Facilitated Transport of CO_2 in Ion Exchange Membranes

The facilitated transport of CO_2 through ion exchange membranes containing organic amine counterions was studied. Steady state CO_2 fluxes were measured from pure gas streams and mixtures with CH_4. Facilitation factors for CO_2 up to 26.7 were calculated from transport data. Transport measurements were binary mixtures of CO_2 and CH_4 yielded ratios of CO_2 flux to CH_4 flux ranging from 29.0 to 264. Conversion of flux ratios to permeabilities yielded separation factors up to 551 for CO_2 over CH_4, which are compared to literature data for polymeric membranes. The transport data support a mobile, reactive-carrier facilitated transport mechanism with a carbamate zwitterion complex. Effective diffusivities for CO_2 and the carrier-gas complex were determined from transport data. A reaction equilibrium model predicted facilitation factors that were in very good agreement with experimental values. Potential applications are also discussed.

J. D. Way, R. D. Noble,
D. L. Reed, and G. M. Ginley
National Bureau of Standards
Center for Chemical Engineering, 773.1
Boulder, CO 80303

L. A. Jarr
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, WV 26505

Introduction

The implicit simplicity and potential energy efficiency of membrane processes have stimulated basic and applied research for many years. To date, however, few membrane processes other than reverse osmosis and hydrogen recovery have been applied to solve industrial separation problems because of coupled problems of the selectivity and the magnitude of the flux. An approach to solving these coupled problems of flux and selectivity is to use liquids as membrane materials and to incorporate reversible complexation agents in the liquids. This concept, known as facilitated transport, is ideal for the separation and concentration of dilute solutes both in the gas and liquid phases.

Facilitated transport of gases has been the subject of numerous investigations that are summarized in recent review articles by Way et al. (1982) and Noble et al. (1986a). Immobilized liquid membranes (ILM's) were prepared for the majority of these studies by impregnating the pore structure of very thin, microporous polymeric substrates with a solution of a solvent and a complexation agent (Way et al., 1985). Such ILM's have two primary experimental problems: loss of solvent phase and loss or deactivation of the complexation agent or carrier. Solvent loss occurs when solvent evaporates or is forced from the support pore structure by large transmembrane pressures. Carrier loss can also occur when pressure gradients force condensed solvent through the support pore structure, leaching the carrier out of the ILM. Irreversible reaction of the carrier with impurities in the feed or product gas stream could lead to deactivation or breakdown of the carrier.

A recent approach has been to use ion exchange membranes as a support for complexation agents (LeBlanc et al., 1980). A cationic or anionic carrier is exchanged into an appropriate nonporous ion exchange membrane (IEM) to form the facilitated transport membrane. This configuration has the advantage that the carrier cannot easily be forced out of the support since the carrier is retained by strong electrostatic forces. Ion exchange membrane supports may provide longer operating lifetimes where conventional ILM's may be subject to carrier or solvent loss.

In this study, monopositive ethylene diamine (EDA) ions were exchanged into perfluorosulfonic acid ionomer films to prepare facilitated transport membranes. The flux of CO_2 was measured with and without carrier present at ambient conditions as a function of CO_2 mole fraction in the feed gas stream. The selectivity of these membranes was determined by simultaneous measurements of CO_2 and CH_4 fluxes from binary mixtures as a function of composition. Reaction equilibrium models were derived to predict the observed experimental data.

The present address of J. D. Way is Chemical Engineering Laboratory, SRI International, Menlo Park, CA 94025.

The present address of G. M. Ginley is Dept. of Chemical Engineering, University of California, Berkeley, CA 94720.

Background

CO_2 facilitated transport

Facilitated transport of gases has been the subject of numerous review articles in recent years (Smith et al., 1977; Kimura et al., 1979; Way et al., 1982; Matson et al., 1983; Noble et al., 1986a). Much of the work in the literature deals with facilitated transport of CO_2, both from an engineering and a physiological standpoint. Many of these studies have examined CO_2 transport through immobilized liquid membranes using aqueous carbonate and bicarbonate solutions immobilized in a variety of microporous substrates such as ultrafiltration membranes, reverse osmosis membranes, and common filter paper (Enns, 1967; Ward and Robb, 1967; Otto and Quinn, 1971; Suchdeo and Schultz, 1974; Donaldson and Quinn, 1975). In the absence of catalysts, the system was determined to be reaction-rate limited by the CO_2 hydrolysis reaction. Performance of the membrane was improved by the addition of catalysts such as carbonic anhydrase (Enns, 1967) and anions of weak acids such as selenite, tellurite, and hypochlorite (Meldon, 1973; Meldon et al., 1977; Kimura et al., 1979).

Donaldson and Nguyen (1980) measured the kinetics of CO_2 reactions with monoethanolamine (MEA), diethanolamine (DEA), triethanolamine, and triethylamine using a tracer $^{14}CO_2$ facilitated transport membrane technique. Facilitation factors up to 4.8 were measured for aqueous ILM's containing 0.083 M MEA. The authors' transport data at low concentrations for MEA and DEA support the following carbamate formation reaction mechanism:

$$RNH_2 + CO_2 = RNHCOO^- + H^+ \qquad (1)$$

Triethanolamine (TEA) and triethylamine also increased the transport rate of CO_2. The authors proposed that the TEA facilitation mechanism was that of base catalysis of the CO_2 hydrolysis reaction and that triethylamine acts as a weak base to produce OH^-, which reacts with CO_2 to form the bicarbonate ion.

