Pervaporation of Water–Ethanol Mixtures through Polydimethylsiloxane Block-Copolymer Membranes

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ABSTRACT: Pervaporation and sorption behavior of water–ethanol mixtures was investigated on block copolymers of polydimethylsiloxane (PDMS)–polysulfone (PS) and of PDMS–PS–poly(4-hydroxystyrene) (PHS) as well as on PDMS. The preferential permeation of ethanol through PDMS membranes was attributed to both the preferential sorption of ethanol and rather small differences in the diffusivities between ethanol and water components (6.4×10^{-6} and 14×10^{-6} cm^2 s^{-1}, respectively, at 25°C and an ethanol content in the feed (x_E) of 10 wt%). The block copolymers were considered to have microphase-separated structures, of which the continuous PDMS phase practically contributed to the permeation. The high sorption in the block copolymers was mainly attributed to the disperse phases and contributed little to the permeation. PDMS–PS–PHS block copolymers having PDMS weight fraction (w_{PDMS}) of 0.6—0.7 showed permeabilities as high as commercial silicone rubber ($w_{PDMS} = 0.7$) and a little lower selectivity of pervaporation ($\alpha_p = 7.7$ at $x_E = 10$ wt%) as compared with that of PDMS ($\alpha_p = 8.8$—9.4). They were superior to PDMS–PS block copolymers ($w_{PDMS} = 0.5$—0.6) as for both the selectivity and the permeability. Composite membranes comprising a uniform ultrathin layer of a PDMS–SP–PHS block copolymer on a microporous support had fairly high performance (the permeation rate of 4.5 kg m^{-2} h^{-1} and $\alpha_p = 6.8$) and durability in the pervaporation of a dilute ethanol solution.

KEY WORDS   Pervaporation / Sorption / Water-Ethanol Mixtures / Block Copolymers / Polydimethylsiloxane / Polydimethylsiloxane–Polysulfone Copolymers / Polydimethylsiloxane–Polysulfone–Poly(4-hydroxystyrene) Copolymers / Composite Membranes /

Pervaporation process has been of much interest because of the prospect of the separation of azeotropic, close-boiling or aqueous organic mixtures with saved energy. Many studies have focused on the separation of water–ethanol mixtures by pervaporation.[1-15] Most membranes so far investigated permeate water preferentially.[1-10] The water-permeable membranes can be effectively used to dehydrate ethanol solutions concentrated upto near the azeotrpic point by distillation.[4,5] On the other hand, ethanol-permeable membranes may be applied directly to dilute aqueous solutions instead of distillation, if their perm-selectivity is enough high. Polydimethylsiloxane (PDMS) is a typical example of ethanol-permeable membranes.[11-13,16] PDMS has poor film-forming properties; it is usually used as a cross-linked, silica-filled film thicker than 25μm.[17] This disadvantage has been overcome by block-copolymerizing PDMS with a polymer having the excellent film-forming properties such as bisphenol-A polycarbonate (PC),[18] polysulfone

(PS) and poly(4-hydroxystyrene) (PHS).[19] From these types of copolymers, uniform, defect-free and ultrathin membranes have been fabricated and used for gas separation processes.[18,19] However, the liquid permeation properties of these copolymer membranes have not been investigated hitherto. It is interesting to investigate membrane performance of these copolymers in the water–ethanol system in comparison with that of PDMS.

In the present paper, pervaporation and sorption experiments in the water–ethanol system were carried out for alternating block copolymers of PDMS–PS and ternary ones of PDMS–PS–PHS as well as for PDMS.

EXPERIMENTAL

Materials and Membrane Preparation

PDMS films containing 30 wt% silica were supplied by Shin-etsu Chemical Industries Ltd. Another type of filled PDMS film was prepared by casting a toluene solution of KE-42S (or 45S)-RTV (Shin-etsu) containing fine silica particles (10—15 or 15—20 μm in diameter) on clean Teflon plates. Unfilled PDMS films, which were prepared by press-curing a gum containing 0.1% of vinyl groups with 0.5% 2,5-dimethyl-2,5-*bis*(*t*-butylperoxy)hexane for 10 min at 170°C followed by a postcure at 200°C for 4 h, were supplied by Shin-etsu Chemical Industries Ltd. Another type of unfilled PDMS film was also prepared from a sample of KE-42S-RTV without filler. These films were immersed in ethanol for a day and dried at 70°C under a vacuum.

