Selective Permeation of Sour Gases Through Polymeric Membranes Modified by Sulfolanes. I. Study of Selective Permeation of CO₂ Through Modified Polymeric Membranes Determined on Different Systems

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SYNOPSIS

Several sulfolanes such as 3-methylsulfolane, sulfolane, and 3-sulfolene were tested as modifiers in poly(trimethylsilylmethyl methacrylate) (PTMSMMA) and poly(trimethylsilyl propyne) (PMSP) to improve the selectivity of CO₂. The gas permeabilities for the PTMSMMA-blend membranes containing high 3-methylsulfolane content were determined on a nonvacuum system in which the membranes started to be measured at their steady states at 30°C; those for all the other membranes were determined in a vacuum system in which those membranes were measured after they reached their unsteady states at 30°C. The PTMSMMA-blend membrane containing 40% 3-methylsulfolane was found to give the best separation of CO₂ under the conditions in this study compared to all the PTMSMMA-blend membranes and the others prepared in our work; its ideal separation factors for CO₂ over N₂ were above 40 and its permeability coefficients of CO₂ increased to above 250 Barrer. The modifications of PMSP membranes by impregnating with sulfolane and blending with sulfolene were found to be effective in improving the selectivity for CO₂ over N₂ for the PMSP membrane. The ideal separation factors for CO₂ over N₂ for the modified PMSP membranes impregnated with 30% sulfolane and blended with 25% 3-sulfolene were improved to above 10 and 13, respectively. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the subjects in the gas membrane separation field is to remove sour gases from the CO₂ emission sources such as power stations, steelworks, and chemical industries, which are burning fossil fuels such as coal, oil, and natural gas. Because, in fact, this leads to the removal of CO₂ from N₂ to complete this task, it is always employed that CO₂ is made to permeate through a membrane faster than N₂ in the selective permeation membrane process. Currently, intensive studies are being carried out on the preparation of new polymeric membranes which not only possess high gas permeabilities but also high selectivities for CO₂ over N₂.

For gas membrane separation, a high flux and high separation factor are always desirable for membrane materials. It is generally known that a polymeric membrane which has high gas permeability may exhibit low selectivity and vice versa. One technique to achieve high values for these properties is to modify high-flux membrane materials in the form of blending or impregnation using some modifiers.[1,2] Some polymeric materials containing silicone on the polymer branches such as poly(trimethylsilylmethyl methacrylate) (PTMSMMA) and poly(trimethylsilyl propyne) (PMSP) as shown in Figure 1 were widely recognized to be promising membrane materials due to their high permeabilities, but the disadvantages of these materials were their low selectivities.[1-3] Thus, stud-

PMSP   PTMSMMA

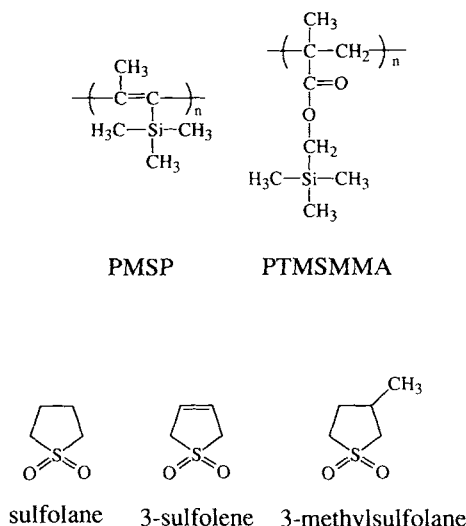sulfolane   3-sulfolene   3-methylsulfolane

Figure 1 Structures of PMSP, PTMSMMA, and various sulfolanes.

ies have been highly focused on how to prepare high selectivity membranes using those polymers.[4,5]

From the standpoint of improving their selectivities for CO_2 over N_2, the enhancement of solubility selectivity for CO_2 over N_2 was proposed as an effective method.[6,7] Based on the fact that some modifiers such as sulfolane and sulfolene possess affinity for sour gases,[6,8,9] we used 3-methylsulfolane, sulfolane, and 3-sulfolene as modifiers to prepare membranes with high selectivities.

In this work, we prepared a series of PTMSMMA-blend membranes with 3-methylsulfolane, PMSP membranes impregnated with sulfolane, and PMSP membranes blended with 3-sulfolene. The performances and characteristics of these membranes relative to selectivities were studied through the determination of gas permeabilities on two different systems.