The majority of the above studies reported data taken at ambient temperature and pressure conditions. Kimura et al. (1979) measured CO_2 transport through ILM's at industrially important conditions (6.90×10^2 kPa CO_2 feed, 363–403 K). The membrane consisted of an aqueous 4.2 M $CsCO_3$ solution immobilized in 80% porous cellulose membranes of 45–80 μm thickness. The uncatalyzed CO_2 permeabilities at 403 K ranged from 263 to 863×10^{-9} cm^3(STP)cm/s · cm^2 · kPa for transport in the intermediate regime between diffusion- and reaction-controlled transport. The addition of catalysts such as sodium arsenite to increase the rate of CO_2 hydrolysis was found to increase the CO_2 permeabilities by more than a factor of 2 at low CO_2 partial pressures in the feed gas. An economics study based on the permeability data taken showed that the use of facilitated transport membranes for acid gas removal could produce cost savings of 30–50% compared to conventional processes such as hot potassium carbonate scrubbing or physical absorption in cold methanol.

LeBlanc et al. (1980) demonstrated the feasibility of facilitated transport of ethylene and CO_2 in ion exchange membranes. Singly protonated ethylene diamine (EDA) was exchanged into a 110 μm thick, 200 g/eq cation exchange membrane prepared by grafting sulfonated polystyrene onto a polytetrafluoroethylene polymer matrix. Permeabilities for CO_2 and N_2 mixtures were measured for the membrane as a function of temperature. The CO_2/N_2 separation factor was 600 for a CO_2 partial pressure of 2.9 kPa. The CO_2 permeability was 23×10^{-9} cm^3cm/s · cm^2 · kPa for a pure CO_2 feed gas at ambient conditions. A facilitation factor of 20 was observed for a 2.9 kPa CO_2 feed gas.

CO_2-EDA chemistry

The kinetics of the reaction of CO_2 with EDA has been studied by several authors for possible applications in gas absorption (Weiland and Trass, 1971; Hikita et al., 1977; Sada et al., 1977). The principal reaction is the formation of a carbamate zwitterion:

$$CO_2 + H_2N(CH_2)_2NH_2 = {}^+H_3N(CH_2)_2NHCOO^- \qquad (2)$$

The equilibrium constant for the reaction is 1×10^5 M^{-1} (Jensen and Christensen, 1955).

Structure of perfluorosulfonic acid cation exchange membranes

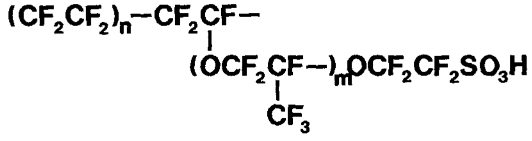
In the early 1970's a perfluorosulfonic acid ionomer was developed for use in electrochemical applications, especially the chloralkali process for the production of chlorine and caustic (Leitz et al., 1972). The structure of these ionomers is shown in Figure 1, where $m = 1$. The acid form of the ionomer can easily be neutralized to cationic form by reaction with an appropriate base such as NaOH. The mechanical, chemical, and ionic transport properties of these membranes have been extensively studied (Grot et al., 1972; Yeo and Eisenberg, 1977; Yeager and Steck, 1981). Mathematical models of the transport of electrolytes through ion exchange membranes have been developed (Gierke, 1977; Pintauro and Bennion, 1984).

There are many studies in the literature that, taken together, provide a clearer picture of the microstructure of perfluorosulfonic acid ionomers. Data presented lead to a microstructure model of a fluorocarbon polymer backbone phase, polar ionic regions containing the sulfonate ions and the majority of the absorbed water, and an interfacial region between the polar ionic and nonpolar polymer phases (Yeager and Steck, 1981). In the present study, we are postulating that the facilitated transport of gas molecules occurs through the water-containing ionic regions of the ionomer support.

Experimental Procedure

Flux measurement

The apparatus and procedure used to measure membrane fluxes were described in detail by Bateman et al. (1984). The apparatus was modified in order to use multicomponent mixtures, and the new flow diagram is shown in Figure 2. Briefly,



$$(CF_2CF_2)_n{-}CF_2CF{-}\,(OCF_2CF(CF_3){-})_m OCF_2CF_2SO_3H$$

Figure 1. Structure of perfluorosulfonic acid ionomers.
Membranes used in study have a value of $m = 1$

