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Studies in Facilitated Transport of Nitric Oxide through Immobilized Liquid Membranes

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Abstract

An experimental technique for studying facilitated transport through immobilized liquid membranes in a batch mode is presented along with its mathematical analysis. Results obtained with two carrier ions [Fe(II) and Zn(II)] in the solvent *N*-cyclohexyl-2-pyrrolidone are compared. The effects of carrier ion concentration and of initial pressure difference are studied. Facilitation factors (ratio of facilitated flux to the flux without any carrier ion) up to 8.1 were observed.

INTRODUCTION

With increased awareness for pollution abatement, the need for a better flue gas clean-up process remains. There are numerous wet scrubbing processes for absorption of NO_x and simultaneous removal of SO_x and NO_x (*1*). All of these, however, are limited by the extremely low solubility of NO_x and have removal efficiencies in the range of 45 to 70%. The membrane separation processes which have emerged over the past two decades seem to have tremendous potential for applicability to the removal of acid gases due to their higher energy efficiency, simplicity, and lower capital cost.

Achieving high flux and selectivity is a common problem of membrane separation processes. Facilitated transport, also known as carrier mediated transport, could be an effective way to overcome this problem, as it involves a reversible chemical reaction between the carrier species and the transported species. Bateman and coworkers (*2*) have cited several examples of improved selectivity when facilitated transport was employed.

BACKGROUND

Ward (*3*), during his pioneering work in facilitated transport of nitric oxide through immobilized liquid membranes, studied the nitric oxide–Fe(II)–formamide system. In addition, he developed a mathematical treatment of the phenomenon. He employed a thin "pool" of liquid, immobilized between two semipermeable membranes. His experiments were carried out in a batch mode by admitting nitric oxide to one side of the membrane while the other side was kept under vacuum.

Recently, Bateman and coworkers (*2*) carried out experiments on the same system, using much more sophisticated equipment. Their experiments involved feed and sweep gas streams passing countercurrently on either side of the membrane. The membrane was made by vacuum impregnation of the liquid onto a support. They employed an on-line gas chromatograph, interfaced with a microcomputer to analyze the streams and compute the mass balance and flux. They studied carrier ion concentrations up to 0.3 *M* and observed facilitation factors (ratio of facilitated flux to flux without any carrier ion) as high as 5.4 for 0.3 *M* Fe(II) solution with 20% nitric oxide in the feed and 2.2 with pure nitric oxide feed.

EXPERIMENTAL DETAILS

Materials

In this study the solution of the carrier ion was immobilized, using the vacuum impregnation technique, onto a polymeric substrate membrane. It was therefore necessary that the solvent liquid wet the substrate membrane well. The liquid used as the solvent for the carrier ion was *N*-cyclohexyl-2-pyrrolidone (CHP) purchased from GAF Corporation. It had a very low vapor pressure (less than 0.05 mmHg at 25°C) and could dissolve up to a 0.3 *M* concentration of $FeCl_2$ or $ZnCl_2$ salts that were used to provide either Fe(II) or Zn(II) ions. Freshly prepared solutions were used for all the runs, and there was no evidence of oxidation of Fe(II) ions to Fe(III) ions, which would have changed the color of the solution to brownish-red. Hydrophobic membranes of 0.1 μm GORE-TEX (made up of expanded polytetrafluoroethylene on nonwoven polypropylene) and hydrophylic membranes of 0.04 μm CELGARD-5550 (made up of expanded polyethylene on nonwoven polypropylene) were used as the supporting substrate membranes for immobilizing the solution. Nitric oxide gas was obtained from Matheson.