PDMS–PS and PDMS–PS–PHS block copolymers were prepared as described elsewhere by one of the authors.[19] In order to control the content of PDMS copolymerized with PHS, the concentration of hydroxy group in PHS was adjusted by trimethylsilylation prior to the copolymerization reaction. This was necessary to contain the solvent–soluble ternary copolymers. Films of the copolymers were prepared by casting their 2—5 wt% benzene solutions on clean mercury surfaces and then by evapoaring the solvent slowly for a day at room temperature. Table I shows the characterization of the homogenous membranes used in this paper.

Composite membranes of PDMS were prepared by means of dip-coating.[13] Poly(vinylidene fluoride) (PVDF) (hydrohobic type of Durapore filters with pore size of 0.22 or 0.45 μm, Milipore Corp.) and polypropylene (PP) (Celgard-2400 and -2500, Celanese Corp.) were used as support layers. Support layers were immersed in toluene solutions (5—20 wt%) of KE-42S (or 45S)-RTV for 1—5 min at room temperature and, after slow evaporation of solvent, composite membranes were obtained. In some cases, dipping-treatment was repeated.

Composite membranes of a PDMS–PS–PHS block copolymer (T-2) were prepared as follows. A single drop of a dilute benzene solution (2—3 wt%) of the copolymer was cast on a water surface at room temperature. After solvent evaporation, a ultrathin film remained on the surface and was applied to the microporous support mentioned above.

All the membranes prepared thus were dried under a vacuum at 70°C before use.

Measurements

The pervaporation experiments were carried out by an ordinary method.[12] The pervaporation apparatus consisted of a pervaporation cell made of stainless steel, a circulation pump or a mechanical stirrer to agitate the feed (100—300 cm^3), traps cooled by liquid nitrogen to condense the permeate, and a vacuum line. The cell was placed in a thermostated water-bath. The down-stream pressure was maintained below 130 Pa. The membrane area in contact with the feed was 19.6 cm^2.

The composition analysis was performed on a Shimadzu 8AT gas chromatograph equipped with 1 m-long columns packed with either Porapak Q or polyethylene glycol 1000 supported on Shimalite F.

Pervaporation of Water–Ethanol through PDMS Copolymers

Table I. Characterization of homogeneous membranes

Code	Membrane	w_{PDMS} [—]	Density g/cm³	Typical thickness μm	Block sequence length			$\bar{M}_w$
					l (PHS)	m (PDMS)	n (PS)	
H-1	PDMS (press-cured, nonfiller)	1	0.974	500				
H-2	PDMS (KE42S-RTV, nonfiller)	1	0.974	500				
H-3	PDMS (KE42S-RTV, 15% SiO$_2$)	0.85	1.065	300				
H-4	PDMS (KE45S-RTV, 15% SiO$_2$)	0.85	1.057	300				
H-5	PDMS (commercial, 30% SiO$_2$)	0.70	1.176	137, 50				
B-1	PDMS–PS block copolymer	0.60	1.090	87		35	15	1×10^5
B-2	PDMS–PS block copolymer	0.50	1.096	39, 49		51	8	6×10^4
T-1	PDMS–PS–PHS block copolymer[a]	0.67	1.044	72	20	40	11	10^5–10^6
T-2	PDMS–PS–PHS block copolymer[a]	0.60	1.057	59	40	50	10–15	10^5–10^6
T-3	PDMS–PS–PHS block copolymer[a]	0.65	1.074	56	40	18	10–15	10^5–10^6

[a] Fractions of the trimethylsilylation (see the text) are 70, 70, and 45% for T-1, -2, and -3, respectively.

