

# Selective Permeation of Carbon Dioxide through Synthetic Polymer Membranes Having Pyridine Moiety as a Fixed Carrier

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## Synopsis

Sorption and permeation of CO<sub>2</sub> were investigated by using synthetic polymer membranes having pyridine moiety or pyridine–Cu(II) complex group as a fixed carrier. The solubility data for CO<sub>2</sub> were interpreted by the dual sorption model, Henry's law plus Langmuir-type adsorption. The permeation results of CO<sub>2</sub> through the present membranes containing pyridine moiety were analyzed in terms of the partial immobilization model, while the solubilities and permeabilities of O<sub>2</sub> and N<sub>2</sub> obeyed Henry's law. Permselectivity of the present membrane for CO<sub>2</sub> was achieved. These results were explained by the acid–base interaction between CO<sub>2</sub> molecules and fixed carrier in the present membrane.

## INTRODUCTION

Remarkable development of industries in recent years induced an abrupt transition of atmospheric environment, hydrosphere environment, and soil environment, in which living creatures including human beings live. There have come to various problems concerning these environments. Turning our eyes to the atmospheric environment, the concentration of carbon dioxide in atmosphere in early 20th century was around 290 ppm by volume.<sup>1</sup> However, that in these days increased to 330 ppm owing to fossil fuel combustion and deforestation for expansion of cultivated area.<sup>2,3</sup> CO<sub>2</sub> concentration in atmosphere increases at the rate of 1 ppm/year.<sup>2,3</sup> The climatic change induced by CO<sub>2</sub> concentration gives us misgivings.<sup>4,5</sup> It is an important subject to reduce the CO<sub>2</sub> amount released into the atmosphere and to make use of CO<sub>2</sub> as recovery of carbon sources. As a link in a chain of such study, we investigated selective separation (removal) of CO<sub>2</sub> with synthetic polymer membranes.

Studies on selective permeation of CO<sub>2</sub> through artificial membranes were achieved via two types of membrane constitution, such as a liquid membrane (mobile carrier membrane) and a fixed carrier membrane (immobilized carrier membrane). As examples of the former, a selective facilitated transport of CO<sub>2</sub> with aqueous liquid membrane was achieved by inorganic salt such as CsHCO<sub>3</sub><sup>6</sup> or K<sub>2</sub>CO<sub>3</sub>.<sup>7</sup> As examples of the latter, studies on a cation-exchange membrane of sulfonated polyphenylene oxide, having monoprotonated ethylenediamine,<sup>8</sup>

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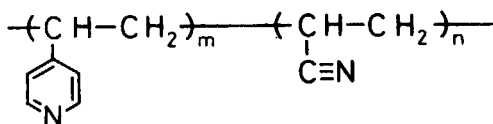
or poly(ethylene glycol) membrane impregnated with inorganic salt were reported.<sup>9-11</sup>

We investigated CO<sub>2</sub> separation with the latter membrane system, that is, a fixed carrier membrane. As a fixed carrier, we adopted pyridine moiety to make use of acid-base interaction for separation of CO<sub>2</sub>, or some Cu(II)- or Pd(II)-based organometallic compounds by making use of reversible insertion reaction with CO<sub>2</sub>.<sup>12</sup> In the present article, we describe the feasibility of selective separation of CO<sub>2</sub> through poly(4-vinylpyridine-co-acrylonitrile) membrane.

## EXPERIMENTAL

### Materials

Poly(4-vinylpyridine-co-acrylonitrile), with a mol fraction of 4-vinylpyridine of either 0.038 or 0.098, was synthesized by the usual radical copolymerization of 4-vinylpyridine and acrylonitrile in benzene initiated by 2,2'-azobis(2-methylpropionitrile) as previously reported<sup>13</sup>:



code	m	n
038	0.038	0.962
098	0.098	0.902

### Preparation of Membranes

038 membrane and 098 membrane were prepared as follows: a DMF solution of the polymer (88 g dm<sup>-3</sup>) was poured onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 40°C for 3 h.

