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R. D. Noble[ab]; J. J. Pellegrino[a]; E. Grosgogeat[ac]; D. Sperry[a]; J. O. Way[ad]
[a] National Bureau of Standards Center for Chemical Engineering, Boulder, CO [b] Chemical Engineering Dept., University of Colorado, Boulder, CO [c] Chemical & Nuclear Engineering Dept., University of Cincinnati, Cincinnati, OH [d] SRI Int., Chemical Engineering Laboratory, Menlo Park, CA

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CO_2 SEPARATION USING FACILITATED TRANSPORT ION EXCHANGE MEMBRANES

R.D. Noble[1], J.J. Pellegrino[4], E. Grosgogeat[2], D. Sperry,
and J.D. Way[3]
National Bureau of Standards
Center for Chemical Engineering, 773.1
325 Broadway
Boulder, CO 80303

ABSTRACT

The use of ion-exchange membranes as supports for facilitated transport of CO_2 is demonstrated. Two different ionomer films were evaluated. The ionomers were a perfluorosulfonic acid film and a sulfonated polybenzimidazole film. Sodium (Na^+) was exchanged into the membrane for diffusion experiments and ethylenediamine (EDA) was exchanged for facilitated transport experiments. The results indicate that thin perfluorosulfonic acid membranes provide the best CO_2 flux and can also provide exceptionally high selectivity.

INTRODUCTION

Facilitated transport is a process whereby a complexing agent (carrier), contained in a liquid membrane, can reversibly react with a solute of interest. This results in an increased solute flux, as well as increased selectivity. A schematic of

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[1] Present address: University of Colorado, Chemical Engineering Dept., Boulder, CO 80303

[2] Present address: University of Cincinnati, Chemical & Nuclear Engineering Dept., Cincinnati, OH 45221

[3] Present address: SRI Int., Chemical Engineering Laboratory, Menlo Park, CA 94025

[4] Author to whom correspondence should be addressed

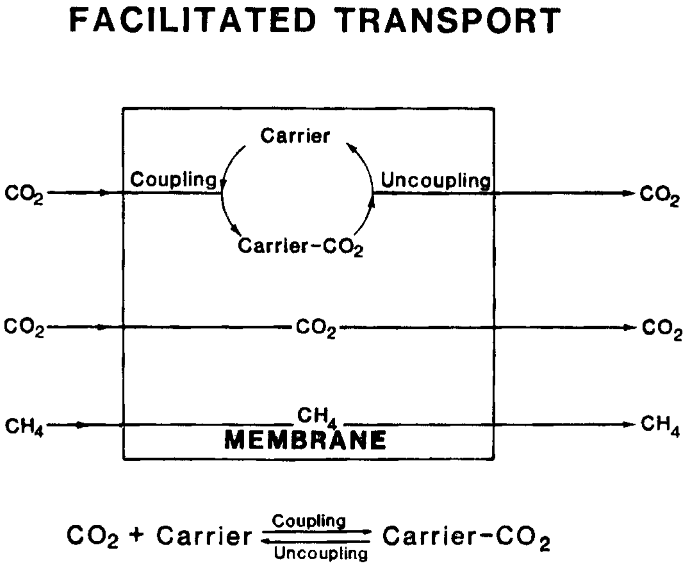


FIGURE 1: Schematic of facilitated CO_2 transport.

this process is shown is in Figure 1. Some recent review articles can provide additional details (1-5).

There are two major problems associated with immobilized liquid membranes (ILMs). These are loss and/or deactivation of the complexing agent through solvent loss from the pore spaces. "Short-circuiting" occurs, and the gas passes through the pore with little or no selectivity. This results in a loss of the facilitation effect.

One method to overcome these problems is to use ion-exchange membranes as the support. These films are nonporous, so no "short-circuiting" occurs if the membrane loses solvent. The complexing agent is held in the membrane by electrostatic forces. This prevents carrier loss and can aid in resisting carrier deactivation. For example, oxidation of the carrier is minimized by the high charge density in the vicinity of an ion-exchange site. A third benefit of ion-exchange membranes is that you can load larger amounts of the carrier than is possible with ILMs. This is due to the fact that carrier loading is limited only by ion-exchange site density and not by the physical solubility of the carrier in the solvent.