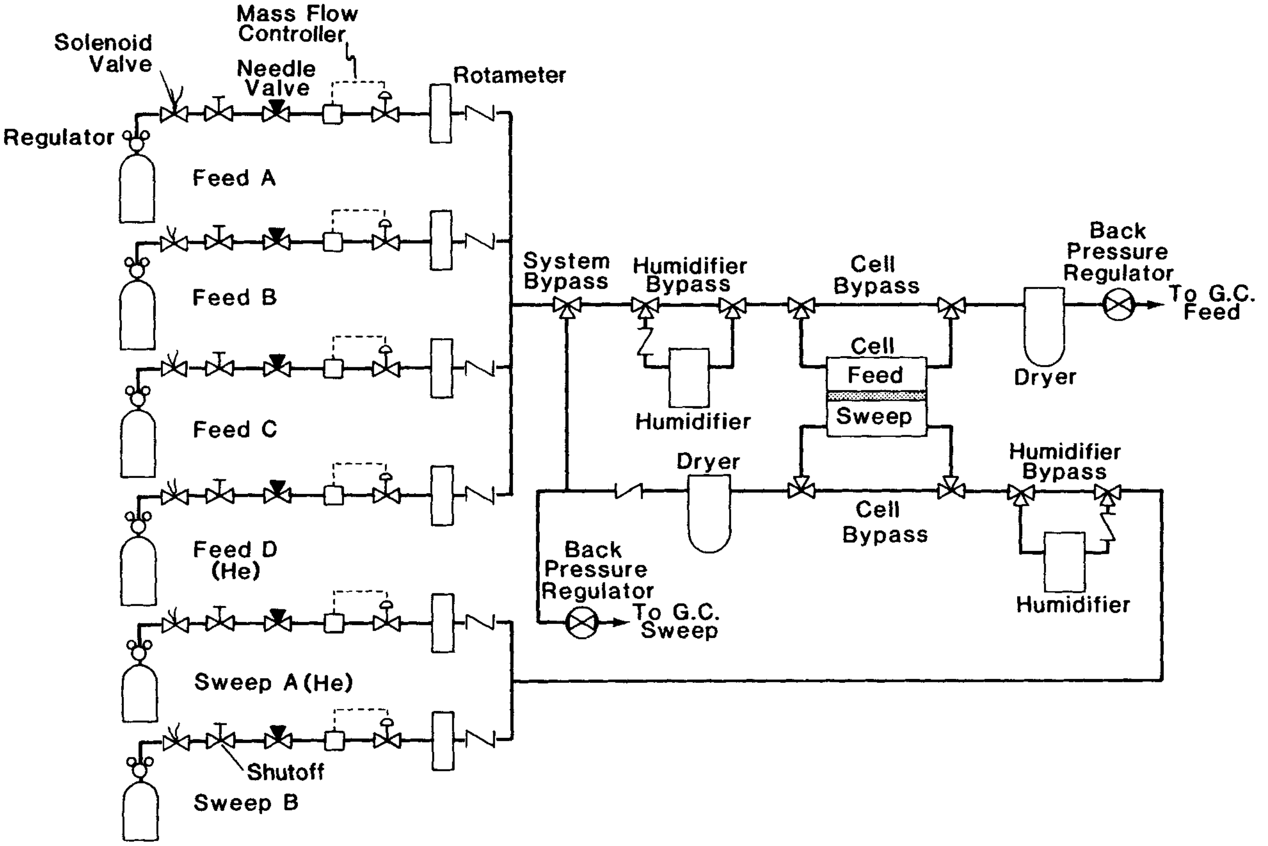


Figure 2. Flow diagram of membrane transport apparatus.

the flux measurement system consists of the gas flow system, which delivers a gas mixture of known concentration to a membrane cell, a gas chromatograph with thermal conductivity detector for analysis of the feed and product side gas streams, and a computer for data acquisition and reduction. As shown in Figure 2, the gas streams were saturated with water upstream of the membrane cell. A cold trap removed the water prior to chromatographic analysis. All measurements were made at ambient conditions of 298 K and 84.0 kPa. The chromatograph was calibrated by injecting 1.0 cm^3 aliquots of premixed gases of interest (1.0% in He).

Membrane preparation

The ion exchange films (1,100 g equivalent molecular weight, 170 μm thickness) were obtained from the manufacturer in the acid form. The dry mass of the membranes was determined and the number of ion exchange sites was calculated using the equivalent molecular weight of the ionomer. The membranes were converted to the Na salt form by soaking them in NaOH solutions overnight. The amount of the NaOH used to prepare the solution was at least 100 times the number of ion exchange sites available in the membrane. The Na salt form was used as a nonreactive membrane for measurements of the diffusive contributions of the individual gases necessary to calculate the facilitation factor. After the transport measurements were made, the Na membrane was converted to reactive EDA salt form by soaking the membrane in an aqueous solution of EDA overnight. A fiftyfold excess of EDA was used to obtain complete exchange of the EDA for Na counterions. To create the monopositive ion of EDA, one equivalent of HCl was added to the solution prior to the exchange. The extent of exchange was measured by analysis of the exchange solutions for Na by atomic emission spectroscopy. Partial exchanges of EDA for NA were also performed to prepare a series of membranes with increasing EDA concentrations. The water content of the membranes at equilibrium was measured using the gravimetric method of Yeager and Steck (1981). Table 1 presents the results of the measurements. The water content of the EDA membranes was needed to calculate the effective membrane concentrations of the EDA carrier species. The thickness of the water-swollen membranes was 200 μm.

