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The correlation between free volume and gas separation properties in high molecular weight poly(methyl methacrylate) membranes

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Abstract

Poly(methyl methacrylate) membranes of different fractional free volume (FFV) were prepared by dry casting from different solvents. Free volume data were determined by means of Bondi method and positron annihilation lifetime spectroscopy (PALS). It was found that both the boiling point and the solubility parameter of casting solvent affect the membrane's free volume. It was believed that the difference in free volume was arisen from the difference in polymer packing.

The gas permeability is higher when membranes are cast from higher molecular weight PMMA. But the plasticizing effect of CO_2 is less serious compared with the low molecular weight one. The high molecular weight PMMA membrane also has an extremely high O_2/N_2 selectivity, indicating its high structure uniformity. These results indicate that membranes made from polymer of higher molecular weight have the advantages of high permeability, gas selectivity and are less sensitive to CO_2 plasticization. The intrinsic gas transport properties such as the permeability, solubility and diffusivity of O_2, N_2, and CO_2 are measured or calculated. The effects of fractional free volume on membrane gas separation properties were investigated. It was found that the fractional free volume had no definite effects on gas solubility, but the gas permeability and diffusivity increased accordingly to the measured free volume.

Keywords: Fractional free volume; Gas sorption; Gas permeation; PMMA membranes

1. Introduction

Membrane gas separation technology has been extensively applied in oxygen enrichment, nitrogen purification, stripping of carbon dioxide from natural gas, hydrogen recovery from reactor purge gas, etc [1]. Recent advances in membrane formation and module design have made membrane-based gas separation more competitive relative to traditional gas separation technologies such as cryogenic distillation, adsorption, and pressure swing adsorption.

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However, gas separation membranes have usually suffered from their low permeability if high gas selectivity is required. Therefore, improving the permeability and selectivity of polymer membranes has become a subject of intense research with worldwide participation in both academic laboratories and industry [2–6].

To improve the membrane permeability with limited loss in selectivity, it is necessary to have a good understanding of the gas transport mechanism. Permeation of a penetrant through a polymeric membrane was often described by the solution-diffusion model [7], in which the gas molecules first dissolved at the membrane surface, then diffused through the membrane, and finally desorbed at the other side of the membrane. Free volume has been shown to have strong influence on gas diffusivity in membrane [8–11]. The free volume of membranes of various chemical structures has been measured and the gas permeability coefficients of these membranes have been compared [12–16]. High correlation has been found between the free volume and gas permeability, but the effect of free volume on gas sorption has hardly been demonstrated. The gas solubility is thermodynamics in nature and may be affected by (i) the polymer–penetrant interactions, (ii) the inherent condensability of the penetrant, and (iii) the free volume in the polymer [17]. For a dense membrane obtained by the dry phase inversion process, the properties of the casting solvent often affect the final properties of the membrane [18–21]. Shao et al. investigated the casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA-TMMDA copolyimide membrane and its derived carbon membranes [22]. They conclude that solvents play an important role on the 6FDA/PMDA-TMMDA membrane morphology and separation performance. Solvent has a closer solubility parameter with polymer, thus provides better environments for the rearrangement of molecular chains to achieve a thermodynamically favored lower entropy configuration. The effects of casting solvent on membrane permeability have been studied for a series of PTMSP membranes [23]. Bi et al. found that the membrane cast from THF has higher gas permeability than the membrane cast from toluene or cyclohexane. It was believed that the conformation of polymers in solution and the rate of solvent evaporation would affect the packing of polymer chain in the membrane. We, therefore, try to prepared membranes with different free volumes but made from the same polymer. Such membranes can be obtained by preparing the casting solution in different solvents. Using membranes with different free volume but made from the same polymer, in this work, we could investigate the effect of free volume on gas separation properties at the same polymer–penetrant interactions.

Poly(methyl methacrylate) (PMMA) has a high O_2/N_2 separation factor and is soluble in various organic solvents. Previous study has shown that the PMMA membrane was brittle and could not be operated at high pressure [24]. This made it difficult to understand the whole picture of gas transport phenomenon. In this study, very high molecular weight PMMA was employed to obtain high pressure gas separation information of PMMA membranes. Furthermore, the effect of polymer molecular weight on membrane gas separation properties was investigated.

