Synthesis of Pyridine-Moieties-Containing Poly(acylhydrazone)s and Solute Separation Through Their Membranes

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SYNOPSIS

Poly(acylhydrazone)s containing pyridine moieties were synthesized from 2,6-pyridinedicaboxaldehyde and each of five dihydrazides. Although most of the polycondensates were insoluble or sparingly soluble and of low molecular weight, the polymers from malonyldihydrazide were highly soluble and readily gave tough films. Their performances as separation membranes were examined in reverse osmosis, gas separation, and pervaporation (PV). The membranes showed a good performance in PV and were water permselective for aqueous alcohols and aprotic solutes, showing to be very effective to break azeotropes with high separation factors and to preferentially separate water from high concentration feeds, particularly in butanols and THF. Deviation from ideal flux, swelling degree, and some physicochemical parameters such as solubility parameter, molar volume, and vapor pressure were correlated to the membrane performances in a wide range of feed concentrations of the above two solute groups. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Among a number of hitherto prepared polycondensates, polyazomethins,[1,2] and poly(acylhydrazone)s[3,4] are the two representative examples of the polycondensates that are yielded by forming carbon–nitrogen double bonds in the backbone on combining monomers. They have been utilized as thermally stable polymers[2,5,6] and electrically conducting polymers.[7,8] Poly(acylhydrazone)s are also useful for ligand polymers due to the action of nitrogens and carbonyl groups. Although most of polyazomethins, including those prepared from acetonitrile in our early study,[9] are insoluble in ordinary solvents, poly(acylhydrazone)s possess fairly high solubility towards the solvents. In addition, $-C(=O)-NH-N=CH-$ linkage in poly(acylhydrazone)s is highly polar and seems hydrophilic in view of a sequence common with the amide and hydrazide linkage. On the other hand, we have prepared various kinds of pyridine-moieties-containing polymers for water permselective membrane,[10,11] because pyridine moieties are able to form hydrogen bond with water. Our recent study has revealed that hybrid Schiff base membranes prepared from poly(allylamine), 2-pyridinecarboxaldehyde, and salicylaldehyde preferentially separated water from water-miscible organics solution under pressure and showed a more water permselective character when complexed with a transition metal salt in contact with the salt solution feed.[12] In this article we have synthesized pyridine-moieties-containing poly(acylhydrazone)s from 2,6-pyridinedicarboxaldehyde and investigated separation performance of their membranes for different kinds of feeds. As pervaporation is known to be a promising process in separation technology, pervaporation was dealt with in detail for the permselective separation of water-miscible organics solution in the various concentration including azeotrope, and for the study on the effect of physicochemical

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Table I   Polycondensation of PDCL with Various Dihydrazides[a]

Dihydrazide	Polymer Code	Temperature (°C)	Pressure (Torr)	Yield (%)	η_i^b (dL/g)
MDH	MP	70	~ 100	85.7	0.385
ODH	OP	70	atm.	83.5	—
IPDH	IPP	50	120	83.2	0.075
TPDH	TPP-1	70	atm.	83.2	0.092
	TPP-5	50	120	62.9	0.093
OBSH	OBSP-1	50	atm.	87.2	0.112
	OBSP-6	50	120	81.9	0.091
	OBSP-8	50	50	81.3	0.057

[a] Monomer concentration: 10 wt % DMSO solution except for TPDH in which HMPA was used. Reaction time : 2h.
[b] At 25°C for 0.5 wt % formic acid (IPP and TPP) and DMF (OBSP) solution.

features of the organics on their separation performance.

EXPERIMENTAL

Materials

2,6-Pyridinedicarboxaldehyde (PDCL) was prepared from 2,6-pyridinedicarboxylic acid via three steps according to the procedure for the synthesis of 4-benzyloxy-2,6-diformylpyridine:[13] esterification of the acid with methanol and thionyl chloride; reduction of the ester into dialcohol with sodium borohydride in tetrahydrofuran (THF); and oxydation of the dialcohol with selenium(IV) oxide in 1,4-dioxane (DOX), in overall yield of 34%, mp. 147.5–148°C. ^{1}H-NMR in dimethyl sulfoxide (DMSO)-d_6: δ 10.2 (s, 2H, CHO), δ 8.2 (single peak, 3H, pyridine ring). Dihydrazides were purchased from Wako Pure Chemical Industries, Ltd. (Wako) or Tokyo Kasei Kogyo Co. Ltd. (Kasei) and recrystallized before use. Dihydrazide, recrystallization solvent and mp (°C) are noted in this order: malonyl dihydrazide (MDH, Wako), ethanol, 147.5–148.0; oxalic dihydrazide (ODH, Wako), water, 233 (dec.); isophthalic dihydrazide (IPDH, Ka-