PS

PDMS

PHS

PDMS–PS block copolymer

PDMS–PS–PHS block copolymer
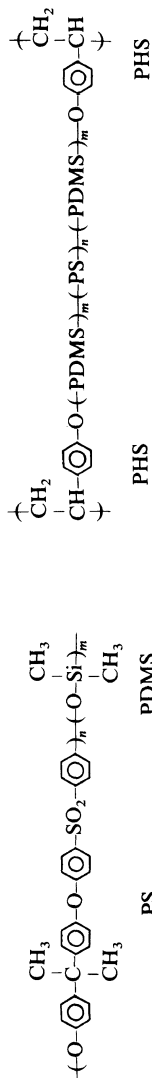
In sorption experiments, the following thick films were used because of the low solubility of water–ethanol mixtures: 1—3 mm in thickness and about 2 g in weight for H-1, H-2, and H-3, and 0.5 mm and 1 g for B-2 and T-2. Three to ten film-samples were dried in a vacuum at 70°C and then weighed. They were soaked in a binary mixture at 25°C for 10—40 h. When the sorption equilibrium was reached, each of the samples was quickly taken out of the mixture, wiped with tissue paper, and weighed in a closed flask to determine the solubility (S, defined as g-solvent per 100-g-dry-polymer). After that, they were soaked in the mixture for another 3 h. After being wipped with tissue paper, two or four samples were placed in a glass tube initially-dried and subjected to the following desorption procedure to determine the composition of the sorbed liquid. The glass tube was then connected to a vacuum line through a trap cooled by liquid nitrogen. The films were desorbed and the sorbed liquid was collected in the trap and analyzed by gas chromatography. The desorbed film-samples showed the same weights as the initial ones within ± 0.15 mg. The sorption data presented below are the average of 6—15 measurements for the solubility and 2—4 measurements for the composition.

RESULTS AND DISCUSSION

Pervaporation and Sorption through and in Homogeneous Membranes

Figure 1 shows effect of feed composition (weight percentage of ethanol, x_E) on permeation rates for a PDMS–PS–PHS block copolymer membrane (T-2). In the dilute solutions ($x_E \leq 20$—30%), both the total permeation rate (Q) and the partial one of ethanol (q_E) increased linearly with an increase in x_E as shown by the solid and dotted lines, respectively, while the partial permeation rate of water (q_W) decreased linearly with an increase in x_E as shown by the broken line. In the region of 20—30% $< x_E < 90\%$, both Q and q_E
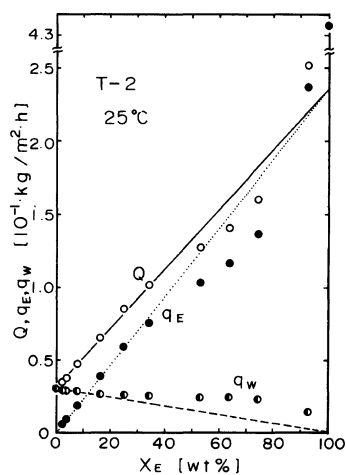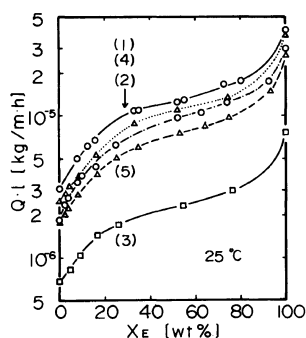

Figure 1. Effect of feed composition on permeation rates for a T-2 membrane.

deviated downward from the line. In the region of $x_E \geq 90\%$, both Q and q_E increased significantly because of swelling of the membrane ($S = 1$—8 g-solvent/100g-dry-polymer as will be shown in Figure 6). The similar dependence of the permeation rates on x_E was observed for the other membranes investigated in this paper.

For the steady state, the partial permeation rate q_i of a component i may be expressed by eq 1.[4]

