Study of Transport of Pure and Mixed CO_2/N_2 Gases through Polymeric Membranes

C. K. YEOM, S. H. LEE, J. M. LEE

Chemical Process and Engineering Center, Applied and Engineering Chemistry Division, Korea Research Institute of Chemical Technology, P. O. Box 107, Yusong, Taejon, South Korea

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ABSTRACT: The permeations of pure CO_2 and N_2 gases and a binary gas mixture of CO_2/N_2 (20/80) through poly(dimethylsiloxane) (PDMS) membrane were carried out by the new permeation apparatus. The permeation and separation behaviors were characterized in terms of transport parameters, namely, permeability, diffusion, and solubility coefficients which were precisely determined by the continuous-flow technique. In the permeation of the pure gases, feed pressure and temperature affected the solubility coefficients of CO_2 and N_2 in opposite ways, respectively; increasing feed pressure positively affects CO_2 solubility coefficient and negatively affects N_2 solubility coefficient, whereas increasing temperature favors only N_2 sorption. In the permeation of the mixed gas, mass transport was observed to be affected mainly by the coupling in sorption, and the coupling was analyzed by a newly defined parameter permeation ratio. The coupling effects have been investigated on the permeation and separation behaviors in the permeation of the mixed gas varying temperature and feed pressure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 179–189, 2000

Key words: gas permeation; mixed gas; coupling effect; flux transient; diffusion coefficient; solubility coefficient; permeability; rubbery membrane

INTRODUCTION

Usually, the gas transport behavior depends strongly on the state of the polymer. In the rubbery state, the permeability of a polymer is independent of the applied pressure difference across the polymer film, and the permeability is very reproducible because the polymer matrix responds elastically to the sorption of the permeating species.[1] In the permeation of gas mixture, the presence of a gas is known not to affect the permeation of the other gas through rubbery membrane as much as through glassy membrane. It is reported that the coupling effects on the separation property of a polymer are prominent only when a transport parameter of each component differ by more than an order of magnitude.[2] The complete understanding of the mixed gas permeation process through a membrane is limited by lack of experimental data. Very few studies are available in the literature which deal with the effects of the couplings during mixed gas transport through polymeric membranes. The major limitations for such an investigation are experimental restrictions. To acquire a better understanding of permeation behavior in gas permeation, it is necessary to resolve the permeation coefficient into its two components, namely, the diffusion coefficient and the solubility coefficient.

The foreknowledge of the diffusion of a permeant through a membrane requires proper understanding of the transient permeation behavior of the permeant.[3,4] Permeation transient data in the beginning stage of the permeation will mini-

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Correspondence to: C. K. Yeom (ckyeom@pado.krict.re.kr).

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mize such cumulative error. A continuous-flow technique[4,5] was employed for the direct measurement of the dynamic permeation which gives permeation transients. In technique, the downstream is continuously pumped and then permeation transients are immediately yielded. In previous works,[6,7] we developed a novel permeation apparatus which could measure precisely the permeation transients by the continuous-flow technique. The permeation apparatus was designed to be able to measure the flux transients of permeants quickly and accurately by solving the problems associated with the drawbacks in the existing continuous-flow technique. The confidence and accuracy of the measurements with the apparatus were proven through both the successful measurement of the permeation properties of various gases through the polyimide and silicone membranes and comparison with the literature values.[6,7]

The objective in this study is to investigate the permeation behavior of mixed CO_2/N_2 gas through poly(dimethylsiloxane) (PDMS) at various operating conditions. The flux transients of the pure CO_2 and N_2 gases and the mixed gas were measured by the newly developed permeation apparatus, respectively. The flux transients are essential to study the permeation behavior and kinetics of permeants through membrane. From the flux transients, permeability, diffusion and solubility coefficient, and apparent activation energies were evaluated, respectively. The permeations of each gas were discussed in terms of the effects of operating temperature and feed pressure. The permeation behavior of the mixed gas was analyzed by comparing with those of the pure component gases. Also, the deviated permeation behaviors of the mixed gas from the ideal case were discussed through the analysis of the newly defined permeation ratio, which could explain the coupling effects occurring in the permeation of mixed gas.

EXPERIMENTAL

Materials

PDMS (RTV6166) was generously provided by Dongyang Silicone (Seoul, Korea). It was composed of two parts: Part A is mainly PDMS oligomers terminated with vinyl groups and part B is a mixture of Platinum (Pt) catalyst and PDMS oligomer with active hydrogens. Ultrapure deionized water was used. *n*-hexane and PDMS oligomers were used without any further purification.

Membrane Preparation

A casting solution was prepared by dissolving part A and part B with a ratio of 9 to 1 in *n*-hexane. The casting solution was poured into a glass Petri dish and then allowed to dry in a fume hood. Subsequently, it reacted at 100°C for 2 h. The crosslinking reaction took place by an addition reaction in which the active hydrogens attack the vinyl groups under Pt catalyst. The prepared membranes were 90–160 μm in thickness.

Gas Permeations

The measurement of flux transients by the permeation apparatus is well described elsewhere.[6,7] A schematic of the apparatus is illustrated in Figure 1. The membrane cell was placed in the heating oven to be controlled at a desired temperature. The effective membrane area in the membrane cell was 13 cm^2. The membrane was supported on a filter paper and a stainless steel porous disk. After mounting the membrane in the membrane cell, both the upstream and downstream sides in the cell were degassed simultaneously until the pressure reached below 0.1 Pa. Then permeation transients were measured by introducing the permeant gas in the upstream side and taking the mass flow readings with time. The feed pressure was controlled by keeping the pressure regulator virtually constant during the measurements.

