NOTE

Selective Permeation of Sour Gases Through Polymeric Membranes Modified by Sulfolanes. II. Study of Selective Permeation of SO_2 Through Polytrimethylsilyl Methyl Methacrylate and Its Blend Membranes Containing 3-Methylsulfolane

INTRODUCTION

For the separation of sulfur dioxide (SO_2) as one of the major air pollutants, existing processes require significant power and have drawbacks such as poor efficiency and problems with the disposal of solid waste. Therefore, in developing new technologies which are more efficient, less costly, and environmentally acceptable, membrane separations have been suggested to be the most promising process for this task.

In improving the permeability and selectivity of SO_2, it was suggested that developing a membrane containing affinity sorbents for SO_2 should be an effective way.[1] Polytrimethylsilyl methylmethacrylate (PTMSMMA) has drawn great attention as a promising membrane material for its high gas permeability, although its low selectivity has to be improved before its practical use.[2] It is well known that sulfolane possesses a high affinity for sour gases.[3] A study about the selectivity permeation of CO_2 through the 3-methylsulfolane- and PTMSMMA-blend membranes has pointed out that membranes blended with a high 3-methylsulfolane content not only showed high selectivity of CO_2 but also a much higher CO_2 permeability with respect to the PTMSMMA membrane.[4] In this study on preparing new kinds of membranes with high SO_2 permeability and selectivity, we examined the effect of 3-methylsulfolane in blends containing 8, 16, and 20% on increasing the permeability and selectivity of SO_2 through the measurement of SO_2 permeability on a vacuum system.

EXPERIMENTAL

Preparation of membranes

PTMSMMA was synthesized by radical bulk polymerization under the conditions described previously.[2] The method of dissolution-reprecipitation was used in the purification of PTMSMMA; it was dissolved in toluene, and then the solutions were poured into methanol. The PTMSMMA- and 3-methylsulfolane-blend membranes used for this study were prepared by casting a 3% toluene solution 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 mm, depending on the weight of the casting solution.

Permeation and Sorption Measurements

The vacuum system used for this study was equipped with an MKS Baraton pressure transducer. The membranes determined on this system were measured after they reached their unsteady states at 30°C[5]; the apparent diffusivity coefficients were determined by the time-lag method, and the apparent solubility coefficients were calculated according to the solubility-diffusivity model. The CO_2 and N_2 gases used in this study were obtained from Keihin Koatsu Gas Co., and their purity was at least 99.5 mol %. The SO_2 gas was obtained from Takachiho Chemical Industry, Ltd. The CO_2 sorption isotherms for the PTMSMMA and its 3-methylsulfolane membranes at 30°C were determined by the gravimetric method using a quartz spring.

Measurement of Membrane Characterization

The membrane density was determined by its weight and volume. The glass transition temperature, T_g, was 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:

$$\lambda = 2d \sin \theta (\text{Cu} - \text{K}\alpha, \lambda = 1.54\text{Å}) \qquad (1)$$

RESULTS AND DISCUSSIONS

Table I lists the characterizations of PTMSMMA and its blend membranes containing 8, 16, and 20% 3-methylsulfolane. The d-spacings and densities of PTMSMMA and its blend membranes did not show much difference in the openness between the polymers in the PTMSMMA and its blend membranes after

Table I   Characterizations of PTMSMMA and its Blend Membranes Containing 3-Methylsulfolane

	d^a	d-spacing^b	T_g^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

^{a} Density, determined by volume and weight; unit: g/cm^3.
^{b} d-spacing, determined by WAXD using Bragg's equation; $\lambda = 2d \sin \theta$; unit: Å.
^{c} Determined by differential scanning calorimetry at a heating rate of 20°C/min; unit: °C.

blending 3-methylsulfolane. The study of the poly(1-trimethylsilyl-1-propyne) (PMSP) membranes filled with liquid poly(dimethylsiloxanes) has pointed out[6] that the Langmuir sorption abilities for CO_2 were depressed and the mobility of polymers was increased due to the decrease in the volume of microvoids in the PMSP-modified membranes. We found that a certain fraction of 3-methylsulfolane was still kept in the PTMSMMA blends after a vacuum period, as shown in Figure 1. Therefore, the low T_g of the blends with respect to that of the PTMSMMA membrane implied that the addition of 3-methylsulfolane to the microvoids in the blends should decrease the Langmuir sorption abilities for CO_2 in the PTMSMMA blends.