Results and Discussion

CO_2 and CO_2/CH_4 transport

The CO_2 single-component mass transfer experiments were performed with the objectives of determining the steady state CO_2 flux at ambient conditions and of obtaining information about the mechanism of mass transfer. Figure 3 is a plot of CO_2 flux vs. CO_2 feed gas mole fraction for both the EDA membrane and the Na membrane. The points plotted in Figure 3 are averages of at least five steady state flux values. Confidence intervals (95%) calculated for the diffusive and facilitated flux values were all less than 0.01×10^{-9} gmol/$cm^2 \cdot s$. The Na membrane flux is a linear function of feed gas concentration, which is evidence of Fickian diffusion. The data are fitted well by a least-squares line, which is shown in Figure 3. The presence of EDA

Table 1. Water Content of Acid-Form and Salt-Form Ion Exchange Membranes

Sample	H^+ Membrane	Na Membrane	EDA Membrane
1	—	0.18	0.10
2	—	0.17	0.12
3	0.25	0.17	—
4	0.25	0.17	—
5	—	0.18	0.11
Avg	0.25	0.17	0.11

in the membrane markedly increases the fluxes, which range from 5.22×10^{-10} to 2.82×10^{-9} gmol/cm^2 · s, and the fluxes are a highly nonlinear function of feed gas mole fraction. The pure CO_2 facilitated flux corresponds to a permeability at 298 K of 17×10^{-9} cm^3 · cm/cm^2 · s · kPa. The nonlinearity is an indication that a reaction is taking place within the membrane, which is consistent with the facilitated transport mechanism. The flux vs. feed mole fraction curve flattens out for higher CO_2 mole fractions, indicating saturation of the carrier.

The ratio of the flux with EDA present to the flux without the carrier is called the facilitation factor F, which is a measure of the flux enhancement. The facilitation factor is 1.44 for a mole fraction of 1.0, increasing to 3.68 at $y = 0.25$. Facilitation factors continue to increase with decreasing feed gas mole fraction to a value of 26.7 at a CO_2 mole fraction of 0.01. These very high facilitation factors are primarily due to two factors. The inverse Damkohler number, $D_{AB}/(k_r L^2)$, the ratio of reaction time to diffusion time, is 1.39×10^{-4}. Therefore, mass transport is limited only by the diffusion rate because of fast kinetics, which maximizes the facilitation effect. Secondly, the carrier loading in the membrane is limited by the ion exchange site density in the ionomer support rather than the carrier solubility in a solvent phase. Based upon the amount of water present in the membrane, the EDA carrier concentration is 8.3 M.

In the reaction equilibrium or diffusion-limited regime, the facilitated flux should increase linearly with the carrier concentration. Figure 4 is a plot of the CO_2 flux as a function of the EDA concentration in the membrane expressed as the fraction of ion exchange sites available which contain EDA. The plot is linear and is fitted very well by a least-squares line. The intercept of the line is 2.12×10^{-9} gmol/cm^2 · s, which is very close to the flux measured for a pure CO_2 feed gas for the Na membrane of 2.00×10^{-9} gmol/cm^2 · s. This small discrepancy may be due to the differences in water content between the Na and EDA form membranes as shown in Table 1.

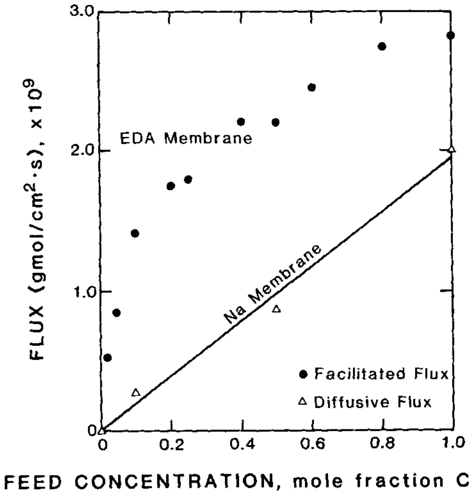


Figure 3. CO_2 flux for an EDA membrane and a Na membrane as a function of CO_2 mole fraction in feed gas.

The results of the CO_2/CH_4 binary mixture transport experiments are shown in Figure 5. The ratio of the CO_2 flux to the CH_4 flux is plotted against the feed gas CH_4 concentration. The solid points represent data for an EDA membrane while the open square is the flux ratio for a Na membrane. The flux ratios increased from 29.0 to 264 for feed gases of 0.05 CO_2/0.95 CH_4 and 0.75 CO_2/0.25 CH_4, respectively. These flux ratios can be converted to separation factors of 87.9 to 551, corresponding to flux ratios of 264 to 29.0, respectively. Table 2 compares these separation factors and permeabilities to those for cellulose ester hollow-fiber membranes used at the SACROC tertiary oil recovery facility (Parro and Hamaker, 1985) for stripping CO_2 from hydrocarbons prior to reinjection into the petroleum reservoir. The range of separation factors obtainable with the cellulose hollow fiber membranes was 16–24. The very high selectivities that can be obtained with facilitated transport membranes are what makes them potentially attractive for industrial application.