sei), ethanol, 216 (dec.); terephthalic dihydrazide (TPDH, Kasei), ethanol, 228–229; 4,4'-oxybis(benzenesulfonylhydrazide) (OBSH, Wako), ethanol, 159 (dec.). A high-quality grade of cobalt(II) chloride hexahydrate was used as received. Water-miscible organic liquids employed as organic solutes and hexamethylenediisocyanate (HMDI) were distilled before use.

Polycondensation

In a three-necked flask was placed 10 wt % DMSO solution of dihydrazide, and to this solution was added 10 wt % DMSO solution of equimolar amount of PDCL, as shown in Scheme 1. The reaction was continued with magnetic stirring under the determined conditions of temperature, pressure, and time. The solution was poured into a precipitant to precipitate the polymer. The precipitant was

Scheme 1.

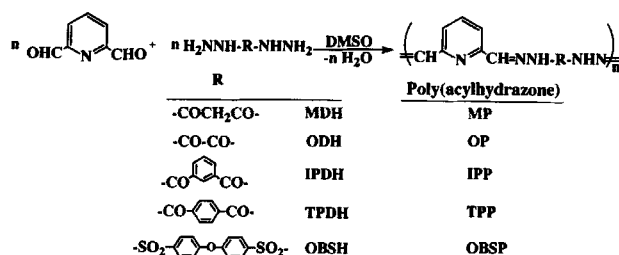**Table II   Copolycondensation of OBSH and MDH with PDCL[a]**

Polymer No.	OBSH[b] (mol %)	Yield (%)	η_i^c (dL/g)
2	67	83.7	0.099
7	50	84.3	0.114
9	40	83.7	0.122
10	30	82.9	0.120
11	20	81.0	0.144
12[d]	0	88.2	0.310

[a] Reaction conditions: 10 wt % monomer in DMSO, 40°C, 120 Torr, 2 h.
[b] Addition ratio of OBSH in total dihydrazides.
[c] At 25°C for 0.5 wt % DMF solution.
[d] A MP polymer.

Table III Results of Polycondensaton with MDH[a]

Polymer MP	Reaction Conditions			Yield (%)	η_i^b (dL/g)
	Temp. (°C)	Pressure (Torr)	Time (h)		
17	50	760	2	91.0	0.309
18	50	120	2	90.2	0.328
15	50	30	2	84.0	0.325
19	50	20	2	90.0	0.275
25-2	31	120	2	90.1	0.334
24-2	40	120	2	89.2	0.347
18	50	120	2	90.2	0.328
22-1	70	120	2	85.3	0.210
4	70	~ 20	2	85.7	0.305
24-1	40	120	1	90.6	0.337
24-2	40	120	2	89.2	0.347
25-1	31	120	1	90.1	0.354
25-2	31	120	2	90.1	0.334
25-3	31	120	4	90.9	0.327
35	40	120	2	95.5	0.233
37	40	120	2	92.3	0.267
38	40	120	2	91.7	0.249
39	40	120	2	95.7	0.309

[a] Monomer concentration: 10 wt % DMSO solution.
[b] At 25°C for 0.5 wt % DMF solution.

methanol for MDH, diethyl ether for IPDH and TPDH, and chloroform–diethyl ether mixture (1 : 1 vol) for OBSH. The solvent for reprecipitation was *N,N*-dimethylformamide (DMF) for MDH and OBSH and formic acid for IPDH and TPDH. For the last two polymers, water was used as the precipitant. The polymer from ODH was insoluble in ordinary solvents. ^{1}H-NMR of MP prepared from PDCL and MDH in DMSO-d_6: δ 3.73–4.00 (d, 2H, CH$_2$), δ 7.8–8.22 (m, 5H, pyridine ring and CH=N), and δ 11.7 (s, 2H, =N—NH—).