THEORETICAL

Gas Permeability

The permeability of a gaseous penetrant, P, can be represented as the product of the average diffusivity, D, and the effective solubility, S, of the penetrant in the polymer matrix[10,11]:

$$P = D \cdot S \tag{1}$$

To investigate the effects of sulfolanes on selectivity conveniently, we used the apparent diffusivity,

which can be obtained easily from the simple eq. (2)[12-14] instead of true diffusivity:

$$D = l^2/6\theta \tag{2}$$

where θ is the time lag, and l, the thickness of the membrane. Thus, the apparent solubility coefficient can be estimated from the permeability and the diffusivity. In fact, the sorption and transport behavior of gases in a glassy polymer is more complex than that in rubbery polymers.[15]

Gas Sorption and Transport in Rubbery Polymers

The sorption of gases in rubbery polymers is similar to the sorption of gases in low molecular weight liquids, and the gas concentration in the polymer, C, often obeys Henry's law[16]:

$$C = k_D \cdot p \tag{3}$$

where k_D is the Henry's law constant, and p, the gas pressure in contact with the polymer. Diffusion of gases in rubbers which do not undergo structural rearrangement in the presence of the gas typically obeys Fick's law.[17,18] At low penetrant concentrations, the diffusion coefficient is often independent of the gas concentration[17] and gas permeability is independent of pressure. In this case, S can be expressed by C/p, i.e., k_D; thus, P can be given by eq. (4):

$$P = k_D \cdot D \tag{4}$$

For highly sorbing penetrants, such as organic vapors or gases at high pressures, penetrant concentration in the polymer may deviate from Henry's law.[19]

Gas Sorption and Transport in Glassy Polymers

It is known that many of the differences in the sorption and transport properties between rubbery and glassy polymers arise from the nonequilibrium nature of glassy polymers. Different from rubbers, which are equilibrium materials, the physical properties of glassy polymers, which include sorption and transport properties, drift over time toward a seemingly unattainable equilibrium. This phenomenon, known as physical aging, is closely related to the existence in glassy polymers of nonequilibrium excess volume.[20] Sorption isotherms for gases in glassy polymers are often modeled successfully by the dual mode.[19] In this model, penetrant molecules are viewed as being partitioned between the dense equilibrium structure of the polymer (Henry mode) and

the nonequilibrium excess volume of the glassy polymer (Langmuir mode). The dual mode is expressed by eq. (5):

$$C = C_D + C_H \qquad (5)$$

where C is the total concentration of the penetrant in the polymer; C_D, the dissolved mode penetrant concentration; and C_H, the penetrant concentration in the microvoids of the Langmuir mode. C_D is written as a linear function of pressure and C_H is expressed by a Langmuir isotherm to give[21]

$$C = k_D p + \frac{C'_H b p}{1 + b p} \qquad (6)$$

where k_D is the Henry's law constant; C'_H, a constant of Langmuir sorption capacity; and b, the Langmuir affinity parameter.

In the dual-mode model, the nonequilibrium excess volume associated with the glassy state also presents an additional mechanism for the penetrant. As a result, when the downstream pressure is effectively zero and the upstream pressure is p, the permeability of penetrant A is given by

$$p_A = k_D D_D + \frac{C'_H D_H}{1 + b p} \qquad (7)$$

where D_D and D_H are the gas diffusivities in the dissolved and Langmuir modes, respectively. D_D is typically much larger than is D_H.[21]

Gas Selectivity

In the expression of gas selectivity of component A over B, the gas separation factor is generally related to the ratio of the pure gas permeabilities as an ideal separation factor when the downstream pressure is negligible. Consequently, the ideal separation factor can be considered to be composed of solubility and diffusivity selectivities as shown by eq. (8):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right) \qquad (8)$$

where S_A/S_B is the solubility selectivity and D_A/D_B is the diffusivity selectivity. In some cases, separations depend mainly on the solubility selectivity or the diffusivity selectivity.

EXPERIMENTAL

Preparation of Membranes

Sulfolanes and PMSP used to prepare membranes in this study were obtained from Wako Pure Chem. Ind. and Shin Etsu Chem. Ind., respectively. PTMSMMA was synthesized by radical bulk polymerization under the conditions described in Ref. 3. The method of dissolution–reprecipitation was employed in the purification of PMSP and PTMSMMA in which PMSP and PTMSMMA were dissolved in toluene and then the solutions were poured into methanol. The PTMSMMA and 3-methylsulfolane, PMSP, and sulfolene-blend membranes used for this study were prepared by casting a 3% toluene solutions of them onto a flat-bottomed Petri dish in a glass bell-type vessel at room temperature. The solvent was allowed to evaporate slowly over a period of about 7–10 days. The thickness of the dry membranes ranged from 80 to 120 μm depending on the weight of the casting solution. The sulfolane-modified PMSP membranes were prepared by impregnating PMSP membranes in saturated sulfolane vapor. The sulfolane contents in the impregnated PMSP membranes were controlled by the time dependence on the sorption and desorption of sulfolane in PMSP membranes as shown in Figure 2. The sorption of sulfolane in PMSP membranes was started after the sorption system was evacuated for 24 h at 29°C. The desorption of sulfolane in PMSP membranes was carried at 29°C under the same vacuum conditions as those for the membranes in the vacuum system before determination.