There have been previous reports of CO_2 separation using ion-exchange membranes. LeBlanc et al. (6) first described the use of an ion-exchange film as a support for facilitated transport. They studied both CO_2 and ethylene transport. Way et al. (7) studied the separation of CO_2 from CH_4 using an ion-exchange film. They used ethylenediamine as the carrier. They measured separation factors up to 551 for CO_2 over CH_4.

The objective of this study is to compare two different ionomer films as supports for CO_2 transport. The films were a perfluorosulfonic acid (PFSA) ionomer and a sulfonated polybenzimidazole (PBI) ionomer.

MEMBRANE PREPARATION

PFSA Films

We used two PFSA membranes, designated N117 and NE111, a commercial, nominally 200 µm (7 mil) film and an experimental, nominal 30 µm (1 mil) film, respectively. Both of these films were supplied in the dehydrated, acid form and have an 1100 gram/equivalent molecular weight (g/eq).

We tested rectangular pieces which were put in the Na form (for diffusive flux measurements) by boiling in NaOH (0.05 and 0.15 M) for 4 hours and then soaking in a fresh 0.05 NaOH solution overnight. The amount of NaOH represented, minimally, a hundred-fold excess with respect to the number of total available ion- exchange sites.

After diffusive flux experiments are run the film is put into the EDA form. Monopositive EDA is created by adding one equivalent of HCl to the EDA solution. The amount of EDA used is, minimally, a fifty-fold excess with respect to the total available ion-exchange sites. The membrane is immersed in the EDA solution and allowed to soak in it (with stirring) overnight.

PBI Films

The PBI membranes are developmental films with a nominal 35 µm (1+ mil) thickness. According to the manufacturer there were two sulfonate groups per polymer repeat unit leading to a equivalent molecular weight of 237.

The PBI films were put in Na form by soaking overnight in 1 M NaCl. This represented a hundred-fold excess of Na with respect the total available ion-exchange sites. After diffusive flux experiments the membranes were soaked, as above, with a solution of monopositive EDA (with stirring) overnight. The amount of EDA was typically a fifty-fold excess with respect to the total theoretical ion-exchange sites available.

For both the Na and EDA form experiments the membranes are kept in their original soaking solutions between experiments.

Carrier selection

The carrier molecule chosen was ethylenediamine. It was chosen for the following criteria:

a) It can be singly protonated and exchanged into the ion-exchange film as a cation.
b) Its reaction properties with CO_2 are well documented.
c) It provides a basis for comparison of the performance of the two ionomer films.

EXPERIMENTAL DESCRIPTION

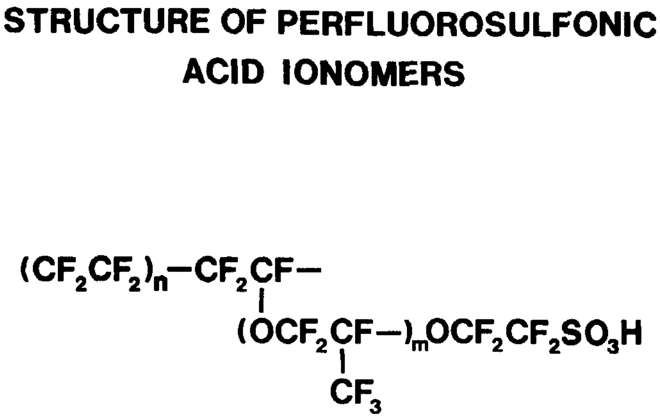
The apparatus and procedure used to measure membrane fluxes were described in detail in previous papers (7,8). The experimental procedure involves flowing CO_2 in He mixtures on the feed side of a flat membrane with a sweep gas of pure He. The flow rates are measured with mass flow meters, calibrated for the specific gases. The membrane area is 202.9 cm^2. Both sweep and feed inlet streams are humidified by bubbling through deionized water before contacting the membrane. The outlet streams from the cell are chilled to 213 K, to remove the moisture before they enter the gas chromatograph (GC) system. We use a thermal conductivity detector to measure both the feed and sweep side compositions. The GC is calibrated daily, with the specific experiment's gases. The flux calculations are based on the measured flow rates of the sweep gas, it's composition and the membrane area. Periodic mass balances are performed using the feed gas composition exiting the membrane cell.

The mass flow meters are accurate to 1 sccm, which represents a 2% error at our experimental flow rates. The gas chromatograph is calibrated before each day's experiments and the calibration gas's composition is reproducible within 0.5%. Independent material balances, based on gas mixture compositions set by flow meter settings and subsequent GC analysis, close within 5%. This represents a possible source of error in our assignment of the feed mole fraction, with a bias to the high side.

All experiments reported here were done at ambient conditions of approximately 298 K and 84 kPa. Only those experiments where the flux reaches and maintains a steady state for at least 1 hour before the experiment is terminated are reported. The 95% confidence intervals for the flux measurements are a function of the actual flux and vary from 0.1 to 2 mol/(cm^2•s).

RESULTS

The structural formula of the PFSA film is shown in Figure 2. The H^+ attached to the SO_3^- is exchanged with the Na^+ to obtain



STRUCTURE OF PERFLUOROSULFONIC ACID IONOMERS

$$\begin{array}{l}(CF_2CF_2)_n-CF_2\underset{|}{C}F- \\ \qquad\qquad\qquad (OCF_2\underset{\underset{CF_3}{|}}{C}F-)_mOCF_2CF_2SO_3H\end{array}$$

FIGURE 2: Structural formula of Perfluorosulfonic Acid ionomers. (Membranes in this study have a value of m= 1).

the non-reactive form of the membrane for diffusive flux experiments. A singly-protonated EDA^+ is exchanged for the Na^+ to obtain the reactive form.

Our initial experiments were performed with the N117 (200 µm) PFSA membrane and are reported by Way et al. (7). The CO_2 flux results are shown in Figure 3. The straight line for the Na^+ data indicates Fickian-type diffusion and no reaction occurring within the membrane. The EDA form flux data are higher and the curve is nonlinear. This indicates enhanced transport and is evidence of reaction between EDA and CO_2.

The same type of experiment was then performed using the developmental PFSA membrane, NE111 (30 µm). The Na^+ form data are shown in Figure 4. Data are presented for three separate membranes. Note that there is a great deal of scatter between membranes but each individual membrane can be fitted to a linear relationship. A "best-fit" straight line was drawn through all the data to determine a basis for comparison with the reactive membrane results. The R^2 was 0.67 and the standard error of the flux estimate is 22.9 $mol/(cm^2 \cdot s)$.

The EDA form results are shown in Figure 5. These flux data are very consistent and again produce the nonlinear relationships between flux and driving force. The CO_2 flux is again much higher (especially at low driving forces) for the EDA^+ versus Na^+ form.

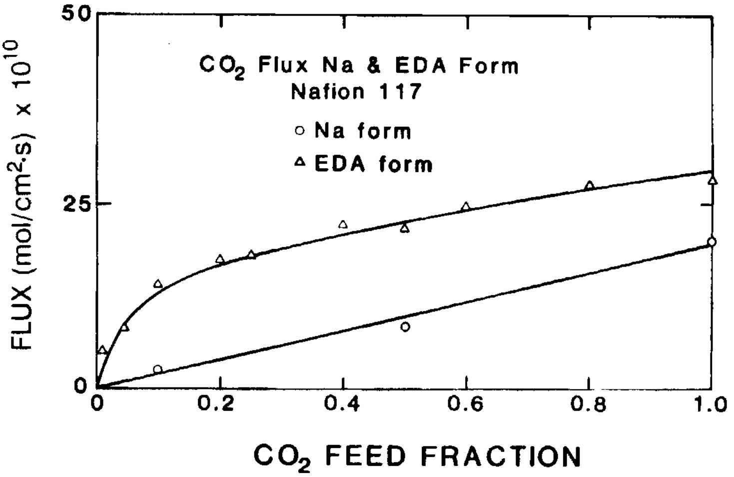


FIGURE 3: CO_2 flux for an EDA (upper) membrane and a Na (lower) membrane as a function of CO_2 feed mole fraction; Perfluorosulfonic Acid ionomer (N117-200 micron).