Apparatus

The membrane cell used to hold the impregnated membrane is shown in Fig. 1. It consisted of two aluminum disks of 4.0 in. diameter and 0.5 in. thickness. Both disks had three 5/8 in. diameter holes across their faces,

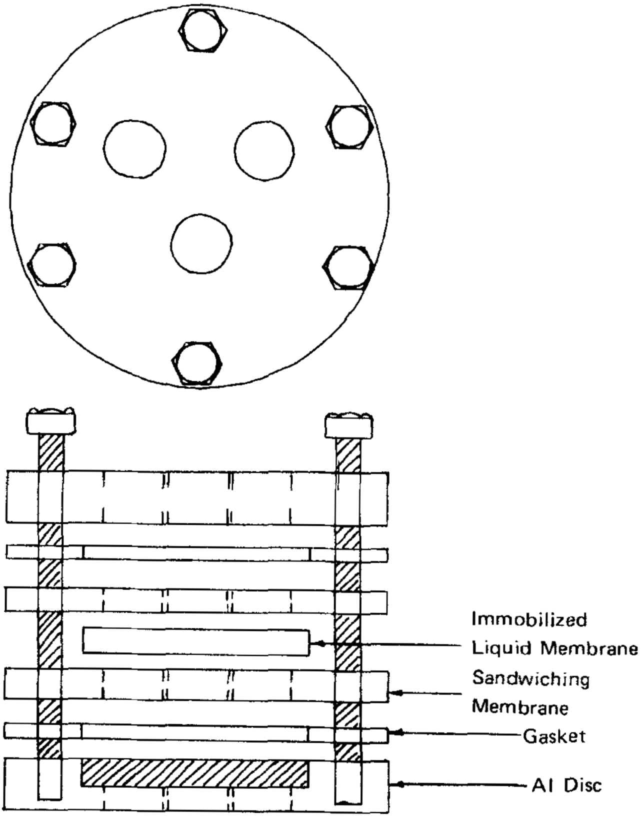

FIG. 1. The membrane cell.

drilled at a pitch circle diameter of 1.25 in. These three holes provided the exposed membrane area when the cell was assembled. The two disks, with the membrane sitting between them, could be assembled using six screws. A thin sheet of polysilicone membrane was used as the gasket on each disk. Also, the impregnated membrane (having either a GORE-TEX or a CELGARD membrane as the substrate) was sandwiched between two dry GORE-TEX membranes of 5 μm pore size. The dry GORE-TEX membranes also had three 5/8 in. holes, corresponding to those on the disks. The polysilicone gaskets, with the dry GORE-TEX sandwiching membrane, provided a completely leakproof membrane cell as verified using a helium leak detector.

In order to provide additional mechanical strength to the membrane, a porous stainless steel screen was embedded in a groove at the surface of the disk, on the low pressure side of the diffusion apparatus. The disk did not offer any significant resistance for the transport of nitric oxide.

The diffusion apparatus consisted of two chambers made out of 1 in. glass pipe. Both the chambers had a flange, used to bolt them together, with the membrane cell placed between them. The assembled view of the diffusion apparatus, with the membrane cell, is shown in Fig. 2. Both the