2. Experimental

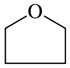
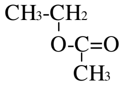
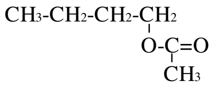
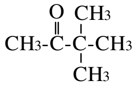
2.1. Materials

Poly(methyl methacrylate) (PMMA) was supplied by the Aldrich Chemical Co. Commercially available dichloromethane, ethylacetate, tetrahydrofuran (THF), butylacetate, and methyl isobutyl ketone (MIBK) were used as solvents without further purification. The boiling point, solubility parameter, and molecular weight of the solvents used were summarized in Table 1.

2.2. Preparation of membranes

The high molecular weight ($M_w = 996{,}000$ g/mol) PMMA membranes were prepared using dichloromethane, ethylacetate, tetrahydrofuran, butylacetate, and methyl isobutyl ketone, respectively. A cast solution consisting of PMMA at 14.3 wt% was cast on a glass plate to a thickness of 600 μm. The solvent was then allowed to evaporate slowly under ambient conditions. After 24 h, the solid membranes were dried in a vacuum oven at 110 °C for 24 h to remove the last traces of residual solvent. The mean thickness of the membrane was measured using a micrometer and was based on the average of at least 25 points on the membrane. All the membranes were between 50 and 70 μm thick. The low molecular weight ($M_w = 120{,}000$ g/mol) PMMA membranes were prepared using dichloromethane, and butylacetate. The preparation process of low and high molecular weight PMMA membranes was the same.

Table 1
Physical properties of the casting solvents used for the preparation of the PMMA membrane

Solvent	T_b[a] (°C)	δ[b] (J cm^{-3})$^{0.5}$	δ_p[c] (J cm^{-3})$^{0.5}$	Chemical structure
Dichloromethane	40	20.2	11.7	$Cl\text{–}CH_2\text{–}Cl$
Tetrahydrofurane	66	18.5	11.0	
Ethyl acetate	77	18.2	8.6	 $CH_3\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}CH_3$
Butyl acetate	126	17.8	7.8	 $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}CH_3$
Methyl isobutyl ketone	115	17.6	8.1	 $CH_3\text{-}C(=O)\text{-}C(CH_3)(CH_3)\text{-}CH_3$

PMMA solubility parameter = 19.0 (J cm^{-3})$^{0.5}$.

[a] Boiling point of solvent.

[b] Solubility parameter.

[c] Polarity item of solubility parameter.

2.3. Characterization

The density of the membrane was measured by buoyancy technique. A well-dried membrane sample was first weight in air and then immersed in water at 25 °C and the difference in weight before and after immersion was determined. The specific volume of the membrane (V) is calculated from the weight difference of the measurements divided by the density of water. The fractional free volume (FFV) was calculated according to the following equation [12]:

$$\mathrm{FFV} = \frac{V - V_0}{V}, \tag{1}$$

where V is the specific volume and V_0 is the occupied volume of the polymer. The occupied volume was calculated by [7]

$$V_0 = 1.3\, V_\mathrm{W}, \tag{2}$$

where V_W is the van der Waals volume which was estimated by the group contribution method by Bondi [25].

2.4. Positron annihilation lifetime (PAL) spectroscopy

The positron annihilation lifetimes of PMMA membranes were determined by detecting the prompt γ-rays (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the subsequent annihilation γ-rays (0.511 MeV). A fast-fast coincidence circuit of PAL spectrometer with a lifetime resolution of 260 ps as monitored by using a ^{60}Co source was used to record all PAL spectra. Each spectrum was collected to a fixed total count of 1×10^6. All of the PAL spectra obtained analyzed by a finite-term lifetime analysis method using the PATFIT program. In the current PAL method, we employ the results of o-Ps lifetime to obtain the mean free-volume hole radius by the following semiempirical equation [26,27]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{3}$$

where τ_3 (o-Ps lifetime) and R (hole radius) are expressed in ns and Å, respectively. R_0 is equal to $R + \Delta R$, where ΔR is a fitted empirical electron layer thickness (=1.66 Å). The cavity volumes were calculated from $V_h = 4\pi R^3/3$.

2.5. Permeation study

A gas permeation analyzer (Yanaco GTR10) was used to measure the pure gas permeability coefficients of the polymeric membranes for O_2, N_2, and CO_2. The tests were carried out under isothermal conditions at 35 °C (±0.5 °C). Permeability is usually expressed in barrer (10^{-10} (cm^3 (STP) cm)/

(cm^2 s cmHg)). The ideal selectivity was calculated based on the ratio of permeability coefficients:

$$\alpha_{A/B} = \frac{P_A}{P_B}, \tag{4}$$

where P_A and P_B are the permeability coefficient of pure gases A and B. The gas sorption measurements were made using a microbalance (Cahn model D202 Electrobalance) to determine the amount of gas absorbed. The membrane was thoroughly evacuated for 12 h and than equilibrated at increasing pressures. For each polymer–solvent system, permeation and sorption experiments were carried out on six samples, for each gas. Therefore, the permeation parameters (P, S) were obtained with an accuracy ranging from 5% to 10%. It was also verified that the results were reproducible over a long period of time.

3. Result and discussion

3.1. Characterization of the membranes

PMMA ($M_w = 996{,}000$ g/mol) is dissolved in dichloromethane, ethylacetate, tetrahydrofuran (THF), butylacetate, or methyl isobutyl ketone (MIBK) and cast on a glass plate. Dense PMMA membranes were obtained by normal casting-evaporation procedure. It was found that the casting solvents had significant effects on the physical properties of the membranes. The boiling point of the casting solvent affects the membrane's free volume. Khulbe et al. obtained the similar results like us [18]. They concluded that the results obtained from X-ray diffraction of dense poly(2,6-dimethyl-1,4-phenylene oxide) membranes, prepared from different casting solvents, show that the physical properties of solvents have a significant effect on the conformation of the membrane. As shown in Tables 1 and 2, the increase in FFV basically follows the increase in solvent's boiling point. Fast solvent evaporation results in immediate vitrification and causes polymer chain aligned in their stretched state which increased inter-chain alignment and subsequently reduced the free volume. On the other hand, slow solvent evaporation allows each polymer chain undergoing self-coiling and interchain penetration which might create higher free volume. The polarity of casting solvent may also affect the polymer packing. As shown in Table 2, MIBK had a lower boiling point than that of butylacetate, but the resulting membrane had a higher FFV. It may be able to explain this observation by the solubility parameter difference between solvent and polymer. The solubility parameter difference between PMMA and MIBK is higher than that between PMMA and butylacetate. The higher solubility parameter difference may induce self-coiling of polymer chains and subsequently reduces inter-polymer alignment.

As showing in Table 2, the measured FFV varies from 0.173 to 0.188, owing to the different casting solvent used. Notice that the measured FFV of high molecular weight PMMA is much higher than the values previously reported in the literature. Wright and Paul [24] reported that the FFV of a PMMA membrane ($M_w = 105{,}400$ g/mol) was 0.135. Base on the above comparison, the much higher FFVs may be due to the high molecular weight of the PMMA we use. Using the free volume concept based on viscosity, a fractional free volume FFV = 0.025 at the glass transition temperature has been found for a number of glassy polymers. Simha and Boyer have used the free volume concept to describe glass transition temperatures and they have derived a value of FFV = 0.11, which is far higher than that quoted above. However, these two values should be considered to be quite genuine, because in the case of diffusion not all the free volume is available for transport. In our present work, membrane permeation test was carried out at room temperature, so we analyzed experiment data according the fraction free volume measured at room temperature. The PALS result of PMMA membrane is consistent with the FFV estimated by

Table 2
Characterization of the PMMA membrane

Membrane	Casting solvent	Density (g/cm^3)	FFV	τ_3 (ns)	R (Å)	V_h (Å^3)
PMMA-D	Dichloromethane	1.135	0.173	1.98	2.83	95
PMMA-T	Tetrahydrofurane	1.126	0.179	2.04	2.88	100
PMMA-E	Ethyl acetate	1.124	0.181	2.08	2.92	105
PMMA-B	Butyl acetate	1.119	0.184	2.14	2.97	110
PMMA-M	Methyl isobutyl ketone	1.114	0.188	2.18	3.00	114

the group contribution method by Bondi. The magnitude of τ_3, hole radius (R), and cavity volume (V_h) grow in the order of

$$\text{PMMA-D} < \text{PMMA-T} < \text{PMMA-E} < \text{PMMA-B} < \text{PMMA-M}$$

The free volumes data in Table 2 suggest that PMMA membranes cast from different solvent indeed have dissimilar free volume.

