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Selective Permeation of Carbon Dioxide through Synthetic Polymeric Membranes Having Amine Moiety

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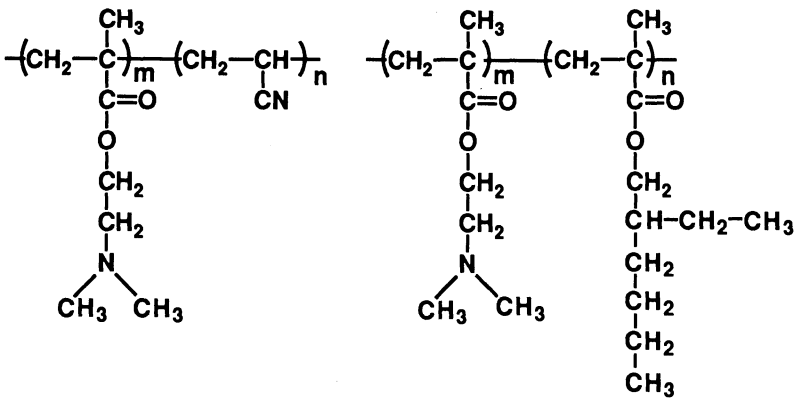
Permeation of CO_2 was investigated by using synthetic polymeric membranes having a tertiary amine moiety, 2-(N,N-dimethyl)aminoethoxycarbonyl group. Permselectivity of the present membranes for CO_2 was achieved. Through the DMAEMA/AN-199 membrane, separation factor towards CO_2 for CO_2/N_2 separation ranged from 60 to 90.

Removal and concentration of CO_2 by artificial membranes from the CO_2 emission sources such as power stations, steelworks, and chemical industries are an important subject. The development of novel membrane materials, which membranes efficiently separate CO_2 from the combustion gas, is indispensable to establish the membrane separation technique feasible in the industries.

There have been three kinds of artificial membranes that can be used to remove or concentrate CO_2: Liquid membranes[1,2] (mobile carrier membranes), polymeric membranes,[3-5] and fixed carrier membranes[6-10] (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 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 shape and molecular weight of gas itself, but it is hard to obtain the polymeric membranes possessing suitable diffusivity. 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.

On the basis of this idea, acid-base interaction was adopted as a molecular recognition interaction to CO_2 so that solubility of polymeric materials towards CO_2 can be improved. We introduced tertiary amine moieties 2-(N,N-dimethyl)aminoethyl methacrylate, which are easily copolymerized by radical polymerization, as a fixed carrier into polymeric membranes and investigated the feasibility of selective separation of CO_2 through these synthetic polymeric membranes newly prepared.

Membrane materials, 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 synthesized by the usual radical copolymerization of 2-(N,N-dimethyl)-aminoethyl methacrylate (DMAEMA) and corresponding vinyl monomer acrylonitrile (AN) or 2-ethylhexyl methacrylate (2EHMA) initiated by 2,2'-azobis(2-methylpropionitrile) at 45 °C. All chemical structures are shown in the scheme. DMAEMA/AN membranes were obtained by casting from N,N-dimethylformamide solution. Membranes from DMAEMA/2EHMA were prepared by casting from chloroform solution. Thickness of the DMAEMA/ AN membranes thus obtained was 20 - 30 μm and that of DMAEMA/2EHMA membrane was 50 - 60 μm. The permeation of CO_2, O_2, and N_2 through the present membranes were measured at 25 °C and



DMAEMA/AN **DMAEMA/2EHMA**

	m	n
DMAEMA/AN-199	0.199	0.801
DMAEMA/AN-107	0.107	0.893
DMAEMA/2EHMA-205	0.205	0.795
DMAEMA/2EHMA-095	0.095	0.905

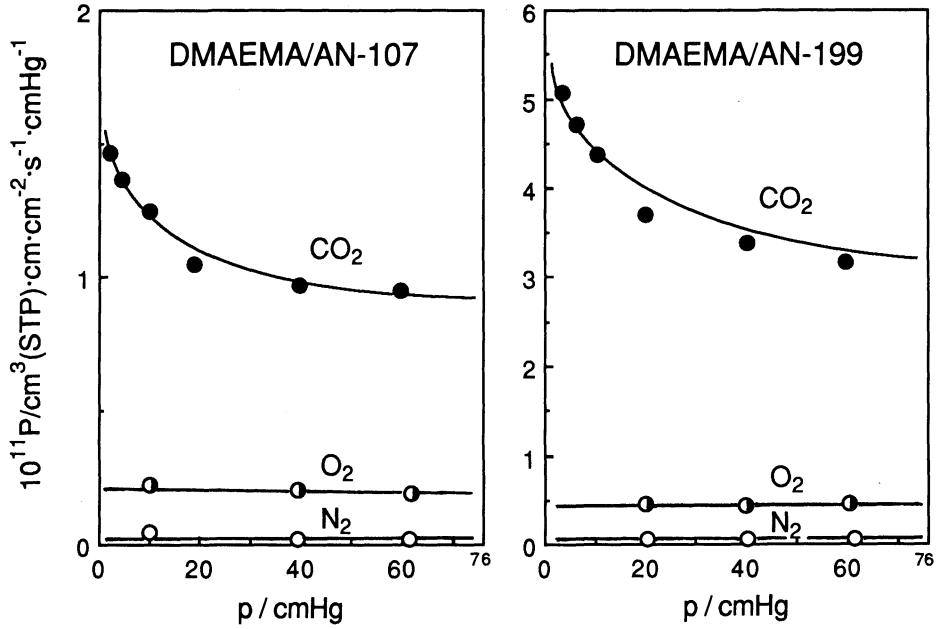


Fig. 1. Pressure dependence of the permeability coefficients of CO_2, O_2, and N_2 through DMAEMA/AN membranes at 25 °C.

under prescribed pressures. From the steady-state straight line of the permeation curve, the permeability coefficient was evaluated.[11] Separation factors $\beta_{CO2/O2}$ and $\beta_{CO2/N2}$ were defined by[12]

$$\beta_{CO2/gas} = P_{CO2}/P_{gas}$$

where the subscript gas is either O_2 or N_2.