As a relative result, the addition of 3-methylsulfolane to the microvoids in the blends made the soluble ability to CO_2 in the blends low, which can be seen from the CO_2 gas sorption isotherms of PTMSMMA and its blends. The contents of CO_2 in these membranes were depressed with blending 3-methylsulfolane, as shown in Table II. It was proposed that with respect to the PTMSMMA membrane,

the increased soluble amount of CO_2 for Henry solubility in these blends, resulting from the affinity of 3-methylsulfolane to CO_2, could not exceed the decreased amount of CO_2 sorbed in the Langmuir mode of these blends.

Table III lists permeabilities, diffusivities, and solubilities of SO_2 for PTMSMMA and its blend membranes containing 3-methylsulfolane at 30°C measured on the vacuum system. The blends showed higher permeabilities of SO_2 than the PTMSMMA membrane under the same condition with increasing 3-methylsulfolane content in the blends. The changes in the solubilities of SO_2 listed in Table III showed the same tendency as that in the permeabilities. The difference in the diffusivities of SO_2 between PTMSMMA and its blend membranes was very slight, so it is suggested that the increased solubilities caused by the strong affinity of 3-methylsulfolane for SO_2 should be the main contributor to the improved solubilities and permeabilities of SO_2 for the blends, although the affinity of 3-methylsulfolane for sour gases did not prove to have a positive effect on improving the solubilities of CO_2 under the same condition (as can be seen in Tables
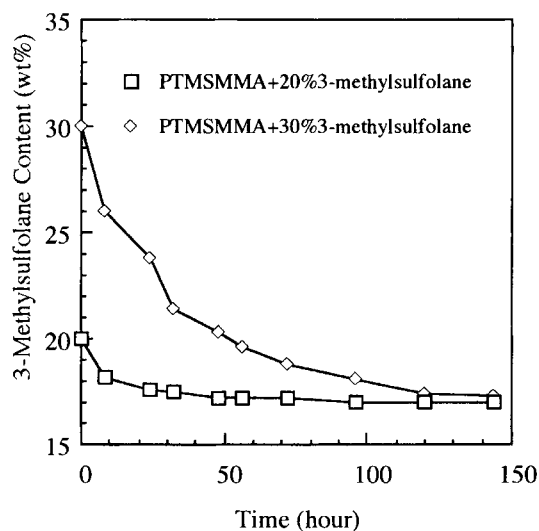

Figure 1   Time dependence on 3-methylsulfolane content in the PTMSMMA-blend membranes under vacuum condition at 28°C and a pressure lower than 1 mm Hg.

Table II CO_2 Sorption Isotherms at 30°C of PTMSMMA Membrane and its 3-Methylsulfolane-Blend Membranes

p (cm Hg)	C_0^a	C_8^b	C_{16}^c
10	0.594	0.593	0.314
20	1.189	1.186	1.093
30	1.720	1.678	—
40	2.124	—	1.411
50	3.478	2.966	1.957
60	4.262	3.390	1.961
70	4.730	4.490	3.516
80	6.083	4.914	4.178

^{a} The content of CO_2 at 30°C in PTMSMMA membrane; unit: cm^3 (STP)/cm^3 polymer.
^{b} The content of CO_2 at 30°C in PTMSMMA + 8% methylsulfolane-blend membrane; unit: cm^3 (STP)/cm^3 polymer.
^{c} The content of CO_2 at 30°C in PTMSMMA + 16% methylsulfolane-blend membrane; unit: cm^3 (STP)/cm^3 polymer.