Copolycondensation was carried out between the mixture of various ratios of OBSH/MDH and equimolar PDCL under the conditions similar to above runs.

Membrane Preparation

Reverse osmosis membranes of MP were prepared by a solution-casting method from a DMF solution of a high concentration (15–18 wt %); the solution was cast on a glass plate with an applicator and evaporated under a reduced pressure of 10 mmHg or less at about 30°C for 4 ~ 7 h. The glass plate was put into water and the membrane was peeled off. The membrane was immersed in water at least over night before use.

For PV membranes, a frame-casting method was employed, which gave a membrane of reproducible performance and was favorable for using a larger quantity of a dilute solution containing CoCl$_2$. On a

Table IV Reverse Osmosis of MP Membranes

Membrane	Thickness $\Delta x(\mu m)$	Solute	J_1 (g/cm^2 h)	R (%)	$K_1 \times 10^8$ [cm^2/(s atm)]
MP4-12[a]	40.4	NaCl	0.0526	74.5	0.079
MP4-24[b]	95.2	NaCl	12.9	28.5	54.4
		CoCl$_2$	6.78	95.1	24.2

[a] Cast from 17.9 wt % DMF solution on a glass plate with an applicator gap of 300 μm and evaporated for 4 h.
[b] Cast from 15.0 wt % DMF solution of MP-4 containing 25.3 wt % LiCl based on MP-4 with an applicator gap of 350 μm and evaporated for 7 h.

**Table V   Pervaporation through Blend Membranes[a] of MP and the Copolycondensate**

Membrane OBM	OBSH (mol %)	Δx[b] (μm)	P × 10⁴ [(g m)/(m² h)]			α (H₂O)
			Overall	H₂O	EtOH	
1	0	131	58.2	55.0	3.19	17.3
2	10	125	53.4	50.7	2.67	19.0
3	15	141	51.9	49.4	2.52	19.6
4	20	159	48.9	46.5	2.36	21.0
5	23	90	31.0	29.6	1.41	20.9
6	25	105	22.4	21.4	0.98	21.9

[a] Polymers 2 and 12 in Table II were blended on casting along with 10 mol % HMDI based on the repeat unit. The OBSH content was calculated based on 67 mol % of Polymer 2. Feed: 50 wt % EtOH (Yanaco GTR-12L gas chromatography for concentration determination).

[b] Net thickness.

clean glass plate a metal ring frame of about 8 cm diameter and 3 cm height was put, and its outside periphery was fixed on the plate with a poly(vinyl acetate) adhesive in order to prevent the casting solution from leaking. A DMSO solution of 5.0 wt % polymer was placed into the frame and evaporated at 70°C for 15 h. When CoCl₂ was added, a complexed membrane of brown transparent appearance was formed.

