Specialty Polymeric Membranes. V. Selective Permeation of Carbon Dioxide Through Synthetic Polymeric Membranes Having 2-(N,N-Dimethyl)aminoethoxycarbonyl Moiety

MASAKAZU YOSHIKAWA,[1,*] KIYOSHI FUJIMOTO,[1] HIROKAZU KINUGAWA,[1] TOSHIO KITAO,[1] YOSHINORI KAMIYA,[2] and NAOYA OGATA[3]

[1]Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan, [2]National Institute of Materials and Chemical Research, Tsukuba 305, Japan, and [3]Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

SYNOPSIS

Permeation of CO_2 was investigated by using synthetic polymeric membranes having a tertiary amine moiety, 2-(N,N-dimethyl)aminoethoxycarbonyl moiety. Permselectivity of the present membranes towards CO_2 was achieved. Through poly{2-(N,N-dimethyl)aminoethyl methacrylate-co-acrylonitrile} (DMAEMA/AN-199) membrane, where DMAEMA mol fraction was 0.199, the separation factor towards CO_2 for CO_2/N_2 separation ranged from 60 to 90, ranging in the CO_2 partial pressure in the feed gas from 61 to 3.6 cmHg. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Since the Industrial Revolution, we human beings have caused a large increase in atmospheric concentrations of CO_2, which is perceived as the dominant greenhouse gas. Following are techniques to remove and/or separate CO_2 from the CO_2 emission sources such as power stations, steel works, and chemical industries, which are burning fossil fuels such as coal, oil, and natural gas: wet absorptions (physical absorption and chemical absorption), dry adsorption (physical adsorption), membrane separation, and distillation. Among these five techniques, the separation by using membranes, in which the removal and concentartion of CO_2 are performed by the difference in permeability of each gas in a membrane, is a promising CO_2 separation technique, which might be operated continuously with low running cost. The membrane separation technique, however, has never been widely applied to CO_2 removal from combustion gas so far in the industries because of lack of suitable membrane materials, which give high permselectivity and permeability for CO_2. The de-velopment of novel membrane materials, which efficiently separate CO_2 from the combustion gas, is indispensable to establish the membrane separation technique feasible in the industries.

The artificial membranes for CO_2 separation have been divided into three categories: liquid membranes[1,2] (mobile carrier membranes), polymeric membranes,[3-5] and fixed-carrier membranes[6-11] (immobilized carrier membranes). From the practical viewpoint, the adoption of a polymeric or a fixed-carrier membrane must be more suitable than the use of a liquid one because of the superior durability. There are two possible ideas for designing membrane materials having CO_2 permselectivity: one is the raising of the solubility of polymeric materials towards CO_2, the other is the increasing of diffusivity of CO_2 in the polymeric membranes. In general, diffusivity of a given gas is primarily determined by the shape and dimensions of gas itself, but it is hard to obtain the polymeric membranes possessing desirable diffusivity because the dimensions of penetrant gases, in the present study, CO_2, O_2, and N_2, are very close.[12] On the other hand, the introduction of a moiety into polymeric membranes that may cause a specific interaction to recognize CO_2 selectively may lead the increase in solubility without difficulty.
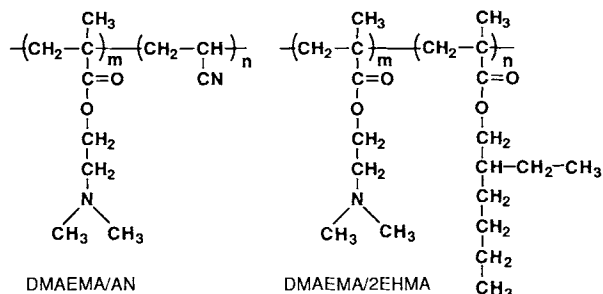
Scheme 1

Because CO_2 is classified into a Lewis hard acid,[13] the molecular recognition to CO_2, based on the acid-base interaction, can be expected to improve the solubility of CO_2 towards the membrane materials, prepared from a polymer having amine moiety. Based on this idea, 2-(N,N-dimethyl)aminoethyl methacrylate, which contains a tertiary amine moiety and is easily copolymerized by radical polymerization, as a fixed carrier into polymeric membranes was copolymerized with acrylonitrile or 2-ethylhexyl methacrylate, and we studied the feasibility of selective separation of CO_2 through these synthetic polymeric membranes newly prepared.

