Gas Permselection Properties in Silicone-Coated Asymmetric Polyethersulfone Membranes

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ABSTRACT: The gas permeation properties of H_2, He, CO_2, O_2, and N_2 through silicone-coated polyethersulfone (PESf) asymmetric hollow-fiber membranes with different structures were investigated as a function of pressure and temperature and compared with those of PESf dense membrane and silicone rubber (PDMS) membrane. The PESf asymmetric hollow-fiber membranes were prepared from spinning solutions containing *N*-methyl-2-pyrrolidone as a solvent, with ethanol, 1-propanol, or water as a nonsolvent-additive. Water was also used as both an internal and an external coagulant. A thin silicone rubber film was coated on the external surface of dried PESf hollow-fiber membranes. The apparent structure characteristics of the separation layer (thickness, porosity, and mean pore size) of the asymmetric membranes were determined by gas permeation method and their cross-section morphologies were examined with a scanning electron microscope. The results reveal that the gas pressure normalized fluxes of the five gases in the three silicone-coated PESf asymmetric membranes are nearly independent of pressure and did not exhibit the dual-mode behavior. The activation energies of permeation in the silicone-coated asymmetric membranes may be larger or smaller than those of PESf dense membrane, which is controlled by the membrane physical structure (skin layer and sublayer structure). Permselectivities for the gas pairs H_2/N_2, He/N_2, CO_2/N_2, and O_2/N_2 are also presented and their temperature dependency addressed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 837–846, 1997

Key words: gas permeation; silicone-coated asymmetric polyethersulfone membranes

INTRODUCTION

Silicone-coated asymmetric membranes are most commonly utilized in industrial membrane gas separation processes.[1,2] The membrane is normally prepared by coating a thin silicone rubber film on the surface of asymmetric membranes prepared from highly selective glass polymers. The gas separation properties through the membrane are controlled by either the coated film or the asymmetric membrane, depending on the membrane structure. Asymmetric membranes with dramatically different structures can be prepared by varying the membrane-making conditions. The effects of the membrane structure characteristics, such as porosity, skin layer thickness, and substructure resistance of the asymmetric membrane, on permeability and selectivity were first analyzed by Henis and Tripodi using the resistance model.[3] Several modified resistance models have subsequently been proposed.[4–8] It is believed that the gas transport behaviors in the silicone-coated asymmetric membrane are different from those of the dense membrane and the asymmetric membrane, depending on the membrane structure. The permselection properties of a membrane

depend not only on its structure but also on the operating pressure and temperature. The gas permselection properties in asymmetric membranes with a porous skin layer[9,10] and "defect-free" skin layer as a function of pressure and temperature have been studied in some detail.[11–13] However, very few attempts have been made to investigate the dependence of pressure and temperature on permselection properties of silicone-coated asymmetric membranes with various structures. Pfromm and colleagues[11] investigated the permeation of various gases through silicone-coated, substantially "defect-free," asymmetric polysulfone (PSf), polycarbonate (PC), and polyestercarbonate (PEC) membranes and compared with those of their respective homogeneous dense membranes. The results show that the activation energies of permeation for O_2, N_2, and O_2/N_2 selectivity in silicone-coated asymmetric membranes are slightly higher than those for the homogeneous dense membranes. The typical dual-mode mobility behaviors commonly found in the homogeneous dense membranes was not observed in these silicone-coated asymmetric membranes.

Aromatic polyethersulfone (PESf) has many advantages as a gas separation membrane material. This polymer, which is commercially available, possesses excellent oxidative and environmental stability as well as good mechanical strength and thermal stability (T_g = 215–230°C).[1,14] Previous investigators have examined gas permeation properties in homogeneous PESf dense membrane (film) with varying pressures and temperatures.[12,15,16] Chiou and associates[15] measured gas permeability coefficients of He, CH_4, and CO_2 through the melt-extrusion PESf dense membrane at different upstream pressures at 35°C and compared them with those of PSf and PC dense membranes. It has been shown that permeability coefficient of He was nearly independent of the operating pressure (whereas those of CO_2 and CH_4 decreased with pressure) and obeys the dual-mode mobility model. The sorption and permeation of CO_2, O_2, and N_2 in the solvent-casting PESf dense membrane were also investigated as a function of pressure.[12] It has been shown that permeability coefficients of CO_2 and O_2 decreased slightly with increasing pressure. The study on the temperature dependence of the mean permeability coefficient for H_2, He, CO_2, O_2, and N_2 in PESf dense membrane has been carried out in our laboratory.[16] The results show that these gases' activation energies of permeation are larger than those reported for PSf and PC dense

membranes, and follow the decreasing order: N_2 > O_2 > He > H_2 > CO_2. These studies reveal that PESf exhibits high selectivity for almost all commercially important gas pairs, but moderate permeability due to its more regular and more polar backbone structure.[12,15,16]

Recently, good progress has been made toward preparing high-flux silicone-coated PESf asymmetric hollow fibers by the introduction of a suitable nonsolvent-additive[16–18] in the polymer dope. Membranes with different structures were prepared from PESf polymer solutions containing various nonsolvent additives.[16,17] This article examines the effects of temperature and pressure on permeability and selectivity of silicone-coated PESf asymmetric membranes with different structures. The relationship between the physical structure of asymmetric membranes and gas permselection properties is elucidated.