Gases

The gases employed in this study were obtained from Keihin Koatsu Gas Co., and their purity was at least 99.5 mol %.
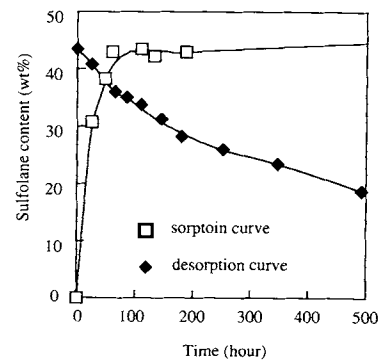

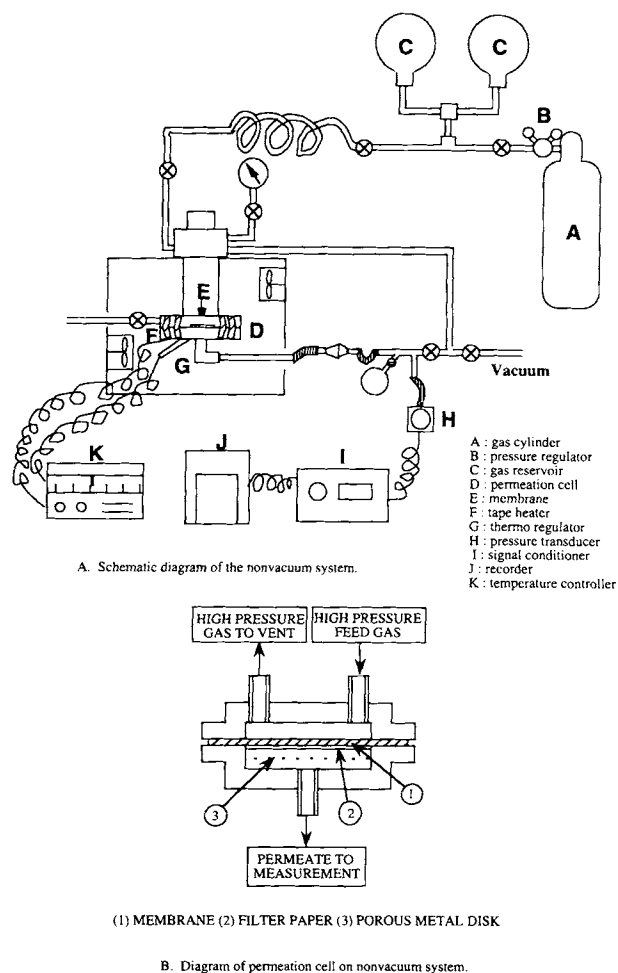**Figure 2**   Time dependence on sorption and desorption of sulfolane in PMSP membrane at 29°C.

A. Schematic diagram of the nonvacuum system.

A : gas cylinder
B : pressure regulator
C : gas reservoir
D : permeation cell
E : membrane
F : tape heater
G : thermo regulator
H : pressure transducer
I : signal conditioner
J : recorder
K : temperature controller

HIGH PRESSURE GAS TO VENT	HIGH PRESSURE FEED GAS

PERMEATE TO MEASUREMENT

(1) MEMBRANE (2) FILTER PAPER (3) POROUS METAL DISK

B. Diagram of permeation cell on nonvacuum system.

Figure 3   Diagrams of the nonvacuum system and its permeation cell.

Permeability Measurements

Two different permeation apparatuses were used in this work: a vacuum system and a nonvacuum system. They all used the vacuum gas transmission technique equipped with an MKS Baratron pressure transducer. The membranes determined using the vacuum system were measured after they reached their unsteady states at 30°C as described in Ref. 22; the apparent diffusivity coefficients were determined by the time-lag method and the apparent solubility coefficients for CO_2 were calculated using eq. (1). To avoid the fact that membranes should have to be in the vacuum environment for a long period before the determination of permeabilities, a new test procedure was employed on a nonvacuum system in which the membranes started to be measured at their steady states at 30°C. This system consists of the following basic sections: gas storage and feeding facilities, constant temperature enclosure, per-

meation cell, pressure measurement, and control facilities. The simplified diagrams of the nonvacuum system and its permeation cell are shown in Figure 3. The nonvacuum system was operated in the new test procedure. The cell temperature was maintained at 30°C for more than 2 h after it was mounted. Then, the feed gas was introduced into the cell at a desired pressure and allowed to pass to the vent for more than 5 min before the permeate side was evacuated. Just before measurement, evacuation was continued for 1 min after the pressure of the permeate side became lower than 5 Torr with the feed gas flowing over the high-pressure side. The permeability coefficients were estimated in the same way as that for the vacuum system, though it is impossible to obtain solubility and diffusivity coefficients with the time lag method from this determination using the nonvacuum system.