EXPERIMENTAL

Materials

2-(N,N-Dimethyl)aminoethyl methacrylate (**DMAEMA**), acrylonitrile (**AN**), 2-ethylhexyl methacrylate (**2EHMA**), and 2,2'-azobis(2-methylpropionitrile) (**AIBN**) were purified in the usual manner. N,N-Dimethylformamide (DMF) and chloroform were used without purification. Membrane materials, such as poly{2-(N,N-dimethyl)-aminoethyl methacrylate-co-acrylonitrile} (**DMAEMA/AN-107** and **DMAEMA/AN-199**) with

the mol fraction of a **DMAEMA** unit of 0.107 and 0.199, respectively, and poly{2-(N,N-dimethyl)-aminoethyl methacrylate-co-2-ethylhexyl methacrylate} (**DMAEMA/2EHMA-095** and **DMAEMA/2EHMA-205**) with the mol fraction of a **DMAEMA** unit of 0.095 and 0.205, respectively, were synthesized by the usual radical copolymerization initiated by **AIBN** at 45°C with shaking. The chemical composition of the polymers thus obtained were determined by elemental analysis. The results are summarized in Table I.

Membrane Preparation

DMAEMA/AN membranes were prepared as follows: a DMF solution (100 g dm^{-3}) was poured onto a glass plate with an applicator, with the casting thickness being adjusted to 0.361 mm. The solvent was allowed to evaporate at 50°C for 2 h, and then the membrane was annealed at 62°C for **DMAEMA/AN-107** and 55°C for **DMAEMA/AN-199** in vacuo for 24 h. The final thickness of the membrane thus obtained was 20–30 μm.

Membranes of **DMAEMA/2EHMA** were prepared as follows: 10 cm^3 of a chloroform solution (30 g dm^{-3}) was poured into a flat laboratory dish (8.6 cm diameter) and the solvent was allowed to evaporate at 25°C for 24 h. The thickness of the membrane was 50–60 μm.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) of the membranes were analyzed with MAC Science DSC-3100. The samples were cooled to -80°C, then heated at 10°C min^{-1} to 150°C. Nitrogen, at a flow rate of 10 cm^3 min^{-1}, was used throughout all DSC measurements.

Table I   Results of Polymer Syntheses[a]

Polymer	Monomer			AIBN[b] (mg)	Time (days)	Yield (g)	Mole Fraction of DMAEMA in	
	DMAEMA (g)	AN (g)	2EHMA (g)				Monomer	Polymer
DMAEMA/AN-107	3.934	11.941	—	205	4.5	14.280	0.100	0.107
DMAEMA/AN-199	7.861	10.612	—	205	4.5	10.506	0.200	0.199
DMAEMA/2EHMA-095	1.415	—	16.068	74	5.0	16.084	0.100	0.095
DMAEMA/2EHMA-205	2.830	—	14.282	74	5.0	15.932	0.200	0.205

[a] Polymerization temperature was 45°C.
[b] (AIBN)/(monomer) = 1/200 (mol/mol).

Determination of Membrane Polarity

Membrane polarity in terms of Dimroth's solvent polarity value $E_T(25°C)$ was measured according to the method described previously, using 1-octadecyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2H-benzopyran) as the indicator.[14] A 500 W xenon lamp was used as the light source. The membrane was illuminated with UV light using a Corning color filter No. 7-54. Absorption spectra were measured with a Spectro Multichannel Photo Detector MCPD-110A (Photal).

Density of Membrane

The densities of the membranes were determined by the hydrostatic weighing method. Heptane was adopted as liquid phase for the measurement of **DMAEMA/AN** membranes and 14 wt % aqueous NaCl solution for that of **DMAEMA/2EHMA** membranes.