For the blends of the copolycondensate and MP, 25 wt % DMSO solution containing 10 mol % HMDI, a crosslinking agent, based on the repeat unit of the polycondensate, was cast with an applicator on a DMSO swollen cellophane sheet support put on a glass plate. The cast solution was evaporated in a desiccator under a reduced pressure of 15–25 Torr at about 30°C for 6–8 h with irradiation by an infrared lamp. All the membranes prepared were immersed in water more than 24 h before use, and
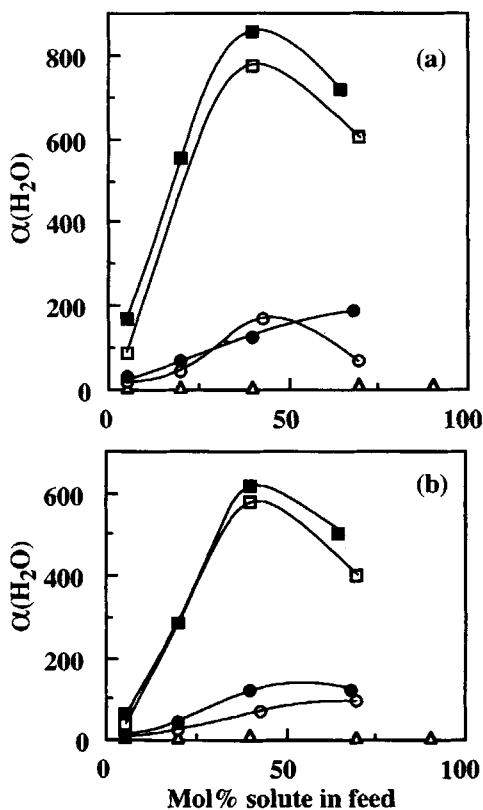
Figure 1   Separation factor of water α(H₂O) vs. feed composition. Membrane: (a) MP38, (b) MP 39 complexed. △: EtOH; ○: n-PrOH; ●: i-PrOH; □: s-BuOH; ■: t-buOH.
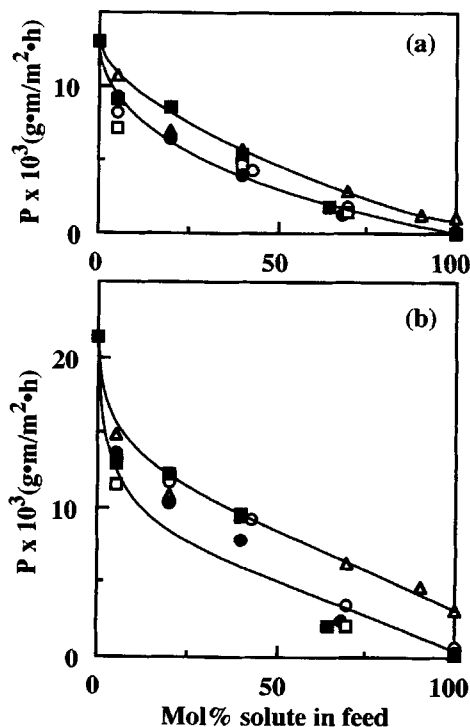
Figure 2   Total permeation coefficient P vs. feed composition. Membrane: (a) MP38, (b) MP39 complexed. △: EtOH; ○: n-PrOH; ● i-PrOH; □: s-BuOH; ■: t-BuOH.

Table VI Swelling Degree (%) at Various Feed Concentrations

Organic	MP Membrane (Complexed Membrane)/Concentration (mol %) of the Organic				
	5	20	30	40	70
EtOH	29.6 (29.4)	30.6 (29.4)		27.7 (27.1)	21.8 (22.3)
n-PrOH	31.1 (31.8)	31.1 (32.9)		29.5 (23.8)	25.7 (25.5)
i-PrOH	23.8 (25.3)	24.4 (25.5)		23.8 (23.8)	19.7 (17.8)
s-BuOH	30.0 (31.0)	32.3 (32.3)		31.3 (28.6)	19.1 (26.4)
t-BuOH	27.5 (25.5)	27.8 (27.8)		25.6 (25.5)	18.8 (21.4)
THF	32.5 (28.6)	34.4 (31.6)	34.4 (31.8)		25.9 (25.5)[a]
DOX	32.8 (30.4)	32.5 (32.3)	26.0 (28.7)	21.2 (21.3)[a]	
DMAc	33.1 (32.8)	35.2 (38.9)	45.5 (43.2)		
DMF	33.7 (31.7)	39.1 (38.0)	42.1 (40.0)		

[a] At the azeotrope concentration of 77.7 mol % for THF and 48.2 mol % for DOX.

the thickness was measured with a Sanko electromagnetic meter SL-110-SP.

Permeation

Reverse osmosis was conducted in the same manner as reported previously[14] with a batch-type apparatus of 300 mL capacity with 18.1 cm^2 effective area, using NaCl and $CoCl_2$ feeds in this order under nitrogen pressure of 7.85 MPa at 25°C. The feed concentration was 0.06 M, and the permeate concentration was measured conductometrically. The solute rejection R and hydraulic permeability K_1 were determined according to the following expressions:

$$R = 100(c - c')/c$$

$$J_1 = K_1(\Delta P - \Delta \pi)/\Delta x$$

where c and c' are feed and product concentration, respectively, J_1 is volumetric flux, ΔP pressure difference, $\Delta \pi$ osmotic pressure difference between feed and product solution, and Δx membrane thickness.

Pervaporation (PV) was carried out by using the same batch-type apparatus connected intermediately to a cold trap in liquid nitrogen. The feed was supplied in the order of increasing number of carbon: ethanol(EtOH), n-propanol(n-PrOH), iso-propanol(i-PrOH), sec-butanol(s-BuOH), t-butanol(t-BuOH), and then THF, DOX, N,N-dimethylacetamