Bonnecaze, R.T. and Johnston, K.P.

J-05-8
Long-Ranged Electrostatic Repulsion and Crystallization of Emulsion Droplets in an Ultralow Dielectric Medium Supercritical Carbon Dioxide
Ryoo, W., Webber, S.E., Bonnecaze, R.T., and Johnston, K.P.

J-05-9
Electrostatically Stabilized Metal Oxide Particle Dispersions in Carbon Dioxide
Smith, P.G.Jr., Ryoo, W. and Johnston, K.P.

J-05-10
High Internal Phase CO2-in-Water Emulsions Stabilized with a Branched Nonionic Hydrocarbon Surfactant
Dhanuka, V.V., J.L.D., Ryoo, W. and Johnston, K.P.
(2005) submitted
Water/Wastewater Treatment

E-92-5
Advances in Separation Technologies for the Treatment of Oily Wastewaters
Humphrey, J.L. and A.F. Seibert
Presented at the AIChE Summer National Meeting, Pittsburgh, Pennsylvania, August 1991
This paper presents an overview of new and emerging separations technologies that are commercially available for the treatment of oily wastewaters. The latest developments in stripping (E-92-5), extraction (E-92-5), adsorption (E-92-5), membrane (E-92-5), and hybrid processes (E-92-5) are covered.

W-87-1
Supercritical Water Oxidation
Gloyna, E.F.
Manuscript prepared for Continuing Engineering Education Seminar at The University of Texas at Austin
This discussion addresses alternatives for treatment and disposal of wastewaters containing toxic and hazardous materials, as well as sludges containing substantial organic materials. Emphasis is directed toward background information on wet air oxidation systems, supercritical water oxidation (SCWO), subcritical deep-well technology (W-87-1), and supercritical deep-well concepts (W-87-1). Also, the UT bench-scale supercritical systems are described.

W-88-1
Supercritical Water Oxidation
Handout for the Separations Research Program Spring Conference, April 1988
Handout used by Gloyna for the Supercritical Fluid Technology Study Group Meeting.

W-89-1
Supercritical and Subcritical Water Oxidation: Deep Well Technology for Toxic Wastewaters and Sludges
Gloyna, E.F.
Manuscript on file, Separations Research Program
This two-part report describes the application of deep-well technology to the treatment of wastewaters and sludges by supercritical and subcritical water oxidation. A general review of the magnitude and scale of the toxic waste and sludge problems is provided with a short discussion on alternative treatment technologies such as wet air oxidation and incineration. Some of the theoretical background of reaction in supercritical fluid is also covered leading to a discussion of SCWO of aqueous wastes. The production of this report was sponsored by Oxidyne, Inc. and covers the application of their deep-well reactor concept to both subcritical as well as SCWO.

W-89-2
Handouts for the Separations Research Program Spring Conference, April 1989
Includes handouts used by Lee, Shanablah, Tonghamachart, Michna, and Wilmanns for the Environmental/Miscellaneous Study Group (W-89-2) Meeting.

W-89-3
Supercritical Water Oxidation of Volatile Acids
Wilmanns, E.G.; L. Li; E.F. Gloyna
The formation and destruction of volatile acids (C1-C4) are important aspects in the treatment of wastewaters and sludges. Acetic acid is often found in effluents from wet air oxidation, subcritical water oxidation, and anaerobic digestion processes. A small pilot-scale SCWO system utilizing two concentric tubes as the oxidation reactor and H2O2 as the oxidant was used to evaluate SCWO for destruction of these acids. The unit had a capacity of 4 liters/min, a maximum operating temperature of 550°C, and operating pressure of 350 bar. The variables described herein
include process temperature, pressure, acid concentration, H2O2 to acid ratio, and feed flow rate. Gas chromatography and TOC analyses results of the effluents from SCWO of acetic acid by H2O2 demonstrated that, under supercritical water conditions (at 276 bar and 400°C to 510°C), acetic acid destruction efficiency increased from 40% to greater than 90% within a reaction time of four minutes. In general, the destruction efficiencies were enhanced by decreasing the flow rate and increasing the H2O2/acetic acid ratio.

W-89-4
SRP/CES Presentation
Handout from the Separations Research Program Fall Conference, September 1989
Includes copies of transparencies used by Gloyna, L., Wilmanns, Shanableh, Little, and Boadway for the Water and Wastewater Technology Study Group (W-89-4) Meeting.

W-90-1 $10.00
Decision Analysis: Stripping and Adsorption to Treat Organic Hazardous Waste
Boadway, D.A.
Master's thesis
The present project was undertaken to simplify the decisions concerning whether liquid adsorption, air stripping, or a combination should be used to treat a particular polluted stream. The decisions were to be made on a rational basis reflecting technical feasibility and economics. The specific objective of this research was to develop the analysis tools to aid the manager or engineer faced with deciding how to treat an organic waste. To meet this objective, it was necessary to determine the effects of chemical properties of the organic compounds on the efficiency of removal in the adsorption and stripping processes. In order to mimic the wide range of possible contamination scenarios that may be present in the environment, it was also important to look at the decision process for low and high concentrations. To carry out this objective, compounds were selected based on Henry's constant, diffusion coefficients in water and air, solubility, and molecular weight. Various mixtures were selected to study the efficiency of removal in the competitive process of adsorption. A program was written to design air stripping towers based on various design parameters. Gas-phase and liquid adsorption programs were adapted to aid in the design of fixed-bed adsorbers. The design results were then analyzed in order to develop a rational decision-making process.

W-90-2 PUBLISHED
Efficiency of H2O2 and O2 in Supercritical Water Oxidation of 2,4-Dichlorophenol and Acetic Acid
Lee, D.S.; L. Li; E.F. Gloyna
Journal of Supercritical Fluids 3:249-55 (1990)
The efficiencies of H2O2 and O2 as oxidants for the destruction of acetic acid and 2,4-dichlorophenol were compared under supercritical water conditions using a batch reactor system. The effects of supercritical water density and oxidant concentration on the destruction of both compounds were studied. Dilute O2 (21% O2 and 79% N2) and H2O2 (32% aqueous solution) were used as the oxidants. The reaction temperatures were 400°C, 450°C, and 500°C. Water densities were fixed at 0.15 g/mL and 0.35 g/mL. The destruction efficiency of H2O2 was significantly higher than that of O2. For acetic acid, the highest conversion of 97.7% was achieved with H2O2 at 500°C for a reaction time of 10 minutes, while 64.3% conversion was achieved with O2 at the same temperature but for a reaction time of 30 minutes. For 2,4-dichlorophenol, conversions higher than 99.995% were obtained with H2O2 at 450°C for a reaction time of 2 minutes compared to 87.6% conversion with O2 at 500°C for the same reaction time.
Change in supercritical water density from 0.15 g/mL to 0.35 g/mL at 400°C only slightly increased the conversion of both compounds. The conversion of acetic acid was enhanced by 10% at 450°C as the H2O2 supply was increased from 100% to 200% of stoichiometric demand. However, concentration of H2O2 higher than 300% of stoichiometric demand did not yield higher conversions of acetic acid. The effect of excess O2 was not conclusive.
Heat Transfer to Water in Countercurrent Flow within a Vertical, Concentric-Tube Supercritical Water Oxidation Reactor
Michna, R.J.

Master's thesis

Information about heat transfer to supercritical water is crucial for the design of SCWO systems. Conventional correlations do not accurately predict heat transfer to supercritical fluids because of dramatic changes in the physical properties of fluids near their critical points. Experimental studies of heat transfer in SCWO reactors have not been reported in the literature. Heat transfer experiments were conducted for near-critical and supercritical water in a vertical, concentric-tube, countercurrent-flow SCWO reactor. Down flowing feed in the annulus of the 6-meter-long stainless-steel reactor was heated by up flowing effluent in the core. Distilled water was used as feed to the reactor. Temperatures and pressures reached as high as 460°C and 250 bar. Variables included temperature, pressure, and mass velocity, as well as the diameter and wall thickness of the center tube. Individual and overall heat transfer coefficients were determined for near-critical and supercritical water. Correlations developed for heat transfer to supercritical water were compared with experimental results. Coefficients were found to be higher in the near-critical region than predicted by heat transfer correlations. Also, deterioration in heat transfer was significant in the critical region. Neither conventional correlations nor correlations developed for heat transfer to supercritical water adequately predicted heat transfer to water in the SCWO reactor used for this study.
W-90-8
Water Oxidation of Sludges and Toxic Wastes
Hartmann, G.; J.M. Eller; E.F. Gloyna
Presented at the American Society of Civil Engineers Conference, Austin, Texas, July 1989
This paper describes alternative approaches to evaluating new technologies for resolving sludge volume reduction (W-90-8) and toxic waste disposal problems. Specific mention is made of the full-scale subcritical sludge processing facility located in Houston, Texas. Also discussed is the subcritical and supercritical water oxidation research facility at The University of Texas at Austin.

W-90-9 PUBLISHED
Supercritical Water Oxidation-Wastewaters and Sludges
Shanableh, A. and E.F. Gloyna
This paper describes the unique system for control of environmental contaminants, the development of a comprehensive SCWO research laboratory, examples of degradation rates of selected organic compounds, and destruction of excess activated sludge derived from an industrial wastewater treatment plant. Also, acetic acid destruction (W-90-9) is discussed because it serves as an example of a major organic compound transformation product, particularly sludge, as the waste material undergoes degradation.

W-90-10
Destruction of Aqueous Hazardous Wastes in Supercritical Water
Gloyna, E.F.; L. Li; J.L. Bravo
Presented at the Second International Symposium on High-Pressure Chemical Engineering, Erlangen, Germany, September 1990
Experiments have been conducted to evaluate the removal efficiency of organic compounds using O2 and H2O2. Synthetic waste solutions, municipal/industrial treatment plant sludges, and industrial wastewaters have been subjected to a range of subcritical and supercritical temperatures and pressures and oxidant concentrations. A batch reactor system and a continuous-flow reactor were used to provide both exploratory and kinetic data. Two vertical, continuous-flow, concentric tube systems were developed for simulating deep-well wet oxidation reactors. In this paper, the destruction of the target compounds and formation of acetic acid in subcritical and supercritical water conditions are presented. Other issues of technological significance, such as heat transfer and corrosion associated with the SCWO processes (W-90-10), are discussed.

W-90-11 $10.00
Supercritical Water Oxidation of Volatile Acids
Wilmanns, E.G.
Master's thesis
A small continuous-flow, pilot-scale SCWO reactor system was used to evaluate the effectiveness of SCWO in destroying volatile acids (W-90-11) (C2-C4). For this study, H2O2 was used as the oxidant. Samples were analyzed by gas chromatography, ion chromatography, or TOC. These analyses demonstrated that under supercritical water conditions acetic acid destruction efficiency was as great as 99%. The higher weight, C3 and C4, volatile acids were transformed into acetic acid. Since acetic acid was the most difficult to oxidize, a kinetic study of this acid was undertaken. Based on these data, a kinetic model for the oxidation of acetic acid by H2O2 at supercritical conditions was developed. The best model for the prediction of the oxidation of acetic acid under SCWO conditions by H2O2 is presented.

W-90-12
Handouts from the Separation Research Program Fall Conference, September 1990
Includes copies of transparencies used by Dell'Orco, Riojas, Lee, Stanford, Tongdhamachart, and Li for the Water/Wastewater Treatment Study Group (W-90-12) Meeting.
A Reciprocating Pump Check Valve Designed for Supercritical Water Oxidation of Sludges
Li, L. and E.F. Gloyna
This paper describes the design and test of a reciprocating pump check valve (W-91-1) suitable for SCWO of sludges. Various designs of pump check valves exist, but few of them meet the requirement for regulating fluids containing particulates (slurries) at high pressures. Check valve leakage is a major problem in pumping particulate fluids. It is desirable to modify existing pump systems for a number of applications. Such was the case for pumping sludges in a novel bench-scale wastewater treatment process operated above the critical pressure of water (221.2 bar or 3207.4 psia). Design and test of the sludge check valve were performed with an American Lew diaphragm pump which had a capacity of 1.5 g/s (0.2 lb/min) at its maximum working pressure of 600 bar (8700 psig). The tests were performed with sludge solutions containing up to 5.7 wt% total solids and particle sizes up to about 100 mm (150 mesh). About one-third of the total solids consisted of fibrous materials as long as one tenth of an inch, which were not accounted in particle size measurement. The modified check valve has been successfully tested for more than 50 hours at a pressure level of 207-276 bar (3000 to 4000 psig) and flow rates ranging from 45 to 135 g/min (0.1 to 0.3 lb/min).

Subcritical and Supercritical Water Oxidation of Industrial Excess Activated Sludge
Shanableh, A. and E.F. Gloyna
PhD dissertation issued as a technical report for the Separations Research Program (November 1990)
The objective of this study was to develop design criteria representative of the destruction of an industrial, excess activated sludge at subcritical and supercritical water conditions by: a) developing kinetic data using O2 as the oxidant; b) evaluating organic compound destruction and sludge volume reduction at subcritical and supercritical conditions; c) investigating sludge by-products resulting from heat/pressure treatment; and d) establish background data for modeling deep-well subcritical and SCWO systems.

Heat Transfer in a Supercritical Water Oxidation Reactor
Michna, R.J.; L. Li; J.R. Howell; E.F. Gloyna
Reactor design modifications are expected to yield even greater removal efficiencies. Information about heat transfer to supercritical water is crucial for the design of these SCWO systems. Conventional correlations do not accurately predict heat transfer to supercritical fluids because of dramatic changes in the physical properties of fluids near their critical points. Heat transfer experiments were conducted for near-critical and supercritical water in a vertical, concentric-tube, countercurrent flow SCWO reactor. Down flowing distilled water in the annulus of the six-meter-long stainless steel reactor was heated by up flowing effluent in the core. Maximum temperatures and pressures were 460°C and 250 bar. Variables included temperature, pressure, and mass velocity. Individual and overall heat transfer coefficients were determined. For this system, coefficients were found to be higher in the near-pseudo critical region than predicted by correlations developed for heat transfer to supercritical water. Also, heat transfer coefficients were found to be significantly lower in the region above the pseudo critical point.

Supercritical Water Oxidation of Acetamide and Acetic Acid
Lee, D.S. and E.F. Gloyna
PhD dissertation submitted as a technical report to the Separations Research Program (September 1990)
The main objectives of this research were to determine the destruction kinetics and to investigate the destruction paths for acetamide and acetic acid (W-91-4) under SCWO conditions. Hydrogen peroxide was used as the oxidant. Hydrolysis and oxidation were the two important reactions for the destruction of acetamide. The preexponential factors, activation energies, and the reaction orders were determined for the hydrolysis and oxidation of acetamide. The rate of oxidation was
more sensitive to the temperature change than that of the hydrolysis. The kinetics were first-order and close to first order (1.2) with respect to the acetamide concentration for the hydrolysis and oxidation, respectively. The effect of pressure on the destruction of acetamide was negligible in both reactions. Acetic acid and ammonia were the main by-products in the destruction of acetamide in supercritical water. A two-step mechanism was suggested for the hydrolysis of acetamide in supercritical water. Three oxidative destruction paths for acetamide were also postulated. The pre-exponential factor, activation energy, and reaction orders were determined for the oxidation of acetic acid. The change in the activation energy was observed at about 450°C. The kinetics were first order with respect to the acetic acid concentration. The effects of pH and the bicarbonate content on the destruction of acetic acid were investigated. The destruction of acetic acid was enhanced at pH above 10. The decarboxylation via charge transfer process might account for the enhanced destruction. No effect of bicarbonate was observed. An oxidative destruction path for acetic acid was suggested. High destruction efficiencies for six toxic organic compounds were obtained under supercritical water conditions. Supercritical water oxidation was an efficient process for the destruction of acetic acid and toxic organic compounds. Hydrolysis, as well as oxidation, might be an important reaction affecting the destruction rate and path of organic compounds in supercritical water.

Corrosion Behavior of High-Grade Alloys in the Supercritical Water Oxidation of Sludges

The oxidation of sludges in supercritical water can prove to be a beneficial, cost-effective means of volume reduction in a totally enclosed treatment facility. The process converts organic components to CO2 and water, recovers energy by means of high-temperature steam, and separates inorganic compounds. However, this enclosed system creates an intriguing engineering problem concerning the corrosion of the reactor material. The presence of O2, chloride ions, elevated temperature, and acidity are the factors of concern in this unique environment. Twelve candidate alloys considered in this study included the following: stainless steel 316, stainless steel 316L, Inconel 625, Incoloy 825, Hastelloy C-22, Hastelloy C-276, Hastelloy G-3, Hastelloy G-30, 2205, 20Cb3, H, Titanium Grade 9, and Titanium Grade 12. Metal coupons were spaced throughout the annular section of a 20-foot-long, vertically mounted, concentric-tube reactor. Industrial sludges at solid concentrations of 0.5 to 3 wt% were processed in the continuous-flow unit. While the studies were conducted at various temperatures and pressures, the maximum temperature was 425°C, and the maximum pressure corresponded to 250 bars.

Supercritical Water Oxidation of Anaerobically Digested Municipal Sludge

This research examined the effectiveness of subcritical and supercritical water oxidation processes for the destruction of anaerobically digested municipal sludge. Data were derived from controlled laboratory-, batch-, and pilot-scale continuous-flow reactors. The parameters affecting sludge destruction included temperature, residence time, influent chemical oxygen demand (COD), solids, and flow rate. Temperature was the most important parameter because it greatly influenced the reduction of COD and solids volume. An increase in temperature from subcritical to supercritical water conditions increased the overall sludge destruction efficiency. More than 99% of the COD was removed using a temperature and residence time of 450°C and 4 min, respectively. The filtrate of the effluent sample, as compared to the influent, contained increased amounts of ammonia, nitrate, and sulfate. Settling characteristics of effluent solids improved because of an increase in particle density. The volume of the wet ash, as compared to the digested anaerobic sludge, was greatly reduced as the temperature was increased. This reduction was greater than 92%. The concentration of metals in the leachate from the ash was below the regulatory limits set by the US EPA.
W-91-7
Subcritical and Supercritical Water Oxidation of Anaerobically Digested Municipal Sludge
Tongdhamachart, C. and E.F. Gloyna
Manuscript on file, Separations Research Program
Summary of W-91-6.

W-91-8
Handouts for the Separations Research Program Spring Conference, April 1991
Copies of transparencies used by Li, Riojas, Wilmanns, Rollans, Matthews, Kanthasamy, Sheets, and Chen for the Water and Wastewater Treatment Study Group (W-91-8) Meeting.

W-91-9 $5.00
Energy Consumption in the Destruction of Wastewaters and Sludges by Supercritical Water Oxidation Deep-Shaft Reactors
Stanford, C.C. and E.F. Gloyna
Master's thesis issued as a technical report for the Separations Research Program (March 1991)
The purpose of this research was to investigate the economic feasibility of an underground, countercurrent flow SCWO reactor based on energy consumption. A method for qualitatively estimating the energy consumption for the destruction of wastes having specific characteristics by SCWO deep-shaft reactors was developed. The results of various reactor designs were compared. The estimated energy consumption of SCWO, deep-shaft reactors was compared with estimates of the energy consumption for incineration of the same wastes.

W-91-10
Supercritical Water Oxidation of Wastewaters
Gloyna, E.F. and L. Li
Prepared for the Seventeenth Meeting of the Japan Cooperative Program in Natural Resources, Tokyo, Japan, May 1991
General background is given on wastewater treatment disposal options, supercritical fluids, and SCWO. Summarizes SCWO activities at UT-SRP, including experimental setup, results on several toxic organic model compounds and sludges, and heat transfer.

W-91-11 $5.00
Corrosion Behavior of Three High-Grade Alloys in Supercritical Water Oxidation Environments
Matthews, C.F.
Master's thesis
This report addresses corrosion of reactor materials within the bounds of the development of the SCWO process. Three alloys were considered: stainless steel 316, Hastelloy C-276, and Monel 400. Metal coupons were used in conjunction with laboratory-scale, batch-reactor systems. The coupons were exposed to three test solutions which had pH levels of 2.1, 5.8, and 8.6. The chloride concentration of the test solutions was 420 mg/L. Three experimental temperatures were used (300°C, 400°C, and 500°C) along with fluid densities which ranged from 0.09 to 0.3 g/cc. Uniform corrosion rates were determined through weight loss analyses, and the corrosion mechanisms were evaluated using a scanning electron microscope.

W-91-12 $5.00
A Literature Review and Analysis of Supercritical Water Oxidation
Adrian, M.B.
Master's thesis
The objective of this report was to review and evaluate the literature relating to wet air oxidation, subcritical water oxidation, SCWO, and supercritical fluids. Based on this literature assessment, a secondary objective was to identify engineering problems that need to be addressed in order to enhance commercialization of SCWO.
**W-91-13**

**Wet Oxidation Bibliography**

Gloyna, E.F. and L. Li

Manuscript on file, Separations Research Program

Compilation of 500 titles from the open literature in the area of wet oxidation.

---

**W-91-14** $10.00

**The Separation of Particles from Supercritical Water Oxidation Effluents**

Dell'Orco, P.C.

Master's thesis

A 10-mm-diameter hydrocyclone with an underflow receiver was evaluated for its ability to achieve the separation of fine particles from water (W-91-14). The temperature was varied from 20°C to 389°C while pressure was maintained at 3600 psi (24.8 MPa). Mass flow rates varied from 0.015 to 0.049 kg/s. Particle concentrations in feed streams ranged from 400 to 1200 mg/L. Three different particulates, Min-U-Sil 5 (quartz SiO2), zirconium dioxide (ZrO2), and titanium dioxide (TiO2) were studied. These particles ranged in diameter from below one micron to ten microns. Low pressure (0-200 psi), room temperature (20°C) studies were also conducted where flow rate and feed concentration were variables. Solids removal efficiencies were determined for all experiments. Solid removals were as high as 99% at elevated temperatures. Particle size distributions provided information on particle sizes separated. Particles removed with efficiencies of 50%, 90%, and 95% (cut sizes) were determined. Ninety percent cut sizes below one micron were reported for several elevated temperature experiments. Empirical models for use in engineering design were developed for the prediction of solid removal efficiencies and pressure drops.

---

**W-91-15**

**The Separation of Particulates from Supercritical Water Oxidation Processes**

Dell'Orco, P.C.; L. Li; E.F. Gloyna

Presented at the Seventh Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 1991

Small hydrocyclones with batch underflow receivers were assessed for their ability to separate micron-sized particulates from near-critical water solutions. Such particulates are expected from the effluent of a SCW reactor. The separation of micron-sized quartz silica, zirconia, and titania particles was investigated. A model was developed for the prediction of gross removal efficiencies as a function of a Stokes number. Particle size distributions provided grade efficiencies for all experiments, and from these data, cut sizes were determined. Gross efficiencies up to 99% were observed for zirconia; cut sizes (d90 and d95) near one micron were measured.

---

**W-91-16** PUBLISHED

**Oxidation Processes in the Separation of Solids from Supercritical Water**

Dell'Orco, P.C.; E.F. Gloyna; S.J. Buelow


The objective of this work was to examine methods for particulate and salt removal from the effluent of a SCWO reactor (W-91-16). Specifically, salt removal efficiencies were assessed using a laboratory-scale reactor equipped with a salt separator. Additionally, a 10-mm-diameter hydrocyclone in conjunction with an underflow receiver was examined for removal capabilities of particles with known size distributions. A high-temperature salt separator was evaluated for the in situ separation of precipitated salts. The separator consisted of a settling reservoir operating at reactor temperatures. At 500°C and 29.8 MPa, salts were separated near their solubility limit. Salts processed included nitrate, chloride, sulfate, and bicarbonate salts of sodium. At temperatures and pressures near the critical point, removal efficiencies achieved by the hydrocyclone were greater than 99% for zirconia test particles, and as high as 80% for silica test particles. An empirical model was developed for predicting removal efficiencies. Cut sizes were determined from particle size distribution data.
**W-91-17 PUBLISHED**

**Kinetic Model for Wet Oxidation of Organic Compounds in Subcritical and Supercritical Water**

Li, L.; P. Chen; E.F. Gloyna


This paper presents a global kinetic model for wet oxidation (WO) of organic compounds. The model is derived from a simplified reaction scheme considering acetic acid as the rate-limiting intermediate. The selectivity of product vs. intermediate formations is quantified by the ratio of the two reaction rate constants. This point selectivity, a, may be used to characterize the "strength" of the feed stream. The model is validated using WO kinetic data reported for temperatures ranging from 150°C to 550°C and pressures varying from 20 bar to 440 bar. The organic conversions predicted by this model, as compared to other models, more accurately reflect the actual performance of WO processes. The WO kinetic model has practical validity for a variety of organic compounds, wastewaters, and sludges, both in subcritical and supercritical water.

**W-92-1 PUBLISHED**

**Generalized Kinetic Model for Wet Oxidation of Organic Compounds**

Li, L.; P. Chen; E.F. Gloyna


A generalized kinetic model for WO of organic compounds was developed based on a simplified reaction scheme considering acetic acid as the rate-limiting intermediate. The selectivity of product vs. intermediate formations was quantified by the ratio of the two reaction rate constants. This point selectivity a may be used to characterize the "strength" of the feed stream to be treated. This global model was validated using WO kinetic data reported for temperatures ranging from 150°C to 550°C and pressures varying from 20 bar to 440 bar. Organic conversions predicted by this model, as compared to other models, more accurately reflect the actual performance of WO processes. The model has practical validity for a variety of organic compounds, wastewaters, and sludges, in both subcritical and SCWO processes.

**W-92-2**

**Effects of Supercritical Water on the Destruction of Toxic Organic Wastes and Biological Sludges**

Gloyna, E.F.

Presented at the Finnish Chemical Congress, Helsinki, Finland, October 1990

An overview of the early SCWO effort at the SRP.

**W-92-3**

**Oxygen Mixing in Near-Critical Media**

Riojas, A.H. and E.F. Gloyna

Presented at the 1991 AIChE Annual Meeting, Los Angeles, California, November 1991

The focus of this research is to establish the mixing characteristics of oxygen with influent wastewater under near-critical temperature and pressure environments. Since SCWO experiments are relatively expensive in contrast to supercritical carbon dioxide, this paper describes the applicability of dimensional similitude in solving this specific mixing problem. Dimensional analyses for turbulent, isothermal, nonreacting flow yielded correlations between dimensionless groups including Sherwood, Reynolds, Schmidt, and Weber numbers. Oxygen-carbon dioxide experiments are being conducted near the critical point of carbon dioxide to ascertain the values of the correlation constants. The secondary objective is to illustrate a possible design for validating simulation. The plan is to conduct oxygen mixing with supercritical carbon dioxide, and ultimately following this experiment with oxygen mixing with supercritical water. These analyses and experiments are relevant because much of the existing kinetic data appears to contain a high level of variability, and possibly this problem is associated with improper interpretation of the mixing characteristics.
Supercritical Water Oxidation of Hazardous Organic Compounds
Lee, D.S.; A. Kanthasamy and E.F. Gloyna
Presented at the 1991 AIChE Annual Meeting, Los Angeles, California, November 1991
Supercritical water oxidation tests were conducted using selected organic compounds. Acetic acid, pyridine, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2,4-dinitrotoluene, ethylene glycol, and diethylene glycol diethyl ether were studied using a batch reactor process. The reaction temperatures and times ranged from 400°C to 500°C, and from 1 minute to 20 minutes, respectively. Water density was fixed at 0.3 g/ml. High levels of destruction were achieved with SCWO. The highest destruction efficiency, greater than 99.999%, was achieved with 2,4-dichlorophenol. Under similar conditions, efficiencies for other compounds exceeded 99.5%. Some compounds such as pyridine and acetic acid required higher temperatures (500°C) and reaction times (20 minutes) to achieve comparable results. In most cases, reported results were limited by the resolution of the analytical techniques employed. Hydrogen peroxide, as compared to oxygen, was consistently more efficient for the destruction of tested organic compounds.

Supercritical Water Oxidation Applications for Industrial Sludges
Gloyna, E.F.
Presented at the Solid and Hazardous Waste Management Symposium, Texas Water Quality Association, January 1992
The magnitude of the industrial sludge problem, the growing regulatory listings, and the rational for alternative sludge treatment were discussed. A case was developed for SCWO of these sludges.