EXPERIMENTAL

Silicone-Coated Asymmetric Hollow-Fiber Membrane

The PESf asymmetric hollow-fiber membranes were first prepared from a spinning solution containing 29.4 wt % PESf (VICTRAX®, 4800P) in the solvent and N-methyl-2-pyrrolidone with ethanol or 1-propanol or water as a nonsolvent-additive (NSA). The spinning solutions were tailored to be near the phase separation point so as to enhance phase inversion kinetics during the membrane formation. The hollow fibers were prepared by the dry/wet phase inversion process on a laboratory scale. The air-gap was adjusted at 15 cm and water was used as both the internal and the external coagulants, which were controlled at 24–26°C. The take-up velocity was maintained at 2–2.5 m/min. Hollow fibers with an outer diameter of about 1.7 mm and an inner diameter of 1.2 mm were prepared. The spinning equipment and the detailed spinning procedures have been described elsewhere.[16] The spun wet hollow-fiber membranes were dried at ambient conditions (room temperature of 24–26°C and relative humidity of 60%). The dried hollow fibers were then coated using a 3 wt % coating solution containing Sylgard-184 and n-pentane for 5 min. A thin silicone rubber film was formed on the external surface of the asymmetric hollow-fiber membranes after 24 h curing at ambient temperature. The

Table I   Skin Layer Structure Characterization and Gas Permeation Properties of PEt-A-2, PPr-A-2, and PHo-A-2 Asymmetric Membranes

Membrane No.	NSA	Structure Parameters			Gas Permeability	
		δ (Å)	ε	r (Å)	$(P/L)_{He}$ (GPU)	$(P/L)_{He}/(P/L)_{N_2}$
PEt-A-2	Ethanol	834	1.9×10^{-7}	575	244 (158.8)[a]	2.7 (58.5)
PPr-A-2	Propanol	1,064	7.8×10^{-7}	629	1,260 (164.5)	2.3 (23.5)
PHo-A-2	Water	440	2.8×10^{-7}	129	470 (194.4)	4.1 (63.6)

NSA: nonsolvent-additive; δ: skin layer thickness; ε: surface porosity; r: mean pore size; (P/L): pressure-normalized flux; 1 GPU = 10^{-6} cm^3(STP)/cm^2-cmHg-s.

[a] Data inside the bracket measured at 50°C and 5 bar for silicone-coated membrane; data outside the bracket measured at 25°C and 2 bar for noncoated membrane.

thickness of the coated film was about 1 μm, determined by the weight method.

Examination of Membrane Structure

Structure characterization of the skin layer of the asymmetric membrane was made based on the gas permeation method reported in our previous paper.[10] The gas pressure-normalized flux, (P/L), of a gas through a defected skin layer of an asymmetric membrane is related to the mean pressure, $\bar{p}$ by the following relationship:

$$\left(\frac{P}{L}\right) = K_0 + B_0\bar{p} \qquad (1)$$

By plotting (P/L) as a function of the mean pressure $(\bar{p})$ at a given temperature, the intercept K_0 and the slope of B_0 can be obtained. Assuming that the pores in the separating layer are cylindrical and their average length is equal to the skin layer thickness (δ), K_0, and B_0 may be expressed as follows[10]:

$$K_0 = P_k^0 \frac{\varepsilon r}{\sqrt{MT}\delta} + \frac{P}{\delta} \qquad (2)$$

$$B_0 = P_v^0 \frac{\varepsilon r^2}{\eta T\delta} \qquad (3)$$

where $P_v^0 = (16R)^{-1}$ and $P_k^0 = 4/3(R)^{-1}(2R/\pi)^{0.5}$ are constant; R is a gas constant; T is absolute temperature; η and M are the viscosity and molecular weight of the test gas, respectively; and P is the gas permeability coefficient of the polymer at a given temperature T. The three unknown parameters, mean pore size (r), surface porosity (ε), and skin layer thickness (δ), can be obtained by

measuring the gas permeation fluxes at various pressure drops and at two different temperatures $(T_1$ and $T_2)$ based on the following equations:

$$\delta = \frac{\sqrt{T_2/T_1}\, P_2 - P_1}{\sqrt{T_2/T_1}\, K_{0,2} - K_{0,1}} \qquad (4)$$

$$r = \left(\frac{P_k^0}{P_v^0}\right)\left(\frac{B_{0,1}}{K_{0,1} - P_1/\delta}\right)\left(\frac{\eta T_1}{\sqrt{MT_1}}\right) \qquad (5)$$

$$\varepsilon = \left(\frac{B_{0,1}}{P_v^0}\right)\left(\frac{\eta T_1 \delta}{r^2}\right) \qquad (6)$$

where $K_{0,1}$, $B_{0,1}$, P_1, and $K_{0,2}$, P_2 are data determined at temperatures of T_1 and T_2, respectively. In this study, hydrogen was used as the test gas. Firstly, the gas permeation flux of H_2 through the three membranes at different pressures (1–8 bar) were measured at the temperatures of 30 and 50 or 80°C, respectively. Then the graphs of the H_2 pressure-normalized flux versus the mean pressure were plotted. Based on the intercept and the slope of the straight line, the skin layer thickness, surface porosity, and mean pore size were calculated using eqs. (4)–(6). The detailed calculation procedure has been presented elsewhere.[10] The cross-section morphology of the membranes was examined with a scanning electron microscope (Hitachi Model S4100).