$$q_i = \frac{\bar{D}_i(C_{i,1} - C_{i,2})}{l} \qquad (1)$$

where $\bar{D}_i$ is the concentration-averaged diffusivity, $C_{i,1}$ and $C_{i,2}$ the concentration of the component at the upstream and the downstream surfaces of a membrane, l the thickness of the membrane. The dependence of the permeation rates on the membrane thickness was examined at x_E of 10 and 35% at 25°C in the range of 0.5—1 mm for H-1, 0.15—1.5 mm for H-3, 0.05—1 mm for H-5 and 0.03—0.2 mm for B-2 and T-2. Q, q_E, and q_W were inversely proportional to l, and the composition of the permeate did not depend on it, implying that eq 1 is applicable to the present system. Thus, we compared the permeability
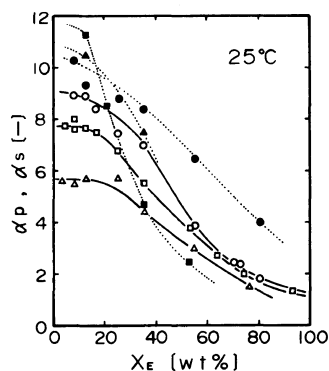
Figure 2. Effect of feed composition on specific permeation rate for (1) H-3, (2) H-5, (3) B-2, (4) T-1, and (5) T-2 membranes.
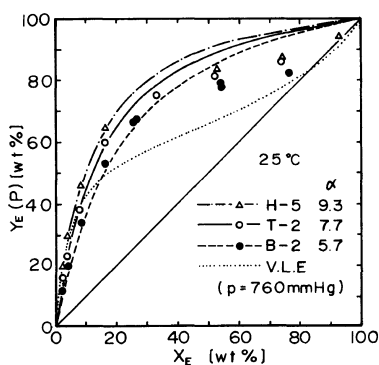
Figure 3. Effect of feed composition on permeate composition for H-5, B-2, and T-2 membranes. The dotted line is the liquid-vapor equilibrium curve. The other lines were calculated from eq 2 using the α_p values observed for the dilute solutions.

Figure 4. Effect of feed composition on separation factors of pervaporation and sorption for H-3, B-2, and T-2 membranes.

Membrane	Pervaporation	Sorption
H-3	—○—	---●---
B-2	—△—	---▲---
T-2	—□—	---■---

Table II. Activation energies of permeation rates at $X_E = 8\%$

Membrane	ΔE_p	$\Delta E_{p,E}$	$\Delta E_{p,W}$
	kJ mol^{-1}		
H-5	35.6	36.7	34.8
B-2	37.7	39.1	36.9
T-2	36.9	38.4	35.9

$$\alpha = \frac{y_E/(1-y_E)}{x_E/(1-x_E)} \qquad (2)$$

of the membanes with different thickness using the specific permeation rate, *i.e.*, the product of Q and l, (Ql). As shown in Figure 2, there were clear differences in the magnitude of Ql among various membranes, but not in its dependence on x_E.

Figure 3 shows effect of feed composition on permeate composition (weight percentage of ethanol, $y_E(p)$) for three types of membranes, as well as the liquid-vapor equilibrium curve. The separation factor of pervaporation (α_p) was calculated from eq 2 and shown in Figure 4.

The α_p was almost constant for dilute solutions ($x_E < 20\%$), while it decreased with an increase in x_E.

The activation energies of Q, q_E, and q_W (ΔE_p, $\Delta E_{p,E}$, $\Delta E_{p,W}$) are listed in Table II. They were very similar among three types of membranes, although being in the order of H-5 < T-2 < B-2 within very small differences. For every membrane, $\Delta E_{p,E}$ was a little larger than $\Delta E_{p,W}$, resulting in the increase in α_p with an increase in temperature, as shown in Figure 5.

Figure 6 shows effect of feed composition on the solubility for three types of membranes. There were clear differences both in its magnitude and in its dependence on x_E among them.
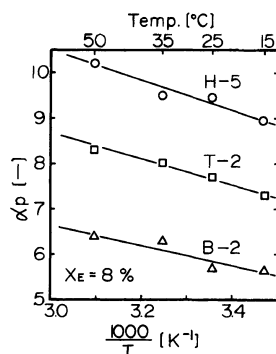
Table III. Pervaporation and sorption data measured for a feed solution of $X_E = 10\%$ at 25°C

Code	v_{PDMS} [—]	α_p [—]	α_s [—]	Ql [a]	S [b]	P/P_{PDMS} [—]	Φ [—]
H-1	1	8.9	18.7	5.5	0.17	1	—
H-2	1	8.8	21.1	6.0	0.21	1	—
H-3	0.92	8.9	10.1 $(2.4)^c$	5.5	0.27 $(0.61)^c$	0.92	1.0
H-4	0.92	9.4	—	5.6	—	0.93	1.0
H-5	0.85	9.3	—	3.8	—	0.69	1.22
B-1	0.65	6.2	—	1.81	—	0.33	2.0
B-2	0:56	5.7	10.6 $(10.1)^c$	1.10	0.80 $(1.45)^c$	0.200	2.8
T-1	0.72	7.7	—	4.2	—	0.76	0.94
T-2	0.65	7.7	11.5 $(11.0)^c$	3.1	1.03 $(2.35)^c$	0.56	1.16
T-3	0.71	6.9	—	2.05	—	0.37	1.9