The Measurement of Membrane Characterization

The membrane density was determined by its weight and volume. The glass transition temperature, T_g, and the melting peak temperature, T_m, were measured by differential scanning calorimetry at a heating rate of 20°C/min. The d-spacing was measured by wide-angle X-ray diffraction (WAXD) using Bragg's equation shown as follows:

$$\lambda = 2d \sin \theta \ (CuK\alpha, \lambda = 1.54 \text{ Å}) \qquad (9)$$

RESULTS AND DISCUSSION

Permeability and Selectivity Determined Using the Vacuum System

Permeations of Gases Through PTMSMMA and Its Blend Membranes

The permeabilities of PTMSMMA and its blend membranes containing 8, 16, and 20% 3-methylsulfolane to CO_2, N_2, CH_4, O_2, and H_2 at 30°C are reported in Figures 4 and 5 in the form of semilogarithmic plots of the permeability coefficients, P, vs. the pressure difference across the membranes and the 3-methylsulfolane content, respectively. It seems in Figure 4 that the permeabilities of CO_2 decreased with the increase in 3-methylsulfolane in the membranes containing 8–20% 3-methylsulfolane. Relative to the others, the permeabilities of CO_2 for the PTMSMMA membrane showed a pressure dependence, but those lines for the blends were nearly parallel to the pressure axis. Although to explain the gas permeation behavior the gas sorption iso-
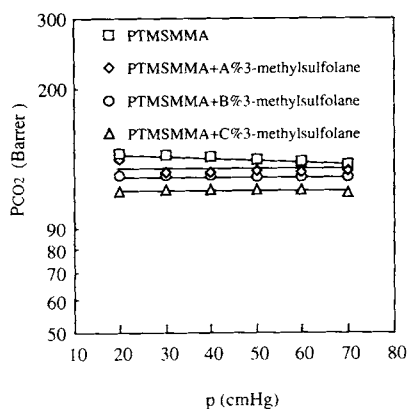
Figure 4 Pressure dependence of permeability coefficients for CO_2 at 30°C determined using the vacuum system.

therms of these blends were needed to understand the gas solubility properties, the determination was too difficult to carry out for the blends containing volatilizable 3-methylsulfolane. The study of the PMSP membranes filled with liquid polydimethylsiloxanes pointed out[23] that the Langmuir sorption abilities for CO_2 were depressed due to the decrease in the volume of microvoids in the PMSP-modified membranes and the modified membranes changed from a glassy state to a rubbery state with increasing liquid content. In this study, the PTMSMMA-blend membranes also changed from a glassy state to a nearly rubbery state with increasing 3-methylsulfolane content as can be seen from the glass transition temperatures, T_g, for the membranes listed in Table I. As can be seen, the T_g values of the blends were lower than that of the PTMSMMA membrane and T_g decreased with increasing 3-methylsulfolane content. Therefore, it is proposed that the volume of the microvoids in the blends should be decreased by the addition of 3-methylsulfolane. It was suggested that with respect to the PTMSMMA membrane the increased soluble amount of CO_2 for Henry solubility in these blends containing 8–20% 3-methylsulfolane measured on the vacuum system could not counteract the decreased amount of CO_2 sorbed in the Langmuir mode of these blends.

That result can be seen from Figure 6 where all the solubilities of CO_2 in the membranes containing 8–20% 3-methylsulfolane were lower than those in the PTMSMMA membrane and the solubilities of CO_2 in the blends became lower with increasing 3-methylsulfolane content. Furthermore, the essential factor that the 3-methylsulfolane in the surface layer of the blend membranes was evaporated under the vacuum condition before measurement has to be

considered. Finally, the affinity effect of 3-methylsulfolane on increasing solubilities of CO_2 in the blend membranes containing 8–20% 3-methylsulfolane was to the contrary, as can be seen from Figure 6. Because the d-spacings and densities of the PTMSMMA and its blend membrane were not obviously changed by blending 3-methylsulfolane, the increase in the diffusivities of CO_2 in the blends shown in Figure 7 should be attributed to the increased mobilities of the polymers in the blends which can be seen from the T_g values of the membranes listed in Table I. Almost the same values of the diffusivity coefficients of CO_2 for the blend membranes containing 8–20% 3-methylsulfolane under the same conditions shown in Figure 7 can also be implied from their near T_g values about 60°C shown in Table I. As the overall result, the permeabilities of CO_2 were low when the 3-methylsulfolane content was high in the blend. Figure 5 also shows the decreasing tendency in the gas permeabilities of CO_2, N_2, CH_4, O_2, and H_2 with the increase in 3-methylsulfolane content from 8 to 20%. Thus, it can be expected that, based on the above results measured on the vacuum system, the ideal separation factors for CO_2 over N_2 for the blend membranes could not be improved satisfactorily through blending 8–20% 3-methylsulfolane, although they were higher than those for the PTMSMMA membrane as shown in Figure 8.