3.2. *Effect of polymer molecular weight on gas separation behavior of PMMA membrane*

The permeability coefficients of carbon dioxide were measured. It seems that the gas permeates faster through PMMA membranes of higher molecular weight. As shown in Fig. 1, the permeabilities of CO_2 through membranes made from high molecular weight PMMA are higher than those of low molecular weight. Wright et al. showed that the CO_2 permeability of PMMA membrane ($M_w = 105{,}400$ g/mol) is 0.36 barrer [24]; however, the CO_2 permeability of PMMA membrane ($M_w = 996{,}000$ g/mol) in this work is 1.28 barrer. The difference in permeability can be explained with molecular weight effect. It can be suspected that a polymer of a higher molecular weight owns stronger intra-molecular interaction, which reduces inter-chain alignment and, subsequently, increases the gas permeability. PMMA is well known to be easily plasticized by CO_2. Our experimental result also showed that the CO_2 permeability of high molecular weight PMMA membrane increases when the pressure is operated above 10 atm. If we assume that the minimum permeability occurs at critical plasticization pressure, CO_2 plasticization is still observed in those membranes of high molecular weight PMMA. However, the critical plasticization pressure at 10 atm shown in Fig. 1 is astonishingly high. Sander [28] had studied the membrane made from PMMA of $M_w = 60{,}000$ g/mol and found that the membrane was plasticized at a pressure lower than 5 atm. We also measured the CO_2 permeabilities of PMMA membranes made from PMMA of $M_w = 120{,}000$ g/mol. As shown in Fig. 1, the critical plasticization pressure was around 5 atm. It was apparent that the membrane made from higher molecular weight polymer was rather resistant plasticization. The solubility of CO_2 in different molecular weight PMMA membranes at 35 °C was shown in Fig. 2. The solubility of CO_2 in high molecular weight PMMA is significantly higher than that absorbed for low molecular weight PMMA. The sorption behavior in Fig. 2 is not follow the well-known dual sorption equation, this behavior has been explained in terms of the plasticizing effect mentioned earlier.

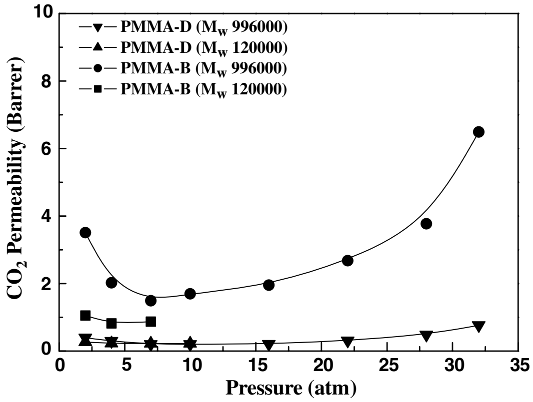


Fig. 1. Effect of molecular weight on the carbon dioxide permeability of PMMA membranes at 35 °C.

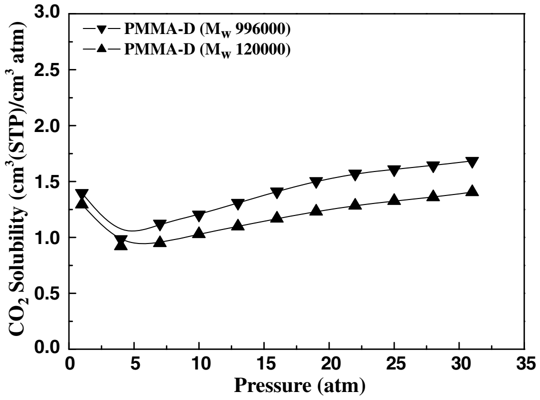


Fig. 2. Effect of molecular weight on the carbon dioxide solubility of PMMA membranes at 35 °C.