Hydrolysis and Oxidation of Acetamide in Supercritical Water
Lee, D.S. and E.F. Gloyna
This paper describes the development of acetamide destruction kinetics in supercritical water. The experimental conditions included temperatures between 400°C and 525°C and pressures between 230 and 335 atm. The empirical rate equations for the hydrolysis and the overall reaction (hydrolysis + oxidation by hydrogen peroxide) were determined as follows: (hydrolysis) $r = -(102.2 \pm 101.3) \exp((-51000 \pm 5600)/RT)[acetamide]1$ and (overall reaction) $r = -(103.6 \pm 102.5) \exp((-68000 \pm 3800)/RT)[acetamide]1$, where the activation energies were in joules per mole and [acetamide] was in moles per liter. First-order kinetics with respect to the acetamide concentration properly described both the hydrolysis and overall reaction rates. The hydrolysis reaction proceeded more rapidly than the oxidation. Therefore, the role of supercritical water as an active reactant should be recognized. The residual byproducts formed from the hydrolysis or the overall reaction of acetamide were acetic acid and ammonia. The effects of hydrogen peroxide concentration and the reaction pressure on the reaction rate were negligible. Therefore, the use of an oxidant slightly above the stoichiometric demand may be sufficient in SCWO processes. The negligible pressure effect implies that, to minimize construction costs associated with containing high pressures, the pressure may be kept as low as possible. Also, the negligible pressure influence may add flexibility for controlling the retention time without loss of destruction efficiency.

Oxidation Kinetics of Acetic Acid in Supercritical Water
Lee, D.S. and E.F. Gloyna
Manuscript on file, Separations Research Program
This paper describes the development of the kinetic relationships of acetic acid oxidation by hydrogen peroxide in supercritical water. The oxidation kinetics for acetic acid in supercritical water environments followed first-order kinetics with respect to the acetic acid concentration. The oxidation rate of acetic acid was enhanced at pH levels above 10. However, the oxidation rate of acetic acid was not changed by variations in the concentration of bicarbonate. The observed SCWO kinetics implied that complete destruction of any organic substances that produce acetic acid was achieved with SCWO.
acid cannot be achieved at temperatures below 400°C at short residence times. The negligible hydrogen peroxide effect demonstrated the adequacy of the stoichiometric oxidant amounts. The observed pH effect suggested that pH adjustment may be used to destroy acetic acid more efficiently. However, further detailed investigations are needed to confirm the applicability of the pH effect.

**W-92-8 $5.00**

**Supercritical Water Oxidation of Acetic Acid Catalyzed by CeO2/MnO2**

Frisch, M.A.

Master's thesis

The objective of this investigation was to evaluate the SCWO of acetic acid when catalyzed by CeO2/MnO2. Destruction efficiencies with and without catalyst were determined and fit to kinetic models. Supercritical water oxidation without catalyst, in a batch reactor, achieved greater than 95% destruction of acetic acid for temperatures greater than 440°C and a residence time of 10 minutes. A kinetic model of this reaction suggested a first-order reaction with respect to acetic acid concentration and an activation energy, Ea, of 165 kJ/mol. Supercritical water oxidation of acetic acid catalyzed by MnO2/CeO2 (fixed in an alumina binder) provided rates faster than noncatalyzed rates. Removals of 95% were achieved at temperatures greater than 395°C and residence times of 5 and 10 minutes. These catalyzed data supported a kinetic model that was first order with respect to acetic acid concentration and an activation energy of 42,500 kJ/mol. This reduced activation energy suggested a catalytic reaction pathway. Differences between destruction efficiencies, with and without catalyst, were greater at lower temperatures. This contrast in destruction at low temperatures further supported a catalytic pathway. Supercritical water oxidation environments reduced the MnO2 when initial oxygen concentration was less than 200% of the stoichiometric demand. Thus, excess oxygen concentration was required in order to maintain the chemical reactivity and physical integrity of the catalyst.

**W-92-9 $5.00**

**A Survey: Destruction of Chemical Agent Simulants in Supercritical Water Oxidation**

Blank, M.R.

Master's thesis

The SCWO process exhibits distinct advantages for destruction of toxic wastes. Examples of these wastes are two chemical agent simulants (W-92-9), DMMP, and thiodiglycol. Dimethyl methylphosphonate is similar to the nerve agent GB Sarin in structure, and thiodiglycol is a hydrolysis product of the blister agent HD Sulfur Mustard. Both simulants are miscible in water and relatively non-toxic in comparison to the actual chemical agents. Using a laboratory-scale batch reactor, three temperatures were investigated: 425°C, 450°C, and 500°C, with an initial concentration of 1% by volume, 11,450 mg/L for DMMP, and 12,220 mg/L for thiodiglycol. Residence times investigated were 1, 2, 3, 6, and 8 minutes. Reactor heat-up was determined to be 1 minute. Both pyrolysis and oxidation tests were conducted. Oxygen levels were uniformly set at 200% of stoichiometric requirements for the parent compounds. The pressure was calculated as a function of reactor temperature and density. In these studies, the density was kept constant to provide a larger sample volume while continuing to achieve supercritical conditions. Both the mass and the sample volume remained constant. The performance of the SCWO system was evaluated as follows: measurement of TOC destruction by TOC analyses; determination of effluent sulfate and phosphate concentrations by ion chromatography analysis; and monitoring the pH. Increases in reactor residence time and temperature resulted in greater destruction of TOC for DMMP and thiodiglycol. The rate and degree of thermal destruction (pyrolysis), oxidation, and hydrolysis, as based on TOC and for similar conditions, was greater for thiodiglycol as compared with DMMP. The strength of P-methyl bond in DMMP was suggested as the reason for this greater TOC destruction.
**W-93-1**

**The Solubility of 1:1 Nitrate Electrolytes in Supercritical Water**

Dell'Orco, P.C.; H.K. Eaton; R.T. Reynolds; S.J. Buelow

Manuscript on file, Separations Research Program

A novel method was developed for determining the solubility of nitrate salts in supercritical water solutions (W-93-1) at pressures ranging from 3600 psi to 4400 psi and temperatures from 450°C to 525°C. Sodium nitrate solubilities ranged from 293 mg/kg at 3600 psi and 525°C to 1963 mg/kg at 4400 psi and 450°C. Solubility was found to vary directly with pressure and inversely with temperature. A simple hydration mechanism was used to model the data. A hydration number near 3 for the solvated sodium nitrate species was determined from an empirical fit to the model. In addition, solubilities were determined for potassium and lithium nitrate salts to assess the effect of ion size on solubility. These experiments determined that the solubility was proportional to size of the cation. These studies were motivated by applications for sodium nitrate in hydrothermal treatment methods, specifically supercritical water oxidation processes where nitrate can be used as an oxidant.

**W-93-2**  PUBLISHED

**Treatability of Dinitrotoluene Process Wastewater by Supercritical Water Oxidation**

Li, L.; E.F. Gloyna; J.E. Sawicki


This study focused on the treatment of dinitrotoluene (DNT) process wastewaters by supercritical water oxidation (W-93-2) (SCWO). Major organic components found in the DNT process wastewaters were 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-ortho-cresol, phenol, and dinitrotoluene. Tests were conducted using a 20-cm³ batch reactor and two 120-cm³/min continuous-flow reactor systems. Separate oxidant tests employed oxygen and hydrogen peroxide. Organic destruction efficiencies of target compounds were obtained at supercritical and subcritical water conditions. Temperatures and pressures, respectively, ranged from 250°C to 500°C and 140 bar to 310 bar. The reaction times varied from one minute to seven minutes. Wastewaters premixed with a biological sludge were also tested. SCWO was capable of destroying the US Environmental Protection Agency (EPA) priority pollutants found in the DNT process wastewater. Under SCWO conditions, destruction efficiencies greater than 99% were achieved.

**W-94-1**  PUBLISHED

**Supercritical Water Oxidation: An Engineering Update**

Gloyna, E.F. and L. Li


This paper reviews the need for innovative treatment technologies and describes a wastewater-treatment system capable of completely destroying toxic organic substances and biological sludges. The basic concepts of supercritical water oxidation (W-94-1) (SCWO), associated engineering research, and technology development are examined. During the last few years a growing body of SCWO knowledge has been assembled. A number of universities, federal agencies, and private companies have participated in both engineering research and technology development. In general, engineering research has focused upon reaction kinetics and mechanisms, salt formation and solubility, mass and heat transfer, transformation product identification, catalysis, corrosion, and additive impacts. As research progressed, technology development has directed its attention to materials of construction, reactor design, heat exchange and recuperative heat recovery, solid-liquid separation, gas-liquid separation, control systems, emuent handling, ash disposal, safety requirements, and process integration. Supercritical water oxidation technology relies on the unique properties of supercritical water to create an excellent reaction medium. The system is capable of operating as a totally enclosed facility, providing complete destruction, and meeting all regulatory emuent requirements. As such, this new technology is an environmentally attractive option. Because of favorable treatability, safety, and economic considerations, a growing number of private and governmental entities are currently involved in the development of more effective SCWO facilities.
Supercritical Water Oxidation of Pulp and Paper Mill Sludge (As an Alternative to Incineration)

Blaney, C.A.; L. Li; E.F. Gloyna; S.U. Hossain

Presented at the AIChE National Convention, San Francisco, California, November 1994

This paper summarizes recent research by Kimberly-Clark Corporation and The University of Texas at Austin in a new technology referred to as supercritical water oxidation (SCWO), an emission- and discharge-free alternative to incineration, to treat wastes such as pulp and paper mill sludges. SCWO has been shown to be an effective method to treat pulp and paper mill sludge, converting it to usable by-products of clean water (for reuse in paper mill), carbon dioxide gas, and dioxin-free ash (mostly CaCO3, which can be used as paper filler or cement aggregate). The majority of all organics are destroyed, including PCBs and 99+ of chlorinated organics such as dioxins (PCDDs) and dibenzofurans (PCDFs). Economic studies indicate that a commercial SCWO process could one day compete on a cost basis with fluidized bed incineration.

Simulation of a Concentric-Tube Reactor for Supercritical Water Oxidation

Chen, P.; L. Li; E.F. Gloyna

Manuscript on file, Separations Research Program

The supercritical water oxidation (SCWO) process is capable of destroying undesirable organic compounds, converting the waste into non-noxious substances, accomplishing this task within an essentially enclosed environment, and requiring a relatively small amount of external heat. The key unit in the SCWO process is the reactor which generally operates at temperatures and pressures ranging from 400°C to 650°C and 25 MPa to 35 MPa, respectively. To further enhance the development of the SCWO process, a concentric-tube reactor model has been developed. Because of the heat generation and transfer processes within the reactor, both reaction kinetics and heat transfer rate factors are incorporated in the model. The simulation model treats the reactor as a number of segments, and each segment is assumed to be isothermal. The residence time in each segment is determined by the properties of water, flow rate and volume of the segment. The reactor simulation model was validated by pilot-plant tests involving the destruction of acetic acid, phenol, and n-octanol. These tests were conducted in a pilot-scale SCWO facility that is equipped with a 6.1-meter long concentric-tube reactor and capable of treating waste water at a rate of 150 liter per hour. All simulation results, using pseudo-first-order kinetic models, agreed favorably with the pilot-plant data. The simulated reactor temperature profiles agreed with the measured profiles.

Kinetics and Reaction Pathways of Pyridine Oxidation in Supercritical Water

Crain, N.S.; S. Tebbal; L. Li; E.F. Gloyna

Industrial Engineering and Chemistry Research 32(10):2259-68

There is a growing interest in applying supercritical water oxidation (SCWO) to the treatment of wastewaters and sludges. Existing mechanistic and kinetic data relate primarily to SCWO of simple compounds, hydrocarbons, and oxygenated hydrocarbons. Since many organic pollutants contain heteroatoms, the knowledge of SCWO reaction pathways, transition products, and kinetics for heteroatom-containing organic compounds is of critical design importance. This study focused on the kinetic and mechanistic aspects of pyridine oxidation; in supercritical water using high-pressure oxygen gas. A laboratory-scale, continuous-flow reactor system was used. The experimental variables included temperatures varying from 426°C to 525°C, reactor residence times varying from 2.1 s to 10.7 s, and oxygen/pyridine molar feed ratios varying from 0 to 2.64. Pressure and feed flow rate, respectively, were maintained at a nominal value of 27.6 ± 0.4 MPa and 35 ± 0.1 g/min. The rate (mol/(L.s)) of pyridine oxidation in supercritical water was found to be 10 13.1 ± 1.65 exp([-209.5 ± 22.4(kJ/gmol)]/RT) [Pyr]1.0 ± 0.30[O2]0.20 ± 0.16. Below 500°C, the extent of pyridine hydrolysis was less than 1%. The largest hydrolysis impact corresponded to 4.2% of pyridine conversion, which occurred at 521°C in less than 7 s. A number of transition products in both liquid and gaseous effluents from the pyridine oxidation experiments were identified. On the basis of these identified compounds, a network of simplified reaction pathways for pyridine oxidation in supercritical water (W-94-4) was constructed.
**W-94-5**  
*Reactions of Inorganic Nitrogen Species in Supercritical Water*  
Dell'Orco, P.C.  
PhD dissertation

Redox reactions of nitrate salts with ammonia and methanol were studied in near-critical and supercritical water, at temperatures from 350°C to 530°C and a constant pressure of 302 bar. Sodium nitrate decomposition reactions were investigated at similar conditions. Reactions were performed using an isothermal tubular reactor, at flow conditions such that plug-flow reactor assumptions were valid. To perform kinetic modeling, nitrate and nitrite reactants were lumped into an NOx - reactant. Kinetic expressions were developed for MNO3/NH4X and sodium nitrate decomposition reactions. Based on experimental evidence, an elementary reaction mechanism for MNO3/NH4X reaction was proposed. This model indicated that NO2 was the primary oxidizing species. The mechanism implied that N2/N2O selectivities could be determined by the form of MNO3 that was used. These reactions immediately suggested a nitrogen control strategy for use in SCWO processes (W-94-5) nitrate or ammonia could be used to remove the other, at reaction conditions far less severe than required by other methods. Reactions of nitrate with methanol indicated that nitrate was a better oxidant than oxygen in supercritical water. Nitrogen reaction products included ammonia and nitrite, while inorganic carbon was the major carbon reaction product. An analysis of excess experiments indicated that the reaction at 475°C was first order in methanol concentration and second order in NOx - concentration. In order to determine phase regimes for these reactions, the solubility of sodium nitrate was determined for some 1:1 nitrate electrolytes. Solubilities were measured at 450°C to 525°C, from 248 bar to 302 bar. A semi-empirical solvation model was shown to adequately describe the experimentally observed sodium nitrate solubilities. Solubilities of lithium, sodium, and potassium nitrates revealed that cations with smaller ionic radii had greater solubilities with nitrate.

**W-94-6**  
*Method and Apparatus for Multiple-Stage and Recycle Wet Oxidation*  
Gloyna, E.F.; L. Li; R.N. McBrayer  
United States Patent 5,358,646 (October 1994)

An organic or inorganic feed compound can be treated in two or more zones to progressively oxidize the compound. The first zone oxidizes the compound to an intermediate product which includes a first intermediate compound which is intermediate the feed compound and end product. The second zone further oxidizes the intermediate product to an end product or a second intermediate compound which is intermediate the first intermediate compound and an end product. One or both zones may operate catalytically and/or at supercritical conditions for water to oxidize the compounds.

**W-94-7**  
*Engineering Aspects of Supercritical Water Oxidation*  
Gloyna, E.F.; L. Li; R.N. McBrayer  
Manuscript on file, Separations Research Program

This paper emphasizes the engineering aspects of supercritical water oxidation (SCWO), including organic destruction, inorganic solubility, corrosion, catalysis, heat transfer, and treatability studies. The development program involving a 2.5 liter-per-minute SCWO pilot-plant (W-94-7) is described. Also, design considerations for the commercial SCWO processing facility, including materials of construction, reactor design, heat recovery, control strategy, safety requirements, and process integration are discussed. The University of Texas at Austin and Eco Waste Technologies, respectively, are involved in research and development of SCWO technology (W-94-7). This R&D effort has resulted in the design and construction of a commercial SCWO processing facility for the Texaco Chemical Company located in Austin, Texas. The facility will become operational in early 1994. The SCWO technology relies on the unique properties of supercritical water to create a useful and effective reaction medium. The SCWO system is capable of operating as a totally enclosed treatment facility, providing complete destruction, and meeting regulatory effluent requirements. As such, this technology is an environmentally attractive, safe and economic wastewater treatment and sludge disposal option.
The Separation of Inorganic Salts and Metal Oxides from Supercritical Water by Cross-Flow Microfiltration
Goemans, Jr., M.G.E.

Master's thesis

The supercritical water oxidation (SCWO) process is an effective treatment technology for organic waste waters and sludges. However, inorganic salts and metal oxides may be generated, and the presence of these materials may create corrosive and erosive environments. In addition, plugging and scaling may occur due to relative low solubility of most inorganic salts and metal oxides in supercritical water. Consequently, the efficiency of reactors, pressure let-down devices, heaters and heat exchangers may be reduced. A solution to the solids problem is to remove precipitates within the supercritical region. However, limited data exist describing solid-fluid separation processes under high temperature and pressure conditions (T = 450°C, P = 27.6 MPa). The purpose of this study was to evaluate the effectiveness of cross-flow microfiltration (W-94-8) to remove inorganic salts and metal oxides from supercritical water under isothermal conditions. Two cross-flow filters capable of operating at high temperature and pressure conditions were designed and fabricated. The cross-flow filters were tested in conjunction with an existing 150 L/hr pilot plant. The filter elements were made of sintered Stainless Steel 316L tubes (pore size = 0.5 mm). Feed streams consisted of sodium carbonate and sodium nitrate solutions and a-Alumina suspensions. Process variables included feed concentration, feed flow rate, feed to filtrate rate ratio, temperature, fluid density and viscosity, transfilter pressure drop, and the physical state of the particulates. Cross-flow filtration was effective in removing sodium nitrate and a-Alumina from supercritical water. Separation efficiencies for sodium nitrate ranged from 60% to 85% for experiments conducted at 420°C and 470°C, respectively. Sodium nitrate separation was limited by the salt solubility under the process conditions. Separation efficiencies ranged from 97.30% to 99.90% for a-Alumina. Filter cake formation was found to be less at SCWO conditions as compared to standard temperature and pressure (STP) conditions. Empirical models for engineering design capable of predicting the filtrate concentration and cake resistance for sodium nitrate filtration were developed and validated. The basis for a theoretical model for salt separation from supercritical water by cross-flow filtration was proposed. Existing theoretical models for predicting the filtrate flux during filtration of metal oxide suspensions were evaluated.

Cyclone Performance for the Separation of Solids from Supercritical Water Oxidation Effluents
Laspidou, C.S.

Master's thesis

The development of a solids separation system is essential to the implementation of supercritical water oxidation as a commercial process. Like all waste disposal processes, supercritical water oxidation produces a residue that must eventually be removed from the effluent stream. Studies for the separation of solids near supercritical water conditions (374.2°C, 3205 psi) are limited. A 25.4-mm diameter hydrocyclone with an underflow receiver was evaluated for its ability to achieve the separation of fine particles from water. Temperature was varied from 25°C to 400°C, while pressure was maintained at 4000 psi (27.6 MPa). Volumetric flow rates varied from 0.012 L/sec to 0.031 L/sec. Particle concentrations in feed streams ranged from 500 mg/L to 2000 mg/L. The particulate studied was a-alumina (A1203), the diameter of which ranged from below one micron to ten micrometers. Solids removal efficiencies were determined for all experiments. Solid removals were as high as 99.9% at elevated temperatures. Particle size distributions obtained by the Coulter Counter provided information on particle sizes separated. Theoretical models were used to predict removal efficiencies, and these values were compared with experimental data.
Pilot-Plant Validation of Kinetic Models for Supercritical Water Oxidation

Li, L.; P. Chen; E.F. Gloyna

Presented at Chemical Oxidation: Technology for the Nineties, Vanderbilt University, Nashville, Tennessee, February 1994

The supercritical water oxidation (SCWO) process is an effective and environmentally attractive option for treating organic wastewaters and sludges. Currently, efforts are being made by several private companies and government agencies to commercialize the SCWO process for the treatment of domestic and industrial wastewaters and sludges, and for the destruction of the noxious organic components of nuclear and military wastes. However, there is a lack of design data based on pilot-scale kinetic studies. While SCWO kinetic models based on laboratory-scale data were available for some simple compounds, the purpose of this pilot-scale study was to validate these models for selected compounds. Specifically, acetic acid, phenol, and n-octanol were studied using a 6.1-m long, concentric-tube reactor with 150-liter/hour (40 GPH) throughput. Process variables included temperature (385°C to 440°C), feed concentration (acetic acid: 4 g/L to 21 g/L; phenol: 0.59 g/L to 0.77 g/L; n-octanol: 0.24 g/L to 0.37 g/L), and flow rate (45 L/h to 115 L/h). All tests were conducted at a pressure of 24.8 MPa and at least 20% excess oxygen. The pilot-plant results confirmed the validity of first-order reaction models for SCWO of acetic acid previously developed at The University of Texas at Austin using laboratory-scale apparatus. It appeared that hydrogen peroxide and oxygen were equally effective in SCWO of acetic acid (W-94-10); when the oxidant and feed were heated separately and then mixed. First-order reaction models for phenol and n-octanol were also obtained. For practical purposes, pseudo-first-order reaction models for these organic compounds can be used in the design and operation of SCWO processes.

Supercritical Water Oxidation Model Development for Selected EPA Priority Pollutants

Li, L.; N. Crain; A. Kanthasamy; C.F. Matthews; S.W. Rollans; E.F. Gloyna

The present regulations defining organic waste destruction and sludge volume reduction are clearly overwhelming if left to conventional treatment concepts. While waste minimization is an important goal, there remain industrial and municipal residuals that must be treated, recycled, and reused. Supercritical water oxidation (SCWO) offers several attractive waste treatment advantages: heat requirements become self-sustaining with wastes having a chemical oxidation demand (COD) of about 30,000 mg/L; seven nine (99.99999%) destruction is achievable; the concept allows enclosed treatment; and costs appear to be favorable compared to existing treatment methods. Supercritical water (SCW) exists above the vapor-liquid critical point of water (374°C and 22.1 MPa). SCW is an excellent solvent for organic compounds and oxygen. The hydrocarbons can be oxidized rapidly in SCW to form carbon dioxide and water. Laboratory and pilot-scale studies involving SCWO (W-94-11) have demonstrated rapid and effective treatment of wastewaters and organic sludges. The SCWO environment exhibits unique characteristics. The destruction rates are likely to be controlled by reaction kinetics instead of the mass transfer rate. The solubility of inorganic salts in SCW is greatly reduced. The resulting solid residuals generally meet EPA leachability requirements. Similarly, gaseous effluents from an SCWO process can readily meet discharge criteria. Therefore, SCWO becomes an attractive treatment/destruction option for environmentally sensitive wastes. (W-94-11)

The Effect of Additives on the Oxidation of Dimethyl Methylphosphonate in Supercritical Water

McKendry, J.K.; L. Li; E.F. Gloyna

The objective of this research was to study the effect of additives on the destruction of dimethyl methylphosphonate (DMMP) at supercritical conditions. The additives chosen for this study were selected primarily to observe their effect on by-product formation upon the destruction of DMMP in supercritical water. Additives which could possibly create a buffering environment were selected as potentially having the ability to neutralize the acidic effluents generated during the
SCWO process. By neutralizing the acidic effluent resulting from certain waste streams, corrosion may be inhibited, and reactor lifetimes prolonged. This research was limited to laboratory bench-scale tests using a batch reactor. Fixed conditions were initial concentration of DMMP (10.00 mg/L), residence time (five minutes), temperature (450°C), and pressure (27.6 MPa). Variables included the use of three additives (NaOH, Na2B4O7, Na2CO3), and three oxygen concentrations (in excess of 100%, 17%, and 0% of stoichiometric demand). Oxidation and hydrolysis by-products were identified and quantified as a function of oxygen concentration. By-products included methylphosphonic acid, phosphates, and methanol in the liquid phase, and methane, carbon dioxide, carbon monoxide, and hydrogen in the gas phase. The final pH was measured. Corrosion products, chromium and iron, were quantified as well.

W-94-13 $10.00
Ceramics for Corrosion Resistance in Supercritical Water Environments
Morin, R.J.
Master's thesis
Ceramic liners and coatings are candidate materials for providing protection against corrosion in supercritical water oxidation (SCWO) systems. Alumina (Al2O3), silicon carbide (SiC), silicon nitride (Si3N4), and zirconia (ZrO2) were evaluated for corrosion resistance in supercritical water at varying pH levels (1.8 through 12.3) and temperatures (350°C, 450°C, and 550°C). Corrosion rates were evaluated based on mass loss. Crystalline deposits were identified by x-ray diffraction, and surficial characteristics were evaluated using scanning electron microscopy. Each of the ceramics experienced corrosion in the SCWO environments. The alumina experienced intergranular corrosion in the pH ranges 1.8 to 8.0, and dissolution in the pH ranges 11.0 to 12.3. Silicon carbide formed a passive oxidation layer of silica in similar acidic and neutral environments, and experienced dissolution in the basic environments. Similar to the silicon carbide, silicon nitride formed a passive layer of silica in the same acidic and neutral environments at 450°C and 550°C, but formed a much thicker and more porous silica layer in basic environments. Zirconia underwent a phase transformation that caused the coupon to crack. This phenomena occurred at 250°C, and was independent of the experimental temperature and pH ranges. Alumina, silicon carbide, and silicon nitride remain candidate materials for corrosion protection in SCWO systems 94-13). Zirconia is not suitable unless the phase transformation can be prevented. Since corrosion characteristics in SCWO are now defined, future ceramic research can focus on more advanced issues. These include: 1) Determining how ceramic corrosion affects the SCWO system, 2) Determining corrosion rates for ceramic components to allow better estimates of component life-expectancies, and 3) Investigating the most efficient and inexpensive means of corrosion protection. Options include tube liners, CVD coatings, and sol-gel coatings.

W-94-14 $20.00
Supercritical Water Oxidation of Dimethyl Methylphosphonate and Thiodiglycol
Turner, M.D.
PhD dissertation
The objectives of this research were to determine global pathways, through analyses of intermediate and final by-products, and evaluate the use of global kinetic models to describe the overall conversion from parent compounds to final stable products, for supercritical water oxidation of dimethyl methylphosphonate (DMMP) and thiodiglycol (TDG). These compounds were chosen as model compounds to simulate the nerve agent GB and mustard gas (agent HD), respectively. Global destruction pathways were postulated for both parent compounds. Mass balances were performed for carbon, phosphorus and sulfur, where closures of 100%±10% were considered adequate to ensure that all major products were identified and analyzed. DMMP rapidly hydrolyzed to methanol and methylphosphonic acid (MPA) at subcritical temperatures. Oxidation of methanol and MPA produced carbon monoxide as an intermediate, and carbon dioxide and phosphoric acid as stable end-products. TDG hydrolysis/pyrolysis produced carbon monoxide, methane, ethanol, ethylene, and hydrogen sulfide. TDG oxidation resulted in carbon monoxide, methane, acetic acid, and sulfuric acid as intermediates, and carbon dioxide and sulfuric acid as stable end-products. A detailed kinetic model, consisting of a set of simultaneous global rate equations, one for each major by-product, was developed to describe the behavior of
DMMP and its transformation products in supercritical water. Arrhenius pre-exponential factors and activation energies, and reaction orders with respect to oxygen and each organic compound were determined. MPA was found to be the rate-limiting intermediate to the overall conversion of DMMP. Pilot-scale tests were conducted to validate the model. Model-predicted yields for all by-products, agreed with the experimental data within 20%. Corrosion, resulting in equipment failures and control problems, limited kinetic evaluations to identification of overall, rate-limiting intermediates for conversion of TDG to stable end-products. Carbon monoxide and methane were the primary rate-limiting intermediates for complete TDG conversion. A new laboratory-scale, continuous-flow reactor was designed and constructed. This reactor system employed high-pressure, gaseous oxygen as the oxidant and provided for separation, collection, and analyses of both the liquid-phase and gas-phase effluents.

W-95-1
A Kinetic Lumping Approach-Supercritical Water Oxidation of Propellant Type Materials
Crain, N.; L. Li; E.F. Gloyna

W-95-2
Catalyst Evaluation Supercritical Water Oxidation Process
Frisch, M.A.; L. Li; E.F. Gloyna
Presented at the Forty-ninth Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May 9-11, 1994

The objective of this research was to evaluate the performance of selected catalysts for use in supercritical water oxidation (SCWO) environments. A three-step procedure was used to evaluate catalyst performance. First, commercially available metal oxide supports were tested for physical stability in SCWO environments. Stability was determined by examination of the supports and dissolved species in the liquid phase before and after exposure to SCWO in laboratory-scale, batch reactors. Second, promising supports were coated with platinum (platinum coated supports were then referred to as platinum catalysts). These platinum catalysts and supports were each packed in a continuous-flow, fixed bed reactor in order to evaluate the catalytic oxidation of DMMP, acetic acid, pyridine, and 2, 4-DCP and their corresponding by-products. Third, selected platinum catalysts and supports were exposed to longevity tests in order to evaluate temporal stability and activity in the catalytic oxidation of acetic acid. Longevity tests also were used to evaluate the effect of sulfuric and hydrochloric acid additions to the feed.