Modeling and analysis

The following equation has been derived for the facilitation factor F (Noble et al., 1986b):

$$F = \frac{\left(1 + \frac{\alpha K}{1 + K}\right)\left(1 + \frac{2}{Sh}\right)}{\left[1 + \left(\frac{\alpha K}{1 + K}\right)\frac{\tanh \lambda}{\lambda}\right] + \left(1 + \frac{\alpha K}{1 + K}\right)\left(\frac{2}{Sh}\right)} \tag{3}$$

where

$$\alpha = \frac{D_{AB} C_T}{D_A C_{AO}} \tag{4}$$

$$K = K_{eq} C_{AO} \tag{5}$$

$$Sh = \frac{kL}{D_A} \tag{6}$$

$$\epsilon = \frac{D_{AB}}{k_r L^2} \tag{7}$$

$$\lambda = \frac{1}{2}\sqrt{\frac{1 + (\alpha + 1)K}{\epsilon(1 + K)}} \tag{8}$$

For reaction equilibrium, $\tanh \lambda/\lambda$ approaches 0. Equation 3 can then be rearranged to yield

$$E^{-1} = (F - 1)^{-1} = \left(1 + \frac{2}{Sh}\right)\alpha^{-1} + \frac{2}{Sh}\left(\frac{\alpha K + 1}{\alpha K}\right) + (\alpha K)^{-1} \tag{9}$$

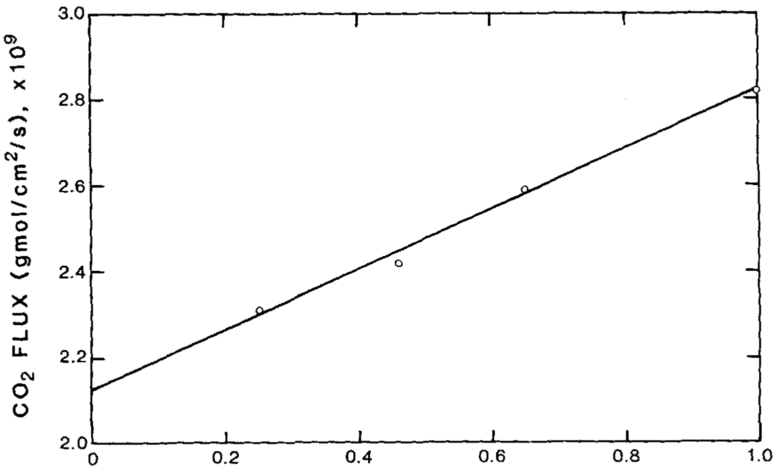


Figure 4. CO_2 flux as a function of EDA concentration in the ion exchange membrane.

Since α^{-1} is directly proportional to y_{CO_2}, a plot of E^{-1} vs. y_{CO_2} should produce a straight line if the reaction equilibrium assumption holds. Also, if αK is large, the intercept of this line is $2/Sh$ and provides a measure of the external mass transfer resistance for the membrane. Figure 6 is a plot of E^{-1} for the CO_2 transport data from Figure 3. The data plot as a straight line with essentially a zero intercept. Therefore, the reaction equilibrium assumption is valid and external mass transfer resistances can be neglected.

Calculation of the diffusivities in the ion exchange membrane was based on the volume of absorbed water. Based on the three-phase model of perfluorosulfonic acid membranes, we have made the assumption that transport of the gas molecules, EDA, and the complexed EDA occurs through the water containing ionic phases of the ionomer. The diffusional path length was taken to be the swollen thickness of the membrane, 200 μm. An effective porosity ϕ of the membrane can be calculated by dividing the volume of water absorbed by the total volume of the membrane. The diffusion coefficient calculations were corrected for the effective porosity of the IEM.

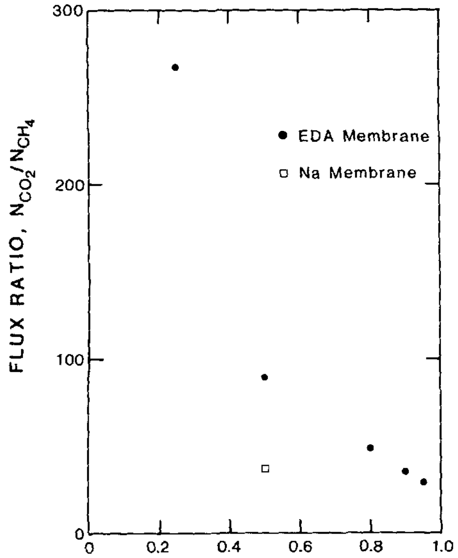


Figure 5. Ratio of CO_2 flux to CH_4 flux as a fraction of CH_4 mole fraction in feed gas CO_2/CH_4 binary mixture.

The effective diffusivities for CO_2 and the CO_2-EDA complex are needed to compute the mobility ratio α. Both diffusivities can be computed from experimental transport data. The effective diffusivity of CO_2 in the IEM was determined from the slope of the linear fit of the flux data for the Na membrane using the following equation,

$$D_A = \frac{\text{slope} \cdot L}{\phi C_{AO}}. \tag{10}$$

A value of 4.93×10^{-6} cm²/s was obtained for CO_2. The effective diffusion coefficient for the complex can be calculated from the slope of the line in Figure 6 using the equation

$$D_{AB} = \frac{D_A C_{AO}}{\text{slope} \cdot C_T}. \tag{11}$$

The effective diffusivity of the CO_2-EDA complex was 9.71×10^{-9} cm²/s, which is also assumed to be the value for the EDA carrier.

