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Studies on Facilitated Transport of Carbon Monoxide Using a Novel Iron(II) Complex

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NOTE

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ABSTRACT

Use of a novel Fe(II) complex for CO facilitated transport across an immobilized liquid membrane has been demonstrated via a batch mode of permeation experiments. The results obtained are compared with those reported for Fe(TIM) and its analogues as the carriers. The effects of carrier concentration and initial pressure difference are examined. Facilitation factors up to 2.39 were realized.

INTRODUCTION

Separation and recovery of carbon monoxide is of great significance in C_1 chemistry processes which utilize CO as the starting material for many chemicals including methanol, formaldehyde, pesticides, herbicides, etc. The rising energy and operating costs of commonly known CO separation processes have called for development of energy efficient and selective separation processes. Facilitated transport or carrier-mediated membrane processes are very attractive for separation of CO from various industrial gas streams. Various carrier membrane systems can be designed for facilitated transport of CO in an immobilized liquid membrane (1, 2) which utilizes the reversible complexation of CO with the relevant carrier. As discussed previously by the authors (1, 2), a nonaqueous environment for the liquid membrane system is advantageous for any gaseous separation application. In view of this, complexes derived from macrocyclic ligands such as Fe(II) compounds and other transition metal complexes of the

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$Pd_2(dpm)_2X_2$ type (3) are thought to be better choices as carriers for the facilitated transport of carbon monoxide. While the choice of solvent for Fe(II) compounds is very specific, a variety of solvents can be selected for the $Pd_2(dpm)_2X_2$ type of carrier and an appreciable solubility of CO in the relevant solvents may be realized (4). On the other hand, various Fe(II) complexes such as Fe(TIM) (2,3,9,10-tetramethyl-1,3,8,11-tetraazacyclotetradeca-1,3,8,11-tetralene) and its analogues are likely to provide desirable CO complexation equilibrium and relevant physicochemical properties which are useful for designing an optimum facilitated transport (5) membrane system.

In our search for an improved Fe(TIM) analogue, we report in this paper an alternative Fe(II) compound and its use in experimental studies of the facilitated transport of CO. The experimental technique involves recording the pressure changes in the membrane cells due to transient (batch) permeation of CO across the immobilized liquid with and without carrier.

EXPERIMENTAL DETAILS

A. Synthesis and Characterization of Carrier

The basic reagents used for the synthesis of anhydrous $FeCl_3$, methanol, iron powder, $SnCl_2 \cdot 2H_2O$, 1,3-diaminopropane, glacial acetic acid, benzil, sodium acetate, and benzonitrile were all of analytical grade and procured from Aldrich Chemical Co. and other reputable firms. Details of the synthesis procedure are reported elsewhere (6). The carrier was Fe(2,3,9,10-tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) $(C_6H_5CN)_2Cl_2$.

B. Facilitated Transport Experiments

Materials

A solution of the carrier ion was immobilized by the vacuum impregnation technique on a hydrophobic membrane of 0.02 m Celgard 2400 with 38% porosity and 25 μm nominal thickness. The solvent benzonitrile was obtained from Aldrich Chemical Co. and was used without further purification. A separate measurement of the solubility of the complex in benzonitrile was made, and it was found to be 63.5 mM. Freshly prepared solutions of the complex were used in all runs in order to prevent oxidation which is likely to occur as a result of long exposure to light. Carbon monoxide gas was procured from Indian Oxygen Ltd. and was of +99.9% purity.