W-95-3
Oxidation Kinetics and Catalyst Transformation of Titania-Catalyzed Supercritical Water Oxidation of Acetic Acid
Frisch, M.A. and E.F. Gloyna
Presented at the AIChE Annual Meeting, November 17, 1994

Refractory transformation products such as acetic acid exist in supercritical water oxidation (SCWO) environments. Higher temperatures and longer residence times are required for their removal. Catalysts may be used to increase the reaction rates, thus destroying refractory organics at lower temperatures and shorter residence times. Catalysts also increase oxidation rates of other organics (Frisch, 1994). The result is a smaller reactor and lower temperatures, which improves the economics and safety of the SCWO system. This is especially useful for mobile SCWO units. The purpose of this research was to globally investigate the use of anatase (TiO2) as a catalyst for the SCWO of acetic acid. The objectives were: identification of process variables affecting catalyzed oxidation rates; development of a kinetic model; and investigation of anatase transformation in SCWO environments.
**W-95-4**

Supercritical Water Oxidation Research and Development

Gloyna, E.F. and L. Li

Presented at the AIChE Spring National Meeting, Houston, Texas, March 19-23, 1995

Research emphasis at UT-Austin includes topics considered to be most important in improving design, operation, and treatability. This research includes: model development, catalysis, salt solubility, fate of heavy metals, procedures for screening survey data, design of continuous-flow systems, behavior of inorganic substances, corrosion, kinetic and reaction pathways, solids separation, treatability, and technology development.

**W-95-5**

Research and Development of a Commercial Supercritical Water Oxidation Process

McBrayer, R.; L. Li and E.F. Gloyna


This paper describes a joint research and development (R&D) effort between The University of Texas at Austin (UT) and Eco Waste Technologies (EWT). The objective was to develop a commercial supercritical water oxidation (SCWO) process (W-95-5). SCWO technology relies on the unique properties of supercritical water to create an excellent reaction medium. The SCWO treatment system is capable of operating as a totally enclosed wastewater treatment facility, providing complete destruction, and meeting regulatory effluent requirements. As such, this technology is an environmentally attractive option. Because of favorable treatability, safety, and economic considerations, a growing number of private and governmental entities have been involved in R&D leading to the commercialization of SCWO waste treatment processes. The cooperative R&D program began in 1990. UT provided research support in the general areas of reaction kinetics and mechanisms, solids separation, salt formation and solubility, mass and heat transfer, transformation product identification, catalysis, corrosion, and additive impacts. EWT focused on the development and testing of a 40-gph SCWO pilot-plant. The objectives were to scale-up the SCWO process. Major design considerations for commercial applications included materials of construction, reactor design, heat recovery, control strategy, safety requirements, and process integration. This R&D effort has resulted in the design of a commercial SCWO processing facility for Texaco Chemical Company located in Austin, Texas. The facility will become operational in early 1994.

**W-95-6** $10.00

Supercritical Water Oxidation Kinetics of Propellant Simulant

Crain, N.E.

PhD dissertation

Supercritical water oxidation (SCWO) has received favorable attention in the treatment of extremely hazardous waste such as hydrolyzed solid rocket propellant. Treatability studies using hydrolyzed propellants have demonstrated the feasibility of using SCWO; however, they did not supply detailed kinetic information. Effective implementation of SCWO requires the development of a reliable kinetic model. A kinetic study of a simulated propellant waste was conducted. The simulant was composed of acetic, formic, oxalic, and tartaric acids. A lumped kinetic model for the SCWO of the simulated propellant was developed. The model was developed from experiments utilizing each of the simulant's components separately. The model successfully reflects experimental data collected from the SCWO of the simulant over the temperature range of 425°C to 475°C at 27.9 MPa. Excess oxygen was maintained in all experiments. Experiments were also conducted using nitric acid as an additive. Six effluent compounds were identified from these experiments. The identified compounds were carbon dioxide, carbon monoxide, acetic acid, formic acid, methane, and hydrogen.
The efficiency of the supercritical water oxidation (SCWO) process depends on the fate of thermally stable oxidation byproducts, such as acetic acid. This research investigated the use of anatase (TiO2) as a catalyst for the SCWO of acetic acid. The specific objectives were to identify process variables that affected catalyzed oxidation rates, develop a kinetic model and investigate anatase behavior in SCWO environments. A fixed-bed reactor was used. Anatase was an effective catalyst. Temperature, residence time, acetic acid concentration, and catalyst exposure time (age) influenced the oxidation rate of acetic acid. Kinetic data were collected and modeled. The initial oxygen concentration did not significantly impact the modeled rate of reaction; thus, it was left out of the rate equation. The following rate equation provided the best fit to 35 kinetic data points.

For temperatures of 400°C and 450°C, respectively, initial catalyzed rates were 44 and 115 times faster than initial noncatalyzed rates. Catalyst samples were characterized in order to relate catalyst properties to transient conversion. Under SCWO conditions, the anatase particles were sintered. Within 200 minutes of exposure time, particle surface areas decreased from 40 m2/g to 20 m2/g and catalyst pore diameters nearly doubled. Qualitative analysis of corrosion-product deposition indicated that iron (III) oxide (hematite) was the most abundant surface contaminant. Surface area, pore diameter and hematite deposition could not be correlated to transient conversion. Sintering and mechanical shock encouraged formation of catalyst fines. Increased catalytic activity of fines may have caused transient conversion; however, further research is needed to confirm this conclusion.

A system for effective utilization of reaction heat and in situ separation of solid and gaseous products in wet oxidation of waste and wastewater. This invention does not require special preheaters for preheating feed streams, therefore reducing the possibility of scale and char formation in the heat exchange zone. The cold feed stream is introduced into the reactor with part of the effluent which has been recycled through a high temperature pumping means to form a hot, near critical oxidant-containing mixture. The cold feed is directly heated up by the oxidant-containing mixture. The reaction mixture is separated by in situ crossflow filtration elements including sintered material. Catalyzed reactions and sintered material gas separation are also described.

The objective of this research was to study the effect of additives on the destruction of dimethyl methylphosphonate (DMMP) at supercritical conditions. Specifically, the objective was to evaluate the effect different additives had on the production of certain by-products in a limited oxygen environment. In addition, the capability of these additives to neutralize the acidic environment generated during the SCWO process was considered. Tests were conducted in a 300-mL Autoclave batch reactor at both subcritical and supercritical temperatures (350°C and 450°C). The effects of three additives (sodium hydroxide, sodium carbonate, and sodium borate) were investigated in three oxygen concentrations. Tests were performed in the absence of oxygen, with less than the stoichiometric oxygen demand, and in excess of the stoichiometric oxygen demand to investigate the extent of hydrolysis and oxidation reaction pathways. Initial concentration and residence time were fixed at 10,000 mg/L and five minutes, respectively. Oxidation and hydrolysis byproducts were identified and quantified in both the gas- and liquid- phases as a function of oxygen concentration. The final pH was measured and corrosion products were quantified. All three additives enhanced hydrolysis by-product formation when less than the stoichiometric
oxygen demand was available. Additives created a more ionic medium supportive of hydrolysis reactions and precipitated certain salts and acids. Moderate increases in final pH were observed as a result of additive addition to the feed. Lower concentrations of soluble corrosion products, chromium and iron, were observed when additives were present.

W-95-10 $5.00
The Fate of Chromium and Lead in a Supercritical Water Oxidation Environment: A Survey
Zimet, D.B.
Master's thesis
Supercritical Water Oxidation (SCWO) is emerging as a promising means to eliminate many forms of municipal and industrial waste. The goal of this research project was to examine the fate of chromium and lead exposed to a SCWO environment. Solutions or mixtures of the following compounds were exposed to SCWO conditions: \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\), \(\text{Cr(NO}_3\text{)}_3\), \(\text{Na}_2\text{CrO}_4\), \(\text{Pb(NO}_3\text{)}_2\), \(\text{Pb(CH}_3\text{COO)}_2\), and \(\text{PbO}_2\). After exposure, the effluent was analyzed in order to characterize transformation products, metallic oxidation states, phase separation, and corrosion products. In batch tests, it was found that chromium and lead were converted from soluble to insoluble species without changing their oxidation states. Soluble \(\text{Cr(NO}_3\text{)}_3\) at a pH of 1.7 was transformed to insoluble \(\text{HCrO}_2\), and soluble \(\text{Pb(CH}_3\text{COO)}_2\) at a pH of 5.9 was transformed to insoluble \(\text{PbCO}_3\). Also, it was possible to reduce the oxidation state of chromium and lead, even under conditions that are known to be highly oxidative to organic compounds. Ammonium dichromate at a pH of 4.5 was reduced to \(\text{Cr}_2\text{O}_3\), and insoluble \(\text{PbO}_2\) at a pH of 6.2 was reduced to insoluble \(\text{PbO}_1.55\). Additionally, one chromium solution and one lead solution were found to be stable in a SCWO environment. At respective pH's of 5.9 and 4.2, \(\text{Na}_2\text{CrO}_4\) and \(\text{Pb(NO}_3\text{)}_2\) were unchanged by SCWO. Corrosion of reactor walls was detected through measurement of chromium in the effluent. Nitrate and acetate ions facilitated corrosion and produced predominantly hexavalent chromium species. In continuous-flow experiments involving \(\text{Na}_2\text{CrO}_4\), it was found that the concentration of soluble hexavalent chromium in the effluent decreased upon the addition of ammonium hydroxide to the influent.

W-95-11
Supercritical Water Oxidation of Pulp and Paper Mill Sludge of Pulp and Paper Mill Sludge (As an Alternative to Incineration)
Blaney, C.A.; L. Li; E.F. Gloyna; S.U. Hossain
Accepted by Supercritical Fluids Science and Technology, ACS Symposium Series
This paper summarizes recent research by Kimberly-Clark Corporation and The University of Texas at Austin in a new technology referred to as "Supercritical Water Oxidation" (SCWO), an emission-free and discharge-free alternative to incineration, to treat wastes such as pulp and paper mill sludges. SCWO has been shown to be an effective method to treat pulp and paper mill sludge, converting it to usable by-products of clean water (for reuse in paper mill), carbon dioxide gas and dioxin-free ash (mostly \(\text{CaCO}_3\), which can be used as paper filler or cement aggregate). The majority of all organics are destroyed, including polychlorinated biphenyls and 99 + % of chlorinated organics such as dioxins and dibenzofurans. Economic studies indicate that a commercial SCWO process can compete on a cost basis with fluidized bed incineration. A new reactor design is discussed which avoids the problem of corrosion.

W-95-12 PUBLISHED
Supercritical Water Oxidation Research and Development Update
Gloyna, E.F. and L. Li
Supercritical water oxidation (SCWO) is a form of hydrothermal treatment. During the early research and development (R&D) period (early 1980s), it has been demonstrated that SCWO can be an effective alternative to the destruction of hazardous organic wastewaters and sludges. Because of this promising potential and growing interest in SCWO technology, R&D efforts have been intensified. As a result, the first SCWO commercial facility (1100 Liter/hour) developed by Eco Waste Technologies was commissioned in August, 1994. Also, a number of demonstration SCWO facilities exist in various companies, national laboratories, and federal agencies. This
recent development has shown that the SCWO process produces environmentally acceptable effluents (gas, liquid and solid), lends itself to resource recovery, and can be economically competitive. As such, the process can be used to serve as a pretreatment unit, an end-of-pipe facility or become an integral part of an industrial process. More recently, the SCWO R&D program has been expanded. The research activities now include more detailed studies involving reaction kinetics, catalysis, salt solubility, corrosion, heavy metal speciation, solids separation, and resource/by-product recovery. Technology development involves process and reactor design, materials evaluation, heat recovery, control systems, effluent handling, safety requirements, and process integration.

W-95-13 PUBLISHED
Separation of Inorganic Salts from Supercritical Water by Cross-Flow Microfiltration
Goemans, M.G.E.; L. Li; E.F. Gloyna
A cross-flow microfilter capable of operating at elevated temperatures and pressures was evaluated for its ability to remove inorganic salts from supercritical water (SCW). The separation characteristics of molten sodium nitrate were investigated. The overall performance of the cross-flow microfilter and the effects of process variables on the separation efficiency were evaluated. Separation efficiencies up to 85% were observed. An empirical model was developed for the prediction of the filtrate salt concentration and the fluidized cake resistance as a function of the salt solubility and salt flux to the filter. Physical principles governing the separation process were defined.

W-95-14 PUBLISHED
Solubility of Potassium Hydroxide and Potassium Phosphate in Supercritical Water
Wofford, W.T.; P.C. Dell'Oroco; E.F. Gloyna
The solubilities of potassium hydroxide and dibasic potassium phosphate in supercritical water solutions have been measured at temperatures from 400 to 525°C and pressures from 22.1 to 32.0 MPa. The solubility of potassium hydroxide varied from 61 mg/kg at 525°C and 22.1 MPa to 594 mg/kg at 450°C and 30.4 MPa. The solubility of dibasic potassium phosphate varied from 2 mg/kg at 450 °C and 26.8 MPa to 416 mg/kg at 400°C and 27.1 MPa. The solubility was found to vary directly with pressure and inversely with temperature. Results were fit to a semiempirical solvation model to yield predictive equations for solubility as a function of water density.

W-96-1
A Tubular Optical Cell for Fluid Dynamic Studies at High Temperatures and Pressures
Goemans, M.G.E.; M.A. Sedillo; J. Romero; S.J. Buelow
A new tubular optical cell was developed for the study of single-phase and multi-phase fluid dynamics at hydrothermal conditions. The intended operational limits were 500°C at 85 MPa. Consequently, this cell should operate reliably in many supercritical fluid applications (e.g. supercritical CO2). The optical cell featured a sapphire tube with the same dimensions as the metal (reactor) tubes, nickel-plated C-seals between the sapphire tube and the metal tube, and a hydraulic assembly to accommodate for thermal expansion differentials between the sapphire and metal components.

W-96-2
The Development of an Effective Treatment Technology Supercritical Water Oxidation of Wastewater and Sludges
Gloyna, E.F. and L. Li
The effective utilization of the world's water resources can be enhanced by an improved wastewater and sludge management system. It is time for the industrial leadership in water resource management to adopt a new vision. While the traditional treatment approaches have served society well, the continued use of end-of-pipe, single media, multi-train treatment
processes must be reevaluated. Too many of the conventional methodologies produce massive amounts of residual chemical sludges, volatile hazardous organic substances, and non-recyclable water. There are innovative treatment solutions available. For example, research, development, and commercialization have demonstrated the applicability of supercritical water oxidation (SCWO) as a viable treatment alternative. Supercritical water (SCW) is an excellent reaction medium. The SCWO process is capable of providing complete destruction of pollutants in a closed facility, meeting effluent criteria, producing a reusable and low-volume ash, providing a usable water resource, emitting no toxic volatile emissions, and recovering valuable by-products. This paper addresses the global water resources issues, the need for innovative, SCWO technology, research and development experiences, and commercialization.

W-96-3
Application of Hydrothermal Oxidation to Waste Treatment
Li, L. and E.F. Gloyna
Second International - Environmental Applications of Advanced Oxidation Technologies Sponsored by EPRI, DOE, and NSF February 28 - March 1, 1996
The treatment of wastewaters, sludges, and munitions containing hazardous organics by conventional technologies is becoming increasingly complex, costly, and from a public point-of-view, environmentally unacceptable. As an alternative, waste treatment by hydrothermal oxidation, in particular, supercritical water oxidation (SCWO), offers a new and attractive waste management approach. Efforts to develop the SCWO process for waste treatment began in the early 1980s, and currently there is a substantial body of knowledge available for SCWO technology development. Most of the past and ongoing SCWO research and development (R&D) efforts have been directed to the establishment of (1) the scientific basis; (2) the technical basis; and (3) the treatment system. This paper describes these three basic requirements for the application of SCWO to waste treatment. The details include system characterizations (such as phase behavior, heat and mass transfer, reaction mechanisms, kinetic models, acid-base reactions, and catalytic enhancement), process development (treatability studies, process design and simulation, material selection, process integration/model validation by pilot-plant studies, and process monitoring/control), and unit operations (reactors, solid separators, pressurization/letdown devices, and heaters/heat exchangers). Also outlines in this paper are typical wastes currently considered treatable by SCWO. Although the emphasis of existing R&D efforts has been given to the application of SCWO to waste treatment, the hydrothermal oxidation methodology has a broad application potential for by-product recovery from wastes, waste minimization by process integration, and new chemical synthesis processes.

W-97-1 PUBLISHED
Separation of Metal Oxides from Supercritical Water by Crossflow Microfiltration
Goemans, Marcel G.E.; F.M. Tiller; L. Li; E. Gloyna
Low-shear crossflow microfilters rated for 34.5 Mpa were evaluated for their ability to remove (-alumina particles from supercritical water. The crossflow microfilters were tested in conjunction with a 2.5 L/h bench-scale apparatus and a 150 L/h pilot plant. The filter elements were made of sintered Stainless Steel 316L tubes with nominal pore size of 0.5 (m. Process variables include volumetric feed concentration, feed flow rate, temperature, and fluid density and viscosity. The mean particle diameter was about 1.6 (m. Filtration characteristics were similar at supercritical water conditions to those at ambient conditions: Increased shear rates and decreased fluid viscosity resulted in increased filtrate fluxes. Filtrate flow deterioration over time and the required transfilter pressure drop were about 40% less at supercritical water conditions as compared to the performance obtainable at ambient conditions. Higher shear rates delayed the establishment of steady state operating conditions. Filtrate flux could be augmented by pressure swings or periodic increases in the shear rate. Particle separation efficiencies typically exceed 99.9%. A modified concentration polarization model for turbulent flow yielded steady state filtrate fluxes that were within a factor of two of the experimental results. Back diffusion was modeled as a process-in-series of molecular diffusion and eddy diffusion. The proposed model was consistent with findings of numerical diffusion studies and the theory of concentration polarization as recently presented in
the literature. To save on energy costs it might be possible to achieve the benefits of filtration at supercritical conditions at near-critical subcritical conditions: viscosity and mass diffusion coefficients are similar but the density of subcritical water is 3 to 4 times higher than supercritical water thus increasing the filtrate mass flow rate by a factor of 3 to 4 for a given filter.

W-97-2 PUBLISHED
Reactions of Nitrate Salts with Ammonia in Supercritical Water
Dell'Orco, Phillip C.; E.F. Gloyna; S. J. Buelow
Reactions involving nitrate salts and ammonia were investigated in supercritical water at temperatures from 450 to 520°C and pressure near 300 bar. Reaction products include nitrite, nitrogen gas, and nitrous oxide. Observed reaction rates and product distributions provided evidence for a free-radical reaction mechanism with NO2, NO, and NH2( as the primary reactive species at supercritical conditions. In the proposed elementary mechanism, the rate-limiting reaction step was determined to be the hydrolysis of MNO3 species, which resulted in the formation of nitric acid and subsequently NO2. A simple second-order reaction model was used to represent the data. In developing empirical kinetic model, nitrate and nitrite were lumped as an NOx- reactant. Empirical kinetic parameters were developed for four MNOx/NH3 reaction rates and mechanisms suggest immediately a practical significance of these reactions for nitrogen control strategies in supercritical water oxidation processes.

W-98-1 $10.00
Solubility of Na2CO3 and Na2CO3/NaNO3 Mixture in Supercritical Water
Mosher, Tyler Jay
Master's Thesis
Supercritical water oxidation is an emerging technology that effectively destroys organic compounds present in wastewaters. Efficiency of this process may be improved by understanding the characteristics of salt precipitation, the fate and transport of these inorganic salts, and the impact of various salts on SCWO facilities. Inorganic salts exhibit low solubilities in supercritical water environments. These precipitates may corrode and plug the SCWO reactor system. Na2CO3 is a common problem because it may adversely impact the performance of SCWP reactors, heat exchangers and associated appurtenances. The presence of sodium in many wastewaters and the production of CO2 in the SCWO process create an ideal environment for precipitation of Na2CO3. Similarly, NaNO3 is another common salt found in these SCWO systems.

W-98-2 $10.00
Corrosion Resistance of Selected Titanium Alloys Under Supercritical Water Oxidation Conditions
Graves, Mark Clinton
Master's Thesis
Supercritical water oxidation(SCWO) is an emerging hydrothermal process. This technology has considerable promise because of its ability to quickly and efficiently break down hazardous organic wastes into harmless inorganic components. Waste destruction is accomplished in a completely enclosed treatment system with no noxious gaseous effluents produced and environmentally acceptable liquid-solid effluents. Unfortunately, some wastes produce corrosive by-products such as inorganic acids and salts. If this corrosion problem can be minimized, the SCWO process can be used to destroy a broader spectrum of hazardous waste components. Previous research showed that titanium alloys were relatively resistant to corrosion in some supercritical water environments. Therefore, to establish a more valid basis for selection of reactor materials, a comprehensive corrosion study was conducted to titanium alloys. This study focused on determining the corrosion resistance of titanium grades 6, 9, 12, 21 and 6-2-2-4 (single grade) in an acidic supercritical water oxidation environment.
**W-99-1**

**Oxidation and Hydrolysis of Lactic Acid in Near-Critical Water**

Lixiong Li; Juan R. Portela; David Vallejo; Earnest F. Gloyna


The purpose of this study was to develop kinetic correlations for hydrolysis and oxidation of lactic acid and identify key reaction pathways associated with reactions of lactic acid in subcritical and supercritical water.

**W-04-1**

**Waste, Nuclear, Reprocessing and Treatment Technologies to Wastewater Treatment, Multilateral Approach**

Gloyna, E.F.

Encyclopedia of Chemical Processing and Design

Supercritical water oxidation (SCWO) is a form of hydrothermal treatment. During 1980s, it was demonstrated that SCWO could be an effective alternative to the destruction of hazardous organic wastewaters and sludges. Because of this promising potential and growing interest in SCWO technology, research and development (R&D) efforts were intensified. The first such commercial facility (1,100 L/h), as developed by Eco Waste Technologies Inc., was commissioned in May 1994. Today, several demonstration SCWO facilities exist in industrial and governmental laboratories. The SCWO process produces environmentally acceptable effluents (gas, liquid, and solid), lends itself to resource recovery, and can be economically competitive. As such, the process can be used to serve as a pretreatment unit, as an end-of-pipe facility, or it can become an integral part of an industrial process. The expanded research activities now include studies involving reaction kinetics, catalysis, salt solubility, corrosion, heavy-metal speciation, solids, separation, and resource-byproduct recovery. Technology development involves process and reactor design, materials evaluation, heat recovery, control systems, effluent handling, ash disposal, safety requirements, and process integration.
Index

A

A A Comparative Study of Partition Coefficients
Determined by Sorption and by Liquid
Chromatography in Alcohol-Water-Cellulose
Acetate Systems, 228
A A Comparison of Steady-State Equilibrium and
Rate-Based Models for Packed Reactive
Distillation Columns, 79, 282
A A Diffusion-Controlled Procedure to Close Pores in
Ceramic Membranes, 195
A A Free Volume Distribution Model of Gas Sorption
and Dilation in Glassy Polymers, 197
A A Fundamental Model for the Prediction of
Distillation Sieve Tray Efficiency, Part I.
Database Development. Part II. Model
Development and Evaluation, 57
A A Fundamental Model for the Prediction of Sieve
Tray Efficiency, 34
A A General Correlation for Predicting the Loading
Point of Corrugated Sheet Structured Packings,
53, 57
A A Generalized Correlation for Mass Transfer in
Packed Distillation Columns, 26
A A Guide to Establishing Hollow Fiber Macroscopic
Properties for Membrane Applications, 203
A A Half-Century of Progress in Separations
Technology, 138
A A Kinetic Lumping Approach-Supercritical Water
Oxidation of Propellant Type Materials, 342
A A Literature Review and Analysis of Supercritical
Water Oxidation, 331
A A Load Dampening System for Vapor Phase
Bioreactors, 23, 76
A A Mass Transfer-Based Process Model of Acid Gas
Absorption/Stripping Using
Methyldiethanolamine, 89
A A Mathematical Model of an Electrochemical
Capacitor with Double Layer and Faradaic
Processes, 14
A A Model of Vapor-Liquid Equilibria for Acid Gas-
Alkanolamine-Water Systems, 94
A A Model of Vapor-Liquid Equilibria in the
Aqueous Acid Gas-Alkanolamine System Using
the Electrolyte-NRTL Equation, 91
A A Molecular Simulation Study of Cavity Size
Distributions and Diffusion in para and meta
Isomers, 148
A A New Cocurrent Gas/Liquid Contacting Device
for High Gas Rate Applications, 29
A A New Model for Predicting Mass Transfer in
Distillation Columns Containing Random
Packings, 46
A A New Model That Describes Adsorption of
Laterally Interacting Gas Mixture on Random
Heterogeneous Surfaces. 2. Correlation of
Complex Binary and Prediction of
Multicomponent Adsorption Equilibria, 13
A A New SRP Program for Packed and Tray-Column
Design, 29
A A New Technique for the Measurement of
Multicomponent Gas through Transport
Polymeric Films, 153
A A New Ultracapacity Tray for Distillation
Columns, 50
A A New, Ultracapacity Tray for Distillation
Columns, 56
A A Nonrandom Two-Liquid Model for
Alkanolamine-Water Systems, 109, 112
A A Novel Particle Engineering Technology: Spray-
Freezing into Liquid, 321
A A Qualitative Skin Layer Formation Mechanism
for Membranes Made by Dry/Wet Phase
Inversion, 176
A A Quantitative Model for the Specific Volume of
Polymer - Diluent Mixtures in the Glassy State,
274
A A Rapid Feedback Characterization Technique for
Polymeric Hollow Fiber Membranes Using
Disperse Dyes, 200
A A Reciprocating Pump Check Valve Designed for
Supercritical Water Oxidation of Sludges, 329
A A Simple Apparatus for Measurement of Liquid
Permeabilities through Polymeric Films, 151
A A Simple Method of Extrapolating the Coexistence
Curve and Predicting the Melting Point
Depression Curve from Cloud Point Data for
Polymer-Diluent Systems, 232
A A Simple Model for Pervaporative Transport of
Binary Mixtures through Rubbery Polymeric
Membranes, 278
A A Simple Model for Prediction of Acid Gas
Solubilities in Alkanolamines, 113
A A Simple Semi-Empirical Model for Prediction of
Hydrogen Sulfide and Carbon Dioxide
Solubilities, 111
A A Statistical Mechanic Perspective on the
Temperature Dependence of the Isosteric Heat
of Adsorption and Adsorbed Phase Heat
Capacity, 13
A A Survey: Destruction of Chemical Agent
Simulants in Supercritical Water Oxidation,
335
A A Tubular Optical Cell for Fluid Dynamic Studies
at High Temperatures and Pressures, 346
A A Unified Classical and Molecular
Thermodynamic Theory of Spherical Water-in-
Oil Microemulsions, 296
A A. A. Patwardhan, 30
A A. Dyer, 229
A A. F. Seibert, 31, 41, 42, 43, 45, 49, 50, 62, 63, 65, 66,
67, 68, 69, 70, 71, 136, 137
A A. F. Siebert, 53
A A. Frank Seibert, 12, 51, 75
A A. J. Bard, 61
A A. J. Toprac, 85
A A. Kanthasamy, 334, 340
A A. Klip, 39
A A. Laxminarayan, 232, 233

350
Absorption (Chemical Engineering), 59
Absorption and Stripping, 13
Absorption of CO2 in Aqueous Piperazine/Methyldiethanolamine Blends, 125
Absorption of Carbon Dioxide in Aqueous Blends of Diethanolamine and Methyldiethanolamine, 102
Absorption of Carbon Dioxide in Tertiary Diamines, 104
Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility, 122, 125
Absorption of Carbolambon Dioxide in Aqueous Blends of Diethanine and Methyldiethanolamine, 105
Absorption of Chlorine and Mercury in Sulfite Solutions, 127
Absorption of CO2 in Aqueous Diglycolamine, 135
Absorption of HCL and So2 From Humidified Flue Gas with Calcium Silicate Solids, 121
Abukhadra, R.K., 178
Accad, J. M., 24, 25
Accelerated Physical Aging of Thin Glassy-Polymer Films: Evidence from Gas Transport Measurements, 194
Acid Gas Treating by Aqueous Alkanolamines - Review of Property Data, 99
Acid Gas Treating by Aqueous Alkanolamines: Review of Property Data, 99
Acid-Base Behavior in Supercritical Water: §-Naphthoic Acid-Ammonia Equilibrium, 314
Acid-Base Behavior of Organic Compounds in Supercritical Water, 308
Activity Coefficients Predicted by the Local Composition Model for Aqueous Solutions Used in Flue Gas Desulfurization, 86
Actual Stage Requirements for Distillation Separations, 33
Adjustable Solute Distribution Between Polymers and Supercritical Fluids, 292
Adjustment of the Selectivity of a Diels-Alder Reaction Network Using Supercritical Fluids, 287
Adrian, M.B., 331
Adsorption, 4, 7, 123, 217
Adsorption Equilibrium and Kinetics for Ethylene-Ethane Separation with a Novel Solvent, 81
Adsorption of Aromatics from Water by Macrorieticular Resins, 9
Adsorption of C1 to C7 Normal Alkanes on BAX Activated Carbon: 1. Potential Theory Correlation and Adsorbent Characterization, 16
Adsorption of Carbon Dioxide by Piperazine Activated Methyldiethanolamine, 123
Adsorption of Cesium, Strontium and Cobalt Ions on Magnetite and Magnetite-Silica Composite, 16
Adsorption of Propane and Propylene, 7
Adsorptive Drying of Hydrocarbon Liquids, 7
Adsorptive Drying of Organic Liquids, 4
Adsorptive Drying of Organic Liquids-An Update, 13
Adsorptive Drying of Toluene, 6
Adsorptive Separation of Propylene-Propane Mixtures, 9
Adsorptive Separation Systems-An Overview, 4
Advanced Gas Separation Membrane Materials: Hyper Rigid Polymers and Molecular Sieve-Polymer Mixed Matrices, 204
Advanced Gas Separation Membrane Materials: Rigid Aromatic Polyimides, 158
Advanced Model-Based Control for Distillation, 38
Advanced Polycarbonate and Polysulfone Materials for Membrane-Based Gas Separation Applications, 252
Advances in Separation Technologies for the Treatment of Oily Wastewaters, 325
Agarwal, R.S, 106, 108, 112
Agglomeration of Damp Calcium Silicate Sorbents for Flue Gas Desulfurization, 101
Aghyad W., 23
Aging of Thin Polyimide-Ceramic and Polycarbonate-Ceramic Composite Membranes, 182
Aguilar-Vega, M., 263, 264, 266, 267
Air Separation Properties for Flat Sheet Homogeneous Pyrolytic Carbon Membranes, 206
Air Stripping of Volatile Organics in Packed Columns: Experiments and Mathematical Modeling, 37
Aitken, C.L, 261, 262, 267
Alawode, A., 135
Alawode, A., 136
Alentiev, A.Y, 143
Al-Hussaini, H, 151
Al-Juaied, M, 135
Al-Rayes, 23, 76
Alternative Separation Processes for Fluid Mixtures, 156
Alkyl Derivatized Cellulose Acetate Membranes with Enhanced Albumin Affinity, 213
Alcock, H.R, 178
Al-Muhtaseb, A, 20
Al-Muhtaseb, S.A, 13, 15, 16, 17, 18, 19
Al-Rayes, 23, 76
Alternative Separation Processes for Fluid Mixtures, 156
351
Ayala, L. B., 44

B. E. Reeves, 30, 65
B. Eldridge, 56, 81, 279, 280
B. K. Kruelskie, 36
B. M. Parker, 29, 31, 42
B. Reed, 71
B. W. Reed, 72
B. Yui, 151
B.C. Johnson, 215
B.J. Hrnjez, 289
B.J. Story, 153

B-82-1, 25
B-84-1, 136
B-85-1, 25
B-86-1, 26
B-86-2, 136
B-86-3, 26
B-86-4, 26
B-86-5, 26
B-86-6, 62
B-86-7, 136
B-87-1, 26
B-87-2, 26
B-87-3, 62
B-87-4, 136
B-87-5, 26
B-87-6, 27
B-87-7, 27
B-87-8, 27
B-87-9, 137
B-88-1, 27
B-88-2, 27
B-88-3, 28
B-88-4, 28
B-88-5, 29
B-88-6, 29
B-89-1, 29
B-89-2, 29
B-89-3, 29
B-89-4, 29
B-89-5, 29
B-89-6, 137
B-89-7, 30
B-89-8, 30
B-90-1, 30
B-90-2, 30
B-90-3, 30
B-90-4, 31
B-90-5, 31, 42
B-90-6, 31, 42
B-90-7, 31
B-90-8, 31
B-91-1, 31
Babai-Pirouz, M, 212, 213, 214
Babatunde A. Oyenekan, 130
Baffle Tray Extraction, 78
Baffle Tray Performance in Liquid Extraction, 77
Balasubramanian, H.A., 241
Balbuena, P.A., 14
Balbuena, P.B., 304, 307, 310, 316
Bangs, K.M., 78
Bartari, T.A., 249, 250, 251
Bard, A. J., 61
Barlow, J.W., 218
Barnicki, 7
Barnicki, S. D., 37, 137, 139, 140
Barrier Polymers, 146
Barrier Polymers and Structures: Overview, 185
Barron, M.K., 321
Bastow, T.I., 147
Bauer, D.L., 66
Beaudoin, S. P., 98
Becker, Oliver, 75
Behles, J.A., 324
Bennett, G.E., 304, 309, 310
Benzene Sorption from Dilute Aqueous Solutions by Crosslinked Polystyrene/Divinylbenzene Microspheres, 178
Berghmans, S, 237
Bergman, T. L, 24
Betts, D.E., 141, 142, 144
Betts, D.S., 226
Bhargava, P, 317
Biddulph, M, 30
BiGiano, F.A., 141
Billet, R, 26
Binary Isosteric Heats of Adsorption in Carbon Predicted from Density Functional Theory, 14
Bioseparations, 22
Bioseparations - An Assessment of Current Technologies and Future Applications, 22
Bioseparations: An Assessment of Current Technologies and Future Applications, 22
Bishnoi, S, 125
Bishnoi, Sanjay, 119, 122, 124, 125
Blaney, C.A., 337, 345
Blank, M.R., 335
Block Copolymers as Stabilizers in Supercritical Fluids, 320
Boadway, D.A., 326
Bode, A, 79
Bodmeier, R, 311
Bondar, V., 147
Bondar, V.I., 143, 146
Bonnecaze, R.T., 324
Bonnecaze, T.R., 237
Borgwardt, R., 96
Boric Acid Equilibria in Near-Critical and Supercritical Water, 317
Botte, G.G, 13, 15
Bravo, J.L., 25, 26, 29, 30, 31, 33, 37, 40, 48, 67, 136, 137
Bravo, J.L., 58, 76, 77, 78
Broadnax, L.F., 125
Brodmax, Lia F., 122
Brown, J, 321
Brugger, M., 50
Bubble-to-Spray Transition on Sieve Trays, 35
Buchanan, J. E, 27

353
Buffer Additives for Lime/Limestone Slurry Scrubbing: Sulfite Oxidation with Enhanced Oxygen Absorption Catalyzed by Transition Metals, 85

Buffer Additives for Lime/Limestone Slurry Scrubbing: Synthesis, Mass Transfer, and Degradation, 85

Buffer Additives for Limestone Scrubbing: A Review of R&D Results, 84

Burgar, M.I, 147
Burns, K, 208
Burns, R, 208

C

C. Carlier, 313
C. Chiang, 235
C. Cozewith, 32
C. Fischer, 29
C. Gonzalez, 53
C. Haynes, 286
C. Hughes, 307
C. Jorgensen, 113
C. L. Gage, 92
C. L. Martin, 39, 40, 60, 136
C. Lewis, 56
C. Slade, 64
C. Staudt-Bickel, 205
C. T. Little, 64, 67
C. Tran, 212, 213
C.A. Eckert, 283
C.B. Sedman, 113
C.F. Matthews, 340
C.G. Panayiotou, 297, 299
C.J. Han, 307
C.J. Nelson, 178
C.J. You, 218
C.M. Burns, 214
C.W. Jones, 192

Calcium Sulfite Hemihydrate Dissolution and Crystallization Dissolution and Crystallization, 86

Calcium Sulfite Hemihydrate: Crystal Growth Rate and Crystal Habit, 85

Calvo, L, 317
Cao, T, 322, 324
Cao, T.K., 322

Capacity and Efficiency of Reactive Distillation of Bale Packing: Modeling and Experimental Validation, 53

Caplan, Michael R, 235

Carbon Dioxide Absorption and Solution Equilibrium in Piperazine Activated Methylidethanolamine, 124

Carbon Dioxide Absorption in Methylidethanolamine with Piperazine or Diethanolamine: Thermodynamic Modeling and Rate Measurement, 117

Carbon Dioxide Absorption Rates and Physical Solubility in 50% Aqueous Methyldiethanolamine Partially Neutralized with Sulfuric Acid, 93
Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine, 134
Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine, 128
Carbon Dioxide Absorption/Desorption Kinetics in Blended Amines, 107
Carbon Dioxide Conditioning Effects on Sorption and Volume Dilation Behavior for Bisphenol-A-Polycarbonate, 164
Carbon Dioxide Regeneration of Block Copolymer Micelles Used for Extraction and Concentration of Trace Organics, 302
Carbon Dioxide Removal from Natural Gas by Membranes in the Presence of Heavy Hydrocarbons and by Aqueous Diglycolamine®/Morpholine, 129
Carbon Dioxide-in-Water Microemulsions, 321
Carbonization and Activation of Sol-Gel Derived Carbon Xerogels, 15

Carey, T. R., 99
Carolyn E. Schmidt, 280
Carruthers, S.B, 211
Cartmel, D, 79
Cartmel, D.B, 79
Cartmel, Dwight B, 281
Cartmel, Dwight Bradley, 280
Castellanos, H, 323

Catalysis in Supercritical Co2 using Palladium Nonparticles Encapsulated in Dendrimer Nanoreactors, 318
Catalyst Evaluation Supercritical Water Oxidation Process, 342
Catalytic Distillation, 40
Catalyzed Supercritical Water Oxidation of Acetic Acid: Kinetics and Anatase Behavior, 344
Caviness, P.L, 20, 21
Cavity Size Distributions in High Free Volume Glassy Polymers by Molecular Simulation, 147
Ceramic Membrane Characterization via the Bubble Point Technique, 201
Ceramics for Corrosion Resistance in Supercritical Water Environments, 341
Cerrada, R.B, 240
Chakravarti, S., 102

Challenges in Forming Successful Mixed Matrix Membranes with Rigid Polymeric Materials, 208
Chan, P. K., 84, 85
Chang, H.T, 100, 102, 103
Chang, Y, 218
Chapter 1 in Supercritical Fluid Science and Technology, 292, 293
Chapter 24 in Supercritical Fluid Engineering Science-Fundamentals and Applications, 333
Chapter 25 in Supercritical Fluid Engineering Science-Fundamentals and Applications, 332
Chapter 5 in Supercritical Fluid Science and Technology, 293
Characterization of CO2-Induced Conditioning of Polycarbonate Films Using Penetrants with Different Solubilities, 157
Characterization of CO2-Induced Conditioning of Substituted Polycarbonates Using Various "Exchange" Penetrants, 166
Characterization of Dense Sulfonated Polysulfone Membranes, 212
Characterization of Integral-Skin Layers in Hollow Fiber Gas Separation Membranes, 211
Characterization of Membranes for Use in Pressure-Driven Membrane Separation Processes, 213
Characterization of Physical Aging of Poly(methyl methacrylate) Powders by a Novel High-Pressure Sorption Technique, 184
Characterization, Analysis and Modeling of Non-ideal Effects in Polymeric Membrane Based Natural Gas Processing, 203
Chemical Complexing Agents for Enhanced Solubilities in Supercritical Fluid Carbon Dioxide, 295
Chemical-Mechanical Photo Resist Drying in Supercritical Carbon Dioxide with Hydrocarbon Surfactants, 323
Chemistry in Supercritical Water: Insights from Theory and Simulation, 318
Chemistry of Limestone Slurry Scrubbing, 106
Chen H. Shen, 115
Chen, Eric, 130
Chen, H, 20, 21
Chen, P, 337
Chen, X, 320, 321, 322
Chern, R.T., 151, 152
Chi, Susan, 124
Chiang, C.Y, 235
Chiang, Chung-Yuan, 233
Chiou, J.S, 241, 242, 243, 244, 245, 247, 248, 251, 252
Chisholm, P.N., 110, 117
Chisholm, Paul N., 121
Chisholm, Paul Norman, 121
Chlístunoff, J, 316, 319
Chlístunoff, J.B., 316
Chlorine Absorption in S(IV) Solutions, 125
Chlorine Absorption in Sulfite Solutions, 125, 132
Chlorine Absorption in Sulfite Solutions: A Mechanism in Mercury Removal, 125
Chlorine Absorption in Sulfite/Bisulfite Solutions, 123
Chlorine Resistance Studies on Membranes, 148
Cho, D, 320
Chris Lewis, 77
Christopher A. Bode, 280
Chu, C.-S., 7
Chu, P, 88
Chumley, L.J., 217
Chung, Youn Suk, 150
Clark, S. M, 53
Clausi, D.T, 200
Clustering in Supercritical Fluid Mixtures, 287
CO2 Absorption into Aqueous MDEA and MDEA/MEA Solutions, 88
CO2 Absorption into Aqueous Mixtures of Diglycolamine and Methyl diethanolamine, 122, 125
CO2 Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water, 124, 126, 128
CO2 Absorption/Desorption in Methyl diethanolamine Solutions Promoted with Monoethanolamine and Diethanolamine: Mass-Transfer and Reaction Kinetics, 90
CO2 Absorption/Desorption in Mixtures of Methyl diethanolamine with Monoethanolamine or Diethanolamine, 98
Co2 and H2S Thermodynamics and Kinetics in Aqueous Alkanolamines, 123
CO2 Capture Performance of an MEA Pilot Plant, 135
CO2 Desorption from DEA and DEA-promoted MDEA Solutions, 90
CO2-Enhanced Transport of Small Molecules in Thin Films: A Fluorescence Study, 322
CO2-Enhanced Transport of Small Molecules in Thin PMMA Films, 324
Coalescence-Induced Coalescence in Polymeric Membrane Formation, 238
Coalescence-induced Coalescence of Inviscid Droplets in a Viscous Fluid, 237
Coalescence-Induced Coalescence of Inviscid Droplets in a Viscous Fluid, 239
Coaxial Nozzle for Control of Particle Morphology in Precipitation with a Compressed Fluid Antisolvent, 314
Cochran, H.D, 317, 319
Coker, D, 144, 145
Coleman, M.R, 169, 174, 183, 188
Colloid and Interface Science for CO2-Based Pharmaceutical Processes, 322
Combes, J.R, 297, 300
Combs, C., 70
Comments on Measurements of Gas-Induced Polymer Dilation by Different Optical Methods, 155
Commercially Attractive Bioseparation Technology, 22
Compaction of Microporous Membranes Used in Membrane Distillation. I. Effect on Gas Permeability, 230
Comparison of Finite Difference and Control Volume Methods for Solving Differential Equations, 15
Comparison of Gas Permeation in Vinyl and Vinlylene Polymers, 257
Comparison of Mixed and Pure Gas Permeation Characteristics for CO2 and CH4 in Copolymers and Blends Containing Methyl Methacrylate Units, 263
Comparison of Pure and Mixed Gas CO2 and CH4 Permeabilities in Polycarbonate: Effect of Temperature, 183
Comparison of Steady- and Unsteady-State Theories for Multicomponent Diffusion/Reaction in Gas Absorption Processes, 91
Comparison of Three Models for Permeation of CO2/CH4 Mixtures in Poly(phenylene oxide), 184
Composite Carbon Fluid Separation Membranes, 192
Compression Molded Membrane Formation via Thermally Induced Phase Separation, 223
Computer Simulation Study of an SN2 Reaction in Supercritical Water, 304
Concentrated CO2-in-Water Emulsions with Nonionic Polymeric Surfactants, 320
Concentrated Potassium Carbonate/Piperazine/Potassium Carbonate for Enhanced CO2 Capture, 130
Concentrating Dilute Sludge Wastes with High Gradient Magnetic Separation: Breakthrough Experiments and Performance, 18
Condo, P.D., 299, 300, 302, 305, 309
Connelly, R.N, 155
Contacting Mechanisms on a Cocurrent Flow Tray, 49
Continuous Mass-Transfer Processes, 33
Continuous Phase Axial Mixing in Packed Large-Scale Liquid-Liquid Extraction Columns, 75
Continuous-Phase Mixing on Crossflow Extraction Sieve Trays, 83
Continuum Electrostatic Model for Ion Solvation and Relative Acidity of HCl in Supercritical Water, 310
Continuum Electrostatics Model for an SN2 Reaction in Supercritical Water, 309
Control of Thickness and Orientation of Solution-Grown Silicon Nanowires, 317
Controlled CO2 Plasticization of Random Copolymers and Miscible Polymer Blends, 253
Controlled Permeability Polymer Membranes, 174
Cooper, A.I, 307
Copolymers of Poly(-alkyl Acrylates): Synthesis, Characterization, and Monomer Reactivity Ratios, 278
Coprecipitation of Formate with Calcium Sulfite Hemihydrate, 105
Coprecipitation of Organic Acids with Calcium Sulfite Solids, 90
Correlation and Prediction of Gas Permeability in Glassy Polymer Membrane Materials via a Modified Free Volume Based Group Contribution Method, 272
Correlation of Flooding in Packed Columns and the Generalized Pressure-Drop Relation, 27
Correlation of Low-Concentration Organic Solubility in Polymers Using the Principle of Corresponding States, 214
Correlation of Organic Solubility in Poly(vinyl acetate), 215
Correlation of Solubility in Polydimethylsiloxane and Polysiloxylene Systems in Polydimethylsiloxane and Polysiloxylene Systems, 215
Correlation of the Double-Layer Capacitance with the Pore Structure of Sol-Gel Derived Carbon Xerogels, 14
Corrosion Behavior of High-Grade Alloys in the Supercritical Water Oxidation of Sludges, 330
Corrosion Behavior of Three High-Grade Alloys in Supercritical Water Oxidation Environments, 331
Corrosion Resistance of Selected Titanium Alloys Under Supercritical Water Oxidation Conditions, 348
Corsi, R., 76
Costain, C.T., 217
Costello, L.M, 177, 183, 187, 189, 192
Couper, J.R, 60
Crain, N, 337, 342, 343
Crain, N.S, 337
Critchfield, J. E, 88, 90
Critical Floculation Density of Dilute Water-in-CO2 Emulsions Stabilized with Block Copolymers, 322
Critical Fluid Extraction of Hydrocarbons from Oil-Field Brines, 65
Crooks, R. M, 61
Crooks. R.M, 318
Crystallization Kinetics of Polymer Diluent Systems. II. Experimental Verification of Model, 235
Crystallization of Isotactic Polypropylene and Dotriacontane: A Study of Kinetics and Morphology, 221
Cullinane, J. Tim, 126, 128, 130
Cullinane, J.T, 135
Cullinane, Tim J, 133, 134
Current Aspects of Membrane-Based Separation of Gases, 151
Cyclone Performance for the Separation of Solids from Supercritical Water Oxidation Effluents, 339

D

D. C. Dixon, 27
D. E. Klein, 138
D. E. Stroud, 99
D. F. Lawler, 47
D. G. Moosberg, 62, 63
D. R. Lloyd, 214, 215, 218, 220
D. R. Owens, 87
D. R. Paul, 32, 241
D.E. Rayne, 299
D.F. Persico, 244
D.G. Peck, 291, 292
D.H. Ziger, 283, 284

356
Development of a Predictive Model for Limestone Dissolution in Wet FGD Systems, 92
Development of Carbon-Metal Oxide Supercapacitors from Sol-Gel Derived Carbon-Ruthenium Xerogels, 14
Development of Scale-Up Procedures for a Microbial Enzyme, 22
DeVincentis, J.W, 118
DeVincentis, Jr., Joseph W, 120
DeVincentis, Jr., Joseph W, 122
Dhamuka, V.V, 324
Dhoot, S.N, 142, 146, 148
Dickson, J.L, 322, 324
Dickson, J.M, 212, 216
Dielectrically Enhanced Drying, 24
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds, 93
Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide, 206
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques, 204
Diffusion in Polymer Glasses, 207
DiGiano, F.A, 144
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate, 153
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption, 160
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption, 164
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer, 177
Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer, 177
Dinno, M.A, 212
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery, 139
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column, 138
Direct-Contact Heat Transfer in Structured Packings, 44
Dissolution and Crystallization of Calcium Sulfite Platelets, 89
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes, 87
DISTILL: A KEE-Based Distillation Column Sequencing System, 37
Distillation, 25, 35, 41, 47, 59, 60
Distillation and Extraction Videotape, 137
Distillation Column Performance Testing: Continuous and Batch Approaches, 53
Distillation Columns Containing Structured Packing, 37

Dielectrically Enhanced Drying, 24
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds, 93
Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide, 206
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques, 204
Diffusion in Polymer Glasses, 207
DiGiano, F.A, 144
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate, 153
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption, 160
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption, 164
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer, 177
Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer, 177
Dinno, M.A, 212
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery, 139
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column, 138
Direct-Contact Heat Transfer in Structured Packings, 44
Dissolution and Crystallization of Calcium Sulfite Platelets, 89
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes, 87
DISTILL: A KEE-Based Distillation Column Sequencing System, 37
Distillation, 25, 35, 41, 47, 59, 60
Distillation and Extraction Videotape, 137
Distillation Column Performance Testing: Continuous and Batch Approaches, 53
Distillation Columns Containing Structured Packing, 37

Dielectrically Enhanced Drying, 24
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds, 93
Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide, 206
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques, 204
Diffusion in Polymer Glasses, 207
DiGiano, F.A, 144
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate, 153
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption, 160
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption, 164
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer, 177
Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer, 177
Dinno, M.A, 212
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery, 139
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column, 138
Direct-Contact Heat Transfer in Structured Packings, 44
Dissolution and Crystallization of Calcium Sulfite Platelets, 89
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes, 87
DISTILL: A KEE-Based Distillation Column Sequencing System, 37
Distillation, 25, 35, 41, 47, 59, 60
Distillation and Extraction Videotape, 137
Distillation Column Performance Testing: Continuous and Batch Approaches, 53
Distillation Columns Containing Structured Packing, 37

Dielectrically Enhanced Drying, 24
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds, 93
Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide, 206
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques, 204
Diffusion in Polymer Glasses, 207
DiGiano, F.A, 144
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate, 153
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption, 160
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption, 164
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer, 177
Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer, 177
Dinno, M.A, 212
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery, 139
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column, 138
Direct-Contact Heat Transfer in Structured Packings, 44
Dissolution and Crystallization of Calcium Sulfite Platelets, 89
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes, 87
DISTILL: A KEE-Based Distillation Column Sequencing System, 37
Distillation, 25, 35, 41, 47, 59, 60
Distillation and Extraction Videotape, 137
Distillation Column Performance Testing: Continuous and Batch Approaches, 53
Distillation Columns Containing Structured Packing, 37

Dielectrically Enhanced Drying, 24
Differential Reaction of SO2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds, 93
Diffusion and Sorption of Methanol/MTBE in 6FDA-ODA Polyimide, 206
Diffusion in Gas Separation Membrane Materials: A Comparison and Analysis of Experimental Characterization Techniques, 204
Diffusion in Polymer Glasses, 207
DiGiano, F.A, 144
Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicon Rubber and Unconditioned Polycarbonate, 153
Dilation of Silicone Rubber and Glassy Polycarbonates Due to High-Pressure Gas Sorption, 160
Dilation of Substituted Polycarbonates Caused by High-Pressure Carbon Dioxide Sorption, 164
Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer, 177
Dimethylacetamide Sorption Kinetics in a Urethane/Urea/Ether Block Copolymer, 177
Dinno, M.A, 212
Direct Contact Gas-Liquid Heat Exchange for Energy Recovery, 139
Direct-Contact Gas-Liquid Heat Transfer in a Packed Column, 138
Direct-Contact Heat Transfer in Structured Packings, 44
Dissolution and Crystallization of Calcium Sulfite Platelets, 89
Dissolution Rate of Calcium Sulfite Hemihydrate in Flue Gas Desulfurization Processes, 87
DISTILL: A KEE-Based Distillation Column Sequencing System, 37
Distillation, 25, 35, 41, 47, 59, 60
Distillation and Extraction Videotape, 137
Distillation Column Performance Testing: Continuous and Batch Approaches, 53
Distillation Columns Containing Structured Packing, 37
Distillation Contacting Devices: II. CMR #2 Metal Packing, 41
Distillation Contacting Devices: III. Structured Packing-90° Corrugation, 41
Distillation Contacting Devices: IV. Metal Pall Rings -1, 1.5 and 2-inch Size, 41
Distillation Contacting Devices: V. Subcooled Reflux Studies on Structured Packing, 42
Distillation Contacting Devices: VI. Sulzer BX Structure Gauze Packing, 43
Distillation Contacting Devices: VI. Sulzer-BXTM Structured Gauze Packing, 43
Distillation Contacting Devices: VII. Mass-Transfer and Capacity Tests on Single and Double Beds; of No. 2 Structured Packing in Distillation Service, 45
Distillation References, 1995 - August 2000, 59
Distillation Results for Structured Packing, 39
Distillation Sieve Trays Without Downcomers: Prediction of Performance Characteristics, 59
Distillation: Energy Savings and Other Benefits from the Use of High-Efficiency Packings, 33
Distillation: King in Separations, 38
Distillation: Research Needs, 32
Distillation: State-of-the-Art and Future Trends, 58
Distillation: Still Towering over Other Options, 48
Distillation: Whither, Not Whether, 35
Distribution Coefficients and Polymer-Solute Interaction Parameters by Inverse Supercritical Fluid Chromatography, 309
Dixon, D.J., 297, 299, 302, 303, 311
Djoejika, G, 207
Dobbs, J.M, 284, 285, 286
Dorhieri, F, 141, 142, 143
Don't Forget the ChEs Who Really Run Things, 59
Doty, R.C, 317, 318, 320
Dougal, R.A, 20, 21
Droplet Interactions in Water-in-Carbon Dioxide Microemulsions Near the Critical Point: A Small-Angle Neutron Scattering Study, 319
Dry Absorption of HCl and So2 with Hydrated Lime from Humidified Flue Gas, 121
Dry Absorption of Hydrogen Chloride and Sulfur Dioxide by Calcium-Based Sorbents from Humidified Flue Gas, 121
Dry Scrubbing: Fly Ash Recycle, 87
Dual-Mode Analysis of Subatmospheric Pressure CO2 Sorption and Transport in Kapton H(r) Polyimide Film, 152
Dugas, R.E, 135
Dunkley-Timmerman, T, 90, 91
DuPont, A, 320
Dutchuk, Michael J, 120, 122
Dvorak, B, I, 47
Dwight Cartmel, 280

Dynamic Mechanical and Gas Transport
Properties of Blends and Random Copolymers of Bisphenol-A Polycarbonate and Tetramethyl Bisphenol-A Polycarbonate, 260
Dynamic Mechanical Behavior of Polysulfones, 261
Dynamic Rate-based and Equilibrium Models for a Packed Reactive Distillation Column, 282
Dynamic Rate-Based and Equilibrium Models for a Packed Reactive Distillation Column, 80
Dynamic Simulation of a Supercritical Fluid Extraction Process, 66
Dzyacky, G, 78

E

E. Gloyna, 347
E. Kiran, 317, 318, 332, 333
E. S. Roothaan, 104
E.A. O'Rear III, 305
E.D. Seo, 275
E.J. Vandenberg, 263
E.M. Nicolaiewsky, 57
E.S. Finkelshtein, 263
E.S. Sanders, 150, 153
E-00-1, 75
E-00-2, 75
E-00-3, 75
E-01-1, 76
E-01-2, 76
E-01-3, 76
E-01-4, 76
E-01-5, 76
E-01-6, 77
E-01-7, 77
E-01-8, 77
E-01-9, 77
E-02-1, 77
E-02-2, 77
E-03-1, 78
E-04-1, 78
E-04-2, 78
E-04-3, 78
E-05-1, 78
E-05-2, 78
E-05-3, 78
E-06-1, 78
E-06-2, 78
E-07-1, 62
E-07-2, 62
E-07-3, 63
E-07-4, 63
E-07-5, 63
E-08-1, 63
E-08-2, 63
E-09-1, 64
E-09-2, 64
E-09-3, 64
E-09-4, 64