Permeations of Gases Through Modified PMSP Membranes

Table II lists the permeabilities of CO_2, N_2, O_2, and CH_4 and the selectivities for CO_2 over N_2 for the PMSP and its blend membranes with 3-sulfolene. The permeability coefficients of CO_2 for the blends
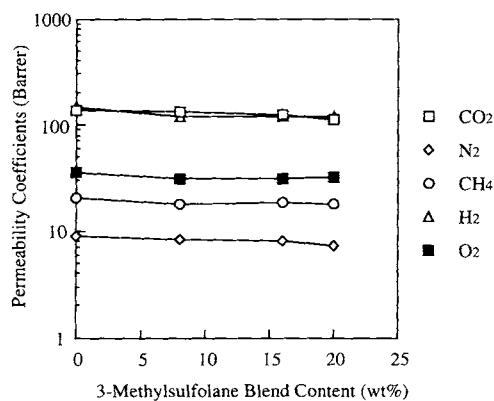

Figure 5 Effect of 3-methylsulfolane blend content on gas permeability coefficients at 30°C and 20 cmHg determined using the vacuum system.

Table I   Characterizations of Poly(trimethylsilylsilylmethyl methacrylate) and Its Blend Membranes Containing 3-Methylsulfolane

	d^a	d-Spacing[b]	T_g[c]	T_m[c]
PTMSMMA	0.951	5.5	82.3	—
PTMSMMA + 8% 3-methylsulfolane	0.942	5.6	64.6	—
PTMSMMA + 16% 3-methylsulfolane	0.950	5.4	65.5	—
PTMSMMA + 20% 3-methylsulfolane	0.916	5.4	60.6	—
PTMSMMA + 30% 3-methylsulfolane	1.01	5.6	61.2	—
PTMSMMA + 40% 3-methylsulfolane	0.923	5.3	35.4	−5.8
PTMSMMA + 50% 3-methylsulfolane	1.08	5.4	30.8	−5.7

[a] Density, determined by volume and weight; unit: g/cm^3.

[b] d-Spacing, determined by wide-angle X-ray diffraction (WAXD) using Bragg's equation; $\lambda = 2d \sin \theta$; unit: Å.

[c] Glass transition temperature, determined by DSC at heating rate of 20°C/min; unit: °C.

[d] The temperature of melting peak in blend membranes; unit: °C.

were one order of magnitude lower but those of the other gases except for CH_4 became two orders of magnitude lower with increasing 3-sulfolene content compared to those for the PMSP membrane, while their ideal separation factors for CO_2 over N_2 for the PMSP and 3-sulfolene blend membranes were higher than that for the PMSP membrane. Though the ideal separation factor for CO_2 over N_2 for the blend containing 20% 3-sulfolene increased to 6.68, that for the blend containing 25% 3-sulfolene reached 13.25. Based on the elucidation about the PTMSMMA and 3-methylsulfolane-blend membranes, it is suggested that most of the 3-sulfolene in the hard PMSP blend with 20% 3-sulfolene may be sorbed in microvoids in the blend, which resulted in the unsatisfactory increase in the selectivity for CO_2. As can be seen from Table II, although the permeability coefficient of CO_2 decreased with the increase in 3-sulfolene content from 20 to 25%, the permeability coefficient of N_2 decreased more seriously than did the former. As a result, the ideal separation factor for CO_2 over N_2 for the PMSP blend

containing 25% 3-sulfolene became about 13, which was about twice that for the PMSP blend containing 20% 3-sulfolene. This may suggest that the affinity of 3-sulfolene for CO_2 made the solubility of CO_2 high in the Henry solubility and compensated somewhat for the decreased Langmuir solubility.