[a] $10^{-6} \, \mathrm{kg \, (m \, h)^{-1}}$.
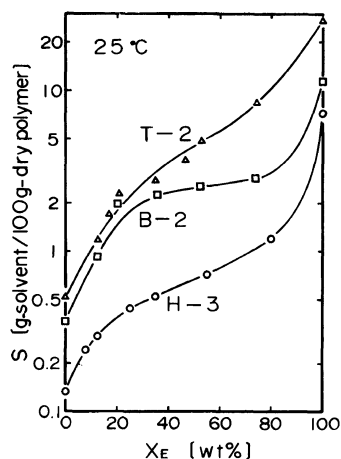[b] g-solvent/100 g-dry polymer.
[c] The values estimated from eq 4 for the disperse phases.

Figure 5. Effect of temperature on separation factor of pervaporation for H-5, B-2, and T-2 membranes.

Figure 6. Effect of feed composition on solubility for H-3, B-2, and T-2 membranes.

The separation factor of sorption (α_s) was calculated from eq 2, using the weight percentage of ethanol in the sorbed liquid ($y_E(s)$) and shown in Figure 4.

In the case of ethanol-permeable membranes, the performance for dilute solutions is important. Table III shows the pervaporation and sorption data measured for a feed solution of $x_E = 10\%$ at 25°C among all the membranes used in this paper.

Filled PDMS membranes have microphase-separated structures which comprise micro-domains of SiO_2 filler in a continuum of PDMS. The glass transition temperatures (T_g) of sulfone blocks were found from DSC measurements to be 157°C and about 145°C for B-1 and B-2, respectively. These values of T_g were much lower than that of PS (182°C) probably because of the short block length. The T_g of PHS blocks was found to be about 100°C for PDMS–PHS block copolymers with

PHS block length of 40. However, for the PDMS–PS–PHS block copolymers, no T_g point attributed to PHS or PS blocks was observed from DSC thermograms. It is well known that PDMS–PC block copolymers have microphase-separated structures.[20] The presence of the microphase separation in PDMS–PS–PHS block copolymers has been suggested from the dependence of O_2 gas permeability on PDMS content.[19] Judging from these facts, it is likely that both PDMS–PS and PDMS–PS–PHS block copolymers have microphase-separated structures comprising microdomains of PS and PHS in a continuum of PDMS.

Both PS and PHS are almost impermeable as compared with PDMS. Therefore, it is reasonable to consider that the permeation in these block copolymers practically occurs in a continuous PDMS phase, as in the case of filled PDMS. This is suppoted by the fact that the dependence of Q, q_E, q_W, and α_p on the temperature and feed composition was very similar among three types of membranes, in spite of clear differences in their magnitude, as described above. For this situation, the permeability P may be expressed by eq 3.[3,21,22]

$$P = \frac{v_{PDMS} P_{PDMS}}{\Phi} \qquad (3)$$

where v_{PDMS} is the volume fraction of PDMS, P_{PDMS} the permeability in the homopolymer of PDMS, and Φ the impedance factor. The Φ values were estimated from eq 3 using the values of P/P_{PDMS} which were obtained from the ratios of Ql to that of the corresponding PDMS (H-1 or H-2). These values are also listed in Table III.

For simple additivity of the sorptions in the two phases, one has eq 4.

$$S = w_{PDMS} S_{PDMS} + w_D S_D \qquad (4)$$

where w is the weight fraction of each phase, and the subscripts PDMS and D denote the continuous PDMS phase and the disperse ones, respectively. Both S and α_s of the dis-

perse phases (SiO_2 filler, PS, and PHS (and PS) for H-3, B-2, and T-2, respectively) were estimated from eq 4 and are shown in parentheses in Table III. The sorption in these disperse phases is considered to hardly affect the steady-state permeation, because the permeation practically occurs in the continuous PDMS phase. The high sorption in the PDMS-PS and PDMS–PS–PHS block copolymers were mainly attributed to the disperse phases and contributed little to the permeation, as can be seen in Table III.