358
Effect of Casting Solvent on the Permeability of Poly (4-methyl-1-pentene), 257

Effect of Column Diameter on Pressure Drop of a Corrugated Sheet Structured Packing, 57

Effect of Condensable Impurities in CO₂/CH₄ Gas Feeds on Carbon Molecular Sieve Hollow-Fiber Membranes, 210

Effect of Crystallinity on Gas Permeation in Miscible Polycarbonate-Copolyster Blends, 241

Effect of Crystallization and Liquid-Liquid Phase Separation on Phase-Separation Kinetics in Poly(ethylene-co-vinyl alcohol)/Glycerol Solution, 239

Effect of Deliquescent Salt Additives on the Reaction of Sulfur Dioxide with Dry Ca(OH)₂, 86

Effect of Extraction and Drying on the Structure of Microporous Polyethylene Membranes Prepared via TIPS, 239

Effect of Film Thickness on the Changes in Gas Permeability of a Glassy Polyarylate Due to Physical Aging: Part I. Experimental Observations, 275

Effect of Film Thickness on the Changes in Gas Permeability of a Glassy Polyarylate Due to Physical Aging: Part II. Mathematical Model, 276

Effect of Fluorocarbon-Hydrocarbon Interactions on Solubility and Permeability Properties of Polymers, 141

Effect of Graphite on the Dehydrogenation and Hydrogenation Kinetics of Ti-Doped Sodium Aluminum Hydride, 21

Effect of Initial Composition Phase Separation Temperature and Polymer Crystallization on the Formation of Microcellular Structures via Thermally Induced Phase Separation, 230

Effect of Isopropylidene Replacement on Gas Transport Properties of Polycarbonates, 258

Effect of Mild Solvent Post-Treatments on the Gas Transport Properties of Glassy Polymer Membranes, 181

Effect of Mixing on Efficiencies for Reactive Tray Contactors, 127

Effect of Nanoparticles on Gas Sorption and Transport in Poly(1–trimethylsilyl-1-propyne), 146

Effect of Orientation on Gas Sorption and Transport in Polysulfone, 245

Effect of Permeation on Gas Sorption and Transport in Polymers, 246

Effect of Initial Composition Phase Separation Temperature and Polymer Crystallization on the Formation of Microcellular Structures via Thermally Induced Phase Separation, 230

Effect of Relative Humidity and Additives on the Reaction of Sulfur Dioxide with Calcium Hydroxide, 87

Effect of Solute Structure on Solute Distribution in Water-Alcohol-Cellulose Acetate Systems, 220, 222

Effect of Structural Modifications on the Gas Transport Properties of Polysulfones and Polycarbonates, 254

Effect of Structural Symmetry on Gas Transport Properties of Polysulfones, 261

Earnest F. Gloyna, 349

Eastoe, J, 320

Ehner, A.D, 14, 15, 16, 17, 18, 19, 20, 21, 22

Ehner, S.A, 20, 21

Eckert, C.A, 283, 284

Edgar, T.F, 79, 80, 282

Edwards, W.M, 80
Effect of Structure on the Temperature Dependence of Gas Transport and Sorption in a Series of Polycarbonates, 192

Effect of Tacticity on Permeation Properties of Poly(methyl methacrylate), 250

Effect of Temperature on Physical Aging of Thin Glassy Polymer Films, 279

Effect of the Polypropylene Type on Polymer Diluent Phase Diagrams and Membrane Structure in Membranes Formed via the TIPS Process. Part 2: Syndiotactic and Isotactic Polypropylenes Produced Using Metallocene Catalysis, 240

Effect of the Polypropylene Type on Polymer-Diluent Phase Diagrams and Membrane Structure in Membranes Formed via the TIPS Process. Part 1: Metallocene and Ziegler-Natta Polypropylenes, 240

Effect of UV Crosslinking and Physical Aging on the Gas Permeability of Thin Glassy Polyarylate Films, 276

Effect of Various Exposure Histories on Sorption and Dilation in a Family of Polycarbonates, 167

Effect of Various Pre-exposure Agents on Methane Sorption and Dilation; in Tetramethyl Polycarbonate, 180

Effect of Viscosity on the Hydraulic performance of a Karr Extractor, 78

Effective Gas/Liquid Contact Area of Packing for CO₂ Absorption/Stripping, 78

Effects of Annealing Below the Glass Transition Temperature on Transport Properties of Three Aromatic Glassy Polymers, 160

Effects of Bromine Substitution on the Physical and Gas Transport Properties of Five Series of Glassy Polymers, 275

Effects of CO₂ Exposure on Gas Transport Properties of Glassy Polymers, 248

Effects of Colloidal Silica Incorporation on Oxygen/Nitrogen Separation Properties of Ceramic-Supported 6FDA-IPDA Thin Films, 197, 201

Effects of Film History on Gas Transport in a Fluorinated Aromatic Polyimide, 158

Effects of Inorganic Salts on Calcium Silicate Sorbents for Flue Gas Desulfurization, 102

Effects of Mechanical Drawing on Gas Transport in an Emulsion Acrylic Multipolymer, 244

Effects of Molecular Orientation and Processing Conditions on Gas Sorption and Transport in Various Polymers, 246

Effects of Molecular Structure and Thermal Annealing Gas Transport in Two Tetramethyl Bisphenol-A Polymers, 158

Effects of Nucleating Agent on Thermally-Induced Phase Separation Membrane Formation, 223

Effects of Orientation on the Transport of d-Limonene in Polypropylene, 193

Effects of Physical Aging on Solubility, Diffusivity, and Permeability of Propane and n-Butane in (Poly(4-methyl-2-pentyne), 148

Effects of Polymide Pyrolysis Conditions on Carbon Molecular Sieve Membrane Properties, 200

Effects of Process Conditions on the Formation of Microporous Membranes via Solid-Liquid Thermally Induced Phase Separation, 233

Effects of Salts on Preparation and Use of Calcium Silicates for Flue Gas Desulfurization, 103

Effects of Sulfur Dioxide Entrainer on the Solubility of Benzoic Acid in Supercritical Carbon Dioxide, 284

Effects of Supercritical Solvents on the Rates of Homogeneous Chemical Reactions, 284, 285

Effects of Supercritical Water on the Destruction of Toxic Organic Wastes and Biological Sludges, 333

Effects of Thermal History on Anisotropic and Asymmetric Membranes Formed by Thermally Induced Phase Separation, 236

Effects of Uniaxial Drawing and Heat-Treatment on Gas Sorption and Transport in PVC, 242

Effects of Uniaxial Drawing and Processing Temperature on Gas Transport in Poly(vinylidene fluoride), 243

Efficiency of a Controlled-Cycle Extractor, 82

Efficiency of Crossflow Sieve Tray Extractors, 82

Efficiency of H₂O₂ and O₂ in Supercritical Water Oxidation of 2,4-Dichlorophenol and Acetic Acid, 326

EL-00-1, 79
EL-00-2, 79
EL-01-1, 79
EL-02-1, 79
EL-02-2, 80
EL-03-1, 80
EL-04-1, 80
EL-04-2, 80
EL-04-3, 81
EL-04-4, 81
EL-04-5, 81
EL-99.1, 79

Eldridge, R. B., 81, 83, 84, 281, 282
Eldridge, R. Bruce, 279, 280
Eldridge, R.B., 80, 81, 280, 281, 282

Electrical Separations, 61

Electrochemistry in High Temperature and Supercritical Water, 289

Electrochemistry in Near-Critical and Supercritical Fluids. 2. Water. Experimental Techniques and the Copper (II) System, 61

Electrochemistry in Near-Critical and Supercritical Fluids. 3. Studies of Br⁻, I⁻, and Hydroquinone in Aqueous Solutions, 61

Electrochemistry in Near-Critical and Supercritical Fluids. 4. Nitrogen Heterocycles, Nitrobenzene, and Solvated Electrons in Ammonia at Temperatures to 150° C, 61

Electrochemistry in Subcritical and Supercritical Water, 284
Electrodialysis of Electrolyte Mixtures on Modified Ion Exchange Membranes (Ion-selective Electrodialysis), 229
Electrogenerated Chemiluminescence of Ge Nanocrystals, 323
Electrolyte Nonrandom Two-Liquid Model for Methyldeethanolamine Solutions, 114
Electrosorption as a Means of Separation, 61
Electrostatic Stabilization of Colloids in Carbon Dioxide: Electrophoresis and Dielectrophoresis, 324
Electrostatically Stabilized Metal Oxide Particle Dispersions in Carbon Dioxide, 324
Elevated Temperature Application of Polymer Hollow-Fiber Membranes, 206
El-Hibri, M.J., 242, 243, 244, 246
Elucidation of the Ion Binding Mechanism in Heterogeneous Carbon Composite Adsorbents, 17
Encapsulation of Protein Nanoparticles into Uniform-Sized Microspheres Formed in a Spinning Oil Film, 324
Endle, J.P, 314
Energetic and Entropic Contributions to Mobility Selectivity in Glassy Polymers for Gas Separation Membranes, 204
Energy Considerations in the Sorptive Removal of Contaminants from Discharge Gases, 8
Energy Consumption in the Destruction of Wastewaters and Sludges by Supercritical Water Oxidation Deep-Shaft Reactors, 331
Energy Performance of Stripper Configurations for CO2 Capture by Aqueous Amines, 135
Energy Recovery by Direct Contact Gas-Liquid Heat Exchange, 138
Energy Savings by Use of Disk/Donut Baffling in Tubular Heat Exchangers, 138
Engineering Aspects of Supercritical Water Oxidation, 338
Enhanced Drug Dissolution Using Evaporative Precipitation into Aqueous Solution, 321
Enhanced Infusion of Gold Nanocrystals into Mesoporous Silica with Supercritical Carbon Dioxide, 324
Enhanced Oxygen Absorption into Bisulfite Solutions Containing Transition Metal Ion Catalysts, 85
Enhancement of Track-etched Membrane Performance via Stretching, 150
Enriching Reflux and Parallel Equalization PSA process for Concentrating Trace Components in Air, 18
Entrainment - Efficiency Effects on Distillation Sieve Trays, 48, 49
Entrainment from Distillation Sieve Trays, 33
Entrainment from Spray Distributors for Packed Columns, 56
Equilibrium Adsorption of Gaseous Volatile Organic Compounds on Activated Carbon, 9
Equilibrium Theory Analysis of a Pressure Swing Adsorption Cycle Utilizing an Unfavorable Langmuir Isotherm 1. Periodic Behavior, 17
Equilibrium Theory Analysis of Dual Reflux PSA for Separation of a Binary Mixture, 19
Equilibrium Theory for Solvent Vapor Recovery by Pressure Swing Adsorption: Analytic solution with Velocity Variation and Gas Phase Capacity, 14
Evaluation of Packed Columns in Supercritical Extraction Processes, 62
Evaluation of Packings for Use in Liquid-Liquid Extraction Processes, 83
Evaluation of Substituted Polycarbonates and a Blend with Polystyrene as Gas Separation Membranes, 248
Evaluation of the Electrode Method for Measuring H2S Vapor Pressure over Alkanolamine Solutions, 88
Evaluation of X-Ray Imaging to Investigate Hydraulic Performance of Vapor-Liquid Contactors, 281
Excited-State Deprotonation of b-Naphthol in Supercritical Water, 309
Experimental Methods for Tracking Physical Aging of Thin Glassy Polymer Films by Gas Permeation, 279
Experimental Procedure Utilizing Head-Space Analytical Method of Obtaining Methanol/MTBE Mixed-Liquid Sorption Isotherms in a Glassy Polymer, 206
Experimental Studies of Dielectric/Convective Drying in Non-Hygroscopic Porous Beds, 24
Extraction, 62
Extraction and Leaching, 78
Extreme Solvent Effects on Reaction Rate Constants at Supercritical Fluid Conditions, 286
Factors Controlling Successful Formation of Mixed-Matrix Gas Separation Materials, 207

Fair, 7
Fair, J., 78
Fair, J. R., 4, 8, 9, 22, 26, 32, 33, 34, 35, 37, 38, 39, 40, 41, 42, 43, 47, 48, 49, 50, 53, 82, 137, 138, 139
Fair, J.F, 59
Fair, J.R, 13, 43, 53, 54, 56, 57, 58, 59, 60, 75, 76, 77, 78, 141
Fair, J.R., 43, 53, 54, 56, 57, 58, 59, 60, 76
Fair, James R, 77
Fanagin, L.W, 315

Factors Controlling Successful Formation of Mixed-Matrix Gas Separation Materials, 207

Fair, 7
Fair, J., 78
Fair, J. R., 4, 8, 9, 22, 26, 32, 33, 34, 35, 37, 38, 39, 40, 41, 42, 43, 47, 48, 49, 50, 53, 82, 137, 138, 139
Fair, J.F, 59
Fair, J.R, 13, 43, 53, 54, 56, 57, 58, 59, 60, 75, 76, 77, 78, 141
Fair, J.R., 43, 53, 54, 56, 57, 58, 59, 60, 76
Fair, James R, 77
Fanagin, L.W, 315
Formation of Water-in-Carbon Dioxide Microemulsions with a Cationic Surfactant: A Small-Angle Neutron Scattering Study, 317

G

G. B. Kitto, 23
G. Bennett, 300
G. Luna-Bárcenas, 304
G. T. Rochelle, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 103, 104, 122
G.B.A. Lim, 225, 227
G.J. McFann, 291, 293
G.K. Fleming, 152, 154, 157, 159, 166, 167, 183, 186
G.L. Tullos, 257
G.R. Husk, 153, 154, 156, 157, 158, 163, 167, 168
G.W. Goldman, 177
Gas Permeation Properties of Poly(1,1’-dihydroperfluoroctylacrylate) (PFOA), Poly(1,1’-dihydroperfluoroctylmethacrylate) (PFOMA) and Poly(styrene-b-FOA) (PS-b-FOA) Copolymers, 142

Gas Permeability and Free Volume Polymers Modified by a Low Molecular Weight Additive, 274

Gas Separation Applications of Miscible Blends of Isomeric Polyimides, 183

Gas Separation Membrane Material Selection Criteria: Differences for Weakly and Strongly Interacting Feed Components, 165

Gas Separation Membrane Material Selection Criteria: Weakly and Strongly Interacting Feed Component Situations, 186

Gas Separation Performance of Poly(4-vinylpyridine)/Polyetherimide Composite Hollow Fibers, 277

Gas Separation Properties of Aromatic Polyimides, 145

Gas Separation Using Polymers, 145

Gas Separations Using Membranes, 150, 151, 154, 161, 249, 252

Gas Solubility, Diffusivity, and Permeability in Poly(ethylene oxide), 146

Gas Sorption and Diffusion within Polymer Crystallites, 252

Gas Sorption and Dilation in Poly(2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene): Comparison of Experimental Data with Predictions of the Nonequilibrium Lattice Fluid Model, 143

Gas Sorption and Permeation in a Series of Aromatic Polyimides in a Series of Aromatic Polyimides, 159

Gas Sorption and Transport in Miscible Blends of Tetramethyl Bisphenol-A Polycarbonate and Polystyrene, 249

Gas Sorption and Transport in Poly(alkyl(meth)acrylate)s. Part II. Sorption and Diffusion Properties, 278

Gas Sorption and Transport in Poly(alkyl(meth)acrylate)s. Part I. Permeation Properties, 278

Gas Sorption and Transport in Poly(tertiary-butyl methacrylate), 273

Gas Sorption and Transport in Semicrystalline Poly(4-methyl-1-pentene), 251

Gas Sorption and Transport in Side-Chain Crystalline and Motlen Poly(octyldecyl acrylate), 277

Gas Sorption and Transport in Substituted Polycarbonates and a Blend with Polystyrene, 249

Gas Sorption and Transport in Substituted Polycarbonates and a Blend with Polystyrene, 247

Gas Sorption and Transport in Substituted Polystyrenes, 252

Gas Sorption and Transport in UV-Irradiated Poly(2,6-dimethyl-1,4-phenylene oxide) Films, 275
Gas Transport Properties of Polycarbonates and Gas Transport Properties of Polyarylates. Part II: Gas Transport Properties of Polymers Based on Gas Transport Properties of Polyarylates Based on

Gas Transport in a Thermotropic Liquid Crystalline Polyester, 247
Gas Transport in Halogen-Containing Aromatic Polycarbonates, 168
Gas Transport in Homogeneous Multicomponent Polymers, 241
Gas Transport in Liquid Crystalline Polymers, 268
Gas Transport in Partially Fluorinated Low-Density Polyethylene, 244
Gas Transport in Polymers Based on Bisphenol-A, 250
Gas Transport in Spirobiindane Polycarbonate, 173
Gas Transport Properties in Amorphous Glassy Polymers and Aging of Thin and Thick Films Made from Amorphous Glassy Polymers, 190
Gas Transport Properties of a Series of Poly(ether ketone) Polymers, 257
Gas Transport Properties of Adamantane-Based Polysulfones, 268
Gas Transport Properties of Aromatic Polyester and Polysulfone Materials, 269
Gas Transport Properties of Bisphenol Polysulfones, 261
Gas Transport Properties of Liquid Crystalline Poly(ethylene terephthalate-co-p-oxbenzoate), 258
Gas Transport Properties of Liquid Crystalline Poly(p-phenyleneterephthalamide), 260
Gas Transport Properties of Liquid Crystalline Polymers, 259
Gas Transport Properties of Poly(2,2,4,4-Tetramethyl Cyclobutane Carbonate), 263
Gas Transport Properties of Poly(3-hydroxyxoytane), 263
Gas Transport Properties of Poly(arylether bisulfone)s and Poly(arylether bisketone), 262
Gas Transport Properties of Polyalrylates Based on 9,9-Bis(4-hydroxyphenyl)anthrone, 269
Gas Transport Properties of Polyalrylates Part I: Connector and Pendant Group Effects, 268, 269
Gas Transport Properties of Polyalrylates Part II: Tetrabromination of the Bisphenol, 270
Gas Transport Properties of Polyalrylates Substituent Size and Symmetry Effects, 270
Gas Transport Properties of Polyalrylates, Part II: Tetrabromination of the Bisphenol, 268
Gas Transport Properties of Polycarbonates and Polysulfones Polycarbonates and Polysulfones with Aromatic Substitutions on the Bisphenol Connector Group, 267
Gas Transport Properties of Polymers Based on Spirobiindane Bisphenol, 194

Gas Transport Properties of Polyphenylene Ethers, 266
Gas Transport Properties of Polysulfone Membrane Materials, 267
Gas Transport Properties of Polysulfones Based on Dihydroxynaphthalene Isomers, 262
Gas Transport Properties of Polysulfones. Part III. Comparison of Tetramethyl Substituted Bisphenols, 259
Gas Transport Properties of Polysulfones. Part I: Role of Symmetry of Methyl Group Placement on Bisphenol Rings, 255
Gas Transport Properties of Polysulfones. Part II. Effect of Bisphenol Connector Groups, 259
Gas Transport Properties of Polysulphones: 1. Role of Symmetry of Methyl Group Placement on Bisphenol Rings, 185
Gas Transport Properties of Thermotropic Liquid Crystalline Copolyesters: I. The Effects of Orientation and Annealing, 260
Gas Transport Properties of Thermotropic Liquid Crystalline Copolyesters: II. The Effects of Copolymer Composition, 260
Gas Transport Properties of Thin Polymeric Membranes in the Presence of Silicon Dioxide Particles, 200
Gas Transport Through Homogeneous and Asymmetric Polyester Carbonate Membranes, 173
Gas Transport through Integral-Asymmetric Membranes: A Comparison to Isotropic Film Transport Properties, 176
Gas-Liquid Contact Area of Random and Structured Packing, 132
Gas-Transport Properties of Polyphenylene Ethers, 264
Gas-Transport Properties of Surface Fluorinated Poly(vinyltrimethylsilane Films and Composite Membranes, 266
Geiszler, V.C, 200
General, 136
General Heuristics for the Design of Catalytic Distillation Columns, 280
General Model for Prediction of Pressure Drop and Capacity of Countercurrent Gas/Liquid Packed Columns, 28
Generalized Correlation for Mass Transfer in Packed Distillation Columns, 25
Generalized Kinetic Model for Wet Oxidation of Organic Compounds, 333
Ghos, J, 79
Gin, D.L., 148
Glass Transition Behavior Including Retrograde Vitrification of Polymers with Compressed Fluid Diluents, 299
Glass Transitions of Polymers with Compressed Fluid Diluents: Type II and III Behavior, 305
Glasscock, D. A., 91, 92, 95, 97, 98
Gleason, C. L., 89, 95, 96
Goyna, E.F., 325, 327, 328, 331, 332, 333, 334, 336, 338, 343, 345, 346, 349
Goemans, Jr., M.G.E., 339

366
Handout for SRP Extraction Study Group Meeting, October 1987, 288
Handout for the Separations Research Program Spring Conference, April 1988, 4, 136, 249, 287
Handouts for the Separations Research Program Spring Conference, April 1989, 29, 221, 253, 290, 325
Handouts for the SRP Extraction Study, 63
Handouts from the Separation Research Program, 66
Handouts from the Separation Research Program Fall Conference, September 1990, 7, 98, 170, 223, 259, 295, 328
Handouts from the Separations Research, 64, 66
Handouts from the Separations Research Program Fall Conference, September 1990, 6, 30, 95, 221, 253, 291
Handouts from the Separations Research Program Fall Conference, September 1990, 31
Handouts from the Separations Research Program Spring Conference, April 1990, 6, 31, 97, 168, 222, 258, 294, 327
Hanrath, T, 320, 323
Haran, B.S, 15
Hardy, R. D., 94
Harrison, K, 305
Hartmann, G, 328
Harvey, R. L, 42
Hasegawa, T, 237
HCL and SO2 Absorption with Calcium Silicate, 121
He, Z, 143, 144, 145, 146
Heat Transfer by Direct Gas-Liquid Contacting, 137
Heat Transfer in a Supercritical Water Oxidation Reactor, 329
Heat Transfer to Water in Countercurrent Flow within a Vertical, Concentric-Tube Supercritical Water Oxidation Reactor, 327
Hellums, M.W, 163, 167, 168, 169, 173, 252
Henriksen, I.B, 319
Henson, M.A., 161, 188
Hermes, J. E., 89
Herron, C. C, 36
HETP and Pressure Drop Prediction for Structured Packing Distillation Columns Using a Neural Network Model, 280
HETP and Pressure Drop Prediction for Structured Packing Distillation Columns Using a Neural Network Model, 79
Hez, X, 141
Hg Absorption in Aqueous Permanganate, 114
High Enrichment and Recovery of Dilute Hydrocarbons by Dual Re reflux Pressure Swing Adsorption, 17
High Gradient Magnetic Separation for the Treatment of High Level Radioactive Wastes, 14
High Internal Phase CO2-in-Water Emulsions Stabilized with a Branched Nonionic Hydrocarbon Surfactant, 324
High Performance Polymer Membranes for Natural Gas Sweetening, 150
High Pressure CO2/CH4 Separation Using Carbon Molecular Sieve Hollow Fiber Membranes, 207
High Yield of Germanium Nanocrystals Synthesized from Germanium Diiodide in Solution, 324
High-Capacity Bubble Columns, 77
Highly Luminous Silicon Nanocrystals with Discrete Optical Transitions, 320
High-Performance Liquid Chromatography Scale-Up for Uracil-DNA Glycosylase Purification, 23
High-Pressure Electrochemical Oxidation of Benzene at a Lead Dioxide Electrode in Aqueous Bisulfate Solutions at 25°C to 250°C, 288
Higuchi, A, 141, 147
Hill, A, 147
Hill, A.J, 142, 143, 144, 145, 146, 147, 149, 150
Hilliard, M.D, 135
Hilliard, Marcus D, 131
Hirata, Y, 141
Hirose, T, 18
Historical Development of Distillation Equipment, 32
H-J. Verschoof, 57
Hoff, K.A, 135
Holland, C.E, 14, 16, 17
Holmes, J.D, 317, 318, 319, 320, 321
Homogeneous, Multicomponent Glassy Polymers as Membranes for Gas Separations, 244
Hong, S.S, 320
Hongyi Dang, 128
Hoshang Eruch Subawalla, 52
Hotta, S, 279
How is Hydrogen Bonding Influenced by Solvent Density? The Spectroscopic Study and Modeling of the Interaction between a Proton Donor and Acceptor from the Gas Phase to Supercritical Fluid States, 305
How Surface Treatment and Geometry Affect the Performance of Structured Packings, 40
Hrnjez, B.J, 290, 292
Hu, J, 320, 321, 322
Huang, C. C., 137, 138
Huang, C.C, 5
Huang, C.-C, 35
Huang, Y, 279
Hufton, J. R., 35, 36
Huggahalli, M, 12
Huggahalli, Madhusudhan, 54
Humphrey, J. L, 31, 67, 69, 82
Humphrey, J.L, 325
Husain, S, 320
Hwang, H.S, 320, 323
Hydration of Isoamylenes in a Catalytic Distillation Column, 51
Hydraulic Study of a Sieve Tray Extractor Operated under High Dispersed to Continuous Flow Conditions, 74
Hydraulic Tests and Performance Evaluation of a Cocurrent Tray for Distillation, 50
Hydraulics and Mass-Transfer Efficiency of a Commercial-Scale Membrane Extractor, 68
Hydrodynamics and Mass Transfer in Spray and Packed Liquid-Liquid Extraction Columns, 63, 82
Hydrodynamics and Mass Transfer in Supercritical Fluid Extraction Columns, 64
Hydrodynamics and Mass Transfer on Three-Phase Distillation Trays, 36
Hydrodynamics of a Section of a Large Sieve Tray Extractor, 84
Hydrolysis and Oxidation of Acetamide in Supercritical Water, 334
Hydrothermal Preparation of High Surface Area Calcium Silicate from Lime and Fly Ash in a Flow Reactor, 110
Hydrothermal Reaction of Lime with Fly Ash to Produce Calcium Silicates for Dry Flue Gas Desulfurization, 106

I. Cabasso, 265
I. Manners, 178
I. Pinnau, 147, 149, 176, 256
I. Trachtenberg, 61
I. Yilgor, 212, 213
I.C. Sanchez, 186, 297, 299, 313, 316
Imizu, T, 141, 147
Improving Ceramic Ultrafiltration Membrane Properties: Gelation of Colloidal Silica in Defects of Alumina Membranes, 180
Improving Hydraulics and Efficiencies with the T-By Sieve Tray, 42
in’t Veld, P.J, 148
Increasing Distillation Column Throughput, 78
Influence of Casting and Curing Conditions on Gas Sorption and Transport in Polyimide Films, 154
Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study, 58
Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study., 74
Influence of Corrugation Geometry on the Performance of Structured Packings: An Experimental Study, 74
Influence of Effective Interfacial Areas in the Operation and Control of Packed Distillation Columns, 30
Influence of Iron (III) Hydroxide on Oil-Water-Separation in Ultrafiltration Systems, 170
Influence of Methanol Conditioning and Physical Aging on Carbon Spin-Lattice Relaxation Times of Poly(1-trimethylsilyl-1-propyne), 147
Influence of Polymer Molecular Weight on Selected Thermodynamic Properties of Polymer/Solvent Systems and the Application of the UNIFAC Theory, 214
Influence of Quench Medium on the Structures and Gas Permeation Properties of Poly(sulfone) Membranes Made by Wet and Dry/Wet Phase Separation, 172
Infrared Spectroscopic Study of Sol-Gel Derived Mixed-Metal Oxides, 16
Innovative Absorber/Stripper Configurations for CO2 Capture for Aqueous Monoethanolamine, 135
Innovative Stripper Configurations to Reduce the Energy Cost of CO2 Capture, 128
In-Situ Investigation on the Mechanism of Dispersion Polymerization in Supercritical Carbon Dioxide, 317
In-Situ Measurement of the Glass Transition Temperature of Polymers with Compressed Fluid Diluents, 302
Interaction Between Organo-Phosphorus Ester and Poly(styrene-co-vinyl benzyl hexafluorodimethyl carbinol), 217
Interaction Parameters of Polyisoprene-Polyisoprene-Toluene Systems at 45°C via Gel Permeation Chromatography, 218
Interfacial Phenomena with CO2-Soluble Surfactants, 319, 322
Interfacial Properties of Fluorocarbon and Hydrocarbon Phosphate Surfactants at the Water-CO2 Interface, 324
Interfacial Studies of the Formation of Microemulsions of Water in Carbon Dioxide with Fluorinated Surfactants, 319
Interfacial Tension of Extractor Test Mixtures, 81
Interfacial Thermodynamics of Surfactants at the CO2-Water Interface, 317
Investigation of Local Scale Phenomena in Vapor Liquid Contactors Using X-Ray Tomography, 280
Investigation of Processing Parameters of Spray Freezing into Liquid to Prepare Polyethylene Glycol Polymeric Particles for Drug Delivery, 321
Investigation of X-Ray Imaging of Vapor-Liquid Contactors 2. Experiments and Simulations of Flows in an Air-Water Contactor, 81
Ion Exchange Processes: Advances and Applications, 229
Ion Hydration in Supercritical Water, 303
Ion Solvation in Supercritical Water Based on Adsorption Analogy, 315
Ion-Containing Polymers. III: Synthesis and Characterization of Sulfonated Poly(arylene Ether Sulfones), 212
Isomer Effects on Transport Properties of Polymers Based on Bisphenol-A, 176
Isomeric Polyimides Based on Fluorinated Dianhydrides and Diamines for Gas Separation Applications, 169
Isomers of Fluorine-Containing Polyimides for Gas Separation Membranes, 174
Isomobal Cry stallization of Isotactic Polypropylene-Hexamethylbenzene Blends: Kinetics Analysis, 235
Isothermal Crystallization of iPP in Dotriacontane. I. Effect of Nucleating Agent Addition on Overall Crystallization Kinetics, 227
Isothermal Crystallization of iPP in Dotriacontane. II. Effect of Nucleating Agent Addition on Growth Rate, 227
Isothermal Crystallization of Isotactic Polypropylene in Dotriacontane. III. Effect of Dilution and Crystallization Temperature on Growth Rate, 229
Isothermal Crystallization of Isotactic Polypropylene in Dotriacontane. IV. Effect of Dilution and Crystallization Temperature on Overall Crystallization Kinetics, 229
Isothermal Crystallization of Isotactic Polypropylene-Hexamethylbenzene Blends: Crystal Morphology, 230
J

