CHEMISTRY LETTERS, pp. 1445-1448, 1980. © The Chemical Society of Japan 1980

SELECTIVE PERMEATION OF CARBON DIOXIDE THROUGH CELLULOSE NITRATE/ POLYETHYLENE GLYCOL BLEND MEMBRANES

Mitsuyasu KAWAKAMI, Hideaki IWANAGA, and Shuichi KAGAWA*
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Nagasaki 852

Permeabilities for N_2, O_2, and CO_2 through cellulose nitrate/ polyethylene glycol blend membranes were determined as a function of film composition. Not only the permeability but the permselectivity for CO_2 increased with an increase in the fraction of polyethylene glycol. It was suggested that the intermolecular force induced by polar groups in the film and the role of polyethylene glycol as a plasticizer may be responsible for such a behavior for CO_2.

In view of the recovery of carbon resources or the control of CO_2 concentration in an artificial atmosphere much attention is being denoted to the membrane separation of CO_2 from a mixture with N_2 and/or O_2. However, no practical membrane has been developed as yet which makes this separation process possible. Although the gas permeabilities of polymer membranes have become expectable to a certain extent from the densities, free volumes, cohesive energy densities,1,2) or Permachor values3) of the polymers, the correlation between the permselectivities and such properties are not yet clarified.

By comparison of the physical properties of N_2, O_2, and CO_2, it will be noted that the polarizability and the quadrupole moment of CO_2 are considerably larger than those of N_2 or O_2, while all of them are nonpolar gases.4) Thus, a stronger interaction can be expected to act between CO_2 molecule and polar substances. In the present work, permeabilities of cellulose nitrate(CN) / polyethylene glycol (PEG) blend membranes for N_2, O_2, and CO_2 were determined as a function of film composition and the permselectivity for CO_2 was examined.

Commercial extra pure PEG-300, -1000, or -4000(Wako Pure Chemical Ind.) and CN membranfilter(Sartorius-Membranfilter GmbH) were used without further purifications. A casting solution was prepared by dissolving appropriate amounts of PEG and CN in tetrahydrofuran(ca. 3wt%). The solution was poured onto a glass plate and dried at room temperature for about 2 days. The film was, then, stripped from the plate, followed by vacuum drying at room temperature for several days. The system of CN/ PEG showed excellent compatibilities and we could obtain transparent or translucent blend membranes of the composition from 100/0 to ca. 30/70. However, those of more than 60wt% of PEG-300 are so sticky and intractable that they could not be subjected to the permeation experiments. The densities of membranes were determined by a floatation method, showing the volume change upon blending to be negligible. The thickness of membranes, ca. 70 - 130μm, was calculated from the density and the weight per unit area of the membrane. These values were in good agreement with those observed with a scanning electron microscope.

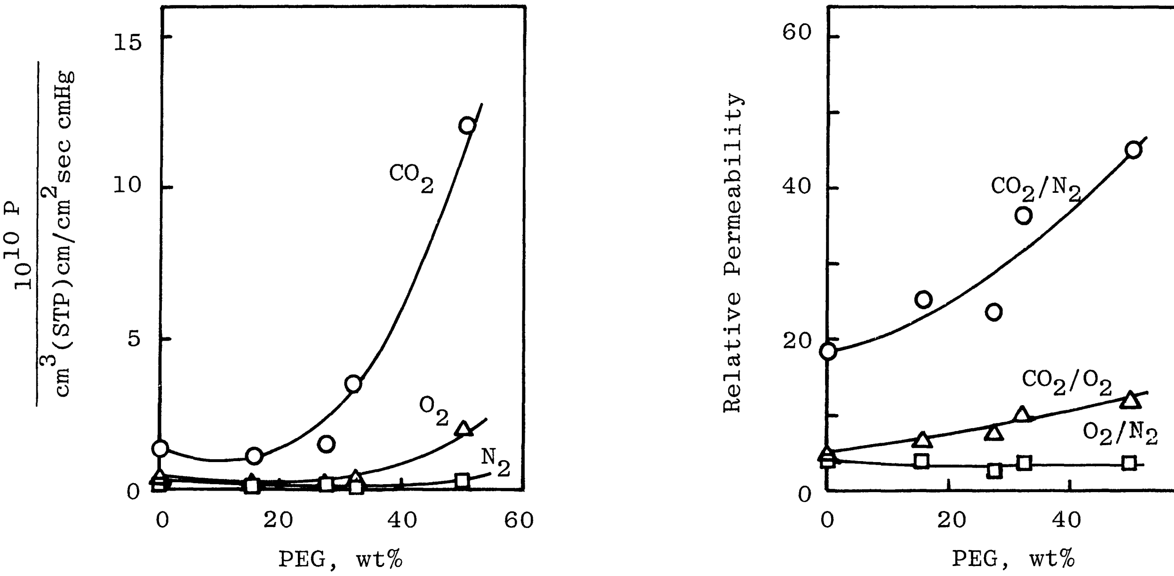
N_2, O_2, and CO_2 of 99.9% minimum purities(Seitetsu Kagaku Co.) were employed as penetrant gases. They were thoroughly dried through a liquid N_2 trap before use.