In the permeation apparatus, the measuring system of permeation properties, which is connected with the permeate side of the membrane cell, consists of a mass flow meter (MFM) and gas chromatography (GC). A MFM (Brooks, Japan) used in this study has a capacity 1000 cm^3(STP)/min. To minimize the pressure drop developed across MFM during permeation, the pressure difference between the inlet and outlet of MFM was adjusted to a low value of 4.5 psi so that permeate pressure could be maintained as low as possible in the downstream side of the membrane cell. When permeation happens through the membrane, a voltage was produced in MFM correspondingly. The produced voltage can be transformed to a mass flow rate in digital value by the read-out connected with MFM according to a relationship between the voltage and mass flow

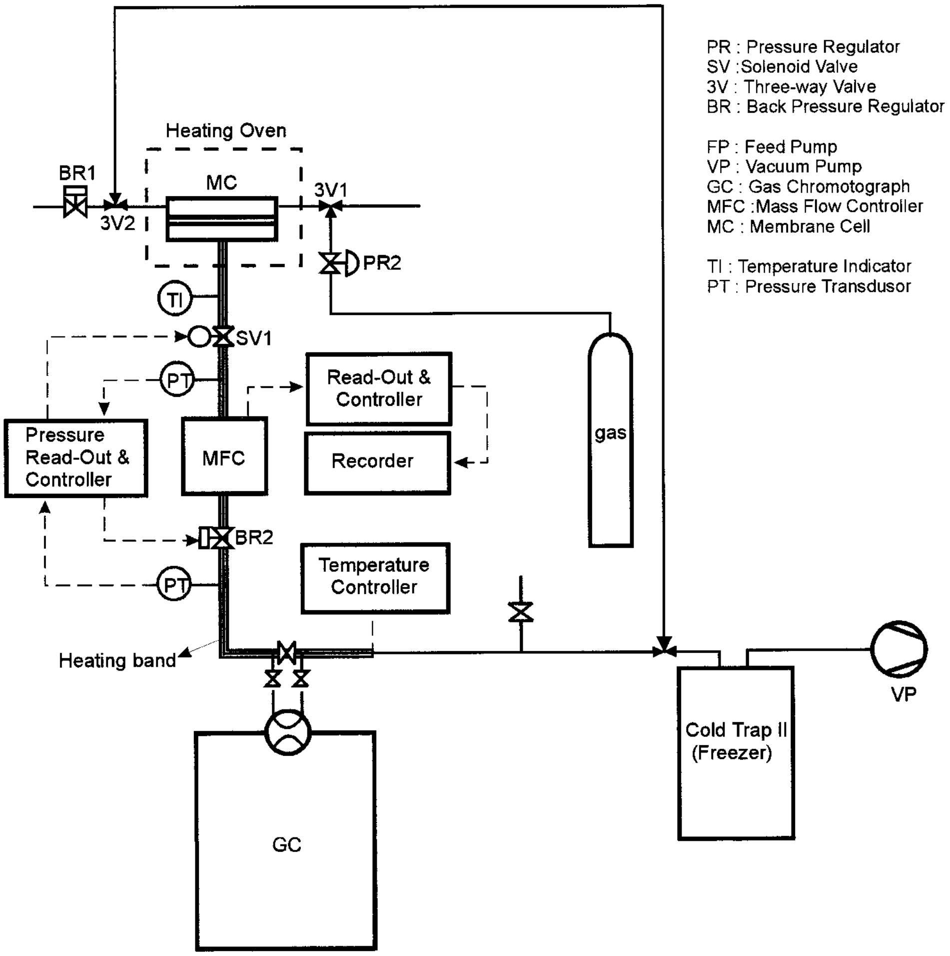

Figure 1 A schematic representation of permeation apparatus.

rate. However, the instantaneous flux through a membrane is normally so small that it cannot easily be monitored by the digital displayer. Therefore, the highly sensitive recorder (model 7155B, Hewlett–Packard) was connected with MFM to directly sense even slight change of voltage produced by the instantaneous flux. The maximum sensitivity of the recorder was 0.1 mV/cm, which is sensitive enough to detect the instantaneous flux in comparison with the maximum voltage of 5 V produced in MFM. Thus, flux could be recorded with operating time even if it is very small.

The GC (5890 Series II Plus HP GC) was equipped with an integrator (HP 3396 Series II), a sample injector (6-port valve) actuated by air, a TCD detector, and a packed column. The column was 6-ft long with $\frac{1}{8}$ in. inside diameter having a Porapak Q. Thus, the permeate can be injected directly into the column by the injector and thereby the composition of the permeate was determined directly and accurately. The evacuation of the permeate was provided by the vacuum pump and the cold trap (JeioTech Ltd., Seoul, Korea) was installed before the vacuum pump.

RESULTS AND DISCUSSION

Measurement of Permeation Transients and Determination of Transport Parameters from Permeation Transients

Figure 2 shows the flux transients of the pure gases N_2 and CO_2 through PDMS membrane, respectively, measured on-line by the new permeation apparatus based on the continuous-flow technique. They are the typical flux transients which can be obtained by the permeation apparatus. The flux transient can be characterized by

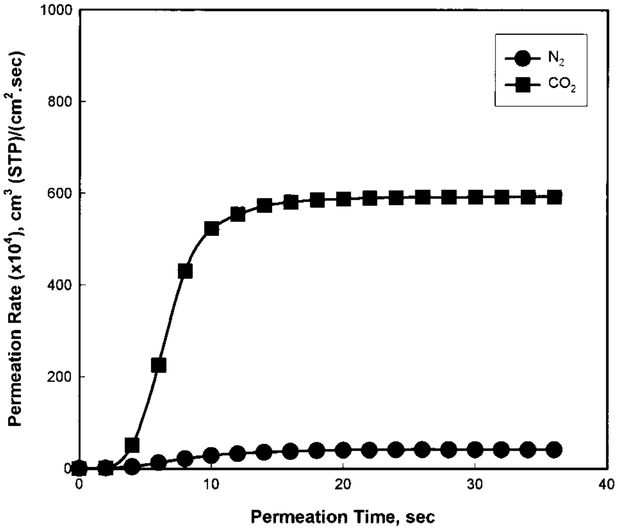

Figure 2 Flux transients of pure gases against operating time through PDMS membranes at 40°C and 0.5 MPa of feed pressure.