The molar free volume V_f is defined as:

$$V_f = V - V_0 \tag{1}$$

where V and V_0 are the molar volume of the repeating unit of polymers at temperature of 298 K and at 0 K, respectively. V can be obtained from the density, ρ, of polymers at 298 K.

$$V = M/\rho \tag{2}$$

where M is the molecular weight of the repeating unit of polymers. A good approximation to V_0[15] is

$$V_0 = 1.3V_W \tag{3}$$

where V_W is the Van der Waals volume, which can be calculated through a group contribution consideration.[16]

Fractional free volume, f, is calculated by

$$f = V_f/V \tag{4}$$

Permeation Experiment

The permeation of CO_2, O_2, and N_2, through membranes, were measured at 25°C. From the steady-state straight line of the permeation curve, the permeability coefficient was evaluated.[17]

Sorption Experiment

Sorption isotherms of CO_2, O_2, and N_2 were measured gravimetrically by a Cahn Model 2000 elec-

trobalance set in a high-pressure chamber made of stainless steel.[18-20] Sorption experiments were made at 25°C. The apparatus consists essentially of a high-pressure chamber mounted in a thermostatically controlled air bath and a gas supply system.

RESULTS AND DISCUSSION

Permeation

The steady-state permeability coefficients of various gases in **DMAEMA/AN-107** and **DMAEMA/AN-199** membranes are presented in Figure 1 as a function of upstream driving pressure p. As for permeability coefficients of O_2 and N_2 for both membranes, they were independent of upstream pressure. In contrast with permeability coefficient independence of O_2 and N_2 on upstream pressure, permeability coefficients of CO_2 for both **DMAEMA/AN-107** and **DMAEMA/AN-199** membranes showed upstream pressure dependence. P_{CO_2} increased with a decrease in upstream driving pressure, as shown in Figure 1.

Figure 2 shows the relationship between the permeability coefficients of various gases in **DMAEMA/2EHMA-095** and **DMAEMA/2EHMA-205** membranes and the upstream driving pressure. P_{O_2} and P_{N_2} for these membranes were independent of upstream pressure. P_{CO_2} for these membranes also showed upstream pressure independence in contrast to CO_2 permeation through **DMAEMA/AN** membranes.

From these results, we deduced, phenomenally, the following plausible permeation mechanisms for these three kinds of gasses as follows[21,22]: (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, permeability coefficients of O_2 and N_2 in **DMAEMA/AN** membranes and those for CO_2, O_2, and N_2 in **DMAEMA/2EHMA** membranes did not show upstream pressure dependence and gave constant permeability coefficients. On the contrary, the permeation mechanism of CO_2 in **DMAEMA/AN** membranes was interpreted by the partly immobilized model[21,22] 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.

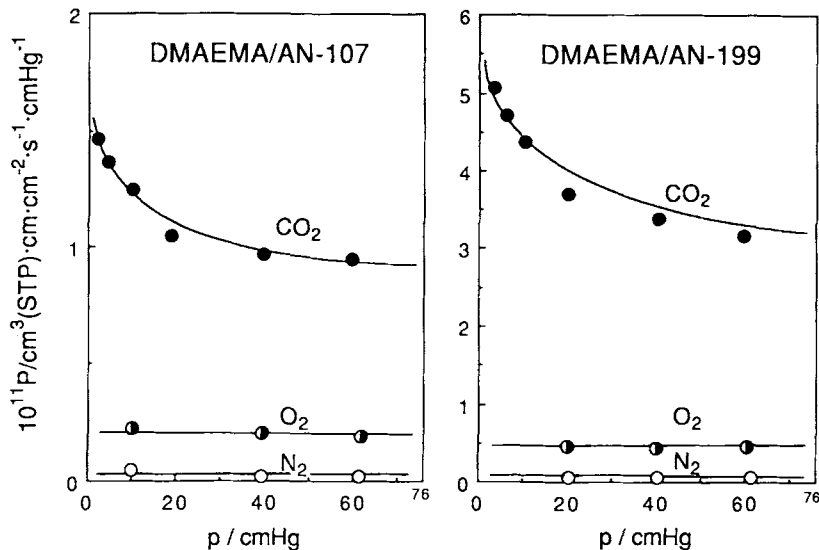In order to ascertain permeation mechanisms of these gases, sorption isotherms of these membranes

Figure 1   Pressure dependence of the permeability coefficients of CO_2, O_2, and N_2 through **DMAEMA/AN** membranes at 25°C.

were investigated. Obtained results are given in the following section.