038-4/1 membrane,<sup>†</sup> which was the Cu(II) containing blended membrane, was prepared by mixing 038 polymer and Cu(ClO<sub>4</sub>)<sub>2</sub> at the ratio of unit mol fraction of 4-vinylpyridine in 038 polymer to Cu(II) of 4/1. Other conditions for membrane preparation were the same as 038 and 098 membranes.

The glass transition temperature (*T<sub>g</sub>*) of the membrane materials 038, 038-4/1, and 098 were determined to be around 134, 130, and 104°C, respectively.

<sup>†</sup>Absorption maximum wavelength in the visible range for 038-4/1 membrane was observed at 595 nm. Those for 038-n/1 (n = 1-10) membranes gave the same maximum wavelength of 595 nm. From this and the results reported by Kirsh et al.<sup>14</sup> there was the predominant formation of the [CuPy<sub>4</sub>]<sup>2+</sup> complex in 038-4/1 membrane (Py = 4-vinylpyridine moiety).

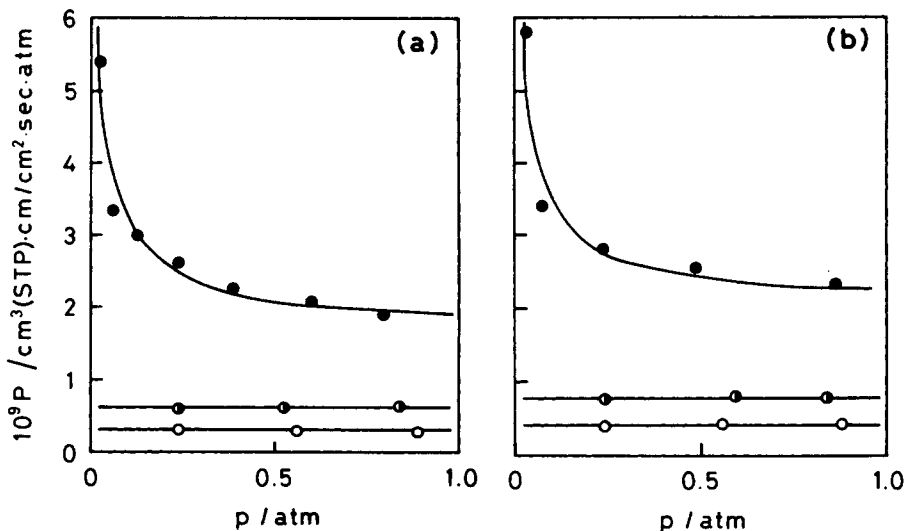


Fig. 1. Pressure dependence of the permeability coefficients of CO<sub>2</sub> (●), O<sub>2</sub> (◐), and N<sub>2</sub> (○) through 038 (a) and 098 (b) membranes at 30°C: (—) calculated from eq. (2) using parameters in Tables I and II.

### Permeation Experiment

The permeation of CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>, through membranes, were measured at 30°C and at certain pressures. From the steady-state straight line of the permeation curve, the permeability coefficient was evaluated.<sup>15</sup>

### Sorption Experiment

Gas sorption experiments were made at 30°C by a standard gravimetric sorption apparatus using a quartz spring. The sample was dried at 30°C under  $10^{-5}$  torr until a variation of its elongation was not observed at all. The sorption amount of gas to the dry sample thus obtained was evaluated by an elongation of the quartz spring.<sup>16</sup>

## RESULTS AND DISCUSSION

### Permeation

The steady-state permeability coefficients of various gases in both 038 and 098 membranes are presented in Figure 1 as a function of upstream driving pressure  $p$ . As for permeability coefficients of O<sub>2</sub> and N<sub>2</sub> for both 038 and 098 membranes, they were independent of upstream pressure, and gave  $P_{\text{O}_2} = 6.33$  barrer and  $P_{\text{N}_2} = 3.00$  barrer for 038 membrane, while 098 membrane gave  $P_{\text{O}_2} = 7.85$  barrer and  $P_{\text{N}_2} = 4.14$  barrer. Permeability coefficients for 038-4/1 membrane were not obtained because of no durability toward permeation experiments except for the upstream driving pressure of 0.24 atm.