The apparatus used for measuring gas permeabilities is essentially the same as that described in the literature.[5)] The pressure increase at the low pressure compartment due to gas transport through a polymer film was followed as a function of time with a Pirani gauge.[6)] Permeability coefficient, P was calculated from the steady state transport rate, $\Delta p/\Delta t$ using the expression,

$$P = \frac{273.2}{76T}\,\frac{V}{p^*}\frac{L}{A}\,\frac{\Delta p}{\Delta t}\,, \qquad (1)$$

where V and T are the volume and the temperature, respectively, of the measuring chamber, p* is the applied pressure of a penetrant gas, A and L are the effective area and the thickness of a film, respectively. At the steady state a plot of p against time, t yielded a straight line, of which the intercept on the t-axis gave the time lag, θ.

From the experimental results that the transport rates of gases increased with increasing temperature and that the higher permeability was found for the heavier gas, the permeation mechanism in the present systems could be regarded as a sorption - diffusion type. Further, P and θ did not show pressure dependence and were practically constant in the applied pressure range which was limited up to 76cmHg(=101325Pa). This fact demonstrated that diffusion coefficient, D and solubility coefficient, S did not depend on the concentration of penetrant. Thus, D and S could be calculated respectively from the relations,



(A) (B)

Fig. 1. Gas permeabilities(A) and relative permeabilities(B) of CN/PEG blend membranes(298K).

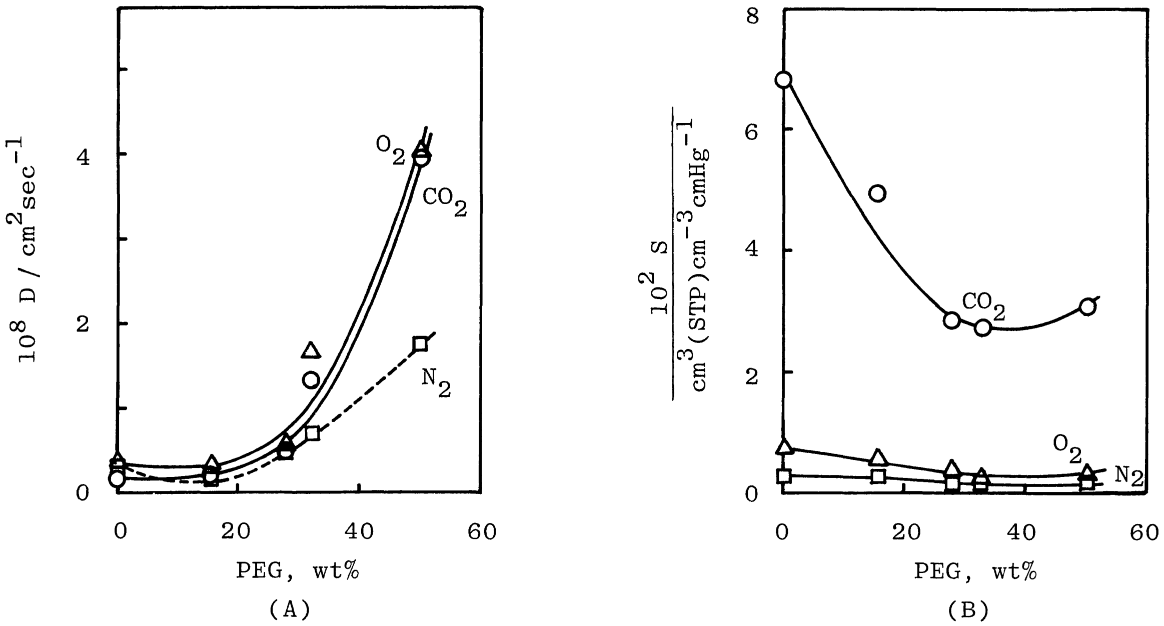


Fig. 2. Diffusion coefficients(A) and solubility coefficients(B) of gases in CN/PEG blend membranes(298K).

$$D = \frac{L^2}{6\theta}, \qquad (2) \quad \text{and} \quad S = \frac{P}{D}. \qquad (3)$$