Gas Permeability Measurement

The experimental apparatus used for measuring gas permeation rates through asymmetric and silicone-coated asymmetric hollow-fiber membranes is the same as that described elsewhere.[10] The hollow fibers, about 20 cm in length, were

tested in bundles. The bore of one end of the bundles was sealed with rapid solidified epoxy resin, while the shell side of the another end was glued on an aluminum holder using a normal solidified epoxy resin. The test module was then fitted into a stainless-steel pressure cell. The test cell was immersed into a thermostat-controlled water bath. The steady-state volumetric gas flow rates were determined using a soap flowmeter at the ambient condition. The gases were studied in the following order: N_2, O_2, CO_2, He, H_2. In measuring gas permeability with pressure, the membranes were pre-pressurized using N_2 at 10 bar for 30 min, then the pressure-normalized fluxes were measured with increasing pressure at 30°C. The pressure-normalized fluxes over the temperature range from 30 to 80°C were measured at a pressure difference of 5 bar.

RESULTS AND DISCUSSION

Structure of Hollow-Fiber Membranes

It is well recognized that gas separation characteristics of asymmetric membranes are determined mainly by skin-layer structure. Unfortunately, the exact skin-layer structure parameters cannot be unveiled by the present available instrument. The gas permeation method is often used to determine the apparent skin-layer structure parameters. Table I shows the apparent skin layer thickness, surface porosity, and mean pore size of the three membranes (PEt-A-2, PPr-A-2, and PHo-A-2) calculated based on hydrogen permeation fluxes measured at different pressure drops and temperatures. As shown, the skin-layer structures are different for the membranes prepared using different nonsolvent-additives. The PPr-A-2 membrane has a much larger surface porosity than those of the PEt-A-2 and PHo-A-2 membranes. The PHo-A-2 membrane has a much thinner skin layer than that of the PEt-A-2 membrane. A comparison of gas permeability and selectivity of noncoated and silicone-coated membranes clearly supports the determined membrane structure characteristics (Table I). The permeability and selectivity of PHo-A-2 membrane are higher than the corresponding ones of PEt-A-2 membrane, suggesting a thinner skin layer, smaller porosity, and less substructure resistance of the former membrane as compared with the latter. The high permeability and low
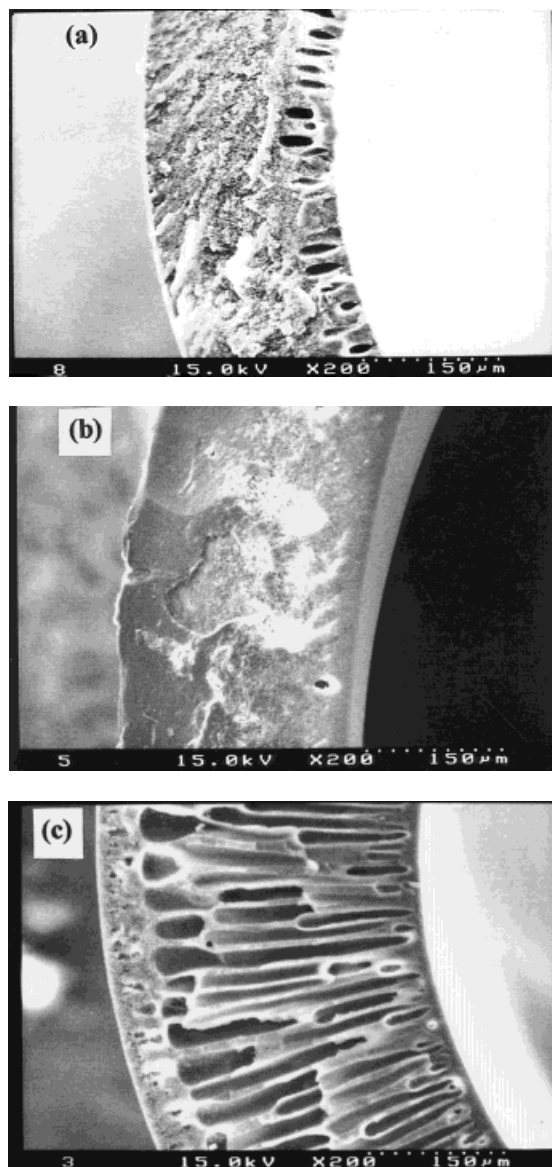

Figure 1 Scanning electron micrographs of the cross section of three PESf hollow fibers; magnification: ×200. (a) PEt-A-2; (b) PPr-A-2; (c) PHo-A-2.

selectivity of the noncoated PPr-A-2 membrane indicates that this membrane has a larger surface porosity. After coating with silicone rubber, this membrane still exhibited a relatively lower selectivity compared with the PESf dense membrane ($P_{He}/P_{N_2} = 65$), but offered a much higher selectivity in comparison with silicone rubber membrane ($P_{He}/P_{N_2} = 1.3$). This implies that there was a significant contribution of gas permeation through the silicone-filled pores.

The cross-section morphologies of the three hollow-fiber membranes were investigated by scan-
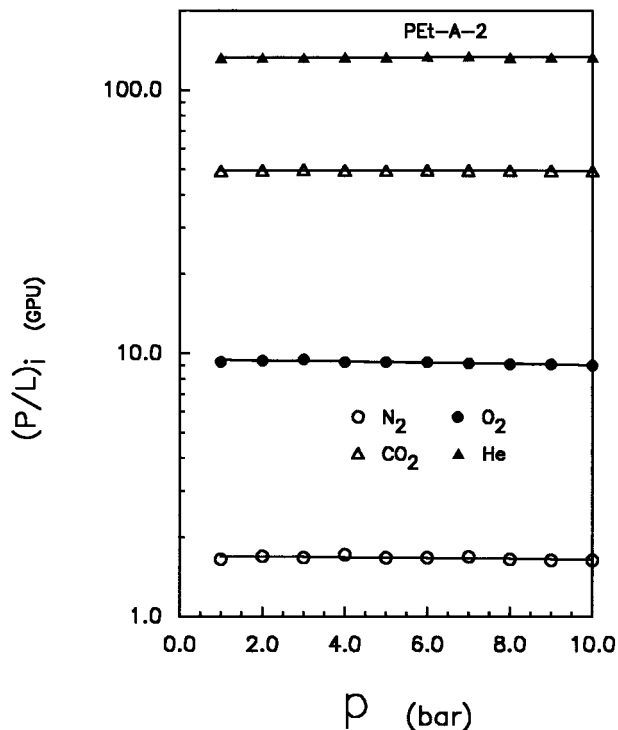
Figure 2 Pressure-normalized fluxes of N_2, O_2, CO_2, and He through the PEt-A-2 membrane as a function of pressure.