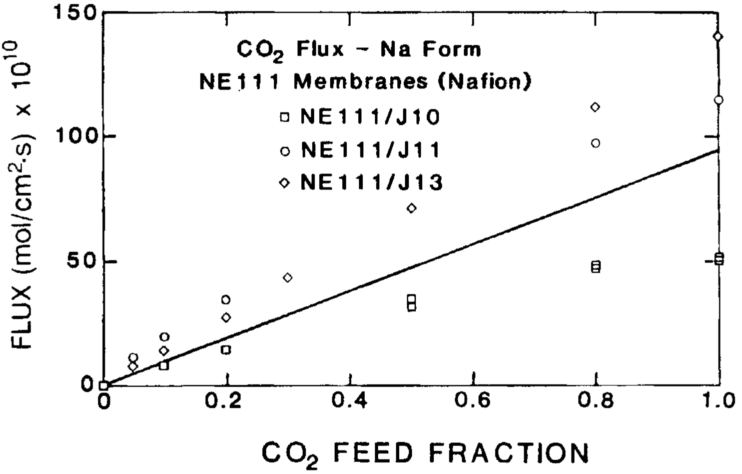


FIGURE 4: CO_2 flux for 3 Na membranes as a function of CO_2 feed mole fraction; Perfluorosulfonic Acid ionomer (NE111-30 micron).

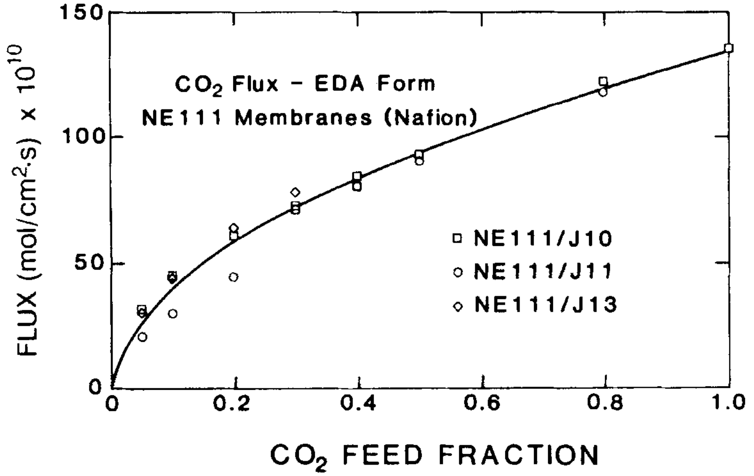


Figure 5: CO_2 flux for 3 EDA membranes as a function of CO_2 feed mole fraction; Perfluorosulfonic Acid ionomer (NE111-30 micron).

An analytical model has been developed to describe facilitated transport (9). The following equation has been derived for the facilitation factor F.

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

where

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

$$K = \frac{k_f}{k_r}\,\frac{C_{AO}}{m}$$

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

$$\varepsilon = \frac{D_{AB}}{k_r L^2}$$

$$\lambda = \frac{1}{2}\sqrt{\frac{1 + (\alpha + 1)K}{\varepsilon(1 + K)}}$$

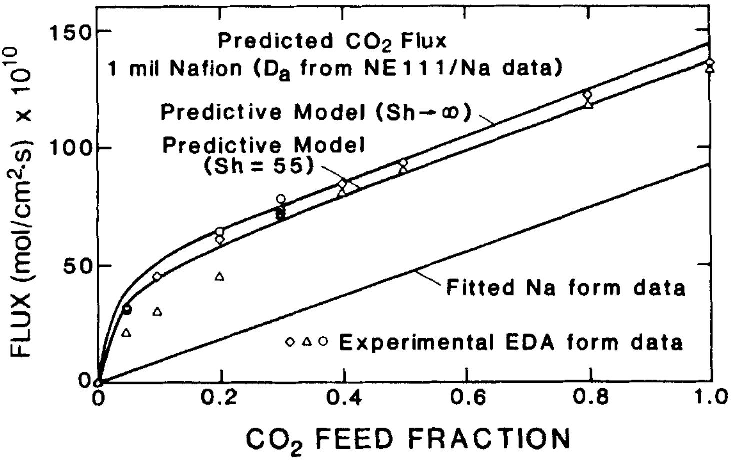


FIGURE 6: CO_2 flux for EDA-NE111 membrane compared with model predictions for the facilitated flux. Upper curve for no mass transfer resistance (Sh-∞) and middle curve for low, but finite, resistance (Sh=55). Bottom line is fitted flux for Na membrane; Perfluorosulfonic Acid ionomer (NE111-30 micron).