In contrast with permeability coefficient dependence of O<sub>2</sub> and N<sub>2</sub> on upstream pressure, permeability coefficients of CO<sub>2</sub> for both 038 and 098 membranes showed upstream pressure dependence.  $P_{\text{CO}_2}$  increased with decrease of upstream driving pressure as shown in Figure 1.

From these results, we deduced the following plausible permeation mechanisms for three kinds of gases as follows<sup>17,18</sup>: (1) The gas was sorbed by the Henry's law and the sorbed gas was free to diffuse in the membrane. (2) Only the gas sorbed by the Henry's law contribution was free to diffuse, while that sorbed by the Langmuir part was not, that is, immobilized. As a result, both  $P_{O_2}$  and  $P_{N_2}$  did not show upstream pressure dependence and gave constant permeability coefficients. The permeation mechanism of  $CO_2$  was interpreted by the partial immobilization model<sup>17,18</sup> as follows: The gas sorbed by the Henry's law contribution was free to diffuse and that sorbed by Langmuir part was partly immobilized, while the remain of sorbed  $CO_2$  by Langmuir part was able to diffuse in the membrane.

In order to ascertain permeation mechanisms of gases, sorption isotherms of these membranes were studied. Obtained results are summarized in the following section.

### Sorption

Sorption isotherms are shown in Figure 2. Sorption isotherms of  $O_2$  and  $N_2$  in these three membranes gave straight lines passing through the origin, leading that both  $O_2$  and  $N_2$  were sorbed by Henry's law. It is concluded that  $O_2$  and  $N_2$  permeated through 038 and 098 membranes by mechanism (1) as shown in the previous section. That is,  $O_2$  and  $N_2$  were sorbed by the Henry's law and the sorbed gases were free to diffuse in the membrane. Though permeation of gases through 038-4/1 membrane was failed, it is expected that permeation mechanism of  $O_2$  and  $N_2$  obeys mechanism (1) mentioned above.

The sorption isotherms of  $CO_2$  increased abruptly at the low upstream pressure range, and increased linearly over certain upstream pressure. The experimental data for  $CO_2$  sorption were analyzed according to the dual sorption model.<sup>19,20</sup>

The dual sorption model postulates that the sorption consists of dissolution ( $C_D$ ) represented by the Henry's law and absorption ( $C_H$ ) on the inner surface of the microvoids represented by the Langmuir equation. The total solubility  $C$  is thus given<sup>19,20</sup> by following equation:

$$\begin{aligned} C &= C_D + C_H \\ &= k_D p + C'_H b p / (1 + b p) \end{aligned} \quad (1)$$

where  $k_D$ ,  $C'_H$ , and  $b$  denote the Henry's law parameter, the capacity constant for the Langmuir adsorption, and the affinity constant of gas for the Langmuir sites, respectively, and  $p$  is the pressure of the penetrant gas. In the present paper, the Langmuir type adsorption might take place mainly through the interaction between  $CO_2$  molecule and pyridine moiety (weak acid-base interaction).