Method and Apparatus

The membrane cell used to hold the impregnated membrane was made of Teflon. Each side of the cell had a volume of 30 cm^3 and an exposed membrane area of 10.46 cm^2. After immobilization the membranes were sandwiched between two hydrophilic millipore membranes with a 0.2-μm pore size. Finally, the sandwiched membranes were held between two perforated metal discs to provide mechanical strength. The solvent neither wets the hydrophilic membrane nor spreads over its surface, which is expected to prevent solvent evaporation loss. After the apparatus was assembled, both chambers of the cell were flushed separately with He gas. The low-pressure side of the membrane was evacuated to around 10 cmHg below atmospheric pressure. The test gas was then allowed to fill the high-pressure side to the desired pressure up to 66 cmHg. The pressure in both chambers was recorded in a precision mercury manometer connected with small bore (3 mm) tubing of equal length for both connections. A question may arise as to whether the pressure shown by the manometer is representative of that found in the membrane cell. As will be shown later, in our analysis of the results the variation of log mean pressure difference between the cell chamber with time will be used, and the probable inaccuracy of the pressure measurement will not be a critical factor.

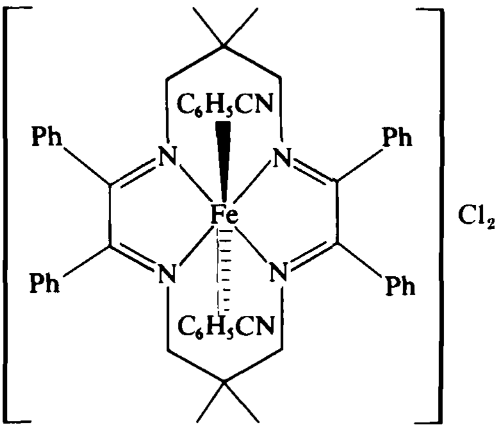
RESULTS AND DISCUSSION

A. Characterization of the Complex

In the IR spectrum of the Fe(II) complex, only two very weak absorption bands appear in the 2300 cm^{-1} region (2300 and 2340 cm^{-1}), and they are associated with the CN stretching vibration. After passing CO to the benzonitrile solution of the compound, the CO complex formed shows two additional bands at 2031 and 1984 cm^{-1}, and they are assigned to the C=O stretching vibration.

The UV spectra of the complex showed a band at λ_{max} 285 μm which is characteristic of the CN vibration band. After passing CO, an additional band appears at λ_{max} 320 μm, revealing complexation with CO.

The H-NMR spectrum of the complex (δ 8.3–7.12 ppm, multiplet aromatic protons; δ 1.7–1.25 ppm, doublet methylene protons) reveals that the proposed structure of the complex is



B. Facilitated Transport

Method of Analysis

As shown by Godbole et al. (7), the integrated form of the pressure profile in the high (1) and low (2) pressure sides of the membrane cell can be written as

$$-\ln\frac{(P_1 - P_2)_{t=t}}{(P_1 - P_2)_{t=0}} = \left(\frac{2DA}{VL}\right)t \tag{1}$$

or

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

The slope of the plot of $-(\Delta P)_{\ln}$ versus t can be used to calculate the apparent diffusivity D of the permeating gas. The facilitation factor F may be defined as

$$F = \frac{D_{\text{with carrier}}}{D_{\text{without carrier}}} \tag{3}$$

The significance of the apparent diffusivity was discussed by Godbole et al. (7) and, for permeation via a simple solution diffusion mechanism, Eq. (2) can be generalized to incorporate the support membrane characteristics and the relevant solute solvent properties, in which case the equation becomes (11)

$$-(\Delta P)_{\ln} = \left(2D_m \frac{\epsilon}{\tau} \frac{A}{VL} \frac{R}{H_A} \frac{T}{L}\right) t \tag{4}$$

The presumption of Eq. (2) that D is independent of the concentration driving force will be validated later on from experimental results.