Table III   Permeabilities (P), Diffusivities (D), and Solubilities (S) of SO_2 at 30°C for PTMSMMA and its Blend Membranes Containing 3-Methylsulfolane

p (cm Hg)[a]	P_{SO_2} (Barrer)[b]			$D_{SO_2} \times 10^8$ (cm²/s)			$S_{SO_2} \times 10^3$ [cm³ (STP)/cm³ cm Hg]		
	20	30	40	20	30	40	20	30	40
PTMSMMA	226	230	237	3.53	3.40	2.71	642	676	873
PTMSMMA + A% 3-methylsulfolane	250	290	327	3.31	3.09	3.65	754	937	896
PTMSMMA + B% 3-methylsulfolane	364	393	411	4.70	4.46	4.08	774	882	101
PTMSMMA + C% 3-methylsulfolane	357	404	404	3.82	4.08	2.92	878	992	139

[a] A, 8% blend content; B, 16% blend content; C, 20% blend content.
[b] Barrer = 1×10^{-10}[cm³ (STP)·cm/cm²·S·cmHg].

II and IV), which has been proposed to be caused by the decreased the sorption of gases in the Langmuir modes of the blends.

Consequently, the permeabilities of CO_2 for the blends were decreased, as shown in Table IV, although the diffusivities of CO_2 in the blends also changed slightly, as did those of SO_2 under the same condition. Because the factors that affected the solubilities of CO_2 also existed for the solubilities of SO_2 in the blends (which were the decreased sorptions in the Langmuir modes of the blends and the evaporation of the 3-methylsulfolane on the surfaces of these blends during the vacuum period before determination[4]) it can be concluded that the higher affinity between SO_2 and 3-methylsulfolane than that between CO_2 and 3-methylsulfolane should be the main reason for the differences in the solubilities and permeabilities of the same blends between CO_2 and SO_2. As a result of the decreased sorptions for N_2 in both the Henry and Langmuir modes of the blends, caused by the exclusion of N_2 from the polar 3-methylsulfolane and the reduced microvoid volume, respectively, the permeabilities of N_2 should decrease with increasing 3-methylsulfolane content.

We used the ratios of the permeability coefficients of pure SO_2 to the permeability coefficients of pure N_2 and pure CO_2 as ideal separation factors for SO_2 over N_2 and CO_2. Consequently, the ideal separation factors for SO_2

over N_2 were increased by blending PTMSMMA with 3-methylsulfolane and were enhanced with increasing 3-methylsulfolane content, as can be seen in Table V. The ideal separation factors for SO_2 over N_2 for the blend containing 20% 3-methylsulfolane were above 50, about twice those of the PTMSMMA membrane under the same condition. Because there was little change in the diffusivity selectivities of SO_2 over N_2 with respect to the increase in the solubility selectivities of SO_2 over N_2 for the blends, as listed in Table V, the improvement in the solubility selectivities of SO_2 over N_2 was proposed to be the main contribution to the enhancement in the selectivities of SO_2 over N_2. Also, the ideal separation factors for SO_2 over CO_2 were increased for the blends containing 8 ~ 20% 3-methylsulfolane with respect to the PTMSMMA membrane. The ideal separation factors for SO_2 over CO_2 for the blends also increased with increasing 3-methylsulfolane content, as can be seen from Table VI. The ideal separation factors for SO_2 over CO_2 for the blend containing 20% 3-methylsulfolane were about twice those of the PTMSMMA membrane under the same condition. It is also clear that the enhanced solubility selectivities of SO_2 over CO_2 should be the main contributor to improving the ideal separation factors for SO_2 over CO_2 after the comparison of the diffusivity selectivities with solubility selectivities of SO_2 over CO_2 for the PTMSMMA and its