Each Henry's law parameter  $k_D$  for  $CO_2$  was obtained from the slope of the straight line over upstream pressure of 0.4 atm. Constants of the Langmuir equation,  $C'_H$  and  $b$ , were evaluated from the Langmuir plot shown in Figure 3. Each Henry's law parameter for  $O_2$  and  $N_2$  was obtained from the slope of each line. These obtained parameters are summarized in Table I. In Table I,  $(C'_H)/(P_y)$  shows the amount (mol number) of  $CO_2$  sorbed to the unit mol of

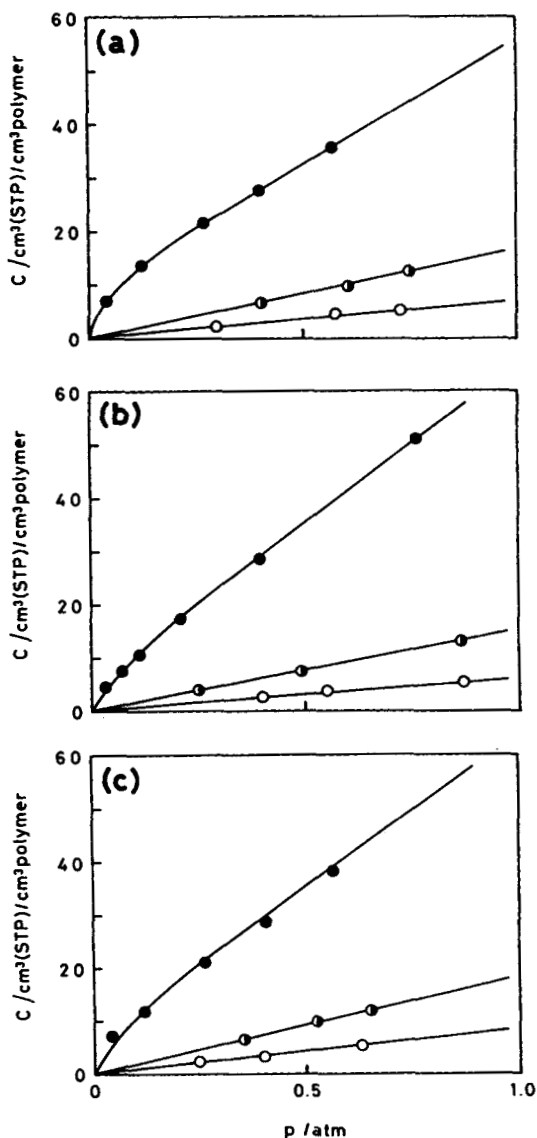


Fig. 2. Sorption isotherms for various gases in 038 (a), 038-4/1 (b), and 098 (c) membranes at 30°C: (●) CO<sub>2</sub>; (◐) O<sub>2</sub>; (○) N<sub>2</sub>; (—) calculated from eq. (1) using parameters in Table I.

pyridine moiety. Obtained  $k_D$  values for CO<sub>2</sub> were relatively high values compared with that for polyacrylonitrile membrane.<sup>21</sup> Such a high value of  $k_D$  for CO<sub>2</sub> might be due to the incorporation of a different monomer sequence which might distort a highly quasicrystalline structure of polyacrylonitrile in the presence of a small amount of different units. As a result, the present membranes gave relatively high  $k_D$  values for CO<sub>2</sub> compared with  $k_D$  values for unmodified polyacrylonitrile. Another plausible reason for the present high  $k_D$  values was as follows: in the present study the removal of residual solvent (DMF) in the membrane might be incomplete. Therefore, we obtained higher  $k_D$  values than those for completely solvent-free polyacrylonitrile membrane.