In this equation α represents the ratio of mobility of the complex to that of the solute; the Sherwood number (Sh) accounts for the boundary layer mass transfer resistance at the feed and sweep gas/membrane interfaces and ϵ, the inverse Damkohler number, represents the ratio of diffusion to reaction time scales.

Figure 6 shows the comparison between the experimental results for the NE111 membranes and the facilitated flux predictions based on the above model. The agreement is very good.

The CO_2 diffusion coefficient was obtained from the fitted line for the Na^+ form experiments. We normalize the effective diffusion coefficient, between the different forms of the membranes, with an effective porosity, defined as the weight fraction of water in the membrane. The porosity of the NE111 membranes was obtained from measuring water uptake in the two forms. Water uptake is measured by first drying the H^+ form of the membrane under vacuum (total pressure 34kPa) at 349 K for 18 hours.

Table 1
Property Values Used in Calculation of Facilitated Fluxes

PROPERTY	VALUE	UNITS	SOURCE
Na form porosity	0.3		measured
EDA form porosity	0.193		measured
C_T	8.32	M	(7)
S_A	2.64×10^{-2}	M	"
k_r	1.75×10^{-1}	s^{-1}	"
k_f	1.74×10^{-4}	$M^{-1}s^{-1}$	"
L	30×10^{-6}	m	measured
Sh	55		1/(F-1) plot of EDA data (9)
D_A	3.61×10^{-6}	$cm^2\ s^{-1}$	Na form data
D_{AB}	9.71×10^{-9}	$cm^2\ s^{-1}$	(7)

The high value of the Sh (Sherwood Number) indicates that external mass transfer resistance was not significant in these experiments.

The dry weight is determined by quicky transferring the membrane to an enclosed analytical balance (Sartorius Model 1712 MP8), in which dessicants have been placed. The wet weight is determined by taking the membrane from the appropriate solution (either Na^+ or EDA^+), patting it to remove excess moisture and transferring it to the enclosed balance. For this measurement the chamber contains saturated paper towels to increase humidity. The other property data were previously determined from the experiments using the N117 membranes (7). All values used in the model and their source are given in Table 1.

The scatter in the Na^+ form data versus the EDA form results can possibly be interpreted in the following manner. The NE111 membranes are developmental and may be subject to some manufacturing process inconsistencies. If the distribution of ion-exchange sites were nonuniform then the hydrophilic cluster-pore network could show variations in its effective tortuosity. Since the CO_2 diffuses through this network, via solubility in the water phase of the ionic clusters, its effective diffusion coefficient, normalized for porosity, would show an effect from the variable tortuosity between samples. Linear fits of the experimental data yields a two-fold spread in the effective diffusion coefficients for the three NE111 membranes tested.

For the facilitated transport case we have speculated that the carbamate zwitterion, formed between the CO_2 and the EDA, is ionically bound at the ion-exchange sites in the cluster network. Due to the ionic attraction, we feel that this complex's effec-

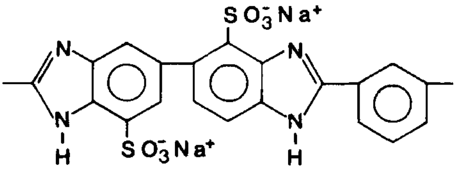


FIGURE 7: Structural formula for the Na salted sulfonated polybenzimidazole membranes.

tive diffusion coefficient is largely influenced by spatial rearrangements of the ionic clusters. The dynamic flexibility of the polymer chain backbone may cause clusters to "jump" (i.e., collapse and reform) to new positions within the absolute volume of the membrane. In this manner the polymer backbone's movement helps carry the ionically associated CO_2 complex to unsaturated positions, and ultimately to the sweep interface.

If this speculated, transport viewpoint is correct, then the lack of scatter in the EDA form results reflects the fact that the rate limiting step, in the facilitated transport, is not the complex's diffusion in hydrophilic regions, but may be related to polymer backbone flexibilty. Thus variable tortuosity between membranes may not cause the same flux data scatter in the EDA form as in the Na^+ form.

A polybenzimidazole (PBI) ionomer film was also studied. A schematic of its structure is shown in Figure 7. The PBI ionomer was reported to have a high ion-exchange site density (237 g/eq versus 1100 g/eq for the PFSA) and was thinner than the N117 membranes (35 μm versus 200 μm). Therefore we expected to have dramatically higher facilitated CO_2 flux.