J. A. García, 41, 42, 60, 69, 72
J. A. Rocha, 25, 30, 33, 40, 42, 48, 65, 82
J. Arellano, 321
J. B. Riggs, 66
J. C. S. Chang, 87, 88
J. E. Critchfield, 98
J. F. Brennecke, 332, 333
J. Goveas, 305
J. Hyun, 316
J. Jagur-Grodzinski, 171
J. Kampa, 264, 265
J. L. Bravo, 10, 26, 27, 28, 29, 30, 34, 36, 37, 42, 62, 63, 65, 67, 68, 138
J. L. Humphrey, 13, 22, 32, 33, 70, 71, 72, 82, 83, 84, 136
J. M. L. Penninger, 292, 293
J. M. Schork, 4
J. Noriyan, 218
J. R. Fair, 4, 5, 6, 7, 9, 10, 12, 13, 25, 26, 27, 28, 29,
30, 32, 33, 34, 35, 36, 37, 39, 40, 41, 42, 43, 45,
46, 47, 48, 50, 52, 53, 62, 63, 65, 66, 68, 69, 71,
72, 73, 81, 82, 83, 84, 136, 138, 139, 140
J. R. Peterson, 90
J. Romero, 346
J. Smart, 232
J. Stichlmair, 50
J. Tim Cullinane, 128, 130
J. W. Barlow, 32, 218
J. Watts, 38
J. A. Garcia, 43
J. C. Mullis, 263
J. C. Schmidhauser, 173, 187, 194
J.C.S. Chang, 113
J.D. Le Roux, 181
J.E. McGrath, 212, 213, 215
J.E. Sawicki, 336
J.K. Beasley, 157
J.L. Bravo, 328
J.M. Desimone, 316
J.M. Dickson, 211, 214, 216
J.M. Eller, 327, 328
J.M. Prausnitz, 283
J.M. Wong, 284, 285, 286
J.P. Wightman, 212
J.P. Wightman, 213, 215
J.R. Carnes, 175
J.R. Combes, 293, 296, 300, 308
J.R. Fair, 40, 73, 74, 75
J.R. Howell, 329
J.S. McHattie, 252, 261
J.W. Barlow, 214, 219, 220, 241, 242, 245, 276
Kinetics of Carbon Dioxide Absorption/Desorption at Stripper Temperature in Mixtures of Aqueous Methylidithanolamine and Diethanolamine, 107
Kinetics of CO2 Conditioning of Copolymers and Blends Containing MMA Units, 233
Kinetics of Droplet Growth in Liquid-Liquid Phase Separation of Polymer-Diluent Systems: Model Development, 233
Kinney, K, 76, 78
Kinzer, K.E, 212, 213, 215
Kiplinger, C.L, 244
Kister, H.Z, 59
Kitto, G.B, 22, 23
Kocher, R.L, 14
Kodama, A, 18
Kollaja, R, 160
Koresh, J.E, 162, 163, 185
Korgel, B.A, 317, 320, 321, 324
Korikiv, A.P, 142
Koros, W, 150, 151, 152, 153, 154, 157, 165, 174, 185, 186, 192, 198, 203, 208, 209, 210, 211, 278
Koros, W.J, 150, 151, 152, 153, 154, 157, 165, 174, 185, 186, 192, 198, 204, 205, 206, 207, 208, 209, 210, 211, 278
Koros, W.K, 207
Koros, William J, 204
Koros, W.J, 208
Kreutzer, S, 104
Kumar, S.K., 288
Kunesh, J.G, 48
Kurimura, H, 103, 108
Kuse, R.J, 161
Kwak, G, 142, 144

L

L. Davidson, 23
L. Li, 325, 326, 328, 329, 331, 332, 336, 337, 338, 340, 342, 343, 345, 346, 347
L.A. Pessan, 178
L.M. Costello, 182
L.Y. Yen, 235
L-00-1, 237
L-00-10, 239
L-00-2, 237
L-00-3, 237
L-00-4, 237
L-00-5, 238
L-00-6, 238
L-00-7, 238
L-00-8, 238
L-00-9, 239
L-02-1, 239
L-03-1, 239
L-03-2, 240
L-05-1, 240
L-05-2, 240
L-06-1, 240
L-06-2, 240
L-06-3, 240

Kaganoi, S., 117, 125
Kai, T, 149
Kaibel, B, 59, 76, 77
Kalakkunnath, S, 148, 149, 150
Kalika, D.S, 148, 149, 150
Kalithod, V.G, 55
Kamaruddin, H.D, 206
Kaminski, M.D, 20, 21
Kandori, K, 65
Karmaruddin, H.D, 206
Kaul, B.K, 14, 15
Kazama, S, 148
Kazarian, S.G, 305
Keiper, J.S, 324
Kelkar, A.I, 276
Kelkar, A.J, 277
Kelleher, T.C, 43
Kelman, S, 148
Kerry A. Kinney, 23
Kim, C.K, 260
Kim, I, 135
Kim, M-M, 239
Kim, S, 222, 224, 225, 284, 285, 287, 288
Kim, S.S, 222, 224, 225
Kim, T.H, 156, 158, 159, 184
Kind, K.K, 103
Kind, K.K, 105, 109, 110
Kinetic Gravimetric Sorption of Low Volatility Gases and Vapors in Polymers, 146
Kinetic Model for Wet Oxidation of Organic Compounds in Subcritical and Supercritical Water, 333
Kinetics and Reaction Pathways of Pyridine Oxidation in Supercritical Water, 337
Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine, 133
Latexes Formed by Rapid Expansion of Polymer/CO2 Suspensions into Water: 1. Hydrophilic Surfactant in Supercritical CO2, 318

Lattice Fluid Hydrogen Bonding Model a Local Segment Density, 303

Lattice-Fluid Self-Consistent Field Theory of Surfaces with Anchored Chains, 306

Lawler, D.F., 150, 240

Lawson, K.W., 230, 233

Lawson, Kevin W, 234

Laxminarayan, A, 230, 231

Le Roux, J.D, 262, 264, 265, 266

Leach, W.T, 322, 324

Lee Jr., C.T, 321

Lee, D.S, 326, 327, 329, 334

Lee, E.K, 207

Lee, G.D, 320

Lee, H.J, 148

Lee, young Moo, 150

Lemert, R.M, 288, 291, 293, 294, 295

Leroux, D, 144

LeVan, M.D, 15

Lewis, C, 76, 78

Lewis, C.L, 76

Lextrait, S, 79, 80, 282

Lextrait, Sebastian, 282

Li, G, 317, 318, 319

Li, L, 327, 329, 333, 336, 340, 347

Lim, G., 217

Lim, G.B.A., 223, 225, 227, 228

Lim, K.-T, 319

Lim, K.T., 318, 320, 323, 324

Limestone Dissolution in Flue Gas Desulfurization Processes, 85

Limestone Dissolution in Modeling of Slurry Scrubbing for Flue Gas Desulfurization, 96

Limestone Dissolution in Stack Gas Desulfurization, 84

Limestone Dissolution: Effects of pH, CO2, and Buffers Modeled by Mass Transfer, 84

Limestone Slurry Scrubbing for SO2 Emission Control-Modeling and Parameter Estimation, 108

Limestone Slurry Scrubbing-Modeling and Parameter Estimation, 112

Lin, C, 14, 15, 18

Lin, G, 148

Lin, H, 141, 146, 147, 148, 149, 150

Linton, R.W., 144

Lipscomb, G.G, 241

Liqui-Cel(r) Membrane Contactors for Liquid-Liquid Extraction, 72

Liquid Distribution and Mixing in Spray Towers, 31

Liquid Entrainment from Spray Distributors for Packed Columns, 55

Liquid Film Flow and Area Generation in Structured Packed Columns, 57

Liquid Film Transport Characteristics of Textured Metal Surfaces, 36

Liquid Flow over Textured Surfaces. 1. Contact Angles, 54

Liquid Phase Mass Transfer in Spray Contactors, 126, 127

Liquid Phase Mass Transfer in Spray Scrubbers, 125

Liquid Side Mass Transfer Resistance of Structured Packings, 78

Liquid-Liquid Extraction References, 75

Liquid-Liquid Extraction Studies on Semi-Commercial Scale Using Recently Commercialized, 71

Liquid-Liquid Extraction Using Microporous Hollow-Fiber Membranes, 68

Liquid-Liquid Extraction: Possible Alternative to Distillation, 82

Liquid-Phase, 47

Liquid-Phase Adsorption of Aromatic Compounds by Macroperticual PS/DVB Resins: Equilibrium and Dynamics, 8

Liquid-side Mass Transfer Resistance of Structured Packings, 60

Little, C. T, 65, 66, 67, 68

Liu, S, 20, 21

Liu, Y, 14, 15

Lixiong, L, 344

Lloyd, D.R, 150, 211, 213, 214, 215, 220, 222, 224, 237, 238, 239, 240, 241

Local Composition Models for Fluid Mixtures Over a Wide Density Range, 286

Long-Ranged Electrostatic Repulsion and Crystallization of Emulsion Droplets in an Ultralow Dielectric Medium Supercritical Carbon Dioxide, 324

Low Interfacial Free Volume of Stubby Surfactants Stabilizes Water-in-Carbon Dioxide Microemulsions, 323

Lozano, A.E, 145

Lu, X, 320, 323, 324

Lu, Y, 147, 148, 149

Luna-Barcenas, G, 316

Luna-Bárcenas, G, 313

M

M. Aguilar-Vega, 260

M. Babai-Pirouz, 211

M. Beauford, 38

M. Behrens, 57

M. Fang, 316

M. Howard, 151

M. Iqbal, 212, 213

M. J. Hudson, 229
Magnetic Field Orientation and Spatial Effects on the Retention of Paramagnetic Nanoparticles with Magnetite, 18
Magnetic Hetero-Flocculation of Paramagnetic Colloidal Particles, 15
Magnetizable Intraluminal Stent and Functionalized Magnetic Carriers. A Novel Approach for Non-Invasive yet Targeted Drug Delivery, 21
Magnetizable Intraluminal Stent and Functionalized Magnetic Carriers. A Novel Approach for Non-Invasive yet Targeted Drug Delivery, 20
Mahajan, R, 207, 208, 209
Making Nanoscale Materials with Supercritical Fluids, 322
Manuel Pacheco, 123
Mapping the Stability and Curvature of Emulsions of Water and Supercritical Carbon Dioxide with Interfacial Tension, 319
Mark Posey, 123
Martin, C.L, 27, 33, 41, 60, 62
Martula, D.S, 237, 238, 239
Mass Transfer in Beds of Modern High-Efficiency Random Packings, 50
Mass Transfer in Beds of Modern, High-Efficiency Random Packings, 46
Mass Transfer in Gauze Packings, 33
Mass Transfer, Kinetics and Rate-based Modeling of Reactive Absorption, 118
Mass-Transfer and Hydraulic Characteristics of a Supercritical Fluid Sieve Tray Extractor, 81
Mass-Transfer and Hydraulic Operating Characteristics of a Pilot-Plant Scale High-Gravity Contacting Unit, 43
Mass-Transfer Characterization of a Counter-Current Spray Column, 32
Mass-Transfer Efficiencies of Column Contactors in Supercritical Extraction Service, 62
Mass-Transfer Efficiency Modeling of Packed Absorbers and Strippers, 30
Mass-Transfer Efficiency of a Large-scale Sieve Tray Extractor, 69
Mass-Transfer Efficiency of a Large-Scale Sieve Tray Extractor, 75
Mass-Transfer Efficiency of a Supercritical Fluid Extraction Column, 81
Mass-Transfer Efficiency of Sieve Tray Extractors, 83
Mass-Transfer Efficiency of Sieve Tray Liquid-Liquid Extraction Columns, 83
Mass-Transfer in Countercurrent Supercritical Extraction, 83
Mass-Transfer Performance of Structured Packings in Distillation Service, 29
Mass-Transfer Studies in Liquid-Liquid and Supercritical Extraction Devices, 62
Masuda, T, 142, 144, 148, 149
Material Science of Polymeric Membranes, 178
Material Selection and Evaluation for Liquid Separation Membranes, 213
Material Selection Considerations for Gas Separation Processes, 153
Material Selection for Membrane-Based Gas Separation, 151
Mathematical Modeling of Gas Separation Permeators for Radial Crossflow, Countercurrent, and Cocurrent Hollow Fiber Membrane Modules, 201
Mathias, P.M, 283
Matsui, S., 277, 278
Matsuyama, H, 237, 238, 239
Matsuyama, Hideto, 236
Matsuyama, K, 318
Matteucci, S, 149
Matthews, C.F., 331
Matthews, F, 32
Matthews, H, 64
Maurizio, C, 142
Mawson, S, 308, 314, 319
McBrayer, R, 343
McCaig, M.S, 275, 276
McDonald, A. C, 61
McFann, G.J, 298, 301, 302, 306, 308, 313
McGlamery, G, G, 36
McGuire, K.S, 227, 231, 232
Mixed Matrix Membranes using Carbon Molecular Sieves II. Modeling Permeation Behavior, 210
Mixed Polymer-Solvent Thermodynamics by Gel Permeation Chromatography, 212
Mixing Characteristics of a Crossflow Sieve Tray Extractor, 81
Moaddeb, M, 193, 197, 200, 201
Mobile Monitored and Modeling of Ozone and Ozone Precursors in Texas, 120
Model Studies of Evaporation under Combined Microwave and Convective Heating, 24
Modeling and Control of a Packed Distillation Column, 39
Modeling and Experimental Study of Carbon Dioxide Absorption into Aqueous Alkanolamines, 97
Modeling and Simulation of Co-Absorption of Water Vapor and Organic Compounds in Fixed Activated Carbon Beds, 11
Modeling and Simulation of Multicomponent, Nonisothermal Adsorption Cycles for Gas Separations, 7
Modeling CO2 and H2S Solubility in MDEA and DEA: Design Implications, 114
Modeling of a Reactive Distillation Column to Produce Tert-Butyl Methyl Ether, 44
Modeling of CO2 Capture by Aqueous Monoethanolamine, 127
Modeling of Limestone Slurry Scrubbing in Plug Flow and Well-Mixed Contactors, 109
Modeling of Limestone Slurry Scrubbing in Spray Towers with Forced Oxidation, 118, 120, 122
Modeling of Microwave/Convective Evaporation and Drying, 25
Modeling of SO2 Removal by Limestone Slurry Scrubbing: Effects of Chlorides, 85
Modeling of SO2 Removal by Spray Dryers, 86
Modeling of Solute Release from Laminated Matrices, 243
Modeling of the Reaction of SO2 with Ca(OH)2, 88
Modeling of Tray-Type Steam Stripping Columns, 9
Modeling Ozone Formation in a Central Texas Power Plant Plume, 126
Modeling Supercritical Mixtures: How Predictive Is It?, 292
Modeling the Relationship Between Free Volume and Transport in Polymers: Theory and Experiment, 142
Modeling the Solubility of H2S and CO2 in Aqueous Solutions of MDEA and Mixtures of MDEA with MEA and DEA Using the Electrolyte-NRTL Equation, 92
Modeling the Solubility of Solids in Supercritical Fluids with Density as the Independent Variable, 288
Modeling Transport Properties in High Free Volume Glassy Polymers, 147, 149
Modeling, Simulation and Design of Reactive Distillation Columns, 52
Modern Plastic Packing for More Efficient Separation Processes, 26
Modern Plastic Packings for More Efficient Separation Processes, 26
Modification and Characterization of Mass-Transfer Properties of Gamma-Alumina Membranes, 199
Modification of Asymmetric Polysulfone Membranes by Mild Surface Fluorination. Part I. Transport Properties, 264
Modification of Asymmetric Polysulfone Membranes by Mild Surface Fluorination. Part II. Characterization of the Fluorinated Surface, 265
Modification of Polysulfone Gas Separation Membranes by Additives, 274
Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents, 284
Modification of Supercritical Fluids Equilibrium and Selectivity Using Polar and Nonpolar Cosolvents, 286
Moe, M.B, 158, 160
Mogri, Z., 276, 277, 278
Mohammed Awad Al-Juaied, 129
Mohr, J.M, 255, 256, 257
Moher, J.M., 255
Molecular Dynamics Simulation of Electrolyte Solutions in Ambient and Supercritical Water: I. Ion Solvation, 310
Molecular Dynamics Simulation of Electrolyte Solutions in Ambient and Supercritical Water: II. Relative Acidity of HCl, 310
Molecular Interactions in Dilute Supercritical Fluid Solutions, 288
Molecular Simulation of a Chemical Reaction in Supercritical Water, 307
Molecular Thermodynamics at Supercritical Fluid Conditions: Solvent Effects on Reaction Kinetics and Separation Processes, 287
Molecular Thermodynamics of Solubilities in Gas Anti-Solvent Crystallization, 297
Molecular Thermodynamics of Solute-Polymer-Supercritical Fluid Systems, 298
Molecular Thermodynamics of Solvent and Density Effects on Interfaces in Microemulsions and on Colloidal Particles, 301
Molecular Thermodynamics of Steroids and Polyfunctional Organic Solids in Supercritical Fluid Mixtures, 286
Monoethanolamine Degradation: O2 Mass Transfer Effects Under CO2 Capture Conditions, 133
Morehouse, J.A, 150, 240
Morin, R.J., 341
Morisato, A, 141
Mosher, Tyler Jay, 348
Msafiri Mshewa, 123
Mshewa, M. M., 68
Mshewa, M.M, 105, 107
Multicomponent Effects in the Pressure-Driven Membrane Separation of Dilute
Multicomponent Solutions of Nonelectrolytes, 220
Multicomponent Gas Sorption in Glassy Polymers, 150
Multiloop Control of a Pilot-Scale Membrane System for Gas Separations, 188
Murrieta, C.R, 60
Murrieta, C.R, 78
Muruganandam, N, 247, 248, 249
Myung, N, 323
N. Crain, 340
N. E. Burke, 67
N. E. Handler, 27
N. Muruganadam, 252
N.B. Bespalova, 263
N.K. Read, 287
N.R. McCoy, 155
Nagai, K, 141, 142, 144, 147, 148
Nagashima, K, 321
Nakagawa, T, 141, 142
Nanocomposites for Gas Separations, 141
Nanocomposites for Vapor Separation, 144
Nanocomposites Formed from Linear Low Density Polyethylene and Organoclays, 279
Nanocrystal and Nanowire Synthesis and Dispersibility in Supercritical Fluids, 323
Nanocrystal Arrested Precipitation in Supercritical Carbon Dioxide, 320
Nanoparticle Engineering Processes for Enhancing the Dissolution Rates of Poorly Water Soluble Drugs, 322
Narasimhan, V, 214
NASA Project-Permeation Studies, 161
Natural Gas Permeation in Polyimide Membranes, 278
Navratil, J.D, 14, 16
Nelli, Christopher H, 117
Nelli, C.H, 108, 111, 114
Neural Network Modeling of Structured Packing Height Equivalent to a Theoretical Plate, 79, 281
Neutralization of Acids and Bases in Subcritical and Supercritical Water: Acetic Acid and HCl, 314
New Analytical Solution for Nonlinear Adsorption and Diffusion in a Single Particle, 17
New Approximate Model for Nonlinear Adsorption and Concentration Dependent Surface Diffusion in a Single Particle, 13
New Correlation for the Capture Cross Section in High Gradient Magnetic Separation, 16
New Developments and Opportunities in Distillation, Absorption, and Extraction, 54
New Developments in Modeling Distillation and Other Separation Processes, 37
New Dimensions in Distillation, 69
New Directions in Supercritical Fluid Science and Technology, 292
New Energy Efficient Method for Cleaning Oilfield Brines with Carbon Dioxide, 68
New Magnetic Field Enhanced Process for the Treatment of Aqueous Wastes, 14
New Methodology for the Measurement and Analysis of Adsorption Dynamics. Butane on Activated Carbon, 20
New Model for Nonlinear Adsorption and Diffusion Based on a Quartic Concentration Profile Approximation, 18
New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration, 20
New Theoretical Correlation for the Capture Cross Section in High Gradient Magnetic Separation, 15
Nicolaiwewsky, Elioni M.A, 54
Ni-Composite Microencapsulated Graphite as the Negative Electrode in Lithium-Ion Batteries I. Initial Irreversible Capacity Study, 15
Ni-Composite Microencapsulated Graphite as the Negative Electrode in Lithium-Ion Batteries II. Electrochemical Impedance and Self-Discharge Studies, 15
Nitrogen Dioxide Absorption and Sulfide Oxidation in Aqueous Sulfide, 120
Nitrogen Dioxide Absorption and Sulfite Oxidation in Aqueous Sulfite, 115
Nitrogen Dioxide Absorption in Aqueous Dithionite, 120, 122
Nitrogen Dioxide Absorption in Aqueous Sodium Sulfite, 115
Nitrogen Dioxide Absorption in Limestone Slurry for Flue Gas Desulfurization, 112
Nitrogen Dioxide Reaction with Alkaline Solids, 111, 114
Nitrogen Dioxide Removal by Advocate Solids, 108
Nitrogen Dioxide Removal by Hydrated Lime with SO2 Present, 111
NMR Studies of Water Transport and Proton Exchange in Water-in-Carbon Dioxide Microemulsions, 321
Nonisothermal Crystallization of iPP in Dotriacontane iPP in Dotriacontane. I. Effects of the, 228
Nonisothermal Crystallization of iPP in Dotriacontane iPP in Dotriacontane. II. Effect of Dilution, Cooling Rate, and Nucleating Agent Addition on Growth Rate, 228
Nonpolar Cosolvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide, 285
Novel Block Copolymers as Nanofiltration Materials, 144
Novel Enriching PVSA Cycle for the Production of Nitrogen from Air, 22
Novel Separations, 279
Novel Technique to Measure Equilibria of Supercritical Solvents and Liquid Mixtures, 138
Novel Techniques for the Enhanced Utilization of Ca(OH)2 under Duct Injection Conditions, 99
Nucleation and Crystal Growth of Calcium Sulfite Hemihydrate, 95, 96
Palladium Microencapsulated Graphite as the Negative Electrode in Li-Ion Cells, 15
Pan, H, 14
Parametric Analysis of Thermal Regeneration of Adsorption Beds, 4
Parametric Analysis of Thermal Swing Cycle for Multicomponent Adsorption, 5
Part 1: Characterization of Ultramicroporous Carbon Membranes with Humidified Feeds, 191
Part 1: Ultramicroporous Carbon Membranes Produced from a Polyimide Precursor, 190
Part 2: Carbon Composite Membranes A Solution to Adverse Humidity Effects, 191
Part 2: Effects of Organic Contamination on Ultramicroporous Carbon Membranes, 191
Permeability of Carbon Dioxide at Elevated Pressures in Substituted Polycarbonates, 166
Permeability of Pure and Mixed Gases in Silicone Rubber at Elevated Pressures, 164
Permeation and Diffusion, 149
Permeation of Pure and Mixed Gases through Polymeric Membranes Based on Bisphenol-A, 249
Permeation of Several Gases through Elastomers, with Emphasis on the Deuterium/Hydrogen Pair, 175
Pervaporation Separation of Aromatic/Aliphatic Hydrocarbons by Crosslinked (Methyl Acrylate-co-acrylic Acid) Membranes, 277
Pervaporative Extraction of Volatile Organic Compounds from Aqueous Systems with Use of a Tubular Transverse Flow Module. Part II. Experimental Results, 237
Pervaporative Introduction of Organic Vapors into High-Pressure Gas Feeds, 207
Peschek, S.C, 177, 180
Pessan, L.A, 176, 178, 189, 194
Peterson, J. R, 89, 92, 95
Peterson, J.R., 106
Pfennig, J.L.G, 244
Pfennig, K.H, 176, 183, 190, 194
Pham, J.Q., 323
Phase Behavior (J-94-13) of Nonionic Surfactant/Oil/Water Systems Containing Light Alkanes, 308
Phase Behavior of Di-2-Ethylhexyl Sodium Sulfoseuccinate Microemulsions in Compressible Liquids, 298

Potential Energy Savings by Using Alternative Technologies for the Separation of Fluid Mixtures, 136
Prabhakar, R, 141, 144, 145, 147, 149
Practical Modeling of Metal Hydride Hydrogen Storage Systems, 19
Prado, M., 34, 35
Predictability and Effect of Phase Behavior of CO2/Propylene Carbonate in Supercritical Fluid Chromatography, 299
Prediction of Mass-Transfer Efficiencies and Pressure Drop for Structured Tower Packings in Vapor/Liquid Service, 34
Prediction of Point Efficiencies on Sieve Trays. 1. Binary Systems, 32
Prediction of Point Efficiencies on Sieve Trays. 2. Multicomponent Systems, 32
Prediction of the Trayed Distillation Column Mass-Transfer Performance by Neural Networks, 80
Prediction of Vapor and Liquid Equilibria for Sparingly Soluble VOCs in Water, 26
Preliminary Distillation Mass-Transfer and Pressure-Drop Results Using a Pilot Plant Scale High-Gra^