Table III lists the permeabilities of CO_2, N_2, O_2, and CH_4 and the ideal separation factors for CO_2 over N_2 for PMSP and its impregnated membranes containing sulfolane. The performances of their gas permeabilities seemed to be the same as those for the PMSP blends with 3-sulfolene, as can be seen from Tables II and III. Although the ideal separation factors for CO_2 over N_2 for the PMSP-impregnated membranes containing sulfolane increased with increasing sulfolane content and that for the PMSP-impregnated membranes containing 30% sulfolane became about 10, it is clear that the effect of modification with sulfolane in the PMSP membrane was poor with respect to that of blending 3-sulfolene with PMSP in the improvement of the selectivity for CO_2.
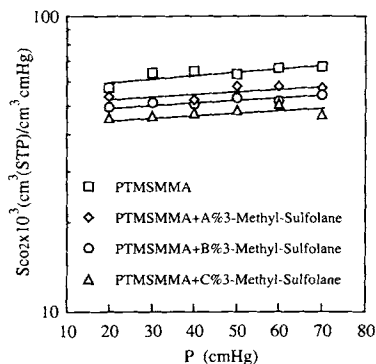
Figure 6   Pressure dependence of solubility coefficients for CO_2 at 30°C determined using the vacuum system.
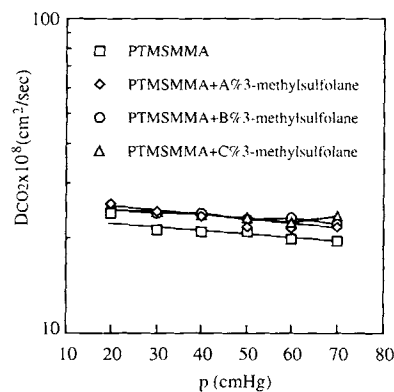
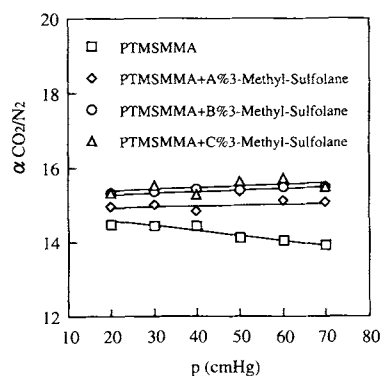**Figure 7**   Pressure dependence of diffusivity coefficients for CO_2 at 30°C determined using the vacuum system.

Figure 8 Pressure dependence of ideal separation factors for CO_2 over N_2 at 30°C determined using the vacuum system.

The explanation for this difference in the effects of sulfolanes between the two kinds of PMSP-modified membranes is suggested to be that, in the vacuum condition before determination, the evaporation of sulfolane in the surface of the impregnated PMSP membranes was easier than that of 3-sulfolene in the surface of the PMSP blends, which might be caused not only by the different methods of modification but also by the different physical properties of solid 3-sulfolene and liquid sulfolane at 30°C.

Permeability and Selectivity Determined on Nonvacuum System

Figure 9 shows the changes in permeability coefficients of CO_2 for PTMSMMA and its 3-methylsulfolane blend membranes with increasing 3-methylsulfolane determined on the nonvacuum system at 30°C. Based on the above discussion, it is proposed that because 3-methylsulfolane could be

Table II Gas Permeabilities and the Selectivities of CO_2 over N_2 for PMSP and Its Blend Membranes with 3-Sulfolene at 30°C and 50 cmHg Determined using the Vacuum System

	PMSP	PMSP + A% Sulfolene	PMSP + B% Sulfolene
$P_{CO_2} \times 10^{-2}$ (Barrer)	419	39.2	17.7
$P_{N_2} \times 10^{-2}$ (Barrer)	99.2	5.87	1.34
$\alpha_{CO_2 N_2}$	4.22	6.68	13.3
$P_{O_2} \times 10^{-2}$ (Barrer)	138	21.7	6.07
$P_{CH_4} \times 10^{-2}$ (Barrer)	252	—	14.3

A, 20% blend content; B, 25% blend content.

Table III Gas Permeabilities and Selectivities of CO_2 over N_2 for PMSP and Its Modified Membranes with Sulfolane at 30°C and 70 cmHg Determined using the Vacuum System

	PMSP	PMSP + A% Sulfolane	PMSP + B% Sulfolane
$P_{CO_2} \times 10^{-2}$ (Barrer)	418	34.6	28.8
$P_{N_2} \times 10^{-2}$ (Barrer)	100	5.90	2.70
$\alpha_{CO_2 N_2}$	4.18	5.85	10.7
$P_{O_2} \times 10^{-2}$ (Barrer)	138	25.8	—
$P_{CH_4} \times 10^{-2}$ (Barrer)	252	43.6	16.9

A, 20% blend content; B, 30% blend content.

sorbed in the Langmuir mode of the membranes in the glassy state 3-methylsulfolane in the blends was not able to play a proper role in increasing the permeability of CO_2 before the 3-methylsulfolane content became high enough. The permeability coefficients of CO_2 for the PTMSMMA blends determined using the nonvacuum system improved with increasing 3-methylsulfolane content and became more than 300 Barrer when the 3-methylsulfolane content reached 50% in the blend, as shown in Figure 9. This is proposed to be in accordance with the explanation for those measured using the vacuum system, although the permeability coefficients of CO_2 for the blend containing 20% 3-methylsulfolane were higher than those of PTMSMMA membrane, because the 3-methylsulfolane on the surface of the blend containing 20% 3-methylsulfolane measured using the nonvacuum system did not experience evaporation before measurement as what occurred in the determination using the vacuum system.
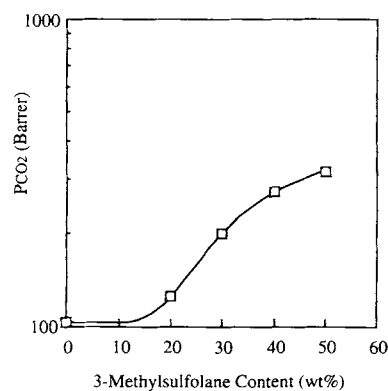