Sorption

Sorption isotherms are shown in Figures 3 and 4. Sorption isotherms for various gases in these membranes, except that for CO_2 in **DMAEMA/AN** membranes, gave straight lines passing through the origin, leading that these gases were sorbed by Henry's law. It can be concluded that permeations of O_2 and N_2 through **DMAEMA/AN** membranes and CO_2, O_2, and N_2 through **DMAEMA/2EHMA** membranes were interpreted by mechanism (1), as given 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 **DMAEMA/AN** membranes. In the case of **DMAEMA/2EHMA** membranes, all gases investigated in the present article were sorbed by the Henry's law and free to diffuse in the membranes.

The sorption isotherms of CO_2 in **DMAEMA/ AN** were concave to the pressure axis, as shown in Figure 3. The experimental data for CO_2 sorption were analyzed according to the dual sorption model.[23,24]

The dual sorption model postulates that the sorption consists of dissolution (C_D) represented by the Henry's law and adsorption (C_H) on the inner surface of the microvoids represented by the Langmuir equation. The total solubility C is, thus, given[23,24] by the following equation:

$$C = C_D + C_H$$

$$= k_D p + C'_H b p / (1 + bp)$$

(5)

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 permeant gas. Obtained sorption parameters for **DMAEMA/AN** membranes are summarized in Table II, and those for **DMAEMA/2EHMA** in Table III. In Table II, dual sorption parameters for polyacrylonitrile (**PAN**),[25] membrane matrix of **DMAEMA/AN**, is also given for convenience of the following discussion. In Figure 3, sorption isotherm for CO_2 in **PAN** is also depicted using the dual sorption parameters[25].

Obtained k_D and b values for CO_2 in the membranes were relatively high values compared with those for **PAN** membrane.[25] This can be also found in Figure 3. Such high values of k_D and b for CO_2 might be due to the introduction of amine moiety into the membrane, that is, the interaction between CO_2 molecules and amine moiety (weak acid-base interaction) made k_D and b values for modified **PAN** membrane higher than those for unmodified **PAN** membrane, as was repoprted in the sorption of CO_2 in poly(4-vinylpyridine-co-acrylonitrile) membranes.[9,10] However, it is impossible to separate two contributions, that from the adsorption on the inner surface of the microvoids and that from the interaction between CO_2 molecules and amine
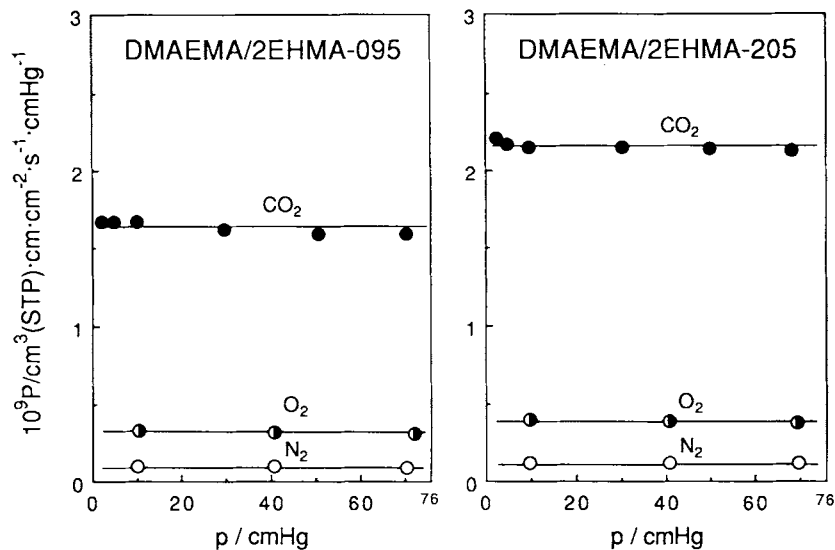
Figure 2 Pressure dependence of the permeability coefficients of CO_2, O_2, and N_2 through **DMAEMA/2EHMA** membranes at 25°C.

moiety, because **DMAEMA/AN** membranes were glassy at the experimental temperature of 25°C.