For unfilled PDMS membranes, α_s was larger than α_p by a factor of about two at $x_E = 10\%$, indicating that the preferential permeation of ethanol through PDMS membranes is due to the preferential sorption of ethanol because of the water-repellent property of PDMS. The diffusivities of ethanol and water components ($\bar{D}_E$ and $\bar{D}_W$) were estimated from eq 1 to be 6.4×10^{-6} and $14 \times 10^{-6} \, cm^2 \, s^{-1}$, respectively, at 25°C and $x_E = 10\%$ for H-1. This difference between $\bar{D}_E$ and $\bar{D}_W$ is rather small considering the fairly large difference in the effective molecular size between ethanol and water (the kinetic radii: 0.2604 and 0.1592 nm, respectively[23]). This seems due to the large free-volume in PDMS because of both almost free rotation of Si–O bonds and the weak molecular interaction (solubility parameter, $15.3 \, (J \, cm^{-3})^{1/2}$). This is another reason why PDMS permeates ethanol preferentially.

Silica filler hardly affects both α_p and the permeation rate through the PDMS phase for silicone-RTV rubbers, while it caused a little impedance effect for the commercial silicone rubbers.

For PDMS–PS block copolymers with PDMS content more than 70%, reproducible and reasonable results were not obtained; most samples showed rather large values of Ql with rather low ones of α_p for the high PDMS content, suggesting the presence of defects or pinholes in the films. Thus, the copolymers with PDMS content of 50—60% were selected

as the optimum. This is similar to the case of PDMS–PC block copolymers for O_2–N_2 gas separation.[18] Both B-1 and B-2 were apparently stiff and looked like PS membranes rather than PDMS ones. They showed fairly large reductions in α_p and Ql, as. compared with H-1. The copolymerized PS blocks caused large Φ values more than two. The similar large impedance effect has been oberved for the permeation of propane gas through PDMS–PC block copolymers[24]; the Φ values were calculated from the reported results to be 2.2 and 3.5 for the samples having v_{PDMS} of 0.60 and PDMS block length of 40 and 20, respectively.[24] The Φ has also been reported to increase with increasing molecular size of penetrant for the styrene-butadiene block copolymers.[22] If this is the case for the PDMS–PS block copolymers, the Φ value will be larger for the ethanol component than for the water one, resulting in reductions in α_p for the block copolymers. Therefore, it seems a poor selection for organics-permeable membranes to block-copolymerize PDMS with rigid polymer chains such as PC and PS upto the content more than 30%, because of the relatively large molecular sizes of the organics.

PDMS–PS–PHS block copolymers have been reported to have excellent film-forming properties even for the high PDMS content of 70—90%.[19] In the present paper, the copolymers with PDMS content of 60—70% were used, taking the fact into account that in the application to composite membranes the limiting effective membrane thickness has been reported to rather increase for the copolymers with PDMS content of 80—90%.[19] Both T-1 and T-2 having PDMS block length more than 40 were as soft as PDMS membranes, while T-3 having that of 18 was apparently a little stiff. For the former membranes, there was no appreciable impedance effect, although the α_p value (7.7) was slightly lower than that (8.8) for H-1. On the other hand, for the latter membranes, there were both the fairly large

impedance effect and a fairly large reduction in α_p. The increase in Φ with a decrease in PDMS block length, which has also been found for the gas permeation through the PDMS–PS–PHS and PDMS–PC block copolymers,[19,24] suggests that the restriction to mobility in the continuous PDMS phase becomes significant with decreasing PDMS block length. The Φ has been found to be 1.36 for the O_2 gas permeation through the PDMS–PS–PHS block copolymer with PDMS content of 72%.[19] This value is a little larger than those (0.94 and 1.16) for the pervaporation of the dilute ethanol solution. A probable explanation of this is that the high sorption in the microdomains in the pervaporation might cause a reduction in the chain immobilization factor, *i.e.*, one of two original factors determining Φ.[21,22]

It is noted that T-1 was more permeable than H-5 or a commercial silicone rubber, and that the PDMS–PS–PHS block copolymers are much superior to the PDMS–PS ones as for the selectivity and permeability in the pervaporation of water–ethanol mixtures.