3.3. *Effects of FFV on gas permeability, solubility and effective diffusivity*

The permeability coefficients of pure helium, oxygen, nitrogen, and carbon dioxide through each PMMA membrane were measured. It was found that the permeability coefficients of all the gases increased with the FFVs of membranes. As demonstrated in Fig. 3, the permeability coefficients of helium gas increased only slightly with the increase in FFV, but the permeability coefficients of other gases increased drastically. As shown in Fig. 3, the

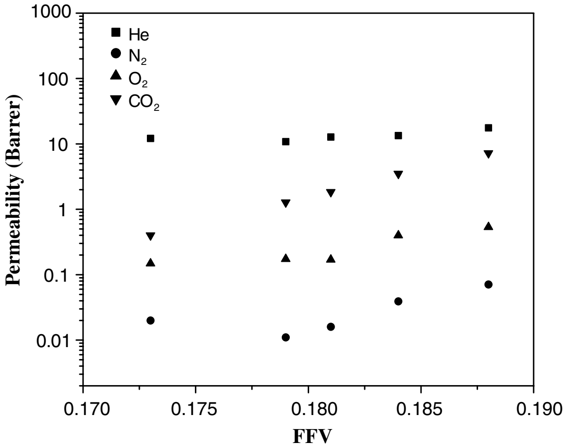


Fig. 3. Effect of FFV on the permeability of PMMA membranes at 35 °C.

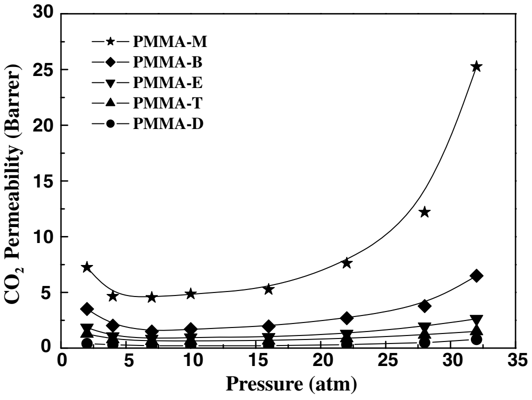


Fig. 5. Effect of pressure on the permeability of carbon dioxide in PMMA membranes at 35 °C.

permeability coefficient of nitrogen and CO_2 increased more than 6-fold as the fractional free volume increased from 0.17 to 0.19 no matter the permeation proceeded at low (2 atm) or high (32 atm) pressure condition. These results imply that free volume is the most important factor affects the gas permeation behavior of membrane. The permeability coefficients were also measured under various operating pressures, which were shown in Figs. 4 and 5. The permeability coefficient of nitrogen decreased slightly with the pressure and soon leveled off to a steady value at higher pressures. The permeability of carbon dioxide, similarly, decreased with the pressure in the beginning, but continuously increased with the increase in operating pressure. The increase of gas permeability at elevated pressure was often considered a consequence of plasticization. Condensable gases plasticized the membrane and increased the polymer chain mobility at high pressure. The permeability ratios of helium to nitrogen and oxygen to nitrogen were strongly affected by the FFV of each membrane. As shown in Table 3, the ideal selectivity basically increased as the FFV decreased. Furthermore, both high O_2/N_2 and He/N_2 permeability ratios are obtained from membranes made from high molecular weight PMMA.

The solubility of pure N_2, O_2, and CO_2 were measured and compared in Fig. 6. As expected, the more condensable gases exhibit higher solubility. Carbon dioxide had the highest gas solubility in PMMA and N_2 had the lowest. As shown in Fig. 6, the solubility of N_2 slightly increased as the increase in FFV but that of O_2 and CO_2 seemed insensitive to the change of FFV. From the present limited data, it seems that the FFV has little effect on the gas solubility. Figs. 7 and 8 showed the pressure dependence of gas solubility. The solubility pressure dependence for a single component is given using a dual mode model [30]

$$S = \frac{C}{p} = k_D + \frac{C'_H b}{1 + bp} \tag{5}$$

where k_D is the Henry's law constant, C'_H is the Langmuir capacity constant, and b is the Langmuir affinity constant. The C'_H term characterizes the amount of unrelaxed free volume in the glassy matrix. This allows describing the non-equilibrium nature of such materials. The b term characterizes the tendency of a given penetrant to sorb into the excess unrelaxed volume in the non-equilibrium matrix. According to the dual mode model, the solubility decreased with pressure at lower applied pressure

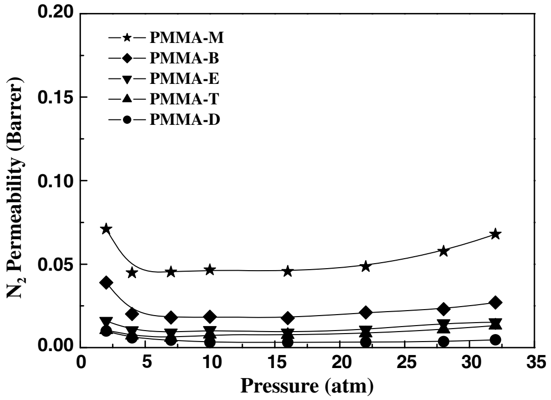


Fig. 4. Effect of pressure on the permeability of nitrogen in PMMA membranes at 35 °C.