Once the diffusivities are known, Eq. 3 can be used to calculate facilitation factors that can be compared to the experimental data. The properties used in the calculation are summarized

Table 2. CO_2/CH_4 Separation Factors

Membrane	Separation Factor P_{CO_2}/P_{CH_4}
Cellulose ester hollow-fiber	16–24
EDA–Ion exchange	87.9–551

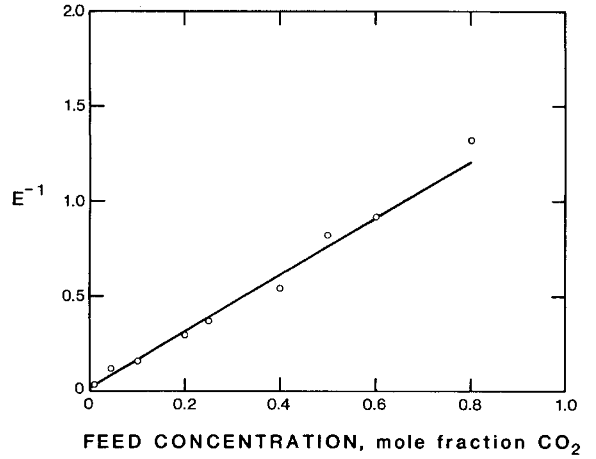


Figure 6. Reciprocal of enhancement factor as a function of feed gas CO_2 mole fraction.

in Table 3. The comparison of predicted and experimental values for F are presented in Table 4. The general agreement is very good. The one exception is the F value for $y_{CO_2} = 0.01$.

The poor agreement at this point is probably due to uncertainties in the reaction properties used as inputs to the model. Values of the reaction rates and the equilibrium constant for bulk solution were used in Eq. 3 to predict the facilitation factors. It is likely that the reaction properties in the high ionic strength environment of the perfluorosulfonic acid membrane could be different from the values in bulk solution. Indeed, Lieber and Lewis (1985) recently compared rate and activation parameters for complexation reactions within perfluorosulfonic acid membranes to the bulk solution values. The rate and activation parameters within the membrane were significantly different from values reported in water. This would explain the poor agreement between the model prediction and experimental data for very low feed gas mole fractions where the contribution of the CO_2-EDA complex flux to the total flux is greatest. Due to the negligible concentration gradient, the flux of uncomplexed CO_2 is small. Therefore, the total flux is dominated by the flux of the CO_2-EDA complex. Consequently, if the equilibrium constant is larger in the bulk solution than in the membrane, then using the bulk solution equilibrium constant will overpredict the facilitation factor at low CO_2 feed gas mole fractions. This is exactly what is observed.

Table 3. Property Values Used in Calculation of Facilitation Factors

Property	Value
D_A	4.93×10^{-6} cm^2/s
D_{AB}	9.71×10^{-9} cm^2/s
S_A	2.64×10^{-2} M (Kohl & Riesenfield, 1979)
C_T	8.32 M
K_{eq}	1.0×10^5 M^{-1} (Jensen & Christensen, 1955)
k_f	1.75×10^4 M$^{-1} \cdot$ s^{-1} (Sada et al., 1977)
k_r	0.175 s^{-1}
L	2.0×10^{-2} cm
ϕ	0.30

Table 4. Model Predictions and Experimental Results

y_{CO_2}	F_{exp}	F_{model}
1.0	1.44	1.62
0.8	1.75	1.78
0.6	2.09	2.03
0.4	2.83	2.55
0.25	3.68	3.48
0.2	4.45	4.10
0.1	7.26	7.18
0.045	9.40	14.7
0.01	26.7	60.8

The effective diffusivity for the CO_2-EDA complex was estimated from the set of facilitated flux data for an IEM fully exchanged with the EDA carrier. As shown in Figure 4, the CO_2 facilitated flux was measured as a function of the degree of EDA loading in the membrane. Equation 3 and the property values in Table 3 were used to predict CO_2 facilitation factors as a function of carrier concentration. As shown in Table 5, the comparison between experimental and predicted F values is excellent. Therefore, the modeling approach used has some utility in predicting facilitation factors under different conditions.

The model was also used to predict facilitation factors for a 50 μm thick IEM in order to compare its performance with an ILM of identical thickness (Noble et al., 1986b). The ILM consisted of a 1 M EDA solution immobilized in a 25 μm microporous polypropylene ultrafiltration membrane. The ILM support had a tortuosity of 2, corresponding to a diffusional path length of 50 μm. As shown in Table 6, the superior facilitation factors for the IEM are due to the higher carrier concentration in the IEM.