Dual sorption parameters for **DMAEMA/AN** membranes seem to depend on content of amine

moiety, 2-(N,N-dimethyl)aminoethyl methacrylate, in the membrane. Henry's law parameters for **DMAEMA/2EHMA** membranes also showed inclination to increase with the increase in amine
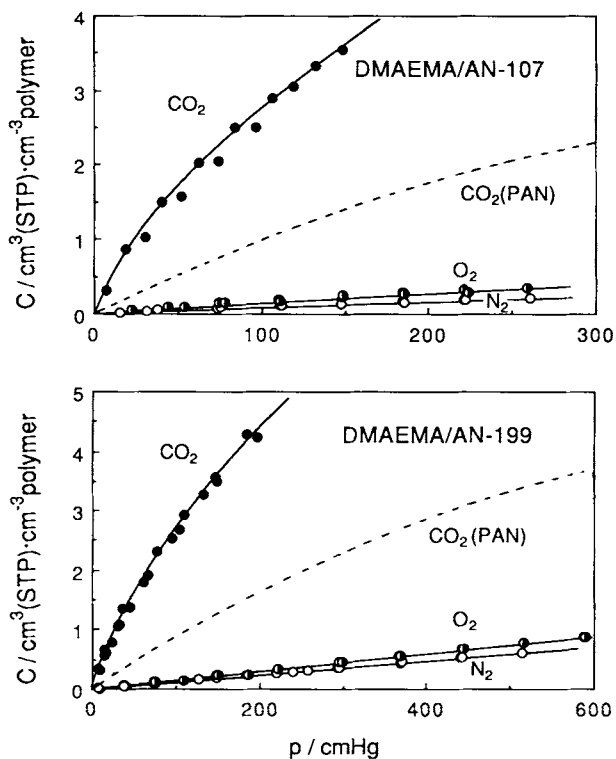

Figure 3 Sorption isotherms for CO_2, O_2, and N_2 in **DMAEMA/AN** membranes at 25°C. Solid lines were calculated from eq. (5) using parameters in Table II.
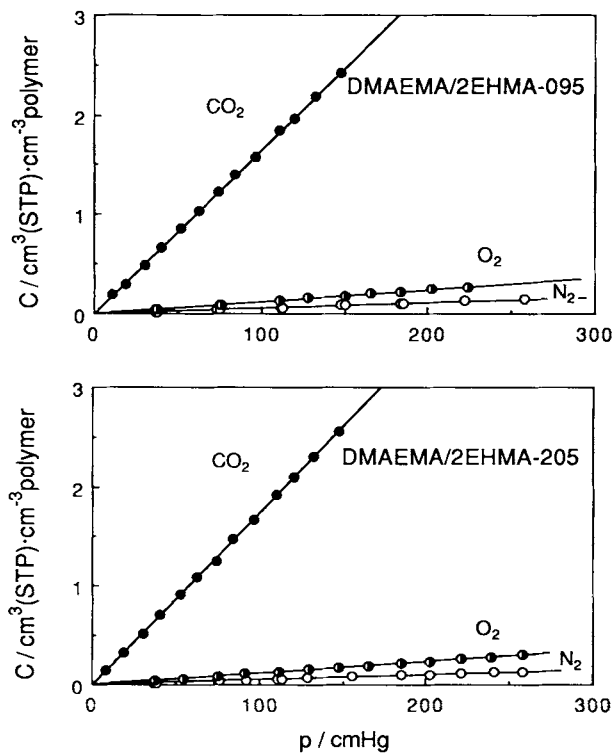
Figure 4 Sorption isotherms for CO_2, O_2, and N_2 in **DMAEMA/2EHMA** membranes at 25°C. Solid lines were calculated from eq. (5) using parameters in Table III.

Table II   Dual Mode Sorption Parameters for DMAEMA/AN Membranes at 25°C

	CO$_2$		O$_2$		N$_2$		
	107	199	107	199	107	199	PAN (CO$_2$)
$10^2 k_D{}^a$	1.62	1.52	0.138	0.151	0.079	0.120	0.271
$C_H'{}^b$	1.49	1.86	—	—	—	—	3.67
$10^2 b^c$	2.48	1.57	—	—	—	—	0.245
$10^2 (k_D + C_H' \cdot b)$	5.32	4.44	—	—	—	—	1.17
$(C_H')/(\text{Carrier})$	0.032	0.026	—	—	—	—	—
$10^9 D_D{}^{d,e}$	0.312	1.15	1.49	2.95	0.272	0.472	—
$10^9 D_H{}^d$	0.257	1.10	—	—	—	—	—