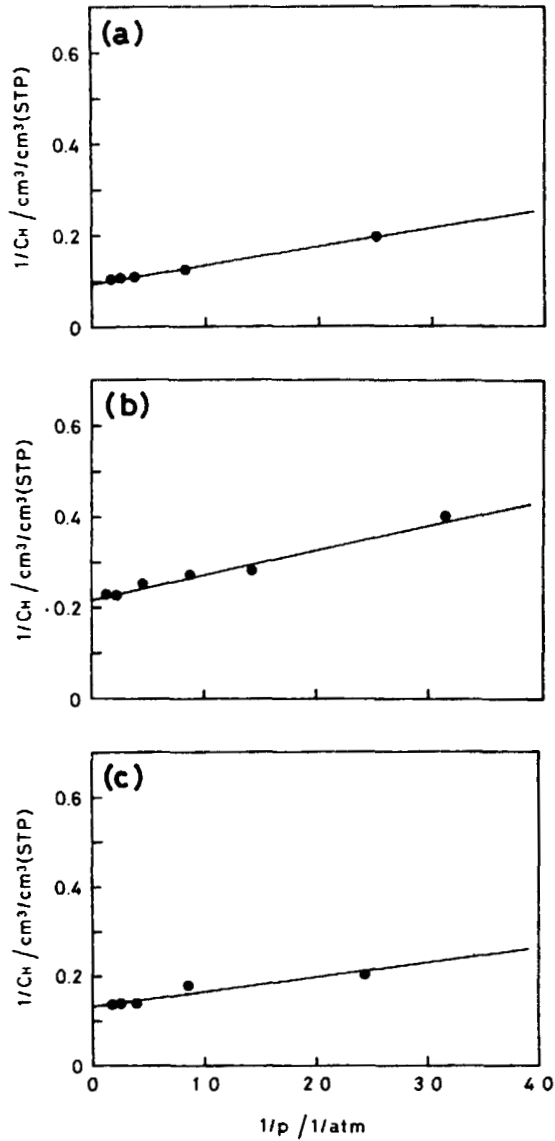


Fig. 3. Langmuir plots for 038 (a), 038-4/1 (b), and 098 membranes ( $1/C_H = 1/(C_H b)p + 1/C_H'$ ).

### Diffusion

One can evaluate the diffusion coefficient  $D$  for  $\text{O}_2$  and  $\text{N}_2$  using  $P = DS$ , where  $S$  is the solubility coefficient ( $k_D$ ) obtained from the sorption experiment. The permeability coefficient is represented<sup>17-19</sup> by

$$P = k_D D_D [1 + FK/(1 + bp)]$$

$$(F = D_H/D_D, K = C_H' b/k_D) \quad (2)$$

TABLE I  
Dual-Mode Sorption Parameters for Gases at 30°C

Membrane	CO <sub>2</sub>						
	$k_D$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> atm)	$C'_H$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> )	$b$ (1/atm)	$K = C'_H b / k_D$	$(C'_H) / (P_y)^a$	$N_2, k_D$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> atm)	$O_2, k_D$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> atm)
038	46.5	10.2	25.3	5.55	0.746	6.92	16.8
038-4/1	61.3	4.61	37.8	2.84	0.357	6.16	15.2
098	52.6	7.50	44.9	6.40	0.238	8.54	18.2

<sup>a</sup> mol/cm<sup>3</sup> polymer/mol/cm<sup>3</sup> polymer.

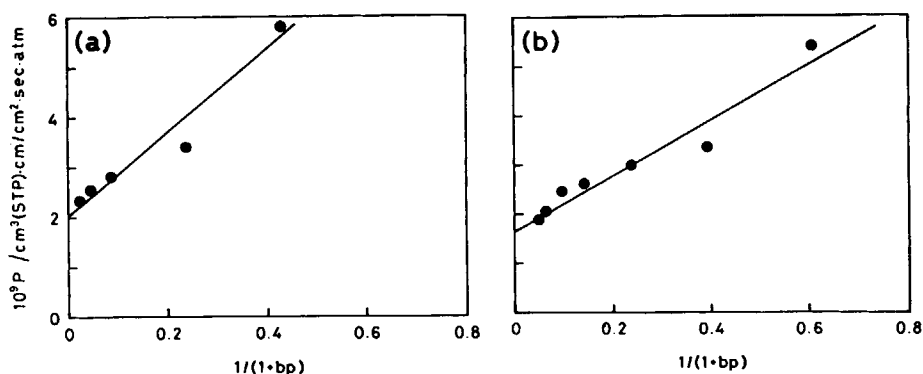


Fig. 4. Permeability coefficients for 038 (a) and 098 (b) membranes plotted in accordance with the partial immobilization model with  $D_D$  constant [eq. (2)].