permeation in homogeneous PESf dense membrane,[12,15] there is no significant variation of pressure–permeability of the four gases in the three silicone-coated asymmetric membranes. The pressure-normalized fluxes of He, O_2, and N_2 decreased slightly with increasing pressure at pressures exceeding about 4 bar. The membranes might be slightly compacted at high pressures. The CO_2 pressure-normalized flux is nearly independent of pressure. A decrease of permeability due to the membrane compactness may be offset by the slight plasticizing effect. The results indicate that skin layer structure of the PESf asymmetric membranes is different from thick homogeneous dense membrane. On the other hand, the voids formed by polymer chains in the ultrathin skin layer are much fewer than in the thick, dense membrane. The contribution of gas permeation by the Langmuir sorption sites may be negligible in the ultrathin separating layer. The results also demonstrate that the defects on the skin layer of the asymmetric membranes were completely sealed with silicone rubber film.

Effect of Temperature on Gas Permeability

The gas pressure-normalized fluxes of the three silicone-coated hollow-fiber membranes (PEt-A-2,
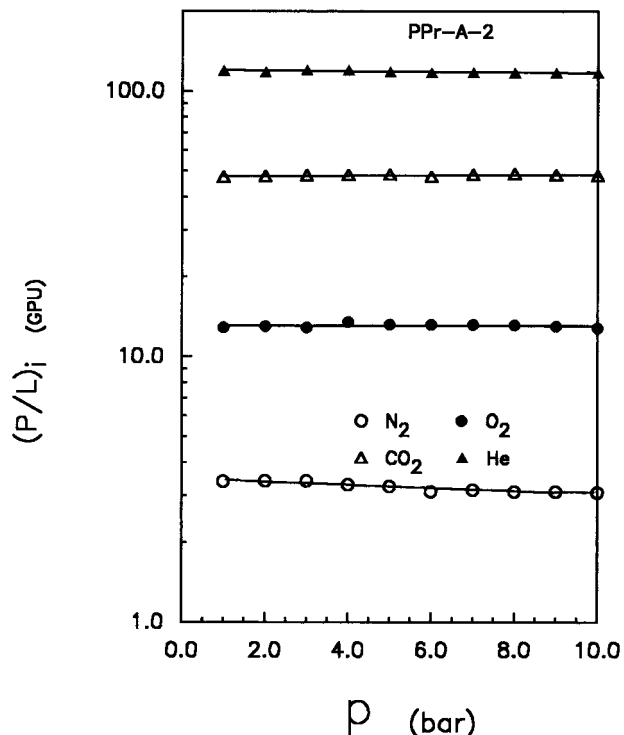
ning electronic microscopy (SEM). The SEM photomicrographs of the PEt-A-2, PPr-A-2, and PHo-A-2 membranes are depicted in Figure 1. As can be seen, with ethanol as a NSA [Fig. 1(a)], only a small number of diminutive macrovoids appeared in the inner edge of the fiber, and a major part of the membrane wall under the dense skin layer was covered by sponge-type of structure. The overall membrane wall of the PPr-A-2 membrane exhibits a fine spongelike structure [Fig. 1(b)]. However, when water was used as an additive, the cross-section of the PHo-A-2 membrane featured numerous big, long, fingerlike voids in the middle of the membrane wall. In general, the fingerlike substructure offers little resistance for gas permeation compared with the spongelike substructure.

Effect of Pressure on Gas Permeability

Pressure-normalized fluxes through the PEt-A-2, PPr-A-2, and PHo-A-2 membranes were measured for He, CO_2, O_2, and N_2 over the pressure range from 1 to 10 bar at 30°C. The results obtained for the three membranes are presented in Figures 2–4. Unlike the previously reported gas

Figure 3 Pressure-normalized fluxes of N_2, O_2, CO_2, and He through the PPr-A-2 membrane as a function of pressure.
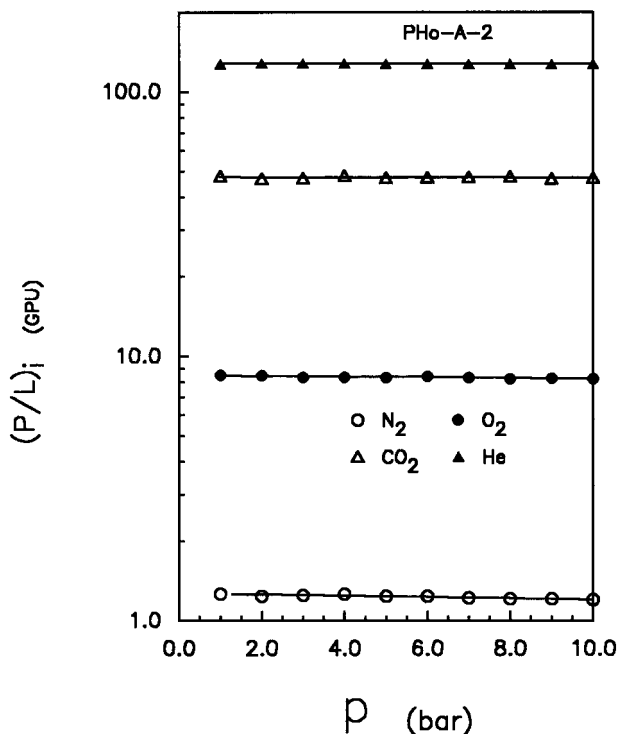
Figure 4 Pressure-normalized fluxes of N_2, O_2, CO_2, and He through the PHo-A-2 membrane as a function of pressure.

PPr-A-2, and PHo-A-2) for the five gases were determined over the temperature range from 30 to 80°C at a pressure difference of 5 bar. The temperature-dependency of permeability follows the typical Arrhenius behavior, as shown in Figures 5–7. As expected, the pressure-normalized fluxes of all gases increase with increasing temperature; however, the rate of increase is different for different gases and different membranes and depends on the activation energies of gas permeation. The activation energy is determined by the size of the gas molecules, the polymer structure, and the membrane structure. The apparent activation energies of these gases through the silicone-coated hollow-fiber membranes were calculated from the slope of the Arrhenius plots and are presented in Table II. For comparison purpose, the activation energies of the five gases in PESf and silicone rubber (PDMS) homogeneous dense membranes determined[16] are also shown in Table II. As illustrated, the activation energies of permeation in the silicone-coated PESf membranes are much higher than those in PDMS dense membrane. This indicates that the gas permeation behavior in the three silicone-coated asymmetric membranes is dominantly controlled by the asymmet-

ric PESf hollow-fiber membranes due to their small porosities as indicated in Table I. The observed different activation energies for different membranes are caused by the different structures of the asymmetric membranes. For the silicone-coated PEt-A-2 membrane prepared using ethanol as NSA, the smaller activation energies for the fast gases (H_2, He, and CO_2) compared with the PESf dense membrane suggest the existence of resistances in the substructure and inner skin layer of the asymmetric membranes. The sponge-like membrane wall and the dense internal skin layer [Fig. 1(a)] may contribute to this resistance. The substructure resistance results in the pressure gradient along the substructure, which increases with increasing gas permeation flux. Therefore, the influence of the resistance on the gas permeability is more significant for a fast gas than for a slow gas. With increasing temperature, the real pressure difference across the skin layer decreased. As a result, the rate of increase in the total gas permeation flux with increasing temperature is less than that of the membrane without the substructure resistance. In contrast to the PEt-A-2 membrane, the activation energies of slow gases (O_2 and N_2) in the silicone-coated PPr-
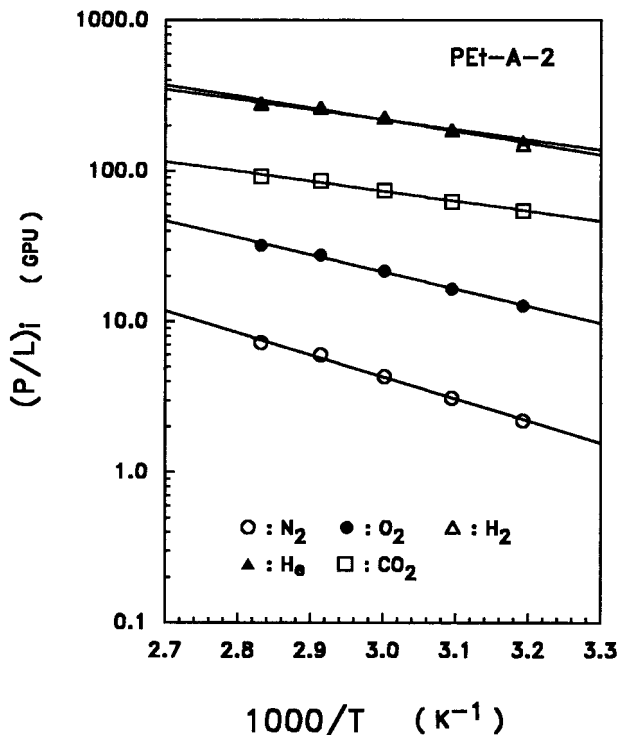

Figure 5 Pressure-normalized fluxes of N_2, O_2, CO_2, H_2, and He through the PEt-A-2 membrane as a function of reciprocal temperature.
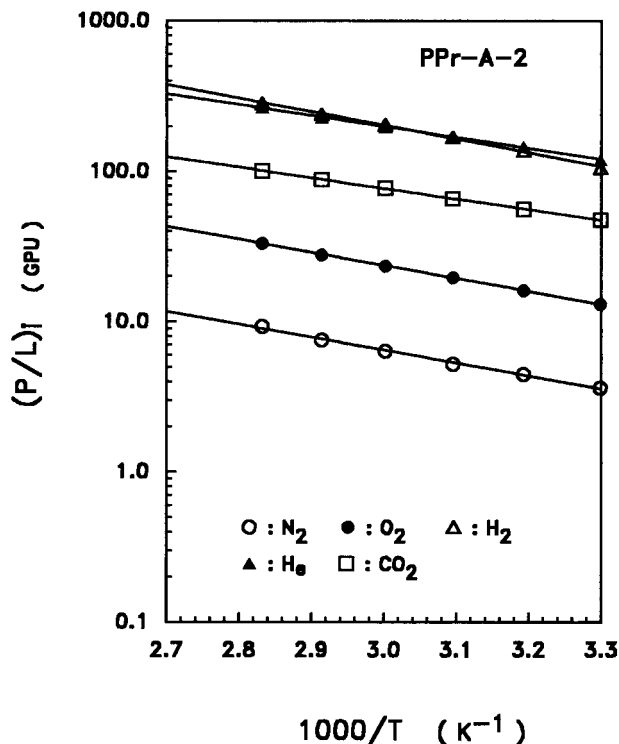
Figure 6 Pressure-normalized fluxes of N_2, O_2, CO_2, H_2, and He through the PPr-A-2 membrane as a function of reciprocal temperature.