Table 3
Permeabilities and ideal selectivities of PMMA membrane at 35 °C

Membrane	P_{He} (Barrer)	P_{O_2} (Barrer)	P_{N_2} (Barrer)	P_{He}/P_{N_2}	P_{O_2}/P_{N_2}
PMMA-D	11.96	0.148	0.010	1196	14.8
PMMA-T	11.62	0.167	0.011	1056	15.2
PMMA-E	12.78	0.170	0.016	799	10.6
PMMA-B	13.43	0.397	0.039	344	10.2
PMMA-M	17.63	0.535	0.071	248	7.5

1 Barrer = 1×10^{-10} m^3(STP) cm/cm^2 s cm Hg. All the data shown measured at 2 atms.

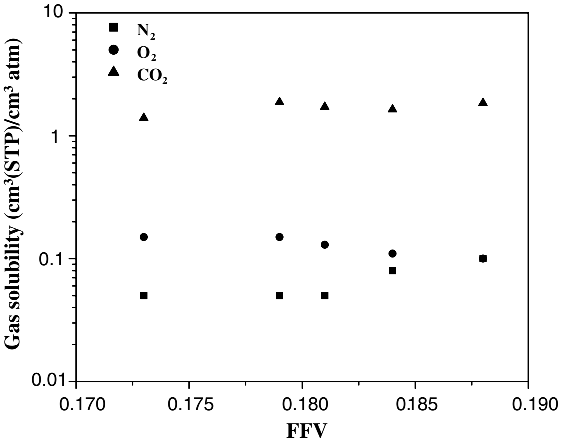


Fig. 6. Effect of FFV on the gas solubility of PMMA membranes at 35 °C.

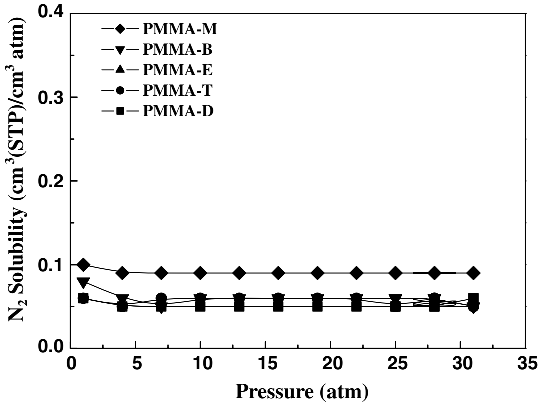


Fig. 7. Plots of solubility of nitrogen vs. gas pressure for PMMA membranes at 35 °C.

then remained almost constant at higher pressures. The nitrogen solubility first decreased with pressure and then remains constant, shown as Fig. 7. It seems that the nitrogen solubility roughly follows the normally observed dual mode sorption pattern. It is instructive to compare the solubility get from this work to other literature. The nitrogen solubility

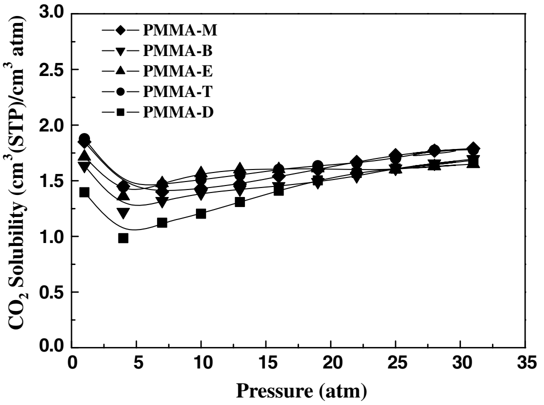


Fig. 8. Plots of solubility of carbon dioxide vs. gas pressure for PMMA membranes at 35 °C.

in this work ($S = 0.15\,cm^3$ (STP) $cm^{-3}\,atm^{-1}$) is similar to Wright et al. result ($S = 0.19\,cm^3$ (STP) $cm^{-3}\,atm^{-1}$) [24]. The solubility of CO_2 first decreases with pressure and then increases after a minimum is reached, shown as Fig. 8. The concave shape of solubility–pressure curve of CO_2 may also be due to plasticization.