The results for the PBI film are shown in Figure 8. The facilitation effect is apparent but not as high as we would expect from the proposed high ion-exchange site density.

An elemental analysis was performed on the PBI film to check the ion-exchange site capacity. The results are shown in Table 2.

Solution 1 was used to generate monopositive EDA and solution 2 to generate the dipositive EDA. The results in Table 2 show that the actual ion-exchange site capacity was lower, by a factor of 4 to 5, than expected from the manufacturer's data. Additionally, only one half of the available sites were accessible to the monopositive EDA because the others had stayed in the acid form versus the Na^+ form, in the first exchange. This translates to much lower carrier loading (2000 g/eq vs 237 g/eq) and less facilitation.

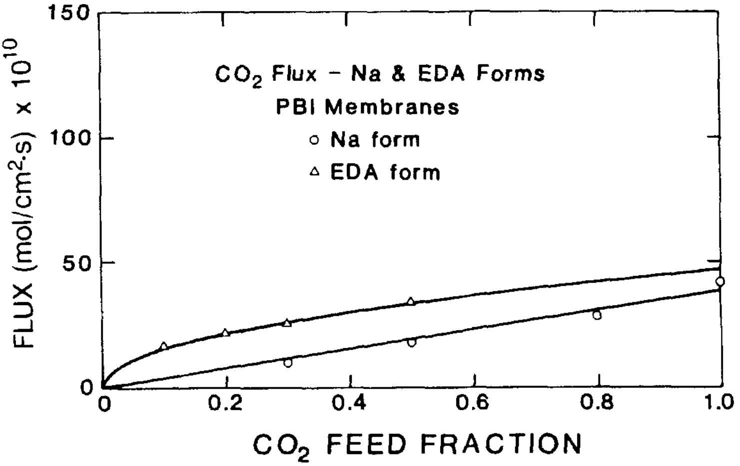


FIGURE 8: CO_2 flux for EDA (upper) and Na (lower) membranes as a function of CO_2 feed mole fraction; Polybenzimidazde (PBI-35 microns).

Table 2
Elemental Analysis

MOLE RATIO	SULF. PBI SOAKED IN SOL. 1	SULF. PBI SOAKED IN SOL. 2	SULF. PBI WITHOUT TREATMENT
S/C observed	0.020	0.019	0.026
S/C expected*	0.083	0.083	0.100
C/N observed	4.72	4.94	5.09
C/N expected*	3.00	3.00	5.00
Na/S observed	0.095	0.063	0.488
Na/S expected	0.0	0.00	1.00

Solution	EDA	HCI	pH
1	0.804 M	0.495 M	9.97
2	0.094 M	0.104 M	2.15

*(2 C added from EDA)

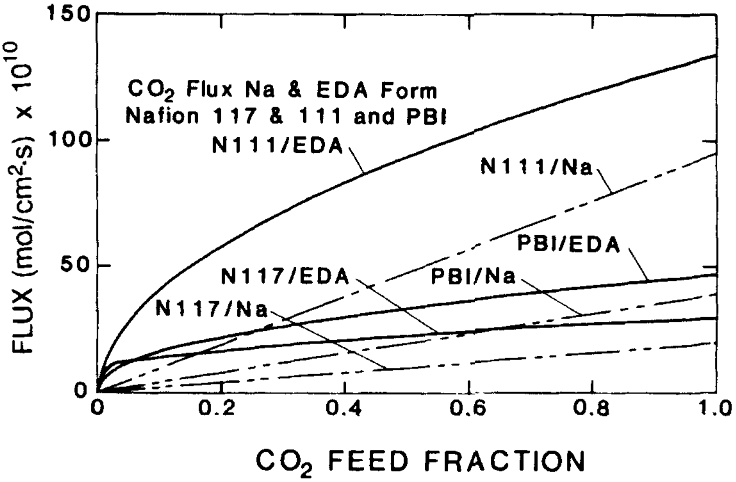


FIGURE 9: Fitted curves of CO_2 flux for EDA and Na membranes as function of CO_2 feed mole fraction. Results from all membranes tested are shown.