the time $t_{1/2}$ for the flux to rise from its initial value to one-half of its final, steady-state value, and by the time t_s for the flux to rise from its initial value to its final value along the time of maximum slope. Also, two diffusion coefficients $D_{1/2}$ and D_s can be evaluated from $t_{1/2}$ and t_s, respectively. The following expression for flux transient is given by[6]

$$J = \frac{DC_1}{l}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-Dn^2\pi^2 t/l^2)\right] \quad (1)$$

where J is the flux in transient state, l is the membrane thickness, D is the diffusion coefficient, and t is the permeation time. The two diffusion coefficients derived from the flux transient are given by the expressions[4]

$$D_{1/2} = \frac{l^2}{7.2t_{1/2}} \quad (2)$$

$$D_{\text{slope}} = \frac{l^2}{5.91t_{\text{slope}}} \quad (3)$$

In this study, D_{slope} was taken as the diffusion coefficient of a gas.

Figure 3 describes schematically how to determine the response times from the flux transient. Diffusion coefficients were calculated from the response times by using eqs. (2) and (3). When the diffusion coefficient D and flux at steady state J_s are determined, the solubility coefficient S and permeability P can be expressed by their definitions:

$$P = \frac{J_s l}{\Delta p} \quad (4)$$

$$S = \frac{P}{D} \quad (5)$$

where Δp is the pressure difference between feed and permeate sides. Thus from the flux transients, permeation properties P, S, D of the gases were determined quickly and accurately.

The permeability, diffusion, and solubility coefficients of the pure gases CO_2 and N_2 through PDMS membrane determined by the continuous technique are presented in Figures 4 and 5. In literature,[8] the permeabilities of N_2 and CO_2 at the PDMS are reported to be 280×10^{-10} and 3200×10^{-10} cm^3(STP) cm/(cm^2 s cmHg) at 35°C, respectively, and the solubility coefficients of N_2 and CO_2 determined at 25°C and 1 MPa are 2.5 and 30 ($\times 10^{-3}$) cm^3(STP)/(cm^3 cmHg), respectively. The permeation properties of the gases evaluated in this study are in relatively good agreement with the literature values even though there is a slight discrepancy between them which might result from the different kinds of PDMS or

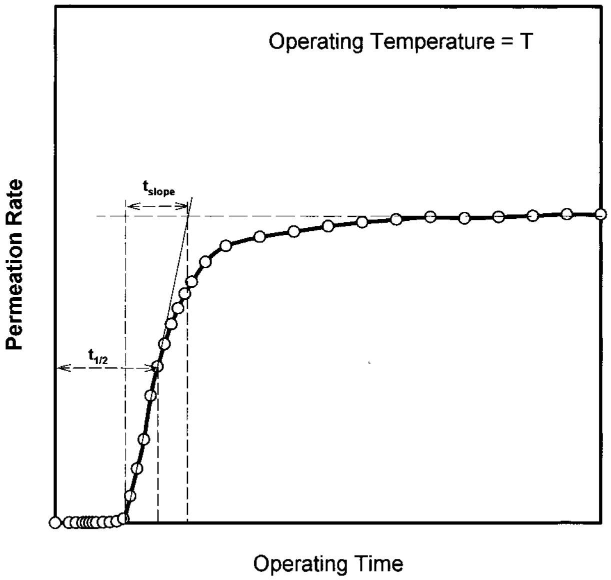

Figure 3 Determination of response times from a gas flux transient through PDMS at a given temperature.

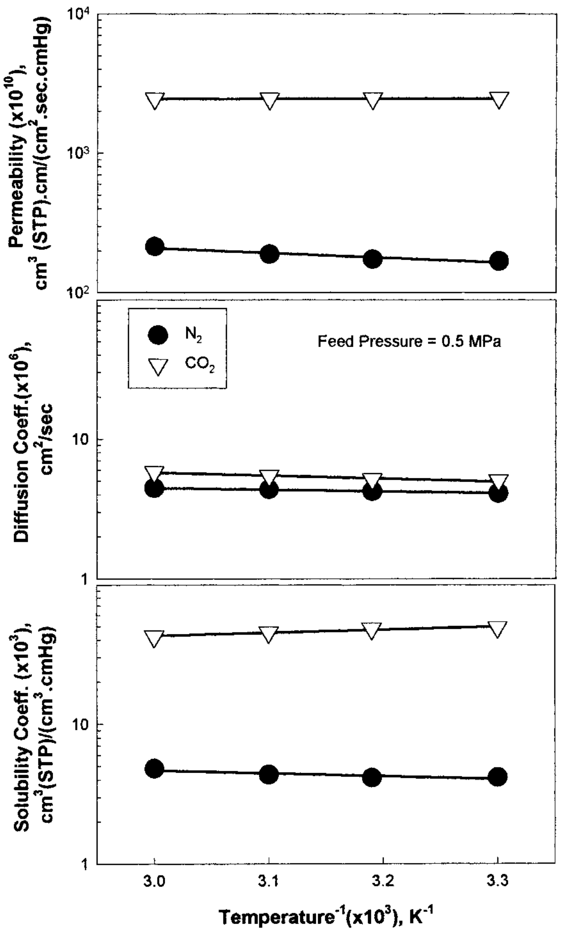

Figure 4 Transport parameters of pure gases through PDMS membrane with temperature at 0.5 MPa of feed pressure.

different determination methods employed. The PDMS membrane used in this study was prepared by an addition crosslinking reaction. To the best of our knowledge, no data on the permeation parameters of gases in the PDMS crosslinked by addition reaction is available in literature.