^{a} cm^3(STP)/cm^3 − polymer cmHg.
^{b} cm^3(STP)/cm^3 − polymer.
^{c} 1/cmHg.
^{d} cm^2/s.
^{e} From sorption parameters and permeability coefficient $[(D_D = 1/k_D(P - D_H\, C_H'\, b/(1 + bp))]$.

moiety content in the **DMAEMA/2EHMA** membranes. The authors tried to explain this dependence by membrane polarity, which was evaluated in terms of Dimroth's solvent polarity value $[E_T(25°C)]$.[14] The following three relationships have already been reported as practical applications of this membrane polarity: (1) the permselectivities for piezodialysis of the binary system K$^+$-Li$^+$ through common polymeric membranes are closely related to the membrane polarities;[26] (2) the mechanism and selectivity of transport of anionic substances such as halogen ions,[27,28] organic acids,[29] and amino acids,[30] through synthetic polymeric membranes bearing heterocyclic compounds as fixed carriers are determined by the membrane polarities; (3) the separation factors for the separation of water/various alcohol mixtures, especially, water/ethanol mixture, through synthetic polymeric membranes by pervaporation showed good correlation to the membrane polarities.[31-35] The membrane polarities of these four kinds of membranes are summarized in Table IV. From

the table, it is concluded that **DMAEMA/AN-107** is more polar than **DMAEMA/AN-199**. **DMAEMA/AN-107** membrane gave greater k_D and b values than **DMAEMA/AN-199** membrane in concert to the change in membrane polarity. The membrane polarity of **DMAEMA/2EHMA-205** was slightly higher than that of **DMAEMA/2EHMA-095**. k_D values of **DMAEMA/2EHMA** showed an inclination to decrease with decrease in membrane polarity. However, such a tendency seems to be only effective among the homologous membrane family. From these results it can be said that membrane polarity is important factors in gas separation as well.

The amine moiety introduced into **DMAEMA/2EHMA** membranes did not show any specific in-

Table III   Permeation Parameters for DMAEMA/2EHMA at 25°C

	CO$_2$		O$_2$		N$_2$	
	095	205	095	205	095	205
$10^2 k_D{}^a$	1.65	1.73	0.122	0.119	0.059	0.054
$10^7 D_D{}^{b,c}$	0.996	1.25	2.59	3.27	1.64	2.20

^{a} cm^3(STP)/cm^3 − polymer cmHg.
^{b} cm^2/s.
^{c} From sorption parameters and permeability coefficient ($D_D = P/k_D$).

Table IV   Characterization of Membranes

	DMAEMA/AN		DMAEMA/2EHMA	
	107	199	095	205
λ^a	557	563	586	583
$E_T(25°C)^b$	48.8	46.6	38.0	39.1
$T_g{}^c$	57	50	−11	−10
ρ^d	1.155	1.095	1.017	1.031
f^e	0.102	0.147	0.153	0.147

^{a} Absorption maximum of the indicator in the visible range (nm).
^{b} Membrane polarity (kcal/mol).
^{c} Glass transition temperature (°C). T_g for homopolymer of **DMAEMA** was reported to be 19°C[36] and that for **2EHMA** to be −10°C.[37]
^{d} Density (g/cm^3).
^{e} Fractional free volume.

teraction towards CO_2 molecules like that in **DMAEMA/AN** membranes. This might be principally due to the difference in the state of **DMAEMA/2EHMA** and **DMAEMA/AN** membranes. It is expected, furthermore, that the membrane polarity can control the effect of amine moiety like transport of anionic species.[27-30]

Diffusion

It is possible to evaluate the diffusion coefficient D for O_2 and N_2 in **DMAEMA/AN** membranes, and CO_2, O_2, and N_2 in **DMAEMA/2EHMA** membranes using $P = DS$, where S is the solubility coefficient (k_D) obtained from the sorption experiment. The permeability coefficient of CO_2 in **DMAEMA/AN** membranes is represented by following equation:[21-23]

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

$$(F = D_H/D_D, K = C'_H b/k_D) \quad (6)$$

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 CO_2 in **DMAEMA/AN** membranes using eq. (6). and the experimental data shown in Figure 1. Those obtained diffusion coefficients are also summarized in Tables II and III. Among the homologous membrane family, diffusivity showed tendency to increase with the increase in fractional free volume in Table IV. The present **DMAEMA/AN** membranes showed higher F values than usual; 0.824 for **DMAEMA/AN-107** and 0.957 for **DMAEMA/AN-199** membranes. This also suggests that the details of the Langmuir type adsorption consists of not only the adsorption of CO_2 on the inner surface of the microvoids but also that induced by the weak acid-base interaction between CO_2 molecule and amine moiety.