where  $D_D$  and  $D_H$  are the respective diffusion coefficients of the Henry's law population and the Langmuir population. We can obtain  $D_D$  and  $D_H$  for  $\text{CO}_2$  using eq. (2) and experimental data shown in Figure 1. The data of Figure 1 were plotted in Figure 4 in the manner suggested by eq. (2) using the sorption parameters given in Table I. From the slopes and the intercepts in Figure 4,  $F$  and  $D_D$  values were deduced. Those obtained diffusion coefficients are summarized in Table II.  $F$  values for 038 and 098 membranes were 0.617 and 0.621, respectively. The  $F$  value, in general, for  $\text{CO}_2$  was reported to be around 0.1, while present membranes gave around 0.6. Present membranes showed higher  $F$  values than other membranes. This led to the conclusion that the details of the Langmuir type adsorption consists of adsorption induced by the weak acid-base interaction between  $\text{CO}_2$  molecule and pyridine moiety rather than of the absorption on the inner surface of the microvoids, as previously mentioned.

### Predicted Permselectivities for Binary Systems

It was impossible for our permeation apparatus to obtain permselectivities of binary systems. So, we evaluated theoretically separation factors for both  $\text{CO}_2\text{-O}_2$  and  $\text{CO}_2\text{-N}_2$  binary systems. Separation factors  $\beta_{\text{CO}_2/\text{O}_2}$  and  $\beta_{\text{CO}_2/\text{N}_2}$

TABLE II  
Permeabilities,<sup>a</sup> Diffusivities, and Solubilities of Gases at 30°C

Membrane	$\text{CO}_2$					$\text{N}_2$			$\text{O}_2$		
	$10^{10}P^b$	$10^{11}D_D$	$10^{11}D_H$	$S(k_D)^d$	$S(C_H b)$	$10^{10}P^b$	$10^{11}D^c$	$S(k_D)^d$	$10^{10}P^b$	$10^{11}D^c$	$S(k_D)^d$
038	26.1	3.57	2.20	46.5	258	3.00	4.34	6.92	6.33	3.77	16.8
038-4/1	25.5	—	—	61.3	174	4.48	7.27	6.16	8.24	5.42	15.2
098	28.1	3.89	2.42	52.6	337	4.14	4.85	8.54	7.85	4.31	18.2

<sup>a</sup> Difference in gas pressures on the two sides, ca. 0.24 atm.

<sup>b</sup> Obtained from permeation experiments ( $P/\text{cm}^3(\text{STP})\text{cm s}^{-1}\text{cm}^{-2}\text{atm}^{-1}$ ).

<sup>c</sup>  $D = P/S(k_D)(D/\text{cm}^2\text{ s}^{-1})$ .

<sup>d</sup> Obtained from sorption isotherms.