Permeation Properties of Pure Gases Through PDMS Membrane

The Effect of Temperature

Generally permeation of a gas through dense polymeric membranes is considered as an activated process which can usually be represented by an Arrhenius type of equation, expressing the temperature dependency of the permeation parameters as follows:

$$P = P_0\exp(-E_p/RT) \qquad (6)$$

$$D = D_0\exp(-E_d/RT) \qquad (7)$$

$$S = S_0\exp(-\Delta H_s/RT) \qquad (8)$$

where E_p, E_d, and ΔH_s are the activation energies for permeation, diffusion, and the heat of solution, respectively; P_0, D_0, and S_0 are preexponential factors or temperature-independent constants. These Arrhenius equations hold for the simple noninteractive gases. For condensable or interactive gases, the permeation parameters have more complex temperature dependency.

Figure 4 shows the Arrhenius plots of the permeabilities, diffusion coefficients, and solubility coefficients of the gases determined from the flux transients against temperature, respectively. Table I lists the physical properties of permeant gases used in this study. Because gas permeabil-

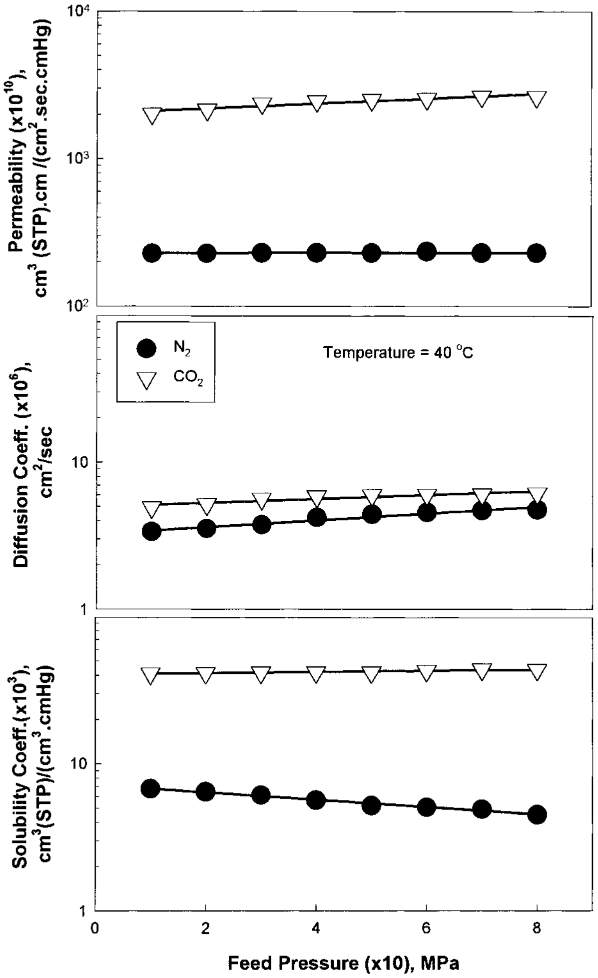

Figure 5 Transport parameters of pure gases through PDMS membrane with feed pressure at 40°C.

Table I Physical Properties of Pure Gases Used in This Study

Gases	Critical Temp., T_{cr} (°C)	Kinetic Sieving Diameter[a] (Å)	Gas Molecular Size[b] (l/mol)
N_2	−147	3.64	0.03913
CO_2	31	3.30	0.04267

[a] Kinetic sieving dimensions of gases based on Zeolite sorption cutoffs.[13]

[b] van der Waals constant, b.[14]

ity is inversely proportional to gas kinetic sieving diameter, the permeability of CO_2 having a smaller kinetic diameter was observed as much greater than that of N_2, $P_{CO_2} > P_{N_2}$, showing a permselectivity toward CO_2. The solubility coefficient of each component differed by more than an order of magnitude, whereas the diffusion coefficient was not different so much from each other. It reflects that the sorption selectivity makes a main contribution to permselectivity in PDMS. The reason for low-diffusion selectivity in rubbery membrane is that the rubbery materials have weak intermolecular forces and a correspondingly broad distribution of intersegmental gap sizes responsible for gas diffusion which can lose the selectivity. Even though it is difficult to observe the changes in the permeabilities with temperature in this figure, CO_2 permeability actually elucidates a slight decrease, whereas on the contrary, N_2 permeability exhibits an increase with increasing temperature. As discussed previously, gas permeability of polymeric membrane depends mainly on both sorptional and diffusional properties. Therefore, for more discussion, it is necessary to investigate how gas permeability can be affected by the two properties.

Diffusion coefficients of gases in a membrane also tend to be inversely proportional to their kinetic molecular diameter as presented in Figure 4. The diffusion coefficients of the gases increased with increasing temperature because more energy at higher temperature produces more active polymeric chain motion resulting in the formation of larger free volumes that permeant molecules can diffuse through. In the absence of specific interaction of gases with the polymer, to a large extent, their solubilities are determined mainly by the force of intermolecular interaction (Leonard–Johns force constant) or critical temperature of the gas, increasing with increasing the values of the parameters.[9] One can see from the figure that the solubility coefficient is increased on the order of the value of the critical temperature of permeant gas in Table I: $S_{CO_2} > S_{N_2}$. It is found that CO_2 molecules are dissolved less with increasing temperature but the N_2 gas behaves in an opposite way. Thus, from the above facts, it can be inferred that the decrease in CO_2 permeability with temperature might be assigned to the significant change in the solubility coefficient among the effects of the parameters that are opposing. The details will be discussed through analysis of activation energies which can provide an insight into the permeation behaviors through membrane.