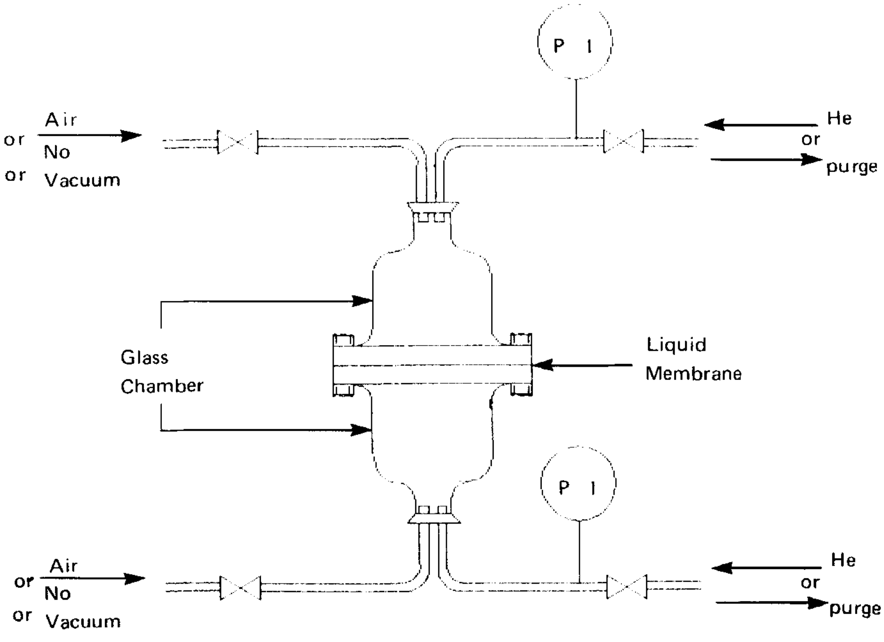

FIG. 2. A schematic representation of the diffusion apparatus.

chambers had two inlet/outlet connections and a pressure/vacuum gauge. Also, both the chambers wree provided with pressure transducers, which were in turn connected to a programmable recorder in order to be able to monitor pressure changes as a function of time.

Procedure

Having assembled the diffusion apparatus holding the membrane cell, both the chambers were flushed with helium separately. Also, the apparatus was checked for any possible leaks. The low pressure side chamber was evacuated to about 20 in.Hg below atmospheric. Nitric oxide was then allowed to fill the high pressure side chamber to the desired pressure (typically 5 to 10 psig). Pressures in both chambers were recorded as functions of time.

At the end of the experiment, both chambers were purged with air into an exhaust duct. The membrane was removed and checked to make sure it was not ruptured during the experiment. A fresh substrate membrane was used for each experiment.

RESULTS AND DISCUSSIONS

Method of Analysis

The experiments for facilitated transport were performed under unsteady state conditions. A standard equation for a diaphragm cell was used for the analysis of data. The equation in its differential form is

$$-\frac{d(C_1 - C_2)}{(C_1 - C_2)} = \left(\frac{2DA}{VL}\right)dt \tag{1}$$

where subscripts 1 and 2 refer to the high pressure chamber and the low pressure chamber, respectively, and V = volume (cm^3), A = exposed membrane area of cross section (cm^2), C = concentration of the permeant species (gmol/cm^3), L = thickness of the membrane (cm), and D = apparent diffusivity of the permeant species (cm^2/s).

It should be noted that D incorporates the parameters for tortuosity and porosity of the membrane as well as a partition coefficient and a concentration dependence due to the presence of the mobile carrier. The differential form can easily be integrated if D is independent of variation in $(C_1 - C_2)$ or t. (The validity of this assumption is discussed in detail later.) Thus, on integration from $t = 0$ to $t = t$ and replacing concentrations by partial pressures,

$$-\ln\left\{\frac{(P_1 - P_2)_{t=t}}{(P_1 - P_2)_{t=0}}\right\} = \left(\frac{2DA}{VL}\right)t \tag{2}$$

or

$$-(\Delta P)_{\ln} = \left(\frac{2DA}{VL}\right)t \tag{3}$$

Hence, the slope of a plot of $-(\Delta P)_{\ln}$ versus t can be used to calculate the apparent diffusivity of the permeant species.

As a measure of the extent of facilitation, a factor, as defined below, was used. The facilitation factor, ϕ, is defined as the ratio of the apparent diffusivity in the presence of a carrier ion to that in the absence of any carrier ion, with the solvent, substrate, and the applied initial pressure difference being the same. Thus,

$$\phi = \frac{D_{\text{with carrier ion}}}{D_{\text{without carrier ion}}} \tag{4}$$

Experimental Findings

Both Fe(II) and Zn(II) ions were found to facilitate the transport of nitric oxide. However, Fe(II) ions were found to give up to 4 times higher values of facilitation factors than those obtained using Zn(II) ions. The results obtained with Zn(II) ions are presented in Table 1.

TABLE 1

Results Obtained with Zn(II) as the Carrier Ion

Support	Liquid	Zn^{2+} concentration (M)	$(\Delta P)_{t=0}$ (psi)	D (cm^2/s)	ϕ
CELGARD (0.04 μm)	CHP	0.0	5	8.6E-06	
		0.3	5	1.3E-05	1.5
CELGARD (0.04 μm)	CHP	0.0	10	3.0E-05	
		0.3	10	5.7E-05	1.9

Thus, moderately low facilitation factors were observed with Zn(II) ions on CELGARD-5500 support.