Experimental Findings

Plots of $-(\Delta P)_{\ln}$ versus time are shown in Figs. 1 and 2, and the calculated facilitation factor (F) is presented in Table 1. The good correlation coefficient (0.98) obtained for linear regression of the $-(\Delta P)_{\ln}$ versus time data indicate that, within the range of the initial pressure difference, $(\Delta P)_{t=0}$, studied in this work, D is independent of the driving force. The facilitation factor of 2.39 obtained in this work with the new Fe(II) com-

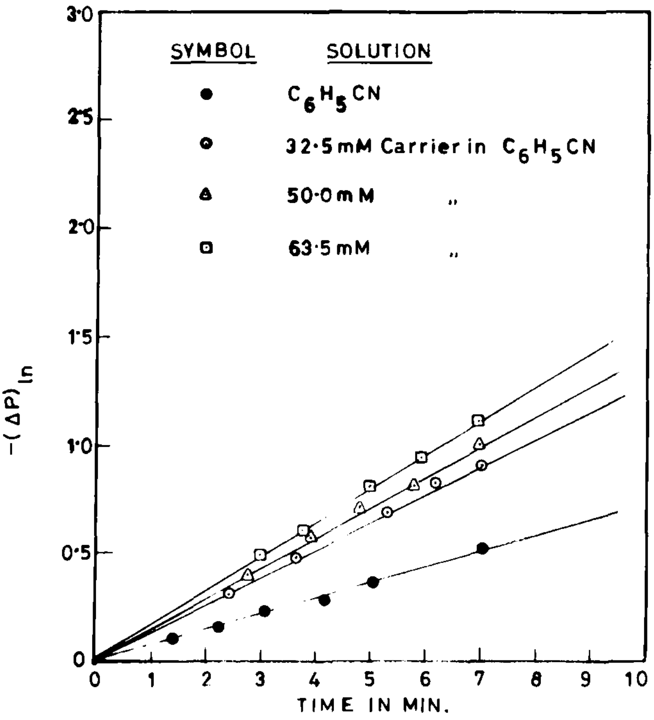


FIG. 1 Effect of carrier concentration on facilitated transport of CO at $(\Delta P)_{t=0}$ = 40 cmHg.

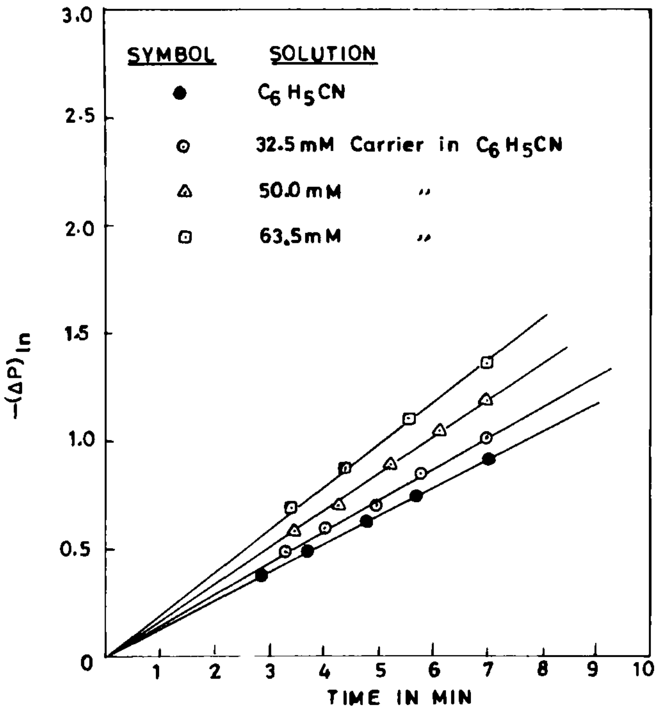


FIG. 2 Effect of carrier concentration on facilitated transport of CO at $(\Delta P)_{t=0}$ = 66 cmHg.

TABLE 1
Facilitation Factor F from Batch Permeation Experiments

C^a (mM)	$(\Delta P)_{t=0}$ (cmHg)	$D \times 10^6$ cm^2/s	F
0.0	40	4.26	—
32.5	″	6.188	1.45
50.0	″	7.881	1.85
66.0	″	10.22	2.39
0.0	66	6.21	—
32.5	″	7.74	1.24
50.0	″	10.65	1.71
66.0	″	13.15	2.117

[a] C: concentration of carrier in solution.

plex is quite attractive in the sense that a marginal improvement over the other reported Fe(TIM) complexes has been realized. Figure 3 shows the relationship of F with the carrier concentration. It is evident that F values increase with carrier concentration up to the solubility limit of the carrier (carrier solubility was separately determined by a simple gravimetric technique). This observation indicates that transport of CO in the liquid membrane follows a diffusion-controlled mechanism (8).