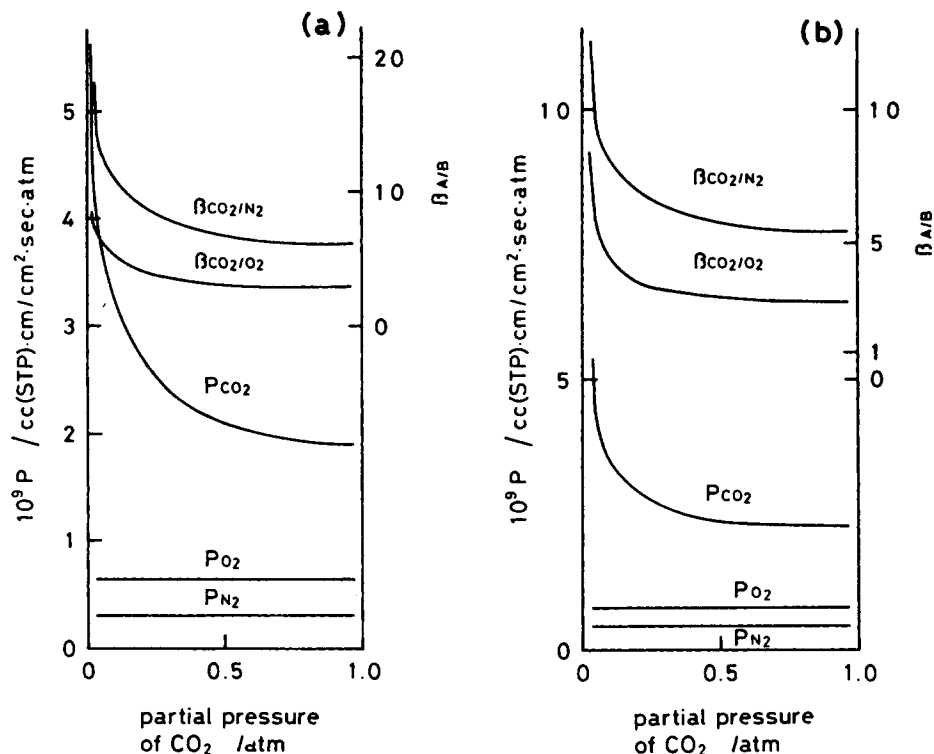


Fig. 5. Predicted permeabilities of various gases and permselectivities for CO<sub>2</sub> relative to O<sub>2</sub> or N<sub>2</sub> as a function of partial pressure of CO<sub>2</sub> for case of a negligible downstream pressure at 30°C for 038 (a) and 098 (b) membranes: Total upstream pressure was 1 atm; (—) calculated from eq. (2) and (3) using parameters in Tables I and II.

were defined by<sup>22</sup>

$$\beta_{\text{CO}_2/\text{gas}} = P_{\text{CO}_2}/P_{\text{gas}} \quad (3)$$

where the gas is either O<sub>2</sub> or N<sub>2</sub>. Figure 5 shows the predicted separation factors as a function of CO<sub>2</sub> partial pressure under the condition that the total upstream pressure was 1 atm and the downstream pressure was assumed to be negligibly small together with experimentally obtained permeability coefficients.

Separation factors, selectivities toward CO<sub>2</sub>, increased with a decrease of partial pressure of CO<sub>2</sub> as expected from the fact that CO<sub>2</sub> gas permeated through 038 and 098 membranes by partial immobilized model. Though separation factors were over unity for both CO<sub>2</sub>-O<sub>2</sub> and CO<sub>2</sub>-N<sub>2</sub> binary systems, those values were less than those for polyacrylonitrile membrane<sup>23</sup> except for those values at the low partial pressure range of CO<sub>2</sub>. The order of permeability coefficients for 038 and 098 membranes, however, gave larger values those for polyacrylonitrile membrane.

To attain higher separation factors toward CO<sub>2</sub> separation with synthetic polymer membranes containing pyridine moiety, there might be the following

two possible ways: (1) increase of fixed carrier (pyridine) content in the membrane; (2) by making use of the interaction of CO<sub>2</sub> with nearly naked counteranions (ClO<sub>4</sub><sup>-</sup>) toward Cu<sup>2+</sup> incorporated into the membrane, i.e., weak acid-base interaction as reported by Kawakami et al.<sup>9-11</sup> We prepared 038-4/1 membrane with a view to separate CO<sub>2</sub> by the latter way (2). However, the permeation result could not be attained because the permeation experiment could not be carried out owing to the break of the membrane as mentioned above.

## CONCLUSION

Permeation of CO<sub>2</sub> through poly(4-vinylpyridine-co-acrylonitrile) membranes (038 and 098 membranes) were interpreted by the partial immobilized model. On the other hand, permeation of O<sub>2</sub> and N<sub>2</sub> were interpreted by the solution-diffusion model based on Henry's law. These two membranes showed feasibility to separate CO<sub>2</sub> from CO<sub>2</sub>-O<sub>2</sub> and CO<sub>2</sub>-N<sub>2</sub> mixtures.

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