As expected from the analysis presented by Ward (*3*) for the case of diffusion-controlled facilitated transport, the flux (and therefore the facilitation factor) was found to increase with the total carrier ion concentration. Table 2 lists the results obtained with varying concentrations of Fe(II) ions in CHP. The results obtained with an initial pressure difference of 5 psi on CELGARD-5550 support are shown in Fig. 3, which is also a typical representative plot for the method of analysis used.

It is observed from Table 2 that the apparent diffusivity in GORE-TEX (0.1 μm) membrane is higher by at least an order of magnitude than that in CELGARD-5550 (0.04 μm) membrane. This susgests that the GORE-TEX membranes were probably not fully wetted by the liquid. This may also be the reason for the lower facilitation factors observed with GORE-TEX membranes.

It was further observed that the higher the extent of facilitation for a particular liquid membrane, the stronger was the effect of concentration. On doubling the concentration of Fe^{2+} in CHP from 0.15 to 0.3 *M* (Fig. 4), the facilitation factor increased by 35% in the case of GORE-TEX (0.1 μm), 75% in the case of CELGARD (0.04 μm) when $[\Delta P]_{t=0} = 5$ psi, and by 84% in the case of CELGARD (0.04 μm) when $(\Delta P)_{t=0} = 10$ psi (Fig. 5). Thus, in this range the facilitation factor was proportional to a power of 0.85 of Fe^{2+} ions concentration on CELGARD support.

As mentioned in the development of the mathematical model, the expression was integrated over a range in which *D* is independent of the driving force. This criterion was satisfied in all the individual experi-

TABLE 2
Effect of Fe(II) Carrier Ion Concentration

Support	Fe^{2+} concentration (*M*)	$(\Delta P)_{t=0}$ (psi)	*D* (cm^2/s)	ϕ
GORE-TEX (0.1 μm)	0.0	5	4.5E-04	—
	0.15	5	6.3E-04	1.4
	0.3	5	8.5E-04	1.9
CELGARD-5550 (0.04 μm)	0.0	5	8.6E-06	—
	0.15	5	3.2E-05	3.7
	0.3	5	5.6E-05	6.5
CELGARD-5550 (0.04 μm)	0.0	10	3.0E-05	—
	0.15	10	1.3E-04	4.4
	0.3	10	2.5E-04	8.1