Transport mechanism

Our hypothesis about the mechanism of transport in EDA-containing IEM's was that of a reactive, mobile carrier, facilitated transport mechanism analogous to that studied in ILM's and biological membranes. Based on the three-phase microstructure model of perfluorosulfonic acid ionomers, we postulated that the mass transfer processes take place in the water containing ionic regions of the IEM. All the data we have taken are consistent with the facilitated transport mechanism. The plot of CO_2 flux vs. feed gas mole fraction for the EDA membrane in Figure 1 is highly curved, indicating that a chemical reaction is taking place. A CO_2 transport experiment was performed using tetramethyl EDA as a carrier in an IEM. No facilitation was observed. Since tetramethyl EDA has methyl groups

Table 5. Prediction of Facilitation Factor as a Function of Carrier Loading in the IEM

Fraction of Ion Exchange Sites with EDA	F_{exp}	F_{model}
0.25	1.18	1.16
0.46	1.24	1.29
0.65	1.33	1.40
1.00	1.44	1.62

Table 6. Predicted IEM Facilitation Factors and Experimental IEM Data

Y_{CO_2}	F_{ILM}	F_{IEM}
1.0	1.00	1.55
0.5	1.16	2.08
0.25	1.38	3.09
0.065	2.75	8.22

Thickness, 5.0×10^{-3} cm

substituted for hydrogens on the amine functional groups, it cannot form the carbamate species with CO_2. This observation supports carbamate formation as the reaction mechanism.

Diffusion coefficients were not directly measured for EDA and the CO_2-EDA complex in this study, but were calculated from transport data under diffusion-limited conditions. The value calculated for the CO_2-EDA complex was of the order 10^{-8} cm^2/s. Studies of alkali metal cation mobility in perfluorosulfonate ionomers have yielded diffusivities of 10^{-7} cm^2/s for Cs^+ ions (Yeager and Steck, 1981). Consequently, a value of 10^{-8} cm^2/s for the CO_2 complex is not unreasonable given the significantly larger size of the diffusing species compared to Cs^+, and is indirect evidence of mobility of the complex.

Conclusions

This is the first study of facilitated transport in perfluorosulfonic acid ionomer films. These ion exchange membranes have usually been used in electrochemical processes such as the chlor-alkali process. We measured CO_2 and CH_4 fluxes through amine-containing ion exchange membranes of 200 μm thickness and observed facilitation factors (ratio of flux with carrier present to flux without carrier) up to 26.7 and flux ratios for CO_2/CH_4 of 29.0 to 264. These flux ratios correspond to separation factors (P_{CO_2}/P_{CH_4}) of 551 to 87.9, respectively. It can be concluded from these data that EDA IEM's can achieve a high degree of facilitation and high selectivities. Very good agreement between a reaction equilibrium analytical model and the experimental data was observed, and predicted facilitation factors at a membrane thickness of 50 μm are promising for industrial applications. The transport data are consistent with our hypothesis of a mobile, reactive-carrier transport mechanism. The excellent performance of the ion exchange support is primarily due to the very high carrier concentrations that can be achieved. Consequently, we have found perfluorosulfonic acid ion exchange membranes to be ideal supports for water-soluble complexation agents. Potential applications of this technology are purification of natural and synthetic gas and the development of acid gas sensors and specific adsorbents.

Acknowledgment

The authors would like to acknowledge the support of the Dept. of Energy Morgantown Energy Technology Center for this work under DOE Contract No. DE-AI21-84MC21271. Jenene F. Bewlay made the measurements of water absorption in ion exchange membranes. We would also like to thank Carl A. Koval of the University of Colorado Chemistry Dept., and Louis L. Burton and C.G. Michael Quah of the DuPont Co. for helpful discussions.

Notation

C_{io} = concentration of species i at feed gas/membrane interface = Y_iS_i
C_i = concentration of species i
D_i = effective diffusion coefficient of species i in membrane
E = enhancement factor
F = facilitation factor, ratio of flux with carrier present to flux without carrier
K = dimensionless equilibrium constant
K_{eq} = equilibrium constant
k = mass transfer coefficient
k_f = forward rate constant
k_r = reverse rate constant
L = membrane thickness
M = molarity, gmol/L
P_i = permeability of species i, volumetric flux of i divided by partial pressure gradient of i
Sh = Sherwood number, kL/D_A
S_i = solubility of species i in water
y_i = mole fraction of species i in gas phase

Greek letters

α = mobility ratio, Eq. 4
ϵ = inverse Damkohler number, Eq. 7
ϕ = effective membrane porosity

Subscripts

A = permeating gas
B = carrier
AB = carrier-gas complex
T = total amount of carrier
i = any species

Literature cited

Bateman, B. R., J. D. Way, and K. M. Larson, "An Apparatus for the Measurement of Gas Fluxes Through Immobilized Liquid Membranes," *Sep. Sci. Tech.*, **19**, 21 (1984).

Donaldson, T. L., and Y. N. Nguyen, "Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes," *Ind. Eng. Chem. Fundam.*, **19**, 260 (1980).

Donaldson, T. L., and J. A. Quinn, "Carbon Dioxide Transport Through Enzymatically Active Synthetic Membranes," *Chem. Eng. Sci.*, **39**, 103 (1975).

Enns, T., "Facilitation by Carbonic Anhydrase of Carbon Dioxide Transport," *Science*, **155**, 44 (1967).

Gierke, T. D., "Ionic Clustering in Nafion Perfluorosulfonic Acid Membranes and Its Relationship to Hydroxyl Rejection and Chlor-Alkali Current Efficiency," Electrochem. Soc. Meet. Atlanta (Oct. 1977).

Grot, W. G. F., G. E. Munn, and P. N. Walnsley, "Perfluorinated Ion-Exchange Membranes," 141st Nat. Meet. Electrochem. Soc., Houston (May, 1972).