The steady state permeability coefficients of various gases in the DMAEMA/AN-107 and DMAEMA/AN-199 membranes are presented in Fig. 1 as a function of upstream driving pressure p. As for permeability coefficients of O_2 and N_2 for these two membranes, they were independent of upstream pressure. In contrast, the permeability coefficient of CO_2 for these membranes showed upstream pressure dependence. P_{CO2} increased with decrease in upstream driving pressure as shown in Fig. 1. From these results and the dependence of P on p reported for glassy polymers,[13] we deduced the following: The fixed carrier, tertiary amine moiety, incorporated into polyacrylonitrile does not show specific interaction towards O_2 and N_2. On the contrary, the fixed carrier does show specific affinity towards CO_2 as designed.

Figure 2 shows the relationships between the permeability coefficients of various gases in DMAEMA/2EHMA membranes and upstream driving pressure. P_{O2} and P_{N2} for these membranes were independent of upstream pressure. P_{CO2} for these membranes also showed upstream pressure independence even though DMAEMA/2EHMA membranes carried tertiary amine moiety. This might be due to the difference in environment surrounding tertiary amine moiety.

It was impossible for our permeation apparatus to obtain permselectivities of binary gas mixtures. So we evaluated theoretically separation factors (β). Figure 3 shows the predicted separation factors as a function of CO_2 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

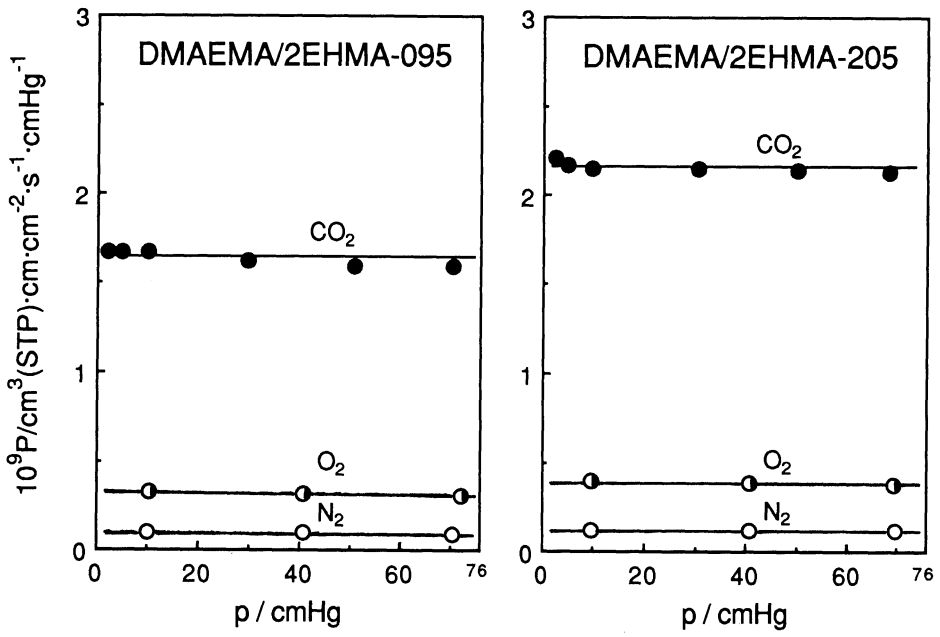


Fig. 2. Pressure dependence of the permeability coefficients of CO_2, O_2, and N_2 through DMAEMA/2EHMA membranes at 25 °C.

obtained permeability coefficients. Separation factors, selectivities towards CO_2 increased with a decrease in partial pressure of CO_2. DMAEMA/AN-199 membrane yielded a $\beta_{CO2/N2}$ value of 90. DMAEMA/AN-199 membrane is one of membranes,[3,5,8] which gave high $\beta_{CO2/N2}$ value, when it is compared with those for a number of polymers. CO_2 is classified as Lewis hard acid.[14] It seems likely that the interaction between CO_2 and the fixed carrier, tertiary amine moiety incorporated into the DMAEMA/AN membrane plays an important role to realize high permselectivity towards CO_2.

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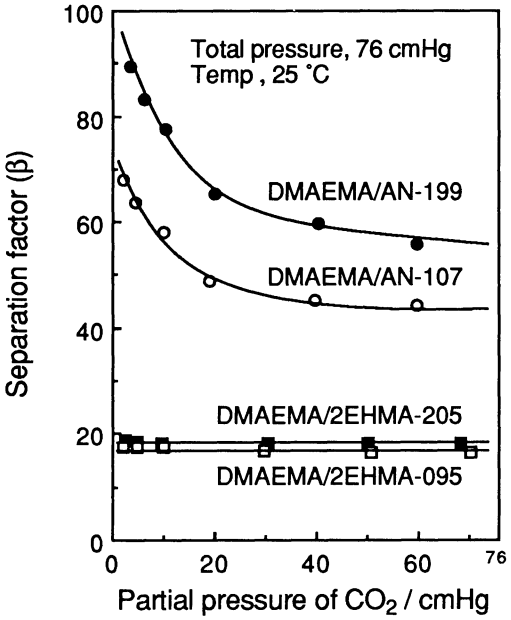

Fig. 3. Predicted separation factors ($\beta_{CO2/N2}$) at 25 °C. (Total upstream press., 76.0 cmHg.)

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