All activation energies were determined from the slope of each Arrhenius plot and are presented in Table II. The permeation activation energies were evaluated larger for a gas having lower critical temperature or larger molecular size. According to the correlation of E_d and gas molecular size in which E_d has a proportional relation to the square of gas molecular size,[9] the value of E_d was larger for CO_2 with larger gas molecular size as predicted. For the noncondensable gas nitrogen, the heat of sorption has a small positive value that indicates that the solubility increases with increasing temperature, whereas for the condensable gas CO_2 the heat of sorption is negative and the solubility decreases with temperature. The permeability of N_2 with temperature is affected by diffusion and sorption in the same way because both ΔH_s and E_d are of positive value. However, for CO_2 the situation is more complex because two effects of diffusion and solubility are opposing. Thus, the transport of CO_2 through PDMS can be diffusion-controlled when the temperature is high and solubility-controlled when temperature is low. Looking at the solubility and diffusion coefficients of the gases, the difference in solubility coefficients between the gases is more significant than that in diffusion

Table II Apparent Activation Energies for the Permeation, Diffusion, and Sorption of the Pure Gases Through PDMS Membrane at 0.5 MPa of Feed Pressure, Respectively

	Activation Energies (Kcal/mol)		
Gases	E_p	E_d	ΔH_s
N_2	1.575	0.567	1.00
CO_2	−0.085	0.948	−0.992

coefficients at a given temperature. It implies that the permselectivity in PDMS is attributable mainly to sorption selectivity as mentioned above.

The Effect of Feed Pressure

Figure 5 exhibits the effect of feed pressure on gas permeations at 40°C. Both of the gas permeabilities illustrate a slight increase with feed pressure and the extent of the permeability increase is greater for CO_2 having the larger critical temperature. The diffusion coefficients of both the gases are found to increase with increasing feed pressure as well, and the coefficients of the two gases are not so much different, which has an implication that the diffusion selectivity is not significant.

The magnitude of solubility coefficient is also on the order of the gas molecular size or critical temperature of the gas permeant in the given range of feed pressure, as discussed earlier. The solubility coefficient of CO_2 increases with increasing feed pressure. The sorption of the condensable gas CO_2 in rubbery polymeric material is characterized by sorption isotherms that are nearly linear, potentially with slight upward curvature with feed pressure.[10] Such relationship between gas concentration and pressure is described by the Flory–Huggins theory as follows:

$$\ln\left(\frac{p}{p_0}\right) = \ln(1 - \phi_2) + \phi_2 + \chi_1\phi_2^2 \qquad (9)$$

where p_0 is the saturated vapor pressure, ϕ_2 is the polymer volume fraction, and χ_1 is the Flory–Huggins parameter. Thus, the increase in solubility coefficient with pressure often occurs in the condensable gas CO_2 in rubbery membrane. In principle, it is predicted for the noncondensable gas N_2, having a low sorption level that the relationship between gas solubility and pressure is linear and Henry's law is applicable. However, in this study, the solubility coefficient of N_2 decreases slightly with increasing feed pressure, implying that the sorption isotherms possess downward curvature as can be observed in the sorption behavior of glassy polymeric membranes. The reason for that is not clear but it may be related to the compactness of the rubbery membrane at high feed pressure. To our knowledge, the sorption characteristics of the noncondensable gas N_2 have rarely been studied. As a result, the ideal selectivity of CO_2 over N_2 has a considerable incline with feed pressure.

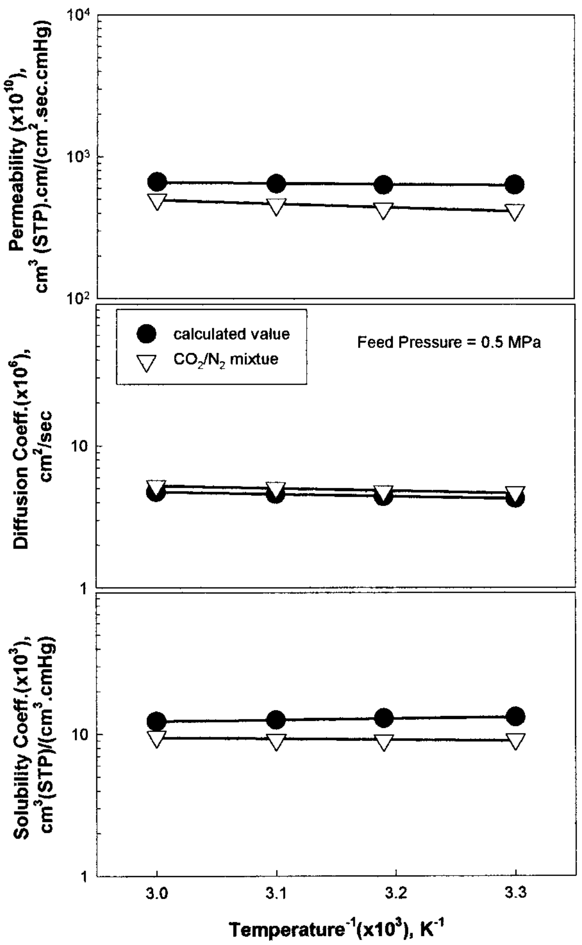

Figure 6 Transport parameters determined in the permeation of mixed gas and calculated in the ideal permeation through PDMS membrane with temperature at 0.5 MPa of feed pressure.

Permeation Properties of Mixed Gas Through PDMS Membrane

In the permeation of a binary gas mixture, the presence of one gas may affect the permeation of the other, which is called a coupling effect. Mixed gas transport involving light gases in rubbery polymeric materials would normally be expected to be ideal. However, both positive and negative deviation in solubility with respect to applied feed pressure have been often observed.[11]

Figures 6 and 7 present the permeation properties of the mixed gas through the PDMS membrane with temperature and feed pressure, respectively. To investigate the coupling effect, the corresponding permeation properties were calculated for the ideal permeation of the mixed gas and plotted in the figures. For the ideal perme-