The effective gas diffusivity in membranes can be estimated by dividing permeability coefficient with solubility according to the traditional solution-diffusion model. The effect of FFV on effective diffusivity is shown in Fig. 9. It was found that the logarithm effective diffusivity increased almost linearly with the inversed fractional free volume. There is no surprise that the effective diffusivity increases along with the increase in FFV. However, it is astonished to find that the effective diffusivity of CO_2 is not always larger than that of O_2. It is suspected that the lower effective diffusivity of CO_2 is arisen from its higher affinity toward PMMA. Fujita [29] has described the relationship between diffusivity (D) and fractional free volume (FFV) as follows: $D = RTA_d \exp\left[\frac{-B}{\mathrm{FFV}}\right]$, where A_d is related to the size and shape of the diffusing molecule and B is related to the minimum hole size necessary for a diffusion

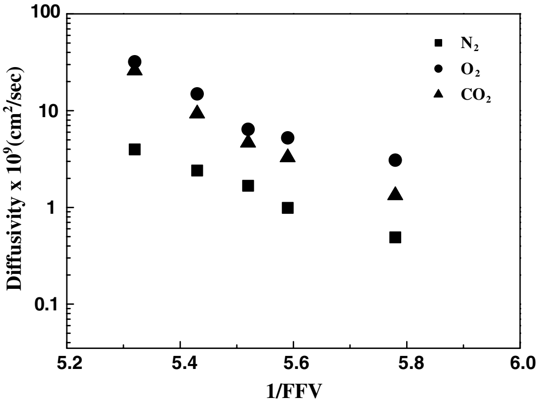


Fig. 9. Effect of FFV on the effective diffusivity of PMMA membranes at 35 °C.

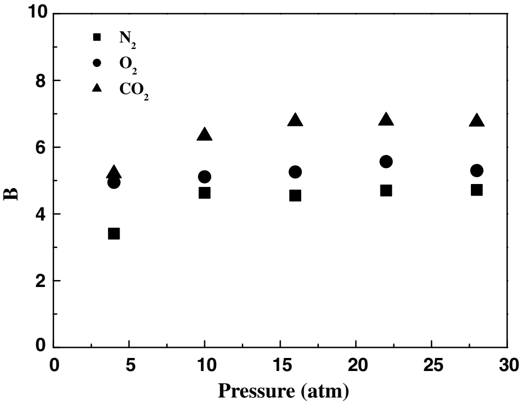


Fig. 10. Plots of B vs. gas pressure for PMMA membranes.

jump. We have derived a value of $A_{\mathrm{d}} = 1.77 \times 10^{-3}$ mol s kg^{-1} in this work. Therefore, we tried to estimate the B values of N_2, O_2 and CO_2 at different pressures. It was expected to observe a decrease in B value if plasticization occurred. However, as shown in Fig. 10, it was found that the B values first increased with pressure and then remained constant when the permeation was operated above 10 atm. This result indicated that there was little observable plasticization effect on gas diffusivity, even in the case of carbon dioxide.

4. Conclusion

The permeability and solubility of high molecular weight PMMA membranes cast from different solvents were studied. The boiling point and polarity of the casting solvent was found to have tremendous effect on the fractional free volume of the membrane. It is also found that high molecular weight PMMA membranes own a higher gas permeability than low molecular weight ones. Stronger intramolecular interaction was considered responsible for the observations. In spite of their higher permeability, higher molecular weight PMMA membranes were less susceptible to CO_2 plasticization.

The permeability and effective diffusivity increased with the increasing in FFV but the FFV had little effect on the gas solubility. Both high O_2/N_2 and He/N_2 permeability ratios were obtained from membranes mad from high molecular weight PMMA. Interestingly, it was found in many cases that the effective diffusivity of CO_2 was smaller than that of oxygen. Strong interaction between CO_2 was considered hindering the movement of CO_2 in PMMA membranes. Furthermore, there was little observable plasticization effect on gas diffusivity, even in the case of carbon dioxide.

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