To compare the performance, Figure 9 shows the CO_2 flux vs. feed mole fraction results for all the membranes tested. The NE111 PFSA membrane had the best performance. The fluxes for the PBI membrane were higher than the N117 primarily due to thickness considerations.

The next comparison is to determine how the permeability of these ionomer films compare with conventional asymmetric polymer membranes used for the same application. This comparison is shown in Figure 10. As expected for facilitated transport, the permeability increases as the solute becomes more dilute. This is due to the fact that the reactive pathway for transport becomes more efficient (per unit pressure driving force) as the partial pressure of the gas decreases. So, for low partial CO_2 pressures, the permeability is comparable to polymer membranes.

The selectivity of PFSA membranes using EDA has previously been reported for CO_2/CH_4 separations (7). These results are shown in Table 3. They demonstrate that these systems can perform very selective separations.

The separation factors cannot be predicted by our current modeling results. In the presence of the other components in a

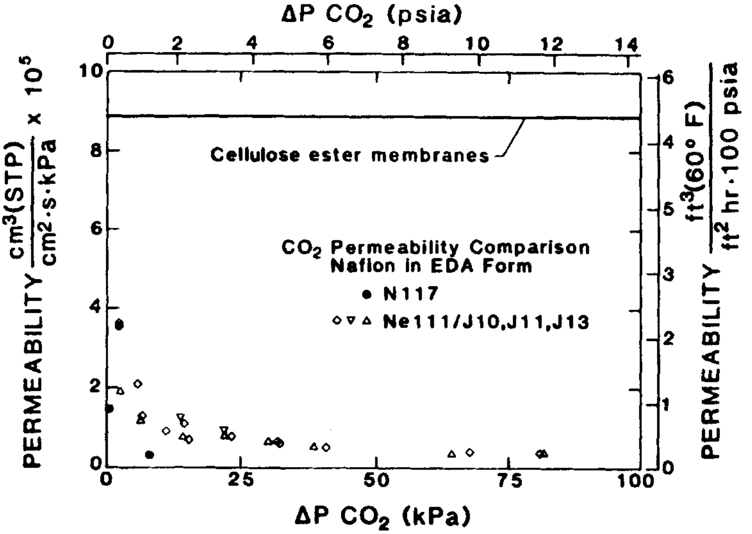


FIGURE 10: CO_2 permiability versus CO_2 partial pressure driving force for Perfluorosulfonic Acid ionomer membranes (data points) and asymmetric cellulose ester membrane (solid line).

Table 3
CO_2/CH_4 Separation Factors

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

multi-component mixture (10) (CO_2, H_2S and CH_4), the flux of CO_2 was significantly higher and the flux of CH_4 was significantly lower (per unit driving force) than what was obtained in the pure component experiments. Therefore we have not tried to predict the effect of membrane thickness on the separation factors. The membrane thickness affects the permeability of the facilitated transport species only (via the inverse Damkohler No.).

CONCLUSIONS

This study has further demonstrated the performance of ion-exchange membranes as supports for facilitated transport. The CO_2 flux measured in several EDA form ion-exchange membranes demonstrated facilitation factors and total fluxes consistent with prior theoretical analysis. We have obtained permeability values (for dilute streams) for thin perflourosulfonic acid ionomer membranes which are getting closer to those obtained with, far less selective, asymmetric cellulose ester membranes. In addition, the experiments on the developmental perfluorosulfonic acid ionomer films have yielded results which support a speculation that polymer chain backbone mobility is a significant part of the complex's diffusion in these membranes.

NOTATION

C_{AO} = concentration of solute in membrane at feed interface
C_T = total concentration of carrier
D_A = diffusion coefficient of solute in uncomplexed state
D_{AB} = diffusion coefficient of solute + carrier complex
F = facilitation factor, the ratio of facilitated to diffusive flux, Eq. 1
S_A = solute concentration in the membrane phase when feed is 100% solute; = C_{AO}/m, mol/l
K = dimensionless equilibrium constant
m = solute partiton coefficient = (external-phase concentration)/(membrane-phase concentration)
k = mass transfer coefficient
k_r = reverse rate coefficient of complexation reaction
k_f = forward rate coefficient of complexation reaction
L = membrane thickness
M = molarity, mol/l
Sh = Sherwood number
α = mobility ratio
ε = inverse Damkohler number

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