Figure 9 Effect of 3-methylsulfolane content on permeability coefficients of CO_2 at 30°C and 4 atm determined using the nonvacuum system.
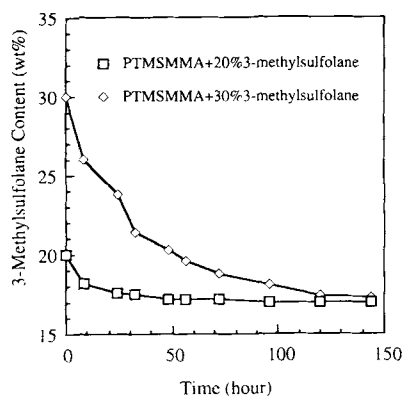
Figure 10 Time dependence on 3-methylsulfolane content in the PTMSMMA blend membranes under vacuum condition at 28°C and a pressure lower than 1 mmHg.

As shown in Figure 10, 3-methylsulfolane in the blends continued to evaporate until the 3-methylsulfolane contents in the membranes were reduced to about 17%. The 3-methylsulfolane on the surface of the PTMSMMA blend containing 20% 3-methylsulfolane was proposed to contribute to improving the permeability of CO_2 determined using the nonvacuum system when it was compared to that for the same blend membrane containing 20% 3-methylsulfolane measured using the vacuum system. The pressure difference between the vacuum and nonvacuum systems could be taken as another factor contributing to the different effect of 3-methylsulfolane on improving the permeabilities of CO_2 for the blend containing 20% 3-methylsulfolane, because the solubility of CO_2 in 3-methylsulfolane could depend on the pressure and become high with increasing pressure. As can be seen from Figure 11, the permeabilities of CO_2 for the blends increased not only with increasing 3-methylsulfolane content, but increased also with increasing pressure. The permeabilities of CO_2 for the PTMSMMA membrane exhibited a pressure dependence in accordance with the behavior of gas permeability for a glassy polymer membrane shown in Figure 11. Because the diffusivities of CO_2 in the PTMSMMA and its blend membranes containing 20 and 30% 3-methylsulfolane should not show much difference, which was implied by the result shown in Figure 7 and by their d-spacings and glass transition temperatures listed in Table I, it should be the effect of the increased solubility of CO_2 in 3-methylsulfolane that the permeabilities of CO_2 for the blends containing 20 and 30% 3-methylsulfolane improved with increasing 3-methylsulfolane content and pressure under the conditions of this study. The diffusivities of both CO_2 and N_2 gases in the blends containing 40 and
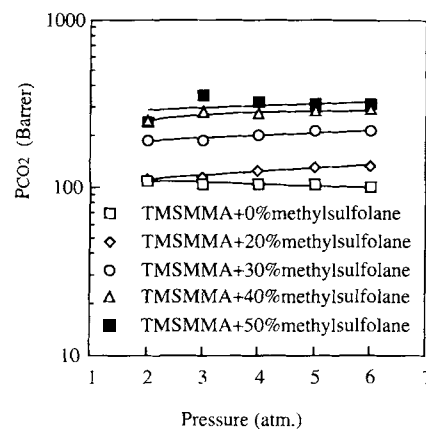

Figure 11 Pressure dependence of permeability coefficients for CO_2 at 30°C determined using the nonvacuum system.

50% 3-methylsulfolane are proposed to be much higher than those in the others, because the polymers in the blends containing 40 and 50% 3-methylsulfolane became rubbery and much more mobile and could allow penetrants to diffuse much more easily than those in the other PTMSMMA blends, as suggested by their glass transition temperatures listed in Table I. Consequently, the blend having 50% 3-methylsulfolane showed the highest permeabilities of CO_2 compared to the others under the conditions of this study, as can be seen from Figure 11.

This performance can also be seen in Figure 12, which shows that the permeabilities of N_2 depended on the 3-methylsulfolane content. The permeabilities of N_2 for the blends became lower with increasing 3-methylsulfolane content before the 3-methylsulfolane content increased to more than 30%.
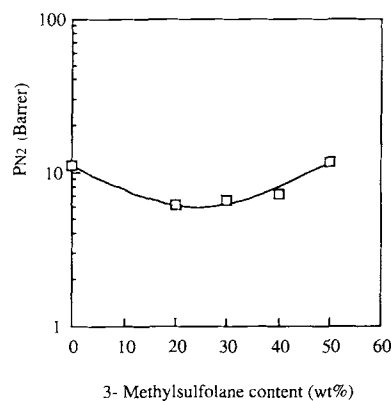

Figure 12 Effect of 3-methylsulfolane content on permeability coefficients of N_2 at 30°C and 2 atm. determined using the nonvacuum system.