Pressure Drop in High-Efficiency Structured Packings, 37
Pressure Drop in Packed Distillation Columns: Evaluation of Predictive Models, 77
Pressure Drop in Structured Packing, 50
Pressure Drop in Structured Packings, 25
Pressure Swing Adsorption Cycles for Improved Solvent Vapor Enrichment, 14
Pressure Swing Adsorption-Solvent Vapor Recovery-III: Comparison of Simulation with Experiment for the Butane-Activated Carbon System, 14
Pressure Tuning of Chemical Reaction Equilibria in Supercritical Fluids, 290
Pressure Tuning of Reverse Micelles for Adjustable Solvation of Hydrophiles in Supercritical Fluids, 293
Pressure-Drop Tests for 1.25-in. Jaeger Plastic Packing, 40
Preston, W.E, 241
Process Tomography: An Option for the Enhancement of Packed Vapor-Liquid Contactor Model Development, 280
Process Tomography: An Option for the Enhancement of Packed Vapor-Liquid Contactor Model Development, 79
Processes for Removing Acid Components from Gas Streams, 113
Production of Calcium Silicate Reagent from Fly Ash and Ca(OH)2, 92
Production of Lime/Fly Ash Absorbents for Flue Gas Desulfurization, 95
Propane and Propylene Sorption in Solid Polymer Electrolytes Based on Poly(ethylene oxide) and Silver Salts, 142
Properties of Concentrated Aqueous Potassium Carbonate/Piperazine for CO2 Capture, 128
Propylene/1-hexene Copolymer as a Tailor-Made Polypropylene for Membrane Preparation via the Thermally Induced Phase Separation (TIPS) Process, 240
Psathas, P, 317, 318, 319, 320, 321
Psathas, P.A, 317, 318, 319, 320, 321
Puleo, A.C, 251, 252
Punsalan, D, 207
Pure Gas and Vapor Permeation Properties of Poly(1-phenyl-2-[p-(trimethylsilyl)phenyl]acetylene) (PTMSDPA) and Its Desalinated Analog, Poly[diphenylacetylene](PDPA), 148
Pushing the Limits on Possibilities for Large Scale Gas Separation: Which Strategies?, 205
Puziy, A.M, 17
Pyrolytic Carbon Membranes for Air Separations, 203
Q. Cao, 316
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Q. Ye, 225</td>
<td>R-02-7, 127</td>
</tr>
<tr>
<td>Quijada, R, 240</td>
<td>R-02-8, 128</td>
</tr>
<tr>
<td>R. A. Koort, 67</td>
<td>R-03-1, 128</td>
</tr>
<tr>
<td>R. Bruce Eldridge, 280</td>
<td>R-03-2, 128</td>
</tr>
<tr>
<td>R. E. Moser, 92, 104</td>
<td>R-03-3, 128</td>
</tr>
<tr>
<td>R. E. Prada, 85</td>
<td>R-04-1, 129</td>
</tr>
<tr>
<td>R. Hardy, 75</td>
<td>R-04-10, 132</td>
</tr>
<tr>
<td>R. J. Smith, 85</td>
<td>R-04-11, 132</td>
</tr>
<tr>
<td>R. Kohn, 183</td>
<td>R-04-12, 132</td>
</tr>
<tr>
<td>R. L. De Sonier, 27</td>
<td>R-04-13, 133</td>
</tr>
<tr>
<td>R. L. Harvey, 9, 47</td>
<td>R-04-14, 133</td>
</tr>
<tr>
<td>R. Macías, 65</td>
<td>R-04-2, 130</td>
</tr>
<tr>
<td>R. Macías, 42</td>
<td>R-04-3, 130</td>
</tr>
<tr>
<td>R. Mahajan, 205</td>
<td>R-04-4, 130</td>
</tr>
<tr>
<td>R. N. Ruiz-Alsop, 88</td>
<td>R-04-5, 131</td>
</tr>
<tr>
<td>R. Perrotta, 64</td>
<td>R-04-6, 131</td>
</tr>
<tr>
<td>R. S. Schechter, 65</td>
<td>R-04-7, 131</td>
</tr>
<tr>
<td>R.A. Bodmeier, 299</td>
<td>R-04-8, 131</td>
</tr>
<tr>
<td>R.A. Fuller, 293</td>
<td>R-04-9, 132</td>
</tr>
<tr>
<td>R.B. Gupta, 305</td>
<td>R-05-1, 133</td>
</tr>
<tr>
<td>R.C. Eberhart, 213</td>
<td>R-05-10, 135</td>
</tr>
<tr>
<td>R.C. Schucker, 237</td>
<td>R-05-11, 135</td>
</tr>
<tr>
<td>R.D. Chebotareva, 229</td>
<td>R-05-2, 133</td>
</tr>
<tr>
<td>R.J. Lagow, 244, 256, 257, 264, 265, 321</td>
<td>R-05-3, 134</td>
</tr>
<tr>
<td>R.J. Lahiere, 284</td>
<td>R-05-4, 134</td>
</tr>
<tr>
<td>R.K. Abukhadra, 181</td>
<td>R-05-5, 134</td>
</tr>
<tr>
<td>R.L. Nolen, 175</td>
<td>R-05-6, 135</td>
</tr>
<tr>
<td>R.M. Lemert, 291, 293, 309, 312</td>
<td>R-05-7, 135</td>
</tr>
<tr>
<td>R.N. McBrayer, 338</td>
<td>R-05-8, 135</td>
</tr>
<tr>
<td>R.S. Pearman, 264</td>
<td>R-05-9, 135</td>
</tr>
<tr>
<td>R.S. Schechter, 181, 193, 195, 198, 199, 202, 296</td>
<td>R-06-1, 135</td>
</tr>
<tr>
<td>R.T. Bonnecaze, 239</td>
<td>R-06-2, 135</td>
</tr>
<tr>
<td>R.T. Chern, 152</td>
<td>R-06-3, 135</td>
</tr>
<tr>
<td>R.T. Reynolds, 336</td>
<td>R-06-4, 136</td>
</tr>
<tr>
<td>R.Y.M. Huang, 214</td>
<td>R-06-5, 136</td>
</tr>
<tr>
<td>R-00-1, 123</td>
<td>R-82-1, 84</td>
</tr>
<tr>
<td>R-00-2, 123</td>
<td>R-82-2, 84</td>
</tr>
<tr>
<td>R-00-3, 123</td>
<td>R-82-3, 84</td>
</tr>
<tr>
<td>R-00-4, 124</td>
<td>R-83-1, 85</td>
</tr>
<tr>
<td>R-00-5, 124</td>
<td>R-83-2, 85</td>
</tr>
<tr>
<td>R-01-10, 125</td>
<td>R-83-3, 85</td>
</tr>
<tr>
<td>R-01-11, 125</td>
<td>R-84-1, 85, 86</td>
</tr>
<tr>
<td>R-01-12, 125</td>
<td>R-84-2, 85</td>
</tr>
<tr>
<td>R-01-13, 125</td>
<td>R-84-3, 85</td>
</tr>
<tr>
<td>R-01-14, 126</td>
<td>R-84-4, 85</td>
</tr>
<tr>
<td>R-01-15, 126</td>
<td>R-84-5, 86</td>
</tr>
<tr>
<td>R-01-2, 124</td>
<td>R-84-6, 86</td>
</tr>
<tr>
<td>R-01-3, 124</td>
<td>R-84-7, 86</td>
</tr>
<tr>
<td>R-01-4, 125</td>
<td>R-85-1, 86, 87</td>
</tr>
<tr>
<td>R-01-5, 125</td>
<td>R-85-2, 86</td>
</tr>
<tr>
<td>R-01-6, 125</td>
<td>R-85-3, 86, 87</td>
</tr>
<tr>
<td>R-01-7, 125</td>
<td>R-85-4, 86</td>
</tr>
<tr>
<td>R-02-1, 126</td>
<td>R-85-5, 87</td>
</tr>
<tr>
<td>R-02-2, 126</td>
<td>R-85-6, 86, 87</td>
</tr>
<tr>
<td>R-02-3, 126</td>
<td>R-85-7, 87</td>
</tr>
<tr>
<td>R-02-4, 127</td>
<td>R-85-8, 87</td>
</tr>
<tr>
<td>R-02-5, 127</td>
<td>R-86-1, 87</td>
</tr>
<tr>
<td>R-02-6, 127</td>
<td>R-86-2, 86, 87</td>
</tr>
<tr>
<td></td>
<td>R-86-3, 87</td>
</tr>
<tr>
<td></td>
<td>R-86-4, 87, 88</td>
</tr>
<tr>
<td></td>
<td>R-86-5, 88, 90</td>
</tr>
<tr>
<td></td>
<td>R-86-6, 88, 90</td>
</tr>
<tr>
<td>Reference</td>
<td>Page</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
</tr>
<tr>
<td>R-86-7</td>
<td>88</td>
</tr>
<tr>
<td>R-87-1</td>
<td>88, 90</td>
</tr>
<tr>
<td>R-87-10</td>
<td>90</td>
</tr>
<tr>
<td>R-87-11</td>
<td>90</td>
</tr>
<tr>
<td>R-87-2</td>
<td>88</td>
</tr>
<tr>
<td>R-87-3</td>
<td>89</td>
</tr>
<tr>
<td>R-87-4</td>
<td>89</td>
</tr>
<tr>
<td>R-87-5</td>
<td>89</td>
</tr>
<tr>
<td>R-87-6</td>
<td>89</td>
</tr>
<tr>
<td>R-87-7</td>
<td>89, 90</td>
</tr>
<tr>
<td>R-87-8</td>
<td>89</td>
</tr>
<tr>
<td>R-87-9</td>
<td>88, 90</td>
</tr>
<tr>
<td>R-88-1</td>
<td>90</td>
</tr>
<tr>
<td>R-88-2</td>
<td>90</td>
</tr>
<tr>
<td>R-88-3</td>
<td>90</td>
</tr>
<tr>
<td>R-88-4</td>
<td>91</td>
</tr>
<tr>
<td>R-88-5</td>
<td>91</td>
</tr>
<tr>
<td>R-88-6</td>
<td>91</td>
</tr>
<tr>
<td>R-89-1</td>
<td>91</td>
</tr>
<tr>
<td>R-89-10</td>
<td>93</td>
</tr>
<tr>
<td>R-89-11</td>
<td>94</td>
</tr>
<tr>
<td>R-89-12</td>
<td>94</td>
</tr>
<tr>
<td>R-89-13</td>
<td>94</td>
</tr>
<tr>
<td>R-89-14</td>
<td>95</td>
</tr>
<tr>
<td>R-89-15</td>
<td>95</td>
</tr>
<tr>
<td>R-89-2</td>
<td>96</td>
</tr>
<tr>
<td>R-89-3</td>
<td>96</td>
</tr>
<tr>
<td>R-89-4</td>
<td>96</td>
</tr>
<tr>
<td>R-89-5</td>
<td>96</td>
</tr>
<tr>
<td>R-89-6</td>
<td>96</td>
</tr>
<tr>
<td>R-89-7</td>
<td>97</td>
</tr>
<tr>
<td>R-89-8</td>
<td>97</td>
</tr>
<tr>
<td>R-89-9</td>
<td>97</td>
</tr>
<tr>
<td>R-89-10</td>
<td>98</td>
</tr>
<tr>
<td>R-90-1</td>
<td>98</td>
</tr>
<tr>
<td>R-90-2</td>
<td>98</td>
</tr>
<tr>
<td>R-90-3</td>
<td>98</td>
</tr>
<tr>
<td>R-90-4</td>
<td>98</td>
</tr>
<tr>
<td>R-90-5</td>
<td>98</td>
</tr>
<tr>
<td>R-90-6</td>
<td>98</td>
</tr>
<tr>
<td>R-90-7</td>
<td>98</td>
</tr>
<tr>
<td>R-90-8</td>
<td>98</td>
</tr>
<tr>
<td>R-90-9</td>
<td>98</td>
</tr>
<tr>
<td>R-91-1</td>
<td>98</td>
</tr>
<tr>
<td>R-91-2</td>
<td>99</td>
</tr>
<tr>
<td>R-91-3</td>
<td>99</td>
</tr>
<tr>
<td>R-91-4</td>
<td>99</td>
</tr>
<tr>
<td>R-91-5</td>
<td>99</td>
</tr>
<tr>
<td>R-92-1</td>
<td>100</td>
</tr>
<tr>
<td>R-92-2</td>
<td>100</td>
</tr>
<tr>
<td>R-92-3</td>
<td>100, 101</td>
</tr>
<tr>
<td>R-92-4</td>
<td>101</td>
</tr>
<tr>
<td>R-92-5</td>
<td>101</td>
</tr>
<tr>
<td>R-92-6</td>
<td>102</td>
</tr>
<tr>
<td>R-92-7</td>
<td>102</td>
</tr>
<tr>
<td>R-92-8</td>
<td>102</td>
</tr>
<tr>
<td>R-92-9</td>
<td>103</td>
</tr>
<tr>
<td>R-93-1</td>
<td>103</td>
</tr>
<tr>
<td>R-93-2</td>
<td>103</td>
</tr>
<tr>
<td>R-93-3</td>
<td>104</td>
</tr>
<tr>
<td>R-93-4</td>
<td>104</td>
</tr>
</tbody>
</table>

**Radial Cross Flow Hollow-Fiber Membrane Extraction**

Raharjo, R, 147, 148

Ramachandran, B, 66

Ramos, G, 211
Rapid Dissolution of High Potency Danazol Particles Produced by Evaporative Precipitation into Aqueous Solution, 322
Rapid Dissolving High Potency Danazol Powders Produced by Spray Freezing into Liquid Process, 322
Rapid Expansion from Supercritical to Aqueous Solution to Produce Submicron Suspensions of Water-Insoluble Drugs, 319
Rapid Release Tablet Formulation of Micronized Danazol Powder Produced by Spray Freezing into Liquid (SFL), 322
RATE Program for Tray or Packed Column Rating or Design, 42
Rate-Based Modeling of Acid Gas Absorption and Stripping Using Aqueous Alkanolamine Solutions, 99
Rate-Based Modeling of Reactive Absorption of CO2 and H2S into Aqueous Methyldiethanolamine, 116
RATESTRIIP Program for Designing Tray or Packed Columns for Stripping & Absorption, 47
Rathkamp, P. J, 62, 81
Raymond, P.C., 253, 254, 263
RB-00-1, 280
RB-00-2, 281
RB-00-3, 281
RB-01-1, 281
RB-02-1, 282
RB-02-2, 282
RB-02-3, 282
RB-02-4, 282
RB-03-1, 282
RB-04-1, 279
RB-98-1, 279
RB-99-1, 280
RB-99-2, 280
RB-99-3, 280
RB-99-4, 280
RB-99-5, 280
Reaction of SO2 with Ca(OH)2 and CaO; at 100 to 800°C, 94
Reactions and Synthesis in Microemulsion and Emulsions in Carbon Dioxide, 319
Reactions of Inorganic Nitrogen Species in Supercritical Water, 338
Reactions of Nitrate Salts with Ammonia in Supercritical Water, 348
Reboilers, 43, 137
Recovery of Organics from Aqueous Solution: An Alternate Approach Using Polymeric Sorbents, 199
Reeves, Bobby, 60
Reformulation of the Solution-Diffusion Theory of Reverse Osmosis, 278
Reine, T.A, 80, 81
Relationship between Gas Separation Properties and Chemical Structures in a Series of Aromatic Polyimides, 156
Relationship Between Substructure Resistance and Gas Separation Properties of Defect-Free Integrally Skinned Asymmetric Membranes, 172
Relaxation Characteristics of Crosslinked Poly(ethylene glycol) Diacrylates and Their Relation to Gas Transport Properties, 148
Removal of Acid Gas Components from Coal-Derived Syngas using Novel, Reverse-Selective Membranes, 144
Removal of Cyclic Hydrocarbons, 213
Removal of Hydrocarbons from Oil-Field Brines by Flocculation with Carbon Dioxide, 67
Removal of Petroleum Hydrocarbons from Oil-Field Brines with Carbon Dioxide, 66, 67
Removal of SO2 and NOx from Stack Gas by Reaction with Calcium Hydroxide Solids, 88
Removal of Suspended and Dissolved Hydrocarbons from Water by the Use of Carbon Dioxide, 67
Removal of Volatile Organic Compounds from Aqueous and Vapor Streams Using Polymeric Sorbents: Friedel-Crafts Modified Polystyrene, 196
Removal of Volatile Organics from Water by Membrane Distillation, 226
Research and Development of a Commercial Supercritical Water Oxidation Process, 343
Research Group Report Handout for SRP Membrane Study Group Meeting, October 1987, 159
Research -Handout for SRP Membrane Study Group Meeting, October 1984, 242
Research Needs for Acid Gas Kinetics and Equilibria in Alkanolamine Systems, 100
Research Needs for CO2 Capture from Flue Gas by Aqueous Absorption Stripping, 125
Research Results for CO2 Capture from Flue Gas by Aqueous Absorption/Stripping, 126
Research-Handout for SRP Membrane Study Group Meeting, May 1984, 241
Research-Handout for SRP Membrane Study Group Meeting, October 1986, 247
Research-Handout for the SRP Membrane Study Group Meeting, October 1985, 244
Response to Comments by Vrentas, Duda and Ling, 251
Results of a Laboratory Investigation to Characterize Coprecipitation of Wet Limestone Flue Gas Desulfurization System Additives in Calcium Sulfite Crystals, 104
Retention by Electrical Field-Flow Fractionation of Anions in a New Apparatus with Annular Porous-Vycor(r)-Glass Channels, 61
Retention of Iron Oxide Particles by Stainless Steel and Magnetite Magnetic Matrix Elements in High Gradient Magnetic Separation, 19
Retention of Paramagnetic Particles by Magnetite Particle Clusters with Multifunctional Character, 19
Retrofitting Distillation Columns for Maximum Energy Efficiency, 31
Retrograde Vitrification in CO₂/Polystyrene Thin Films, 323
Retrograde Vitrification of Polymers with Compressed Fluid Diluents: Experimental Confirmation, 300
Reverse Micelles in Supercritical Fluids. 2. Fluorescence and Absorption Spectral Probes of Adjustable Aggregation in the Two-Phase Region, 291
Reverse Micelles in Supercritical Fluids. 3. Amino Acid Solubilization in Ethane and Propane, 293
Reverse Micelles, Recovery of Proteins and Amino Acids from Reverse Micelles by Dehydration with Molecular Sieves, 307
Reverse Osmosis of Multicomponent Electrolyte Solutions Part I. Theoretical Development, 235
Reverse Osmosis of Multicomponent Electrolyte Solutions Part II. Experimental Verification, 235
Reverse Osmosis Transport Phenomena in the Presence of Strong Solute-Membrane Affinity, 216
Reverse Permselectivity of N₂ over CH₄ in Aromatic Polyimides, 156
Reverse-Selective Membranes for Hydrogen Purification, Polymer Preprints, 146
Reverse-selective Polymeric Membranes for Hydrogen Purification, 147
Review of Supercritical Fluid Technology at The University of Texas at Austin, 287
Reynolds, S.P., 20, 22
Rezac, M.E, 171, 181, 182, 190, 194, 195, 196
Richard L. Corsi, 23
Rietfort, T, 59, 76, 77
Riggs, J. B, 38
Rojas, A.H, 333
Ritter, J.A, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22
Ritter, J.A., 22
Ritter, J.A, 13
Robledo-Muniz, J.G., 212, 215
Rocha, J. A, 10, 30, 45, 63, 83
Rocha, J. Antonio, 75
Rocha, S.R.P, 317, 322
Rocha, T, 78
Rocha-Uribe, J.A, 60
Rochelle, G., 78, 84, 85, 87, 88, 90, 93, 99, 100
Rochelle, G.T, 113, 114, 125, 126, 127, 128, 132, 133, 134, 135, 136
Rochelle, G.T., 135
Rochelle, Gary, 123, 126
Rochelle, Gary T, 123
Rochelle, R.T, 135
Rochelle, T, 78
Rodriguez, J. N, 42
Rogers, T.L, 320, 321
Roles of Surface Heterogeneity and Lateral Interactions on the Isosteric Heat of Adsorption and Adsorbed Phase Heat Capacity, 13
Roman, I, 147, 150
Roothaan, E.S., 105
Rosengart, A.J, 20, 21
Roschke, P.J., 317, 318, 319, 320
Roudman, A, 144
Roy, S, 125
Roy, Sharmi, 127
Roy, Sharmistha, 123, 132
RT-00-1, 13
RT-00-10, 14
RT-00-11, 14
RT-00-12, 14
RT-00-13, 14
RT-00-14, 14
RT-00-15, 15
RT-00-2, 13
RT-00-3, 13
RT-00-4, 13
RT-00-5, 14
RT-00-6, 14
RT-00-7, 14
RT-00-8, 14
RT-00-9, 14
RT-01-02, 15
RT-01-03, 15
RT-01-04, 15
RT-01-05, 15
RT-01-06, 15
RT-01-07, 15
RT-01-08, 15
RT-01-09, 15
RT-02-01, 17
RT-02-02, 17
RT-02-03, 17
RT-02-04, 17
RT-02-05, 17
RT-02-06, 18
RT-02-07, 18
RT-02-08, 18
RT-02-09, 18
RT-03-01, 18
RT-03-02, 18
RT-03-03, 19
RT-03-04, 19
RT-04-01, 19
RT-04-02, 19
RT-04-03, 19
RT-04-04, 19
RT-04-05, 19
RT-04-06, 19
RT-04-07, 20
RT-04-08, 20
RT-04-09, 20
RT-05-01, 20
Sagle, A.C, 148
Sakaguchi, T, 148, 149
Sanchez, I.C, 147, 148, 149
Sanchez, P, 77
Sanda, F, 149
Sander, E.A, 319
Sanjay Bishnoi, 123
Santos, J, 125
Sarkari, M, 320, 321
Sarti, G.C, 141, 142, 143
Saunders, A.E, 324
Scale-Up of Hollow Fiber Extractors, 72
Scale-Up of Laboratory Data for
DistillationColumns Containing Corrugated
Metal-Type Structured Packing, 36
Scale-Up of Protein Purification for Biotechnology
Products, 23
Scaling Up High-Performance Liquid
Chromatography for Biotechnology Products,
23
Scaling Up High-Performance Liquid
Chromatography Liquid, 23
Schaeffer, M, 208
Schell, John, 280
Schmit, C, 81, 281, 282
Schmit, C.E, 79
Schmit, Carolyn E., 281
Schork, J. M, 4, 6
Schult, K.A, 270, 271, 272, 273
Segmental Relaxation Characteristics of
Crosslinked Poly(ethylene oxide) Copolymer
Networks, 149
Segura, C.J., 159
Seibert, A, 49, 62, 63, 64, 65, 68, 69, 70, 71, 72, 73,
82, 83
Seibert, A. Frank, 73, 74, 75
Seibert, A.F, 58, 59, 60, 74, 75, 76, 77, 78
Seibert, F, 78, 135
Selected Reports on Gas Sorption/Transport, 241,
242, 244, 247
Selected Reports on Gas Sorption/Transport
Research, 249, 250, 252, 253, 258, 259
Selected Reports on Gas Sorption/Transport
Research-, 249
Selected Reports on Gas Sorption/Transport
Research-, 250
Selected Reports on Gas Sorption/Transport;
Research-, 245
Selection and Evaluation of Membrane Materials
for Liquid Separations, 215
Selection of Internals for Carbon Dioxide
Absorption/Stripping, 132
Selective Gas Transport in Miscible PPO-PS
Blends, 243
Selective Permeation of CO2 and CH4 through
Kapton(r) Polyimide: Effects of Penetrant
Competition and Gas-Phase Nonideality, 151
Selectivities in Pure and Mixed Supercritical Fluid
Solvents, 285
Self Consistent Model of Concentration and
Temperature Dependence of Permeability in
Rubbery Polymers, 147

S. Berghmans, 236, 237, 238
S. Bishnoi, 123
S. Chakravarti, 100, 105, 229
S. Curtsy, 67
S. Glaser, 229
S. J. Buelow, 348
S. Kanakia, 314
S. Kim, 284, 286, 292, 293
S. Mawson, 311, 316
S. R. Joshi, 136
S. Takishima, 316
S. Tebbal, 337
S.A. Gouye, 214
S.E. Webber, 314, 321
S.G. Kazarian, 307
S.J. Buelow, 332, 336, 346
S.J. Miller, 194, 195, 196
S.K. Kanakia, 313
S.M. Howdle, 306, 307, 313
S.M. Jordan, 153, 157
S.R. Goatees, 299
S.R. Goates, 306
S.R. Sumpter, 306, 309
S.S. Kelley, 252
S.S. Kim, 224, 225, 230
S.U. Hossain, 337, 345
S.W. Rollans, 340
S.W. Theil, 214
S-88-5, 140
S-89-4, 140
S-89-5, 140
S-90-1, 140
S-91-1, 140
S-92-1, 140
S-93-1, 140
S-94-1, 140
S-95-1, 140
Safarik, D.J, 279
Safer Solutions for Chemists, 305
Sagle, A., 147
Semicrystalline Microfibrils and Hollow Fibres by Precipitation with a Compressed-Fluid Antisolvent, 313
Sengupta, A, 71
Separation of Azeotropic Mixtures via Enhanced Distillation, 26
Separation of Gas Mixtures with Polymer Membranes: A Brief Overview, 206
Separation of Gaseous Mixtures Using Polymer Membranes, 152
Separation of Isomers Using Retrograde Crystallization from Supercritical Fluids, 287
Separation of Metal Oxides from Supercritical Water by Crossflow Microfiltration, 347
Separation of Oil/Water Emulsions Using Ceramic and Polymeric Micro- and Ultrafiltration Membranes, 168
Separation of Propane and Propylene, 10
Separation System Synthesis: A Knowledge-Based Approach. 139
Separation System Synthesis: A Knowledge-Based Approach. 2. Gas/Vapor Mixtures, 140
Separation Technologies: An Opportunity for Energy Savings, 31
Separations Research Program Annual Report 1987, 140
Separations Research Program Annual Report 1988, 140
Separations Research Program Annual Report 1989, 140
Separations Research Program Annual Report 1990, 140
Separations Research Program Annual Report 1992, 140
Separations Research Program Annual Report 1993, 140
Separations Research Program Annual Report 1994, 140
Separations: Essential to Life and Well Being, 137
Serad, G.E, 142
Serafine, D, 240
Sexton, A, 136
Shah, J, 70
Shah, P.S, 318, 320, 321, 322, 323, 324
Shanableh, A, 328, 329
Shang, M, 239, 240
Shantarovich, V.P, 142, 143
Sharma, M, 148
Shen, C.H, 112, 115
Shen, Chen H, 120
Shen, J, 14
Shida, Y, 148
Shieh, J.J, 277
Shim, J.J., 292, 294, 296, 298, 318
Shimko, L.A, 150
Shiotsuki, M, 148, 149
Shoichi Kaganoi, 122, 123
Shung, T.S, 277
Siebert, A.F, 59
Sieve Mechanism of Microfiltration, 229
Sieve Tray Extractors: A Closer Look at Capacity Limitations, 76, 77
Sieve-Tray Extractor Continuous-Phase Mixing, 279
Silicate Sorbents for Flue Gas Cleaning, 119
Silica-Treated Ceramic Substrates for Formation of Polymer-Ceramic Composite Membranes, 193
Simmons, M. A., 9
Simplified Analysis of Gas/Polymer Selective Solubility Behavior, 151
Simpson, D.T., 322, 324
Simpson, E.J, 181, 196, 198, 199, 202
Simulation of a Concentric-Tube Reactor for Supercritical Water Oxidation, 337
Simulation of a Hollow-Fiber Gas Separator: The Effects of Process and Design Variables, 152
Simulation of a Thermally-Coupled Metal Hydride Hydrogen Storage and Fuel Cell System, 20, 21
Simulation of an SN1 Reaction in Supercritical Water, 319
Simulation of Gasoline Vapor Recovery by Pressure Swing Adsorption, 15
Simultaneous Absorption of Mercury and Chlorine in Sulfite Solutions, 132
Simultaneous Dry Absorption of HCl and SO2 with Hydrated Lime from Humidified Flue Gas, 117
Simultaneous Sulfur Dioxide and Nitrogen Dioxide Removal by Calcium Hydroxide and Calcium Silicate Solids, 117
Singh, A, 199, 203, 204
Singh-Ghosal, A., 204
Sirard, S.M, 318, 323
Size-Selective Dispersion of Dodecanethiol Coated Nanocrystals in Liquid and Supercritical Ethane by Density Tuning, 321
Skin Formation of Integral-Asymmetric Gas Separation Membranes Made by Dry/Wet Phase Inversion, 172
Smart, Jim, 234, 237
Smith, P.G., 323, 324
Smith, P.G.Jr, 324
Snyder, J, 41
SO2 and NOx Removal from Flue Gas Flue Gas by Reaction with Solids Prepared by Slurrying Fly Ash and Ca(OH)2, 90
Soichi Kaganoi, 123
Sol-Gel Derived Carbon Aerogels and Xerogels Design of Experimental Approach to Materials Synthesis, 17
Solid-Liquid-Gas Equilibria in Multicomponent Supercritical Fluid Systems, 288
Solubilities and Selectivities in Supercritical Fluid Mixtures Near Critical End Points, 291
Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented vander Waals Treatment, 283
Solubility and Diffusivity of Sodium Chloride in Phase-Separated Block Copolymers of Poly(2-dimethylaminooethyl methacrylate), Poly(1,1-dihydropéfluorooctyl methacrylate), and
Spectroscopic Probes for Hydrogen Bonding, Extraction Impregnation and Reaction in Supercritical Fluids, 307
Spectroscopic Studies of Chemical Equilibrium in Supercritical Water: Cr(VI) and NOx Chemistry, 319
Spectroscopic Studies of p-(N,N-Dimethylamino)benzonitrile and Ethyl p-(N,N-Dimethylamino)benzoate in Supercritical Trifluoromethane, Carbon Dioxide, and Ethane, 298
Spherulitic Crystallization: An Analysis of Inverse Stefan Problems in Cartesian, Cylindrical, and Spherical Coordinate Systems, 228
Spray Freezing into Liquid for Highly Stable Protein Nanostructured Microparticles, 323
Spray, Sieve-Tray, and Packed High-Pressure Extraction Columns-Design and Analysis, 63
Sprays, 137
Srinivasan, M.P, 277
Srinivasan, V, 324
SRP Experimental Data on Structured Packings in Distillation Service, 30
SRP Six-Inch Distillation Column, 45
SRP/CES Presentation, 326
Stability of Ionic and Radical Molecular Dissociation Pathways for Reaction in Supercritical Water, 319
Stagewise Mass-Transfer Processes, 33
Stanford, C.C., 331
Starov, V.M, 229, 232
Statistical Thermodynamic Interpretation of Sorption/Dilution Behavior of Gases in Silicone Rubber, 186
Staudt-Bickel, C, 209
Steady-State Rate-Based Simulation of Packed Reactive Distillation: Spatial Discretization, 80
Steady-State Rate-Based Simulation of Packed Reactive Distillation: Spatial Discretization, 282
Steam Regeneration of Activated Carbon Adsorbents, 6, 11
Steam Regeneration of Activated Carbon Beds, 12
Steam Regeneration of Activated Carbon Beds: Mechanisms and Models, 54
Steam Stripping of VOCs from Water, 28
Steam of Activated Carbon Beds, 6
Stebbins, C.K, 144
Steel, K., 207, 208
Steel, K.M., 211
Steric Stabilization of Colloids by Poly(dimethylsiloxane) in Carbon Dioxide: Effect of Cosolvents, 318
Steric Stabilization of Inorganic Suspensions in Carbon Dioxide, 317
Steric Stabilization of Noncrystals in Supercritical Co2 Using Fluorinated Ligands, 318
Steric Stabilization of Silica Colloids in Supercritical Carbon Dioxide, 323
Stern, S.A, 206
Stewart, M.E, 142, 146, 148, 155, 184
Steytler, D.C., 320
Stichlmair, J, 26, 28
Story, B.J., 179, 184, 186
Strategies for Purging the Pellicle Space for 157 nm Lithography, 209
Stripper Models for CO2 Capture by Aqueous Solvents, 131
Stripping Efficiency in a Stirred and Sparged Vessel, 33
Stripping PSA Cycles for CO2 Recovery from Flue Gas at High Temperatures using a Hydrotalcite-Like Adsorbent, 22
Stroud, D. E., 101
Structure Control of Anisotropic and Asymmetric Polypropylene Membrane Prepared by Thermally Induced Phase Separation, 238
Structured Packing Performance - Experimental Evaluation of Two Predictive Models, 57
Structured Packings in Liquid-Liquid Extraction, 71
Structures and Gas Separation Properties of Asymmetric Polysulfone Membranes Made by Dry, Wet, and Dry/Wet Phase Inversion, 171
Studies of Solute-Solvent Interaction in Mixtures of Supercritical Fluids Using Fluorescence Spectroscopy, 300
Study and Prediction of Efficiency of a Controlled Cyclic Extractor, 82
Study of the Adsorption and Desorption of Multiple Adsorbates in a Fixed Bed, 35
Study of the Adsorption and of Multiple Adsorbates in a Fixed Bed, 5
Study of Ultramicroporous Carbons by High Pressure Sorption. Part 3: Complex Transport Phenomena as Sensed by CO2 and N2 Kinetics, 163
Study of Ultramicroporous Carbons by High Pressure Sorption. Part 4: Isotherms and Kinetic Transport in Activated Carbons, 163
Study of Ultramicroporous Carbons by High Pressure Sorption: Part 1. N2, CO2, O2 and He Isotherms, 162
Su, Y, 241
Subawalla, H. J, 53
Subcritical and Supercritical Water Oxidation of Anaerobically Digested Municipal Sludge, 331
Subcritical and Supercritical Water Oxidation of Industrial Excess Activated Sludge, 329
Subramanian, D, 14
Subramanian, V.R, 17
Sugawara, A, 148
Sulfation of Calcium Silicate-Aluminate and Calcium Oxide Below 800°C, 96
Sulfite Oxidation Inhibited by Thiosulfate, 86, 87
Sulfite Solutions as an Absorbent for Chlorine and Fluorine Gases - A Literature Review, 110
Sulfur Dioxide Removal by Reagents Prepared from Lime and Recycled Glass, 110
Su, Y.P, 298, 300