The variations of P with the fraction of PEG-300 in blend membranes are illustrated in Fig. 1(A). P for each gas is almost constant or rather slightly lowers up to ca. 20wt% PEG content, and then increases with the fraction of PEG. Such an increase in P is particularly marked for CO_2. In Fig. 1(B) permeability ratios are plotted against the PEG content. P_{CO2}/P_{N2} rises appreciably with increasing fraction of PEG, while P_{O2}/P_{N2} is practically constant. This illustrates a selective increase in P_{CO2}. The film of CN/PEG-300(50/50) yielded a P_{CO2}/P_{N2} of 45.2, which is the largest value next to 86.4 of polyformaldehyde when it is compared with those for a number of polymers cited in Ref. 7. P is represented by the product of D and S. Variations of permeabilities and relative permeabilities with film composition will be examined from two standpoints of D and S, separately.

D and S are shown in Fig. 2(A) and (B) as a function of film composition. Diffusivities for each penetrant gas increase significantly with an increase in the fraction of PEG in the region higher than 30wt%. It may be considered that a PEG molecule plasticizes CN matrix and results in higher mobilities of CN segments and consequently, in a larger value of D. The glass transition temperature of the blend membranes determined by DSC, in fact, dropped gradually with the PEG content and reached about 300K for CN/PEG-300(57/43). On the other hand, the value of S for each gas decreases initially with the fraction of PEG and then increases after passing a minimum at 30 - 40wt% PEG content. Such a dependence of S is the most remarkable for CO_2. Evidently the marked increase in P_{CO2} above 30wt% PEG content is attributable to both of those in D and S. These remarkable changes in transport properties such as P, D, or S observed at ca. 30wt% PEG might be associated with the change of the glass transition temperature with PEG content. According to Stern, et al.,8) transport properties of cellulose acetate membrane showed discontinuous dependence on temperature at the glass transition point. For the present system blend membranes of lower than 30wt% PEG content were glassy whereas those of higher PEG content were rubbery.

Table 1. Effects of the molecular weight of PEG on gas permeabilities of CN/PEG (57/43) blend membranes (298K).

M.W. of PEG	10^{11} P a)			P_{CO_2}/P_{N_2}
	N_2	O_2	CO_2	
300	2.2	6.7	82	37.8
1000	2.1	6.2	72	33.6
4000	0.5	1.6	14	28.6

a) $cm^3(STP)cm/cm^2sec\ cmHg$

Permeability data for various membranes blended with PEG of different molecular weight are given in Table 1. Each membrane has the same composition. Clearly P is larger when PEG of lower molecular weight is blended. This is because a smaller molecule, which has higher mobility itself and can enter into the CN matrix more easily, may exert a larger plasticizing effect on the mobility of CN segments.

It may be seen from gas transport data available for various polymer films,9) that with increasing the polarity of polymers the diffusivity for a given gas generally decreases, whereas the solubility increases. Thus, permeabilities can not be correlated simply with the polarity of polymers. In the present work, however, both the permeability and the selectivity for CO_2 in CN/PEG blend membranes were found to increase with an increase in the fraction of PEG. CO_2 is a nonpolar gas but has relatively larger polarizability and quadrupole moment. It seems likely that the intermolecular force induced by polar groups of the blend membrane may cooperate with the role of PEG as a plasticizer to realize both increases in permeability and permselectivity for CO_2.

References

1) L.A. Pilato, L.M. Litz, B. Hargitay, R.C. Osborne, A.G. Farnham, J.H. Kawakami, P.E. Fritze, and J.E. McGrath, ACS Polymer Preprints, 16, 41 (1975).
2) U. Konig and H. Schuch, Kunststoffe, 67, 27 (1977).
3) M. Salame, ACS Polymer Preprints, 8, 137 (1967); J. Polym. Sci., C41, 1 (1973).
4) D.E. Stogryn and A.P. Stogryn, Mol. Phys., 11, 371 (1966).
5) R.M. Barrer and G. Skirrow, J. Polym. Sci., 3, 549 (1948).
6) M. Kawakami, H. Iwanaga, and S. Kagawa, Bull. Chem. Soc. Jpn., in press.
7) S.T. Hwang, C.K. Choi, and K. Kammermeyer, Separ. Sci., 9, 461 (1974).
8) S.A. Stern, S.K. Sen, and A.K. Rao, J. Macromol. Sci., Phys., B10, 507 (1974).
9) For example, Y. Ito," Zairyo to Suibun handobukku," ed. by the Society of Polymer Science of Japan, Kyoritsu Shuppan, Tokyo (1968), Chap. B5.

(Received September 8, 1980)