Hikita, H., S. Asai, H. Ishikawa, and M. Honda, "The Kinetics of Reactions of Carbon Dioxide with Monoisopropanolamine, Diglycolamine, and Ethylenediamine by a Rapid Mixing Method," *Chem. Eng. J.*, **14**, 27 (1977).

Jensen, A., and R. Christensen, "Studies on Carbamates. XI: The Carbamate of Ethylenediamine," *Acta Chemica Scand.*, **9**, 486 (1955).

Kimura, S. G., S. L. Matson, and W. J. Ward III, "Industrial Applications of Facilitated Transport," *Recent Developments in Separation Science*, **5**, N. N. Li, ed., CRC Press, Cleveland (1979).

Kohl, A. L., and F. C. Riesenfeld, *Gas Purification*, Gulf Pub. Co., Houston (1979).

LeBlanc, O. H., W. J. Ward III, S. L. Matson, and S. G. Kimura, "Facilitated Transport in Ion Exchange Membranes," *J. Mem. Sci.*, **6**, 339 (1980).

Leitz, F. B., M. A. Accomazzo, and S. A. Michalek, 141st Meet. Electrochem. Soc., Houston (1972).

Lieber, C. M., and N. S. Lewis, "Probing Polymer Effects on Chemical Reactivity: Ligand Substitution Kinetics of $Ru(NH_3)_5\ (H_2O)^{2+}$ in Nafion Films," *J. Am. Chem. Soc.*, **107**, 7190 (1985).

Matson, S. L., J. Lopez, and J. A. Quinn, "Separation of Gases with Synthetic Membranes," *Chem. Eng. Sci.*, **38**, 503 (1983).

Meldon, J. H., "Reaction-Enhanced Mass Transfer in Thin Liquid Films," Ph.D. Thesis, Mass. Inst. Tech. (1973).

Meldon, J. H., K. A. Smith, and C. K. Colton, "The Effect of Weak

Acids Upon the Transport of Carbon Dioxide in Alkaline Solutions," *Chem. Eng. Sci.*, **32,** 939 (1977).

Noble, R. D., J. D. Way, and A. L. Bunge, "Liquid Membranes," *Solvent Extraction and Ion Exchange,* **10,** Y. Marcus, ed., (1986a).

Noble, R. D., J. D. Way, and L. A. Powers, "Effect of External Mass Transfer Resistance on Facilitated Transport," *Ind. Eng. Chem. Fundam.*, **25,** 450 (1986b).

Otto, N. C., and J. A. Quinn, "The Facilitated Transport of Carbon Dioxide Through Bicarbonate Solutions," *Chem. Eng. Sci.*, **26,** 949 (1971).

Parro, D., and B. Hamaker, "CO_2 Hydrocarbon Membrane Separation Systems from Laboratory to Commercial Success," Paper 42b, AIChE Spring Nat. Meet., Houston (Mar., 1985).

Pintauro, P. N., and D. N. Bennion, "Mass Transport of Electrolytes in Membranes. 1: Development of Mathematical Transport Model," *Ind. Eng. Chem. Fundam.*, **23,** 230 (1984).

Sada, E., H. Kumazawa, and M. A. Butt, "Absorption of Carbon Dioxide into Aqueous Solutions of Ethylenediamine: Effect of Interfacila Turbulence," *Chem. Eng. J.*, **13,** 213 (1977).

Smith, D. R., R. J. Lander, and J. A. Quinn, "Carrier-Mediated Transport in Synthetic Membranes," *Recent Developments in Separation Science,* **3,** N. N. Li, ed., CRC Press, Cleveland (1977).

Suchdeo, S. R., and J. S. Schultz, "The Permeability of Gases Through Reacting Solutions: The Carbon Dioxide-Bicarbonate Membrane System," *Chem. Eng. Sci.*, **29,** 13 (1974).

Ward, W. J., and W. L. Robb, "Carbon Dioxide-Oxygen Separation: Facilitated Transport of Carbon Dioxide Across a Liquid Film," *Science,* **156,** 1481 (1967).

Way, J. D., R. D. Noble, T. M. Flynn, and E. D. Sloan, "Liquid Membrane Transport: A Survey," *J. Mem. Sci.*, **12,** 239 (1982).

Way, J. D., R. D. Noble, and B. R. Bateman, "Selection of Supports for Immobilized Liquid Membranes," *Materials Science of Synthetic Membranes,* D. L. Lloyd, ed., *ACS Symp. Ser. No. 269* (1985).

Weiland, R. H., and O. Trass, "Absorption of Carbon Dioxide in Ethylenediamine Solutions. I: Absorption Kinetics and Equilibrium," *Can. J. Chem. Eng.*, **49,** 767 (1971).

Yeager, H. L., and A. Steck, "Cation and Water Diffusion in Nafion Ion Exchange Membranes: Influence of Polymer Structure," *J. Electrochem. Soc.*, **129,** 328 (1981).

Yeo, S. C., and A. Eisenberg, "Physical Properties and Supermolecular Structure of Perfluorinated Ion-Containing Polymers," *J. Appl. Polymer Sci.*, **21,** 875 (1977).

Manuscript received Mar. 25, 1986, and revision received Sept. 15, 1986.