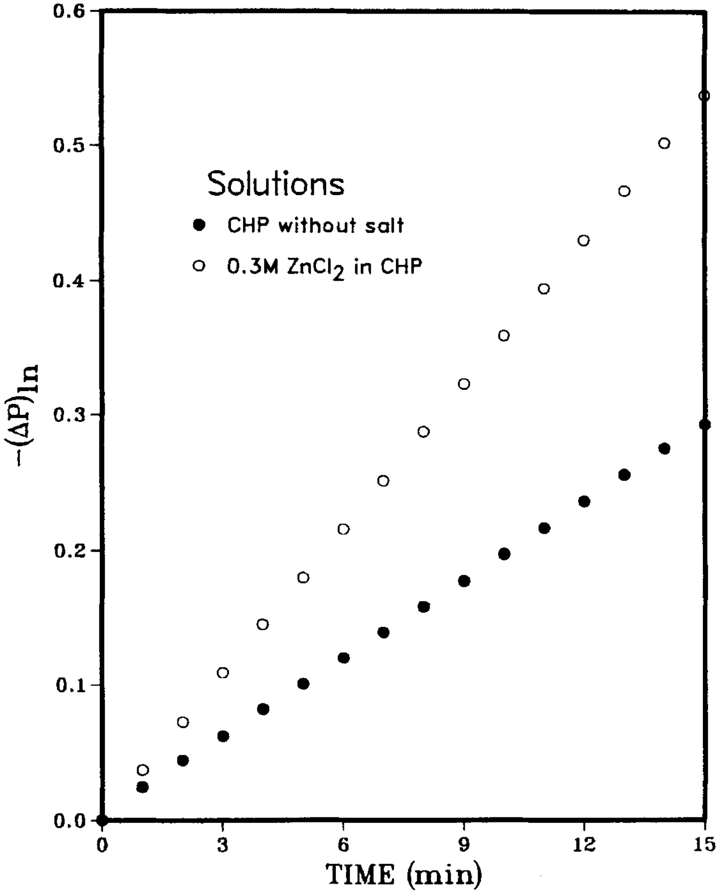

FIG. 3. Facilitated transport with 0.3 M Zn^{2+} ions in CHP on CELGARD-5550 membrane at $(\Delta P)_{t=0} = 10$ psi.

mental runs discussed so far, as demonstrated by the linearity of plots of $-(\Delta P)_{ln}$ against time. Each of these runs was confined to a pressure difference variation of less than 1 psi over the duration of the experiment.

The apparent diffusivity in the model is obviously a lumped parameter, which somehow combines the contributions of pure diffusion and the chemical reaction. Therefore, it was quite reasonable to expect that an increase in initial pressure difference would result in a higher value of D. Two sets of experiments, one with $(\Delta P)_{t=0} = 5$ psi and the other with $(\Delta P)_{t=0} = 10$ psi, were carried out in order to study this effect. These results are summarized in Table 3.

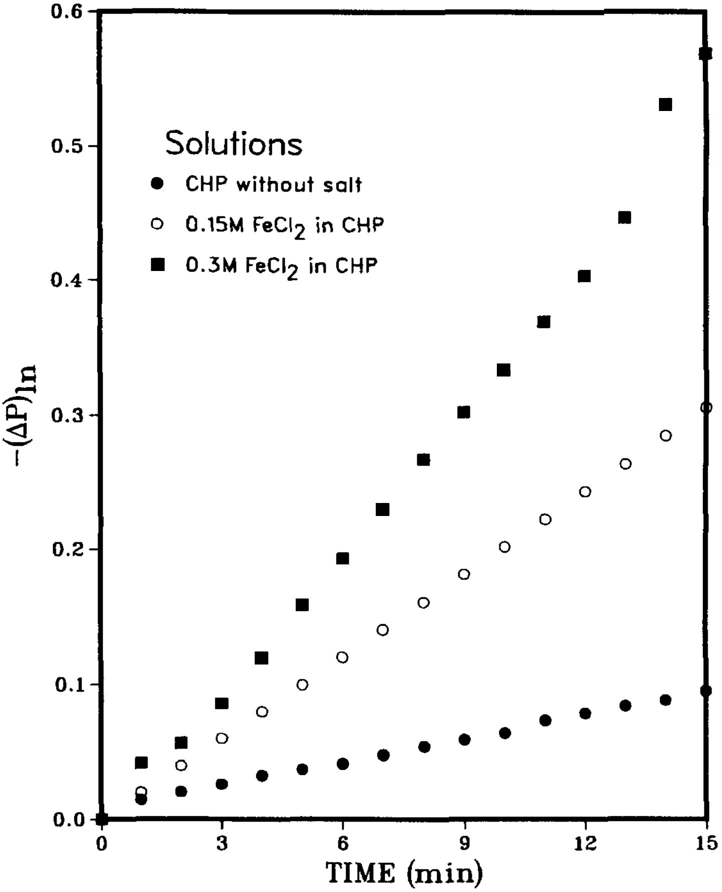

FIG. 4. Effect of concentration of Fe^{2+} ions in CHP on CELGARD-5550 membrane at $(\Delta P)_{t=0} = 5$ psi.

It can be seen from Table 3 that doubling $(\Delta P)_{t=0}$ from 5 to 10 psi increased the apparent diffusivity by about a factor of 4 and increased the facilitation factor by 20–25%. The increase in facilitation factor was unexpected. This increase may arise in this case due to the fact that both the partial pressure of nitric oxide and the total pressure difference were doubled from 5 to 10 psi.