A-2 membrane prepared using 1-propanol as NSA are smaller. This behavior may be caused by two factors: (1) the surface porosity of asymmetric membrane was relatively large; and (2) some big pores on the surface of the membrane were not completely sealed by silicone rubber. An examination of the skin layer structure (Table I) reveals that the PPr-A-2 membrane has very large surface porosity. In this case, the gas permeation of a slow gas through the silicone rubber film on the porous part of the asymmetric membrane has a significant contribution to the total gas permeation, whereas the contribution of the nonporous medium in the asymmetric membranes for fast gases is predominant due to great difference in gas permeabilities between fast gases and slow gases in the PESf medium. Temperature has little effect on the gas permeation rate through silicone rubber because the activation energies of permeation are very small (Table II). As a result, the apparent activation energies of O_2 and N_2 are smaller than the corresponding PESf dense membrane. For the silicone-coated PHo-A-2 membrane prepared using water as NSA, its activation energies are higher than those of the PESf dense membrane. This phenomenon was also observed in

the "defect-free" asymmetric PSf and PEC membranes.[11,13]

The results further illustrate the significant difference in gas separation characteristics between a dense skin layer of an asymmetric membrane and the corresponding homogeneous film. A possible explanation for the observed higher activation energy is that segmental packing density in the skin layer of the asymmetric membrane was increased due to the accelerated phase inversion during the spinning of the PHo-A-2 hollow-fiber membrane.[11]

Effect of Temperature on Gas Selectivity

The relatively higher activation energy of permeation for gases through silicone-coated PESf asymmetric membranes suggests that permeability may be greatly improved by an increase in temperature. However, the selectivity of a fast gas with respect to a slow gas usually decreases with increasing temperature, depending on the difference of activation energies between the two gases. The temperature-dependent selectivities in the PESf dense membrane, silicone-rubber dense membrane, and silicone-coated PESf asymmetric
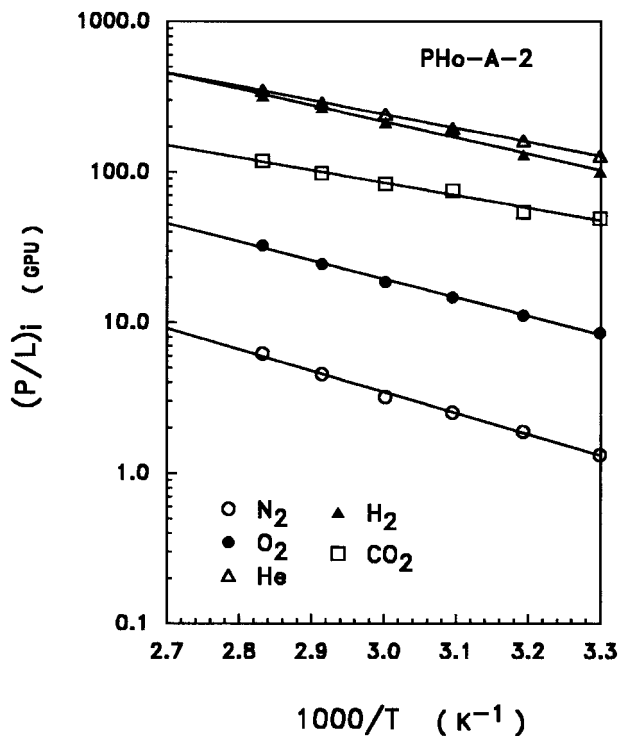

Figure 7 Pressure-normalized fluxes of N_2, O_2, CO_2, H_2, and He through the PHo-A-2 membrane as a function of reciprocal temperature.

Table II Activation Energies of Permeation for Five Gases in Three Silicone-Coated PESf Hollow-Fiber Membranes as Well as PESf and PDMS Dense Membranes

Membrane	Activation Energy of Permeation (J/mol)				
	He	H_2	CO_2	O_2	N_2
PEt-A-2	12,831	14,789	12,604	21,743	27,949
PPr-A-2	13,919	18,183	13,438	16,539	16,505
PHo-A-2	17,768	20,596	16,010	23,682	26,891
PESf[a]	15,470	16,971	12,673	20,170	26,100
PDMS[a]	9,878	7,740	−3,298	6,055	5,617