Predicted Permselectivity for Binary Systems

It was impossible for the permeation apparatus used in the present study to obtain permselectivities of gas mixtures. So, we evaluated theoretically permselectivities towards CO_2. Ideal separation factor β_{CO_2/N_2} was defined by[38]

$$\beta_{CO_2/N_2} = P_{CO_2}/P_{N_2} \quad (7)$$

Figure 5 shows the ideal separation factors as a function of CO_2 partial pressure under the condition

that the total upstream pressure was 76 cmHg (1 atm) and the downstream pressure was assumed to be negligibly small.

Separation factors, selectivities towards CO_2 for **DMAEMA/AN** membranes increased with a decrease in partial pressure of CO_2 as expected from the fact that CO_2 permeated through **DMAEMA/AN** membranes by partial immobilized model. Permselectivity towards CO_2 increased with the increase in amine content in the membrane. **DMAEMA/AN-199** membrane yielded a β_{CO_2/N_2} value of 90. **DMAEMA/AN-199** membrane is one of membranes,[3,5,8] that gave high β_{CO_2/N_2} value, when it is compared with those for a number of polymers. On the contrary, it can be predicted that **DMAEMA/2EHMA** membranes give the constant separation factor, as expected from the results in Figures 2 and 4.

In order to attain higher separation factors towards CO_2 separation with synthetic polymeric membranes containing amine moiety, there might be the following two possible ways: (1) increase in amine moiety content in the membrane; (2) magnitude of interaction between CO_2 and amine moiety might depend on surface area of nitrogen atom in amine group. The surface areas of nitrogen atom in alkyl amine moiety give tendency to decrease in the following order:[16] primary amine > secondary amine > tertiary amine. From this, a primary or secondary amine moiety, instead of a tertiary amine, is adopted as a fixed carrier towards CO_2.
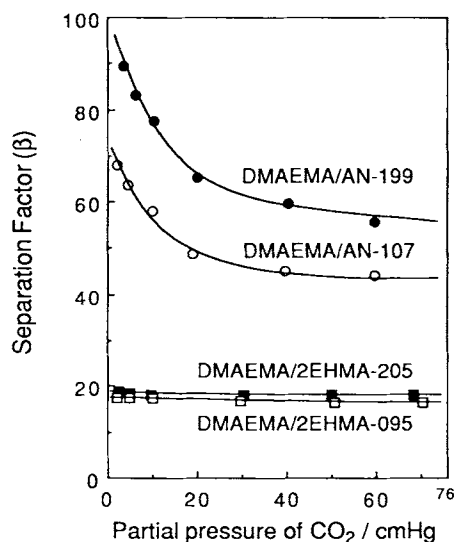

Figure 5 Predicted permeabilities for CO_2 relative to N_2 as a function of partial pressure of CO_2 for the case of a negligible downstream pressure at 25°C for **DMAEMA/AN** and **DMAEMA/2EHMA** membranes. Total upstream pressure was 76.0 cmHg.

CONCLUSIONS

Novel membrane materials for selective separation of CO_2, poly{2-(N,N-dimethyl)aminoethyl methacrylate-co-acrylonitrile} (**DMAEMA/AN**) and poly{2-(N,N-dimethyl)aminoethyl methacrylate-co-2-ethylhexyl methacrylate} (**DMAEMA/2EHMA**) were prepared from corresponding vinyl monomers by radical copolymerization. Membranes from these copolymers showed permselectivity towards CO_2. Through **DMAEMA/AN-199** membrane, where **DMAEMA** mol fraction was 0.199, especially, the separation factor towards CO_2 for CO_2/N_2 separation ranged from 60 to 90, ranging in the CO_2 partial pressure in the feed gas from 61 to 3.6 cmHg. These membranes showed feasibility to remove (or separate) CO_2 from combustion gas.