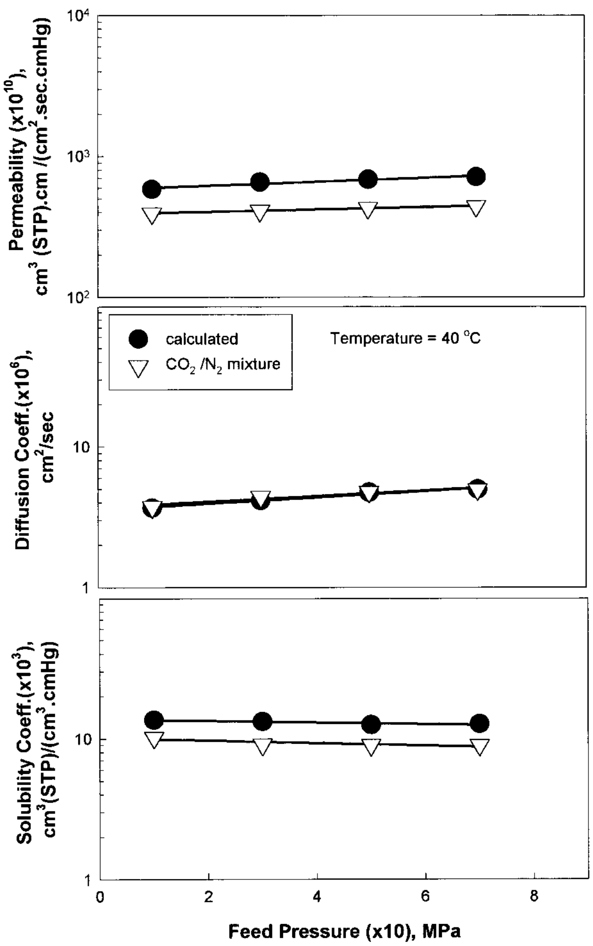

Figure 7 Transport parameters determined in the permeation of the mixed gas and calculated in the ideal permeation through PDMS membrane with feed pressure at 40°C.

ation in which there are no interactions between the gases, as well as no specific gas–polymer interactions in the presence of the second gas, the following additive rule was applied to predict the permeation parameters of the ideal mixed system from those of pure gases,

$$M_{\mathrm{id}} = \phi_1 M_1 + \phi_2 M_2 \tag{10}$$

where M_{id} is the permeation parameter of the mixed system, ϕ and M are mole fraction and permeation parameter of a pure gas, respectively, and the subscripts 1 and 2 are component gases, respectively. The permeabilities of the mixed gas have a negative deviation from those for the ideal permeation, namely, the depression of permeability by negative coupling. On the other hand, the diffusion coefficients of the mixed gas were close to the ideal value, whereas negative deviations in the solubility coefficients with respect both to temperature and feed pressure were found in the figures. Thus, it can be seen that the coupling effect on the permeation is associated mainly with the negative coupling in sorption. More details could be obtained through an analysis on a permeation ratio θ, defined as a ratio of the actual property M_m to the ideal property as:

$$\theta = \frac{M_m}{M_{\mathrm{id}}} \tag{11}$$

The permeation ratio, which is a measure of the deviation of the actual property from the ideal property, was used to explain the coupling effect (Figs. 8 and 9). For the diffusion coefficients with respect to both temperature and feed pressure, all the permeation ratios are near unity, whereas for the permeabilities and solubility coefficient, the ratios were well below unity. It indicates that the negative coupling in sorption causes the depression of the permeability. For the negative sorption, it could be related to the competition of two gases for the limited number of active sites in the polymer, although the said sites interact more with CO_2.[11,12] The negative couplings have been attributed to fixed amounts of sorption sites present in the matrix, which get saturated at a certain feed pressure, thereby leading to a decrease in solubility coefficient. The competition of the gases for a limited number of absorption sites

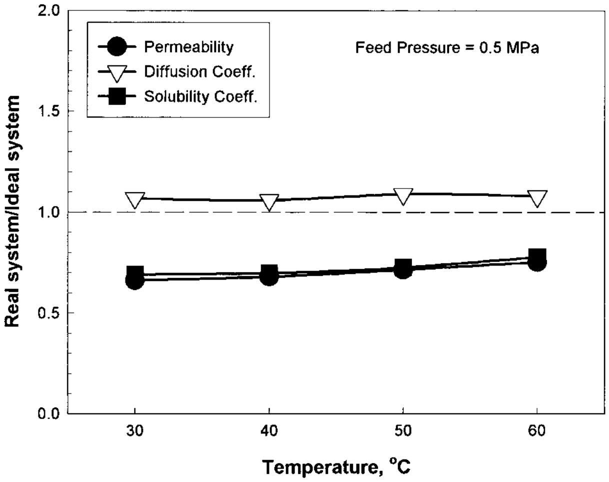

Figure 8 Permeation ratios with temperature in the permeation of the mixed gas (CO_2/N_2) at 0.5 MPa of feed pressure.

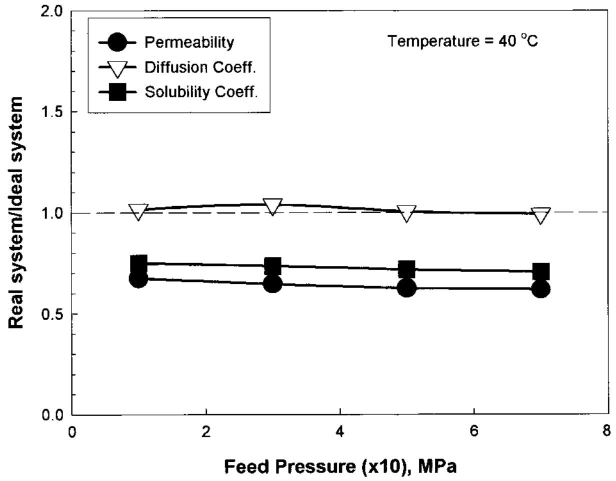

Figure 9 Permeation ratios with temperature with feed pressure in the permeation of the mixed gas (CO_2/N_2) at 40°C.