Pervaporation of a Water–Ethanol Mixture through Composite Membranes

In order to get a high permeation rate without appreciable loss of the selectivity, composite membranes of PDMS and of PDMS–PS–PHS block copolymers were prepared. As a support layer of a composite PDMS membrane, PVDF was superior to PP from the point of uniform coating. As the copolymer for composite membranes, T-2 was used, because T-1 having the highest permeability among the copolymers might be too soft to be used in the ultrathin film state repeatedly. Durapore filters had no selectivity toward an water–ethanol mixture and very high permeation rates, while Celgard 2400 and 2500 filters had low selectivity ($\alpha_p = 4.3$ and 2, respectively) and relatively low permeation rates. As support layers of ultrathin membranes of T-2, Durapore filters with pore
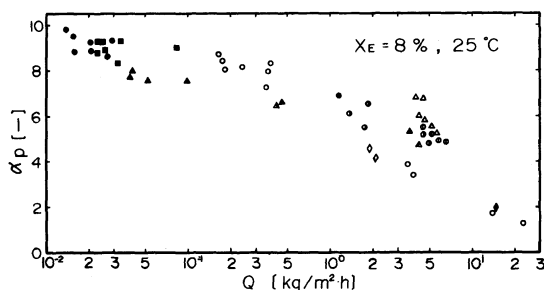
Figure 7. Plots of separation factor of pervaporation *vs.* permeation rate for various homogeneous and composite membranes. For homogeneous membranes: ■, H-5; ●, H-3 or H-4; ▲, T-2; ◇, Celgard-2400; ✦, Celgard-2500. For composite membranes: ○, H-3/PVDF (0.45 μm); ◐, H-3/PVDF (0.22 μm); ◑, H-4/PVDF (0.22 μm); △, T-2/PVDF (0.22 μm); ▲, T-2/PP (Celgard-2500).

size of 0.22 μm were mainly used because of negligible resistance of the support layer.

The pervaporation data of a dilute solution ($x_E = 8\%$) through the composite membranes at 25°C are shown by plots of α_p *vs.* Q in Figure 7. The 50 μm-thick silica (30%)-filled PDMS membranes being the thinnest among the homogeneous PDMS ones had Q and α_p values of 0.085 kg m^{-2} h^{-1} and about 9, respectively. In the case of composite PDMS membranes, Q was enhanced upto 0.4 kg m^{-2} h^{-1} with only a slight loss of α_p from 9 to 8. The effective thickness of the membranes with this Q value was 13 μm. In the region of Q above 0.5 kg m^{-2} h^{-1}, α_p decreased rapidly with an increase in Q. The decrease in α_p hardly depended on the coating materials (KE-42 or -45), although being larger for the membranes prepared from the supporters with the larger pore size of 0.45 μm. Observation by scanning electron micrography showed that the surfaces of the composite PDMS membranes with lower values of α_p were not uniform and smooth but had numerous defects.

In the case of composite T-2 membranes, Q was enhanced upto 4.5 kg m^{-2} h^{-1} with only a slight loss of α_p from 7.7 for the homogeneous ones to 6.8. This value of Q corresponded to the effective membrane thickness of 0.5 μm,

while the one calculated from both casting area and amount of the casting solution was about 0.2 μm. This discrepancy may be due to a decrease in Q because of the presence of the temperature polarization effect; that is, it may be explained by assuming a reduction in the membrane temperature by about 10°C as compared with the feed temperature. Observation by scanning electron micrography showed that these membranes had the uniform and defect-free surface layer of the copolymer on the support layer even after use in the pervaporation experiments for a dilute solution.

As for the films prepared by casting solutions of the PDMS–PS–PHS block copolymers on water surfaces, it has been reported that PDMS component was enriched in the surface layer facing air.[25] This was confirmed from the fact that the contact angle of water was a little larger for the surface layer faced air (95°) than for that faced water (90°). However, both Q and α_p did not depend on which layer was in contact with the feed solution. Similar results have been reported on the gas permeation through the copolymer films.[25]

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