393
Supercritical and Subcritical Water Oxidation: Deep Well Technology for Toxic Wastewaters and Sludges, 325

Supercritical Fluid Extraction, 62, 64, 66, 70, 82, 283

Supercritical Fluid Extraction Applications in the Process Industries, 82

Supercritical Fluid Extraction in Column Contactors, 84

Supercritical Fluid Extraction-Process Simulation and Design, 62

Supercritical Fluid Mixtures: Prediction of the Phase Behavior, 284

Supercritical Fluid Separation Processes, 309

Supercritical Fluid Technology, 283

Supercritical Fluid Technology: Theory and Application, 312

Supercritical Fluids, 283, 311

Supercritical Microemulsions, 313

Supercritical Water and Solvent Oxidation, 327

Supercritical Water Oxidation, 325

Supercritical Water Oxidation Applications for Industrial Sludges, 334

Supercritical Water Oxidation Kinetics of Propellant Simulant, 343

Supercritical Water Oxidation Model Development for Selected EPA Priority Pollutants, 340

Supercritical Water Oxidation of Acetamide and Acetic Acid, 329

Supercritical Water Oxidation of Acetic Acid Catalyzed by CeO2/MnO2, 335

Supercritical Water Oxidation of Anaerobically Digested Municipal Sludge, 330

Supercritical Water Oxidation of Dimethyl Methylphosphonate and Thiodiglycol, 341

Supercritical Water Oxidation of Hazardous Organic Compounds, 334

Supercritical Water Oxidation of Pulp and Paper Mill Sludge (As an Alternative to Incineration), 337

Supercritical Water Oxidation of Pulp and Paper Mill Sludge of Pulp and Paper Mill Sludge (As an Alternative to Incineration), 345

Supercritical Water Oxidation of Volatile Acids, 325, 328

Supercritical Water Oxidation of Wastewaters, 331

Supercritical Water Oxidation Research and Development, 343

Supercritical Water Oxidation Research and Development Update, 345

Supercritical Water Oxidation: An Engineering Update, 336

Supercritical Water Oxidation-A Microreactor System, 327

Supercritical Water Oxidation-Wastewaters and Sludges, 328

Surface Fluorination of Composite Membranes Poly(phenylene oxide). Part I. Transport Properties, 265

Surface Fluorination of Composite Membranes Poly(phenylene oxide). Part II. Characterization of the Fluorinated Layer, 265

Surface Fluorination of Composite Membranes. Part I. Transport Properties, 256

Surface Fluorination of Composite Membranes. Part II. Characterization of the Fluorinated Layer, 256

Surface Fluorination of Gas Separation Membranes, 255

Surface Fluorination of Polysulfone Asymmetric Membrane and Films, 256

Swendsen, H.F, 135

Swelling of Polystyrene Latex Particles in Water by High Pressure Carbon Dioxide, 314

Swinnea, J.S, 150

Swinnea, S, 321

Synergistic Effects of Co-Dopants on the Dehydrogenation Kinetics of Sodium Aluminum Hydride, 20, 21

Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permeability and Permeability in Gas Separation Applications, 154

Synthesis and Characterization of Polypyrrolones for Gas Separation Membranes, 182

Synthesis and Characterization of Sulfonated Poly(arylene ether sulfones), 213

Synthesis and Gas Transport Properties of Aromatic Polyester Membrane Materials, 189

Synthesis and Properties of F-Containing Poly(diphenylacetylene) Membranes, 149

Synthesis and Properties of membranes of Poly(diphenylacetylenes) Having Fluorines and Hydroxyl Groups, 148

Synthesis of Germanium Nanocrystals in High Temperature Supercritical CO2, 324

Synthesis of Germanium Nanocrystals in High Temperature Supercritical Fluid Solvents, 323

Synthesis of TiO2 Nanoparticles Utilizing Hydrated Reverse Micelles in CO2, 323

Synthesis, Analysis, and Albumin Adsorption Properties of Alkylated Poly-4-Vinyl-Pyridine Grafted Polyethylene Terephthalate, 217

T. A. Evans, 24

T. C. Ward, 218

T. F. Edgar, 30, 85

T. G. Brna, 87, 88

T. Hasegawa, 239

T. J. Parker, 29, 31, 42

T. J. Selm, 92

T. Maki, 239, 240

T. Prado, 213

T. Xiang, 309

T.A. Barbari, 153

T.A. Hatton, 302

T.B. Meluch, 213, 215

T.C. Ward, 214, 215, 219
T.E. Mlnsa, 256, 257
T.G. Brna, 113
T.H. Kim, 157, 162, 163, 185
T.K. Ellison, 283
T.R. Holcomb, 287
T.W. Copeman, 283
T.W. Randolph, 313
Taborek, J. J, 138
Tailoring Mixed Matrix Composite Membranes for
Gas Separations, 203
Tailoring Nanospace, 149
Takahashi, H, 241
Takishima, S, 315
Talton, J. E., 33
Tanabe, D, 318
Tanaka, S, 141
Tanaka, T, 241
Taniguchi, M, 241
Taylor, C. E., 86
Taylor, D.L, 240
Taylor, L.S, 240
Techniques for Measurement of Water Vapor,
Sorption and Permeation in Polymer Films, 271
Techniques for Measurement of Water Vapor,
Water Sorption and Permeation in Polymer
Films, 270
Tedder, D, 42
Temperature and Density Effects on an SN2
Reaction in Supercritical Water, 312
Temperature Dependence of Gas Sorption and
Transport Properties in Glassy Polymers, 189
Temperature Dependence of Gas Sorption and
Transport Properties in Polymers;
Measurement and Applications, 177
Temperature Dependence of Gas Sorption and
Transport Properties in Polymers;
Measurements and Applications, 187
Temperature Effects on Gas Permselection
Properties in Hexafluoro Aromatic Polyimides, 184
Teplyakov, V.V, 263
Teraguchi, M, 142
Teraguchi, M, 144
The Bubble-to-Spray Transition on Sieve Trays:
Mechanisms of the Phase Inversion, 34
The Development of an Effective Treatment
Technology Supercritical Water Oxidation of
Wastewater and Sludges, 346
The Distillation Imperative, 58
The Effect of Additives on the Oxidation of
Dimethyl Methylphosphonate in Supercritical,
344
The Effect of Additives on the Oxidation of
Dimethyl Methylphosphonate in Supercritical
Water, 340
The Effect of Crosslinking on Gas Permeability in
Crosslinked Poly(ethylene glycol diacrylate),
149
The Effect of Degree of Acetylation on Gas
Sorption and Transport Behavior in Cellulose
Acetate, 252
The Effect of Moisture on the Reaction of Sulfur
Dioxide with Calcium Silicate Sorbents, 104
The Effect of Moisture on the Reactivity of
Ca(OH)2-Based Sorbents for Flue Gas
Desulfurization, 98
The Effect of N-Pentanol on the Transport of Salt
in Reverse Osmosis, 217
The Effect of Solute-Membrane Affinity on Cyclic
Hydrocarbon-Water Transport in Pressure-
Driven Membrane Separation Processes, 214
The Effect of Sorbed Penetrants on the Aging of
Previously Dilated Glassy Polymers Powders,
Part 2, n-Propane Sorption in Polystyrene, 155
The Effect of Sorbed Penetrants on the Aging of
Previously Dilated Glassy Polymer Powders. IV,
179
The Effect of Sorbed Penetrants on the Aging of
Previously Diluted Glassy Polymer Powders,
Part 1. Lower Alcohol and Water Sorption in
Poly(methylmethacrylate), 155
The Effect of Uni-Axial Orientation on
Macroporous Membrane Structure, 240
The Effect of Uni-Axial Stretching on the
Roughness of Microfiltration Membranes, 240
The Effects of Carbon Dioxide Conditioning on the
Permeation Behavior of Hollow Fiber
Asymmetric Membranes, 167
The Effects of Carbon Dioxide Exposure on
Permeation Behavior in Silicone Rubber and
Glassy Polycarbonates, 162
The Effects of CO2 Conditioning on the Transport
Properties of Glassy Polycarbonates, 159
The Effects of CO2 Exposure on Pure and Mixed
Gas Permeation Behavior: Comparison of
Glassy Polycarbonate and Silicone Rubber, 154
The Effects of Conditioning on Sorption and
Volume Dilation in Rubbery and Glassy
Polymers, 170
The Effects of Crosslinking Chemistry on CO2
Plasticization of Polyimide Gas Separation
Membranes, 209
The Effects of Free Water on the Performance of
Packed Towers in Vacuum Service, 58, 76
The Effects of Humidity on the Activated-Carbon
Adsorption of Organics, 12
The Effects of Humidity on the Adsorption of
Organics on Activated Carbon, 13
The Effects of Morphology and Hygrothermal
Aging on Water Sorption and Transport in
Kapton(r) Polyimide, 152
The Effects of Pendant Groups on Gas Sorption
and Transport in Polymers, 251
The Effects of Structural Order on Barrier
Properties, 254
The Enhancement of Albumin Binding by Alkyl
Derivitization of Cellulose Acetate Membranes,
211
The Essentials of Extraction, 82
The Experimental Application of X-ray
Tomography to a Vapor-Liquid Contactor, 79,
281
The Fate of Chromium and Lead in a Supercritical Water Oxidation Environment: A Survey, 345
The Formation of a Chemically Modified g-Alumina Microporous Membrane, 166
The Formation of Chemically Modified g-Alumina Microporous Membranes, 170
The Influence of Solvent-Solute and Solute-Solute Clustering on Chemical Reactions in Supercritical Fluids, 297
The Kinetics of Membrane Formation via Thermally Induced Liquid-Liquid Phase Separation, 231
The Oldershaw Column: Useful for Solving Distillation Problems, 60, 78
The Operating Characteristics of the Karr Reciprocating Column, 64
The Photodimerization of Isophorone in Supercritical Trifluoromethane and Carbon Dioxide, 290
The Prediction of Trayed Distillation Column Mass Transfer Performance by Neural Networks, 281
The Selection of Surfactants for Micelle Enhanced Ultrafiltration, 65
The Separation of Inorganic Salts and Metal Oxides from Supercritical Water by Cross-Flow Microfiltration, 339
The Separation of Particles from Supercritical Water Oxidation Effluents, 332
The Separation of Particulates from Supercritical Water Oxidation Processes, 332
The Significance of Entropic Selectivity for Advanced Gas Separation Membranes, 199
The Solubility of 1:1 Nitrate Electrolytes in Supercritical Water, 336
The T-By Tray: A Plug-Flow, Low-Pressure Drop Contacting Device for Cross-Flow Columns, 29
The Transport Properties of Polyimide Isomers Containing Hexafluoroisopropylidene in the Diamine Residue, 188
The Use of Bench-Scale and Pilot-Scale Testing Systems to Investigate the Effects of Carbon Dioxide Conditioning on the Permeation Behavior of Asymmetric Membranes, 161
The Use of Gel Permeation Chromatography for the Determination of Polymer-Polymer Interaction Parameters, 214
The Use of Partial Molal Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures, 283
The Workhorse Today & Tomorrow - Distillation, 60
Theil, S.W., 212
Theoretical Analysis of a Transdermal Ferromagnetic Implant for Retention of Magnetic Drug Carrier Particles, 20, 21
Theoretical Approach for Enhanced Mass-Transfer Effects in Duct Flue Gas Desulfurization Processes, 93
Theoretical Approach for Enhanced Mass-Transfer Effects in Duct Flue Gas Desulfurization Processes Volume II: Duct Spray Drying, 101
Theoretical Approach for Enhanced Mass-Transfer Effects in Duct Flue Gas Desulfurization Processes. Volume I: Dry Sorbent Injection, 100
Theory and Simulation of Colloid and Interface Science in Supercritical Fluids, 318
Theory of Hydrogen Bonding in Supercritical Fluids, 297
Theory of the Pressure Effect in Dense-Gas Extraction, 284
Theory of the Pressure Effect on the Curvature and Phase Behavior of Di-2-Ethylhexyl Sodium Sulfosuccinate Water-in-Oil Microemulsions in a Compressible Solvent, 295
Thermal Design of Horizontal Reboilers, 39
Thermal Regeneration of Fixed Adsorption Beds, 4
Thermal Regeneration of Fixed Multicomponent Adsorption Beds, 5
Thermal Treatment of Sol-Gel Derived Nickel Oxide Xerogels, 18
Thermally Induced Phase Separation of Isotactic Polypropylene and Hexamethylbenzene, 226
Thermally Stable Polyimide Isomers for Membrane-Based Gas Separations at Elevated Temperatures, 192
Thermodynamic Interaction in Polybutadiene/Solute Systems by Inverse Gas Chromatography, 219
Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions, 113
Thermodynamic Models for Nonrandom and Strongly Nonideal Liquid Mixtures, 283
Thermodynamic Parameters for Predicting Acid Gas Solubility in Aqueous Alkanolamine Solutions, 102
Thermodynamic Parameters for Predicting Acid Gas Solubility in Methyldiethanolamine Solutions, 100
Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption, 135
Thermodynamics and Phase Equilibria of Polymer-Solute-Supercritical Fluid Systems by Supercritical Fluid Chromatography, 296
Thermodynamics and Structural Study of Thermally Induced Phase Separation Membranes, 222
Thermodynamics of Alkanolamine-Water Solutions from Freezing Point Measurements, 103
Thermodynamics of Aqueous Piperazine/Potassium Carbonate/Barbon Dioxide Characterized by the Electrolyte Nonrandom Two-Liquid Model in Aspen Plus, 131
Thermodynamics of Aqueous Potassium Carbonate, Piperazine, and Carbon Dioxide, 134
| Thermodynamics of Carbon Dioxide in Aqueous Piperazine/Potassium Carbonate at Stripper Conditions, 135 |
| Thermodynamics of Diglycolamine®/Morpholine/Water/Carbon Dioxide, 133 |
| Thermodynamics of Piperazine/Methyldiethanolamine/Water/Carbon Dioxide, 124 |
| Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation. I. Determination of Equation of State Parameters, 224 |
| Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation. II. Solid-Liquid Phase Separation Systems, 224 |
| Thermodynamics of Polymer/Diluent Systems for Thermally Induced Phase Separation: III. Liquid-Liquid Phase Separation Systems, 224 |
| Thermodynamics of Polymer/Polymer/Solvent Systems, 216 |
| Thermodynamics Studies of Polymer/Solvent Interactions Using Inverse Gas Chromatography, 216 |
| Thermo-Mechanical Stability of Polymer-Ceramic Composite Membranes, 196 |
| Thermosiphon Reboilers-Performance Modeling, 137 |
| Thiel, S.W., 213, 216, 218, 220, 221 |
| Thiosulfate Additives for Lime/Limestone Scrubbing, 88 |
| Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes: A Review of R&D Results, 87 |
| Thomas, A.J., 330 |
| Thongpakdi, D, 38 |
| Thundiyil, M.J, 201, 203 |
| Tingey, K.G., 217 |
| Toman, J. J, 93 |
| Tongdhamachart, C., 330, 331 |
| Toprac, A. J, 84 |
| Toy, L., 144, 146, 147, 150 |
| Toy, L.G, 144, 146, 147, 150 |
| Transfer Fluorescence Emission Dependence on Excitation Wavelength for Ethyl p(Dimethylamino)benzoate in Supercritical Trifluoromethane, 292 |
| Transfer of Gases to Liquid Films Flowing Over Enhanced Surfaces, 38 |
| Transient Length Dilation vs. Transient Increase in Permeability of Natural Rubber Films, 171 |
| Translation and Rotation of Penetrants in Ultrapervmeable Nanocomposite Membrane of Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) and Fumed Silica, 148 |
| Transport and Structural Characteristics of Crosslinked Poly(ethylene oxide) Rubbers, 150 |
| Transport Characterization of a Polypyrrolone for Gas Separations, 168 |
| Transport of Carbon Dioxide in Nafion Membranes Enhanced by Relative Humidity and Ethylenediamine Content, 90 |
| Transport of Carbon Dioxide in Perfluorosulfonate Membranes Enhanced by Relative Humidity and Ethylenediamine Content, 91 |
| Transport of Gases and Vapors in Glassy and Rubbery Polymers, 149 |
| Transport of Multicomponent Liquid Solutions of Nonelectrolytes in Pressure-Driven Membrane Separation Processes, 218 |
| Transport Properties, 165 |
| Transport Properties of Native and Chemically Modified Gamma-Alumina Membranes, 175 |
| Transport Properties of Polymers, 241 |
| Trays Versus Packing: Selection of the Optimal Extractor, 78 |
| Treatability of Dinitrotoluene Process Wastewater by Supercritical Water Oxidation, 336 |
| Treatment of Air Pollutants Emitted from Corn-derived Ethanol Production Facilities, 78 |
| Trempel, D. P., 94 |
| Tres Bien! Trays Are Still In!, 54 |
| Trifunctional Ambidextrous Surfactants for Latexes in Supercritical Carbon Dioxide and Water, 318 |
| Tri-n-butylphosphate/Carbon Dioxide and Acetone/Carbon Dioxide Phase Behaviors and Utilities in Capillary Supercritical Fluid Chromatography, 306 |
| Trocha, M., 180, 195 |
| Trompiz, Carlos J, 56 |
| Trompiz, Carlos Jose, 55 |
| Trutna Tray, 60, 69 |
| Trutna Tray Performance Studies, 69 |
| Trutna, W. R, 29, 60, 69 |
| Tseng, H, 214, 215, 216, 218, 219 |
| Tseng, H.S, 214, 215, 216, 219 |
| Tseng, P. C., 85, 86, 87 |
| Tsuchiya, T, 241 |
| Turk, B, 141 |
| Turner, M.D., 341 |
| Two Dimensional Model for the Design of Metal Hydride Hydrogen Storage Systems, 20, 21 |

---

U

Ulbricht, M., 240

Ulrich, R. K, 85

Ultrapermeable Reverse-Selective Nanocomposite Membranes, 143

Understand Distillation-Column Debottlenecking Options, 49

Uniform Encapsulation of Stable Protein Nanoparticles Produced by Spray Freezing for the Reduction of burst Release, 322

Uragami, H, 152

Use of Electrochemistry to Predict Ethylene Absorption Capacities of Reactive Absorption Systems, 80

---

397
Use of Excess Enthalpy Data to Improve Activity Coefficient Models for Water-Monoethanolamine Systems, 107
Use of the Three-Component Solubility Parameter in Asymmetric Phase-Inversion Membrane Preparation, 214
UV-Vis Spectroscopic Determination of the Dissociation Constant of Bichromate from 160°C to 400°C, 316
UV-Visible Absorbance Spectroscopy of Organic Probes in Supercritical Water, 304

V.D. Grebenjuk, 229
V.M. Starov, 229, 234, 235, 237
V.T. Stanett, 152
V.T. Stanett, 151, 152
V.V. Teplyakov, 266
Val, T.N, 324
Vandekemp, R., 109
vanWagner, E, 150
Vapor Sorption and Blend Miscibility Studies of Alkyd Resin and Poly(vinyl chloride), 161
Ventoza, T.P, 214, 217
Verschoof, H. J, 53
Verschoof, Huib-Jan, 50
Viscoelastic Characteristics of U.V. Polymerized Poly(ethylene glycol) Diacrylate Networks with Varying Extents of Crosslinking, 150
Vu, D, 207, 208, 209
Vu, D.Q, 207, 209
Vu, De Q, 209, 210

W. J. Koros Research Group Report, 168
W. Jozewicz, 113
W. Ryoo, 321
W. T. Weems, 85
W.D. Coggio, 178
W.D. Richards, 194
W.J Koros, 259
W.M. Flarsheim II, 283, 289
W.R. Trutna, 56
W.T. Wofford, 315
W-04-1, 349
W-04-2, 325
W-04-3, 325
W-04-4, 327
W-04-5, 327
W-04-6, 327
W-04-7, 327
W-04-8, 328
W-04-9, 328
W-04-10, 329
W-05-1, 331
W-05-2, 331
W-05-3, 331
W-05-4, 332
W-05-5, 332
W-05-6, 332
W-05-7, 333
W-05-8, 333
W-05-9, 333
W-05-10, 336
W-05-11, 336
W-05-12, 336
W-05-13, 337
W-05-14, 337
W-05-15, 337
W-05-16, 338
W-05-17, 338
W-05-18, 339
W-05-19, 339
W-05-20, 340
W-05-21, 340
W-05-22, 341
W-05-23, 341
W-05-24, 341
W-05-25, 341
W-05-26, 341
W-05-27, 342
W-05-28, 342
W-05-29, 342
W-05-30, 342
W-05-31, 342
W-05-32, 342
W-05-33, 342
W-05-34, 342
W-05-35, 342
W-05-36, 342
W-05-37, 342
W-05-38, 342
W-05-39, 342
W-05-40, 342
W-95-4, 343
W-95-5, 343
W-95-6, 343
W-95-7, 344
W-95-8, 344
W-95-9, 346
W-96-1, 346
W-96-2, 346
W-96-3, 347
W-97-1, 347
W-97-2, 348
W-98-1, 348
W-98-2, 348
W-99-1, 349
Wagner, I, 46, 50
Walker, D.R, 168, 182
Wang, B, 80
Wang, J, 20, 21, 22
Wang, R, 277
Wang, T. R., 32
Wang, X.-Y, 147, 148, 149
Wang, Y.F, 221, 228, 229
Warmuth, W., 168
Wasserman, P.D., 102
Waste, Nuclear, Reprocessing and Treatment, Technologies to Wastewater Treatment, Multilateral Approach, 349
Water Extraction of Polyethyloxazoline from Miscible and Immiscible Polymer Blends, 244
Water in Carbon Dioxide Microemulsions with a Fluorocarbon-Hydrocarbon Hybrid Surfactant, 305
Water Oxidation of Sludges and Toxic Wastes, 328
Water Sorption and Transport in a Series of Polysulfones, 271
Water Sorption and Transport in Blends of Poly(vinyl pyrrolidone) and Polysulfone, 272
Water Sorption and Transport in Blends of Polyethyloxazoline and Polysulfone, 273
Water Sorption, Proton Conduction, and Methanol Permeation Properties of Sulfonated Polyimide Membranes Crosslinked with N,N-Bis(2-hydroxyethyl)-2-aminoethanesulfonic Acid (BES), 150
Water Vapor Sorption and Transport in Polysulfones and Their Blends, 273
Water Vapor Transport in a Series of Polyarylates, 276, 277
Water/Vastewater Treatment, 325
Water-in-Carbon Dioxide Emulsions with PDMS-Based Block Copolymer Ionomers, 318
Water-in-Carbon Dioxide Macroemulsions and Miniemulsions with a Hydrocarbon Surfactant, 320
Water-in-Carbon Dioxide Microemulsions: An Environment for Hydrophiles Including Proteins, 313
Water-Vapour Permeation in Semicrystalline and Molten Poly(octadecyl acrylate), 277
Webber, S., 318
Webber, S.E, 318, 320, 324
Weinkauf, D.H, 254, 258, 259, 260, 268
Welding Colloidal Crystals with Carbon Dioxide, 321
Wen, W.-Y, 148
Westacott, R.E, 319
Wet Oxidation Bibliography, 332
Whaley, A.K, 79
Whaley, Amanda K, 280
White, R.E, 14, 15, 17
White, W. B, 93
Wignall, G.D, 317, 319
Williams, R.O, 320, 321, 322, 324
Wilmanns, E.G, 325, 328
Wilson, I, 78, 132
Wind, J.D, 209, 278
Wofford, W.T, 317, 346
Wong, J.M, 283, 284, 285, 286
Wong, P.C., 216
Woods, D, 206
Wooten, C, 27, 28, 161
Worrel, L.S, 150, 240
Wright, C.T, 271, 273, 275

X

X. Py, 68
Xiang, T, 308, 314, 315
XPS Characterization of Surface Fluorinated Poly(4-methyl-1-pentene), 257
Xu, B, 321, 324

Y

Y. Chang, 218
Y. J. Lee, 85, 88
Y. Kang, 212
Y. Kitamura, 238
Y. Maeda, 242, 251
Y. Taru, 256, 257
Y. Yuan, 265
Y.F. Wang, 225
Y.M. Tsou, 61
Yamaguchi, S, 318
Yampolskii, Yu, 142, 149
Yampolskii, Yu,P, 142
Yang, D.K, 152
Yates, M.Z, 317, 318, 319
Yates. M.Z, 318
Yave, W, 240
Yazdi, P.T, 291
Ye, Q., 223
Yeh, N, 125, 127
Yeh, Norman, 126
Yeun, L.K, 318
Yoshida, M, 18
Young, T.J, 318, 319, 320, 321
Yu, P, 15
Yu, Z, 320, 323, 324
Z

Z. Olujic, 57, 58
Zanto, E.J, 17
Zeigler, K.J, 317
Zhang, R, 13
Zhang, X, 323, 324

Zhao, L, 114
Zhao, Lynn L., 116
Zhong, J, 148
Zich, E., 59, 76, 77
Zidan, R, 20, 21
Ziegler, K.J, 319, 320, 323
Zimet, D.B., 345
Zimmerman, C, 203, 204