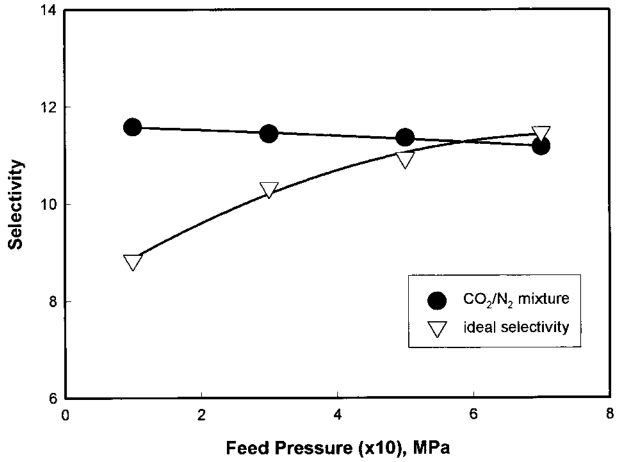

Figure 11 Comparison of real selectivity with ideal selectivity in the permeation of the mixed gas (CO_2/N_2) at 40°C.

finally causes depression of the permeability of one gas by the other.

Figures 10 and 11 present the ideal selectivities of the mixed gas, that is, the permeability ratio of pure component gases with temperature and feed pressure, respectively. With increasing temperature, the selectivity toward CO_2 has a significant decline. These observations can be explained in terms of a difference in permeation activation energy between each gas for a pair of gases. The activation energy of N_2 is greater than that of CO_2, so that the permeability of N_2 can increase more and thereby the selectivity to the other gas over N_2 is reduced with increasing temperature. With increasing feed pressure, the solubility coefficient of CO_2 increases, whereas surprisingly the solubility coefficient of N_2 decreases. As a result, the ideal selectivity to CO_2 over N_2 has a considerable incline with feed pressure.

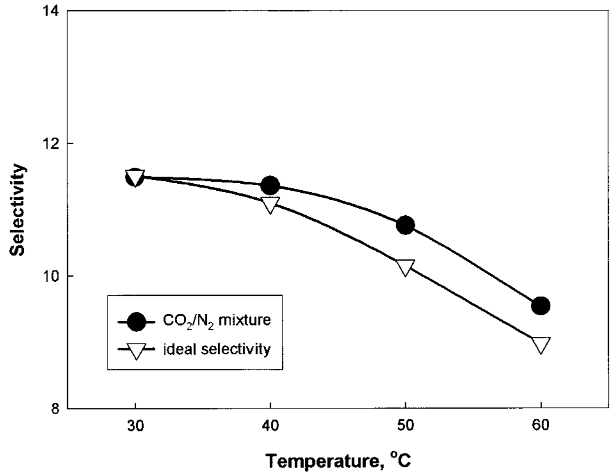

Figure 10 Comparison of real selectivity with ideal selectivity in the permeation of the mixed gas (CO_2/N_2) at 0.5 MPa of feed pressure.

According to whether sorption selectivity or diffusion selectivity is dominant, the coupling effect is reported to be an enhancement or depression of permselectivity, respectively.[11] Mixed gas separation by means of flexible-chain polymer membranes obviously corresponds to the former situation and should, therefore, be favorably affected by the coupling in terms of permselectivity. Hence, permselectivity would, in general, be expected to be enhanced if the basic selectivity of the membrane favors the heavier, stronger interacting gas CO_2, as shown in Figures 10 and 11. Going back to Figures 8 and 9, it is observed that both the permeation ratios of permeability and solubility coefficient slightly increase with increasing temperature and decrease with increasing feed pressure. It implies that the depressed sorption is recovered with increasing temperature, whereas the sorption is more depressed with increasing feed pressure. As a result, the selectivity in the real system is higher than the ideal selectivity at higher temperature, whereas it is reduced and closer to the ideal selectivity with increasing feed pressure. It is summarized that increasing temperature or decreasing feed pressure favors the permselectivity toward CO_2.

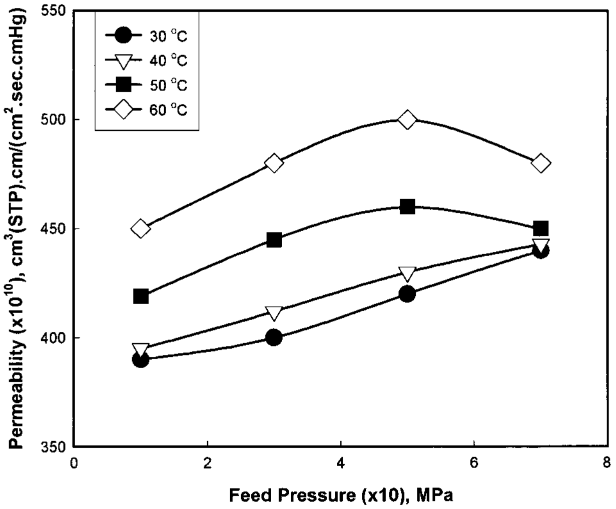

Figure 12 Permeability of the mixed gas through PDMS membrane with feed pressure at different temperatures.

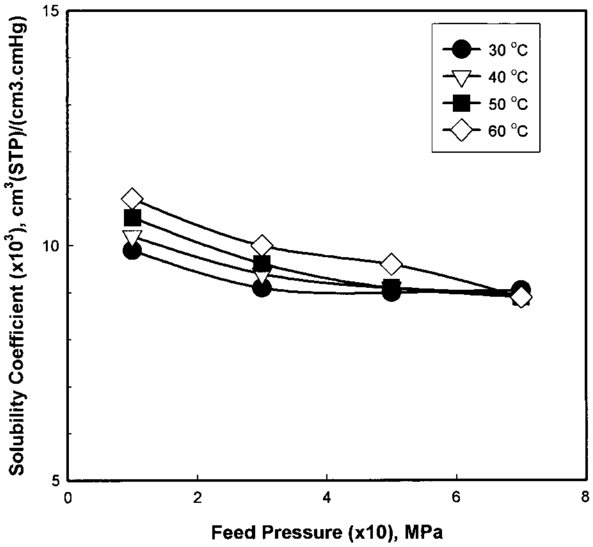

Figure 14 Solubility coefficient of the mixed gas through PDMS membrane with feed pressure at different temperatures.