PESf: polyethersulfone; PDMS: silicone rubber.
[a] From Wang.[16]

hollow-fiber membranes have been calculated by simply taking the ratios of the permeability coefficients or the pressure-normalized fluxes of a gas pair. Figures 8–11 compare the results for the gas pairs of H_2/N_2, He/N_2, CO_2/N_2, and O_2/N_2 in these membranes. It is seen that the selectivities of H_2/N_2, He/N_2, and CO_2/N_2 in PESf dense membranes (PEt-A-2 and PHo-A-2) decrease much more rapidly with increasing temperature

than do those in the PDMS and PPr-A-2 membranes. Gas permeation in these membranes depends mainly on gas diffusion in polyethersulfone, and the diffusion coefficient strongly depends upon the size of gas molecule.[19] This explains the observed sharp drop in selectivity for gas pairs with large differences in gas molecule size, such as H_2/N_2 and He/N_2, as compared with small differences in gas molecule size, such as O_2/N_2 in
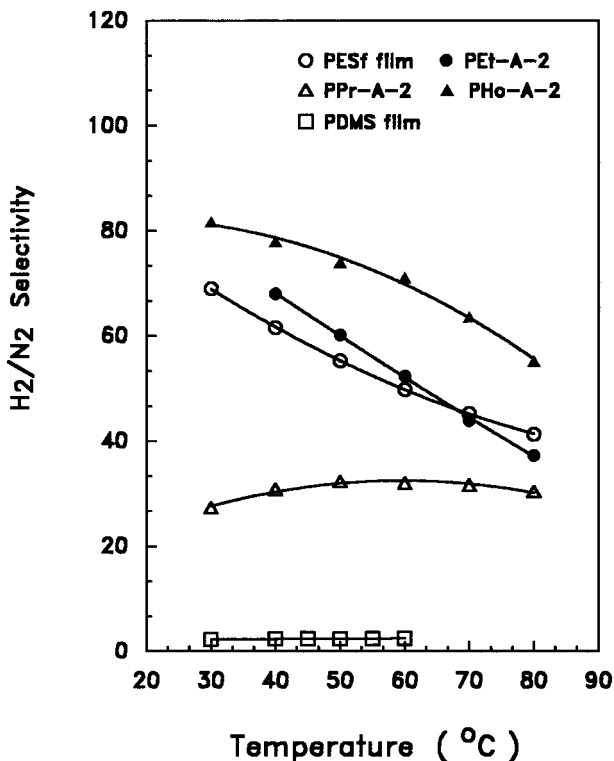

Figure 8 Effect of temperature on the selectivity of H_2/N_2 for PESf dense membrane, PDMS dense membrane, and three silicone-coated PESf asymmetric membranes.

Figure 9 Effect of temperature on the selectivity of He/N_2 for PESf dense membrane, PDMS dense membrane, and three silicone-coated PESf asymmetric membranes.
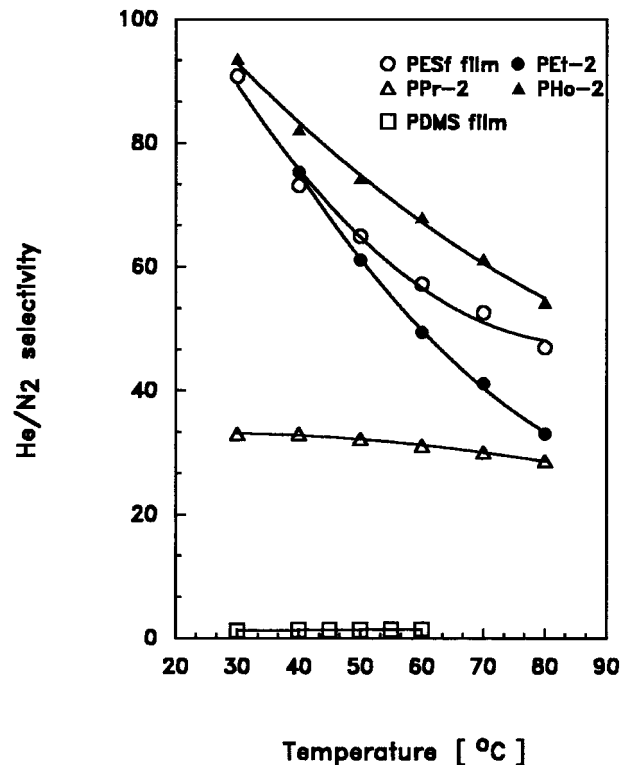
these membranes. For CO_2, the fast decrease in solubility with increasing temperature also results in a sharp drop in CO_2/N_2 selectivity. The results reveal that the existence of the substructure resistance caused the sharp drop in the selectivity with increasing temperature. For PPr-A-2 and PDMS membranes, temperature has little effect on the selectivity because the activation energies of permeation for these gases have smaller differences compared with the other membranes.

CONCLUSIONS

Permeabilities of He, H_2, CO_2, O_2, and N_2 through three silicone-coated polyethersulfone asymmetric hollow-fiber membranes with different structures have been investigated as a function of pressure and temperature and compared with those of PESf and PDMS dense membrane. The pressure-normalized fluxes of the gases through these asymmetric membranes are not sensitive to change in pressure and do not appear to follow the dual-mode mobility model. The activation energies of permeation of the gases through the
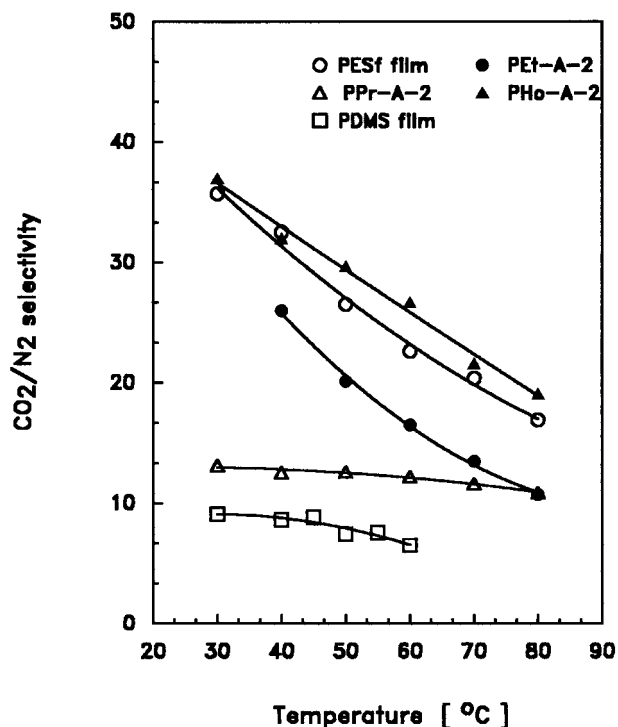