REFERENCES

1. W. J. Ward, III and W. L. Robb, *Science*, **156**, 1481 (1967).
2. S. L. Matson, C. S. Herrick, and W. J. Ward, III, *Ind. Eng. Chem. Process Des. Dev.*, **16**, 370 (1977).
3. O. H. LeBlanc, Jr., W. J. Ward, S. L. Matson, and S. G. Kimura, *J. Membrane Sci*, **6**, 339 (1980).
4. M. Kawakami, H. Iwanaga, and S. Kagawa, *Chem. Lett.*, 1445 (1980).
5. K. Okamoto, N. Umeo, S. Okamyo, K. Tanaka, and H. Kita, *Chem. Lett.*, 225 (1993).
6. M. Kawakami, H. Iwanaga, Y. Hara, M. Iwanaga, and S. Kagawa, *J. Appl. Polym. Sci.*, **27**, 2387 (1982).
7. M. Kawakami, Y. Yamashita, M. Yamasaki, M. Iwamoto, and S. Kagawa, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 251 (1982).
8. M. Kawakami, H. Iwanaga, Y. Yamashita, M. Yamasaki, M. Iwamoto, and S. Kagawa, *Nippon Kagaku Kaishi*, 847 (1983).
9. M. Yoshikawa, T. Ezaki, K. Sanui, and N. Ogata, *Kobunshi Ronbunshu*, **43**, 729 (1986).
10. M. Yoshikawa, T. Ezaki, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.*, **35**, 145 (1988).
11. M. Yoshikawa, K. Fujimoto, H. Kinugawa, T. Kitao, and N. Ogata, *Chem. Lett.*, 243 (1994).
12. A. R. Berens and H. B. Hopfenberg, *J. Membrane Sci.*, **10**, 283 (1982).
13. R. G. Pearson, *J. Chem. Ed.*, **45**, 581 (1968).
14. T. Shimidzu and M. Yoshikawa, *Polym. J.*, **15**, 135 (1983).
15. W. M. Lee, *Polym. Eng. Sci.*, **20**, 65 (1980).
16. A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Gases*, Wiley, New York, 1968.
17. T. Nakagawa, *Maku (Membrane)*, **6**, 197 (1981).
18. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 535 (1986).
19. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1525 (1986).
20. K. Mizoguchi, T. Hirose, Y. Naito, and Y. Kamiya, *Polymer*, **28**, 1298 (1987).
21. D. R. Paul and W. J. Koros, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 675 (1976).
22. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 2171 (1978).
23. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 687 (1976).
24. W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membrane Sci.*, **1**, 177 (1976).
25. D. R. Paul, *Ber. Bunsenges. Phys. Chem.*, **83**, 294 (1979).
26. T. Shimidzu and M. Yoshikawa, *Nippon Kagaku Kaishi*, 958 (1983).
27. M. Yoshikawa, Y. Imashiro, K. Sanui, and N. Ogata, *J. Membrane Sci.*, **20**, 189 (1984).
28. M. Yoshikawa, Y. Yatsuzuka, K. Sanui, and N. Ogata, *Macromolecules*, **19**, 995 (1986).
29. M. Yoshikawa, S. Shudo, K. Sanui, and N. Ogata, *J. Membrane Sci.*, **26**, 51 (1986).
30. M. Yoshikawa, M. Suzuki, K. Sanui, and N. Ogata, *J. Membrane Sci.*, **32**, 235 (1987).
31. M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, and T. Shimidzu, *Polym. J.*, **16**, 653 (1984).
32. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2159 (1984).
33. M. Yoshikawa, N. Ogata, and T. Shimidzu, *J. Membrane Sci.*, **26**, 107 (1986).
34. M. Yoshikawa, S. Ochiai, M. Tanigaki, and W. Eguchi, *J. Appl. Polym. Sci.*, **43**, 2021 (1991).
35. M. Yoshikawa, H. Hara, M. Tanigaki, M. Guiver, and T. Matsuura, *Polymer*, **33**, 4805 (1992).
36. S. Krause, J. J. Gormley, N. Roman, J. A. Shetter, and W. H. Watanabe, *J. Polym. Sci.*, **A3**, 3573 (1965).
37. C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).
38. W. J. Koros, R. T. Chern, V. Stannett, and H. B. Hopfenberg, *J. Polym. Sci., Pokym. Phys. Ed.*, **19**, 1513 (1981).