Table IV   Permeabilities (P), Diffusivities (D), and Solubilities (S) of CO_2 at 30°C for PTMSMMA and its Blend Membranes Containing 3-Methylsulfolane

p (cm Hg)[a]	P_{CO_2} (Barrer)			$D_{CO_2} \times 10^8$ (cm²/s)			$S_{CO_2} \times 10^3$ [cm³ (STP)/cm³ cm Hg]		
	20	30	40	20	30	40	20	30	40
PTMSMMA	138	137	135	24.2	21.3	20.9	57.2	64.3	64.7
PTMSMMA + A% 3-methylsulfolane	134	124	124	25.1	24.4	23.7	53.3	50.8	52.4
PTMSMMA + B% 3-methylsulfolane	122	122	122	24.7	24.0	24.0	49.4	50.7	50.6
PTMSMMA + C% 3-methylsulfolane	112	113	113	24.8	24.5	23.9	45.2	46.2	47.3

[a] A, 8% blend content; B, 16% blend content; C, 20% blend content.

Table V   Ideal Separation Factors (α), Diffusivity (D), and Solubility (S) Selectivities of SO_2 over N_2 at 30°C for PTMSMMA and its Blend Membranes Containing 3-Methylsulfolane

p (cm Hg)[a]	$\alpha P_{SO_2}/P_{N_2}$			$\alpha D_{SO_2}/D_{N_2}$			$\alpha S_{SO_2}/S_{N_2}$		
	20	30	40	20	30	40	20	30	40
PTMSMMA	25.1	25.1	25.2	0.150	0.147	0.117	167	171	221
PTMSMMA + A% 3-methylsulfolane	29.9	35.2	39.2	0.192	0.164	0.205	156	215	192
PTMSMMA + B% 3-methylsulfolane	46.5	50.2	52.5	0.200	0.168	0.181	232	298	291
PTMSMMA + C% 3-methylsulfolane	48.8	55.6	54.7	0.190	0.192	0.138	257	290	395

[a] A, 8% blend content; B, 16% blend content; C, 20% blend content.

Table VI   Ideal Separation Factors (α), Diffusivity (D), and Solubility (S) Selectivities of SO_2 over CO_2 at 30°C for PTMSMMA and its Blend Membranes Containing 3-Methylsulfolane

p (cm Hg)[a]	$\alpha P_{SO_2}/P_{CO_2}$			$\alpha D_{SO_2}/D_{CO_2}$			$\alpha S_{SO_2}/S_{CO_2}$		
	20	30	40	20	30	40	20	30	40
PTMSMMA	1.64	1.68	1.75	0.130	0.159	0.130	11.2	10.5	13.5
PTMSMMA + A% 3-methylsulfolane	1.87	2.34	2.64	0.132	0.127	0.154	14.2	18.5	17.1
PTMSMMA + B% 3-methylsulfolane	2.98	3.23	3.38	0.190	0.186	0.177	15.7	17.4	19.9
PTMSMMA + C% 3-methylsulfolane	3.19	3.58	3.58	0.155	0.167	0.122	20.7	21.5	29.3

[a] A, 8% blend content; B, 16% blend content; C, 20% blend content.

blend membranes, as shown in Table VI.

CONCLUSIONS

On the basis of the measurement of the permeabilities of SO_2, CO_2, and N_2 for the PTMSMMA and its blend membranes containing 8, 16, and 20% 3-methylsulfolane on the vacuum system, it was found that the permeabilities and the selectivities of SO_2 over CO_2 and N_2 for the blends were higher than those of the PTMSMMA membrane and all increased with increasing 3-methylsulfolane content under the conditions in this study. It was concluded that the solubilities of SO_2 in the blends increased, but those of CO_2 did the opposite under the same conditions determined on the same vacuum system, due to the much higher affinity between SO_2 and 3-methylsulfolane than that between CO_2 and 3-methylsulfolane. As a result, the ideal separation factors for SO_2 over CO_2 and N_2 for the blend containing 20% 3-methylsulfolane increased to about twice those for the PTMSMMA membrane under the same condition.

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