Figure 11 Effect of temperature on the selectivity of O_2/N_2 for PESf dense membrane, PDMS dense membrane, and three silicone-coated PESf asymmetric membranes.
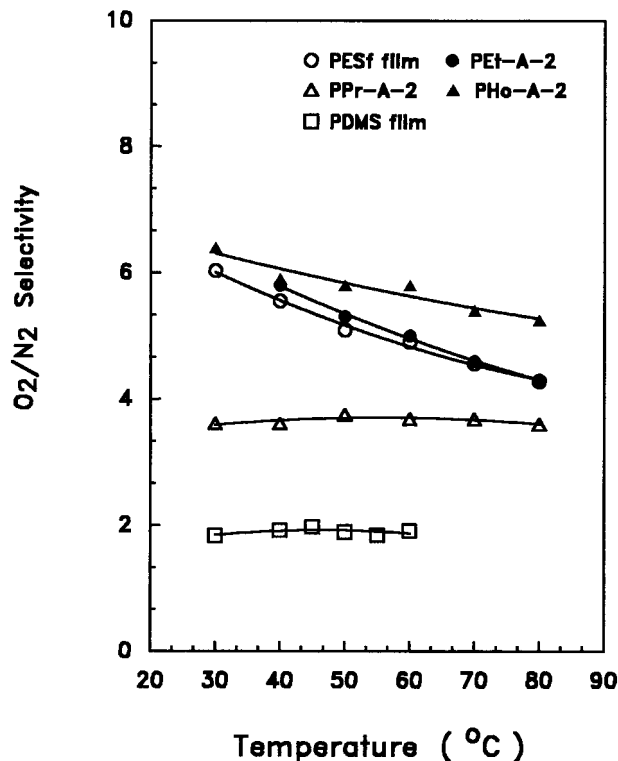
PESf asymmetric membranes may be larger or smaller than those of PESf dense membrane, which was affected by the membrane structure (both skin layer and sublayer). The resistance due to sublayer and/or the inner skin layer of the hollow fiber may reduce the activation energy of gas permeation, particularly for the fast gases. The membrane with larger surface porosity tends to exhibit smaller activation energy of permeation for the slow gases. The difference in activation energies of a gas pair may significantly alter the selectivity with temperature, especially between a fast gas and a slow gas. The data on the pressure dependence and temperature dependence of gas permselection properties in PESf dense membrane and in the silicone-coated PESf asymmetric membranes with different structures provide useful information for the selection of suitable operating conditions for the membrane systems and offer a better understanding of the membrane structure.

Figure 10 Effect of temperature on the selectivity of CO_2/N_2 for PESf dense membrane, PDMS dense membrane, and three silicone-coated PESf asymmetric membranes.

REFERENCES

1. R. E. Kesting and A. K. Fritzsche, *Polymeric Gas Separation Membranes,* Wiley, New York, 1993.
2. W. J. Koros and G. K. Fleming, *J. Membrane Sci.,* **83,** 1 (1993).
3. J. M. S. Henis and M. K. Tripodi, *J. Membrane Sci.,* **8,** 233 (1981).
4. K. Kimmerle, T. Hofmann, and H. Strathmann, *J. Membrane Sci.,* **61,** 1 (1991).
5. A. Fouda, Y. Chen, J. Bai, and T. Matsuura, *J. Membrane Sci.,* **64,** 263 (1990).
6. J. L. Lopez, S. L. Matson, J. Marchese, and J. A. Quinn, *J. Membrane Sci.,* **27,** 301 (1986).
7. K. A. Lundy and I. Cabasso, *Ind. Eng. Chem. Res.,* **28,** 742 (1989).
8. I. Pinnau, J. G. Wijmans, I. Blume, T. Kuroda, and K. V. Peinnemann, *J. Membrane Sci.,* **37,** 81 (1988).
9. K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, *J. Chem. Eng. Japan,* **19,** 431 (1986).
10. D. Wang, K. Li, and W. K. Teo, *J. Membrane Sci.,* **105,** 89 (1995).
11. P. H. Pfromm, I. Pinnau, and W. J. Koros, *J. Appl. Polym. Sci.,* **48,** 2161 (1993).
12. H. Kumazawa, J.-S. Wang, and E. Sada, *J. Polym. Sci., Part B: Polym. Phys. Ed.,* **31,** 881 (1993).
13. I. Pinnau, M. W. Hellums, and W. J. Koros, *Polymer,* **32**(14), 2612 (1991).
14. C. P. Smith, *CHEMTECH,* **May,** 290 (1988).
15. J. S. Chiou, Y. Maeda, and D. R. Paul, *J. Appl. Polym. Sci.,* **33,** 1823 (1987).
16. D. Wang, Ph.D. thesis, The National University of Singapore, 1995.
17. D. Wang, K. Li, and W. K. Teo, *J. Membrane Sci.,* **115,** 85 (1996).
18. R. E. Kesting, A. K. Fritzsche, M. K. Murphy, A. C. Handerman, C. A. Cruse, and R. F. Malon, U. S. Pat. 4,871,494 (1989).
19. P. Meares, *Polymers: Structure and Bulk Properties,* Van Nordstrand, London, 1985, p. 381.