An increase of $(\Delta P)_{t=0}$ at the same carrier concentration increases the apparent diffusivity, but the facilitation factor is decreased. This is quite reasonable because an increase of pressure is likely to shift K (a dimensionless equilibrium constant) away from the optimum value suggested by Kemena et al. (9). A quick estimate of F was made by using the relation suggested by Smith and Quinn (10) for reaction equilibrium conditions. In this calculation, the K_{eq} (equilibrium constant for the complexation reaction with CO) value was estimated from the record in changes in the UV spectrum of the complex dissolved in the CO-saturated solvent following a procedure outlined for Fe(TIM) (5). The solubility of carbon monoxide was determined by a simple volumetric method (4). K_{eq} and the solubility value were found to be 190.1 M^{-1} and 5.56×10^{-3} M, respectively. The diffusivity of the carrier complex necessary for calculation of F was taken from the literature (5) for Fe(Me_2Ph_2TIM) with the assumption that the value of the complex studied by us would not differ

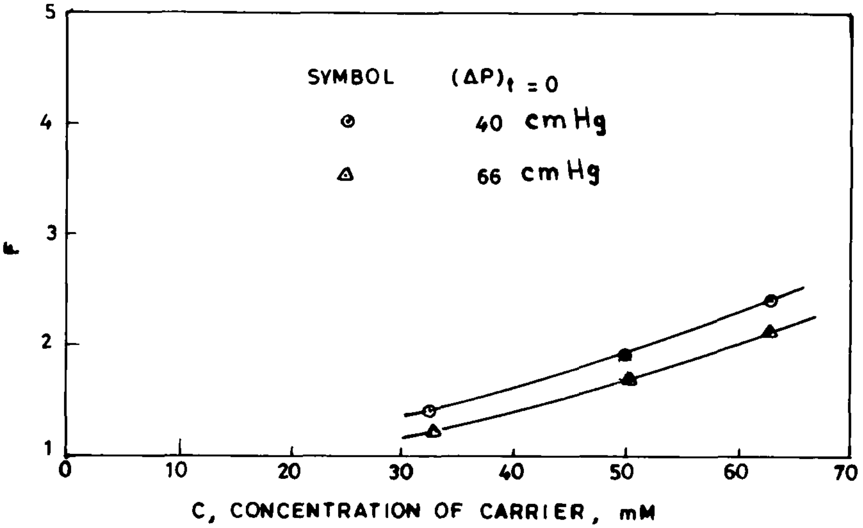


FIG. 3 Relation of F vs carrier concentration.

by a factor of more than 1.5. The F value so calculated was found to be 2.1, which is considered quite reasonable considering the approximation made. Thus, the observed and calculated values of F are comparable.

Some experiments were carried out with Celgard 2500 membranes as the support. The observed F values were found to be almost independent of carrier concentration. We presume that such observations are due to solvent leakage from the pores and to the effect of bulk flow due to the pressure gradient across the Celgard 2500 support which has a larger pore size (0.04 μm). Such factors were found to also affect permeation via a purely solution diffusion mechanism (11). In view of this, we suggest that determination of the F factor from simple batch permeation experiments should be carried out with a membrane of small pore size so that vapor pressure lowering via the Kelvin effect can be realized and Poiseuille flow can be avoided.

CONCLUSION AND RECOMMENDATIONS

A new Fe(II) complex was suggested for facilitated transport of CO in an immobilized liquid membrane
CO facilitated transport was found to be diffusion limited
The facilitation factor is better at low CO partial pressure

However, a systematic investigation of a continuous permeation assembly is required in order to establish the effect of partial pressure.

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