This is suggested to be the result of the decreased solubilities of N_2 both in the Henry and Langmuir modes caused by the exclusion of N_2 from the polar 3-methylsulfolane and the reduced volume of microvoids in the glassy blends. As a result, the ideal separation factors for CO_2 over N_2 for the blends became high and then decreased with the increasing 3-methylsulfolane content from 20 to 50%, as shown in Figure 13. Consequently, it can be seen from Figure 14 that, though the blend containing 40% 3-methylsulfolane showed the higher selectivities of CO_2 over N_2 than the blend containing 50% 3-methylsulfolane under these conditions, the blend containing 50% 3-methylsulfolane still showed the highest selectivity of CO_2, benefiting from the affinity of 3-methylsulfolane for CO_2 with respect to the others except for the blend containing 40% 3-methylsulfolane.

ERROR ANALYSIS FOR THE MEASUREMENT ON THE NONVACUUM SYSTEM

The desorbed gases from the measured membrane and the inside of the permeate tank were suggested to have the biggest influence on permeabilities of gases compared to the other factors during determination. As a result, the apparent permeability coefficients of gases determined using the nonvacuum system were higher than their actual permeability coefficients. Furthermore, the apparent ideal separation factors for CO_2 over N_2 would be lower than the ideal separation factors if they had been determined using the vacuum system, because the measure range for the measurement of the N_2 permeability was one order of magnitude lower than
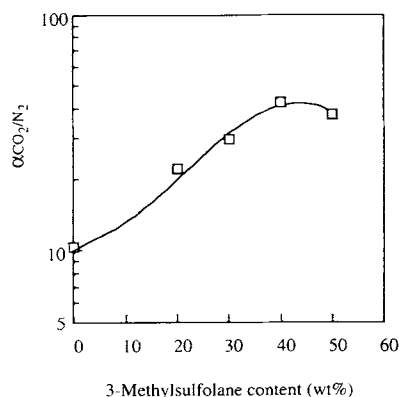

Figure 13 Effect of 3-methylsulfolane content on ideal separation factors for CO_2 over N_2 at 30°C and 4 atm determined using the nonvacuum system.
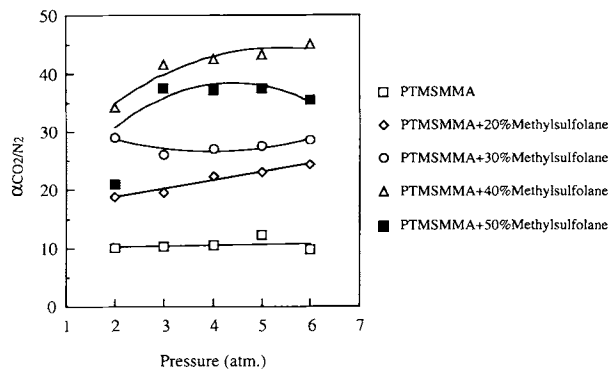

Figure 14 Pressure dependence of ideal separation factors for CO_2 over N_2 at 30°C determined using the nonvacuum system.

that for CO_2, and the permeability coefficients of N_2 should be influenced more highly by the desorbed gases than those of CO_2.

CONCLUSIONS

Sulfolanes have been shown to be good modifiers to improve the permeabilities and selectivities of CO_2, although the PTMSMMA blends with low 3-methylsulfolane content did not display good permeabilities and selectivities of CO_2 measured using the vacuum system. The PMSP membranes modified by 3-sulfolene and sulfolane both showed good selectivities for CO_2 with the trade-off decreased permeabilities of CO_2 but which were still above 1000 Barrer. The PTMSMMA blend membranes containing high 3-methylsulfolane content determined using the nonvacuum system exhibited both extremely higher permeabilities and selectivities of CO_2 over N_2 than those of the PTMSMMA membrane. In addition, the blends with 40 and 50% 3-methylsulfolane did not show the fragility of the PTMSMMA membrane. With its ideal separation factors for CO_2 over N_2 above 40, the PTMSMMA blend with 40% 3-methylsulfolane showed the highest selectivities, while the PTMSMMA blend with 50% 3-methylsulfolane showed the permeabilities of CO_2 above 300 Barrer which were the highest under the conditions of this study. The new procedure employed using the nonvacuum system for the measurement of gas permeabilities in this study proved to be effective for the membranes containing a volatilizable component.

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