Most of the runs were repeated once, and agreements within 15% were obtained.

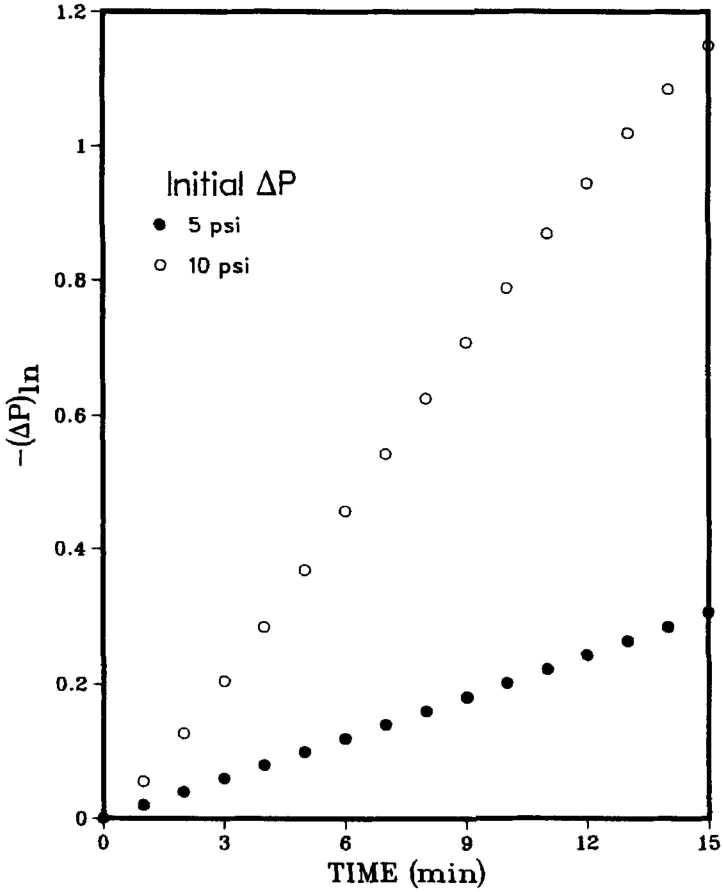

FIG. 5. Effect of $(\Delta P)_{t=0}$ with 0.15 M Fe^{2+} ions in CHP on CELGARD-5550 membrane.

CONCLUSIONS

The partial pressures of nitric oxide used in this study were much higher than those typically found in the gas from a coal-based power plant. Nevertheless, the results obtained in the study are indicative of the transfer process. The following conclusions are drawn from this study.

1. *N*-Cyclohexyl-2-pyrrolidone (CHP) was found to be a good candidate for facilitated transport of nitric oxide.
2. Ferrous (Fe^{2+}) ions were found to be quite active as the carrier ions

TABLE 3
Effect of Initial Pressure Difference; Solvent, CHP; Support, CELGARD-5550

Carrier ion	$(\Delta P)_{t=0}$ (psi)	D (cm^2/s)	ϕ	$\frac{(D)_{10\text{ psi}}}{(D)_{5\text{ psi}}}$	$\frac{(\phi)_{10\text{ psi}}}{(\phi)_{5\text{ psi}}}$
None	5	8.6E-06	—		
	10	3.0E-05	—	3.5	—
0.15 M Fe^{2+}	5	3.2E-05	3.7		
	10	1.3E-04	4.4	4.1	1.19
0.3 M Fe^{2+}	5	5.6E-05	6.5		
	10	2.5E-04	8.1	4.5	1.25
0.3 M Zn^{2+}	5	1.3E-05	1.5		
	10	5.7E-05	1.9	4.4	1.26

in the CHP-Fe(II)-NO system, and facilitation factors up to 8.1 were observed.

3. The facilitation factor was observed to be a strong and direct function of the carrier ion concentration.
4. The apparent diffusivity increased by a factor of about 4, and the facilitation factor increased by 20-25% when the initial applied pressure difference was doubled from 5 to 10 psi.

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