Permeation of the Mixed Gas with Feed Pressure at Various Temperatures

Figures 12–14 demonstrate the plots of permeability, diffusion coefficient, and solubility coefficient of the mixed gas with feed pressure at various temperatures, respectively. It is very interesting to note that the permeability has a monotonous increase with feed pressure at a low temperature of 30–40°C, but it has a more downward curvature with feed pressure as temperature increases further. It is understandable that the permeability of the mixed gas increases with feed pressure at low temperature is due to the increase in each gas permeability, as shown in Figure 7. However, the complex shape of permeability might be explained by the changes of the diffusion and solubility coefficients with feed pressure, as shown in Figures 13 and 14. The diffusion coefficient of the mixed gas increases with increasing feed pressure or temperature over the range of feed pressure. On the other hand, the solubility coefficient decreases with feed pressure. At higher temperature, the decrease of the solubility coefficient with feed pressure becomes more significant. In the permeations of pure gases at various operating conditions presented in Figures 4 and 5, feed pressure and temperature affect the solubility coefficients of CO_2 and N_2 in opposite ways, respectively; increasing feed pressure positively affects CO_2 solubility coefficient and negatively affects N_2 solubility coefficient while N_2 solubility coefficient increases and CO_2 solubility coefficient decreases with temperature. From these facts, it can be seen that the sorption behavior of the mixed gas is exhibited closer to N_2 rather than CO_2, supporting the coupling effect, and at high temperature, the coupling effect in sorption with feed pressure becomes significant. As a result, at high temperature contribution of solubility coefficient to permeability is predominant over that of diffusion coefficient at greater than 0.5 MPa. That is why the permeability curve is downward at high temperature.

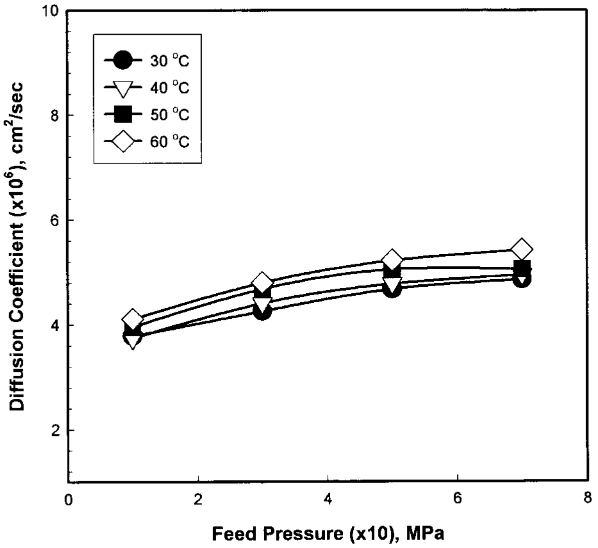

Figure 13 Diffusion coefficient of the mixed gas through PDMS membrane with feed pressure at different temperatures.

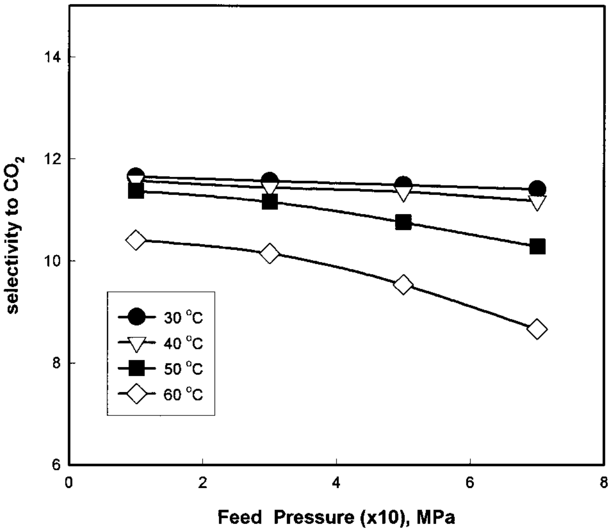

Figure 15 Selectivity to carbon dioxide in the permeation of the mixed gas through PDMS membrane with feed pressure at different temperatures.

Figure 15 presents the real selectivity to CO_2 with feed pressure in the permeation of the binary gas mixture at various temperatures. The selectivity was lower at higher temperature and selectivity decreased with increasing pressure as discussed in Figures 10 and 11. It is also observed that the decrease of selectivity with feed pressure was remarkable at high temperature as a result of the coupling effect significantly occurring.

CONCLUSIONS

The permeation and separation behaviors of the pure CO_2 and N_2 gases and a binary gas mixture of CO_2/N_2 (20/80) through PDMS membrane were characterized in terms of transport parameters, namely, permeability, diffusion, and solubility coefficients, respectively. The transport parameters were precisely determined by the new permeation apparatus in which measurement is made by the continuous-flow technique.

In the permeation of the pure gases, feed pressure and temperature affect the solubility coefficients of CO_2 and N_2 in an opposite way, respectively; increasing feed pressure positively affects CO_2 solubility coefficient and negatively affects N_2 solubility coefficient while increasing feed pressure positively affects CO_2 solubility coefficient and negatively affects N_2 solubility coefficient while N_2 solubility coefficient increases and CO_2 solubility coefficient decreases with temperature.

In the mixed gas system, coupling effects were analyzed by the defined parameter permeation ratio, and thereby mass transport was observed to be affected mainly by coupling effects in sorption. The permeability had a monotonous increase with feed pressure at low temperature. At high temperature, the coupling effect became more significant as the feed pressure increased and finally the effect of solubility coefficient was predominant over the effect of diffusion coefficient at greater than 0.5 MPa, reducing the permeability. Thus the permeability curve was downward with feed pressure. The selectivity was lower at higher temperature and selectivity decreased with increase pressure. It is also observed that the decrease of selectivity with feed pressure was remarkable at high temperature as a result of the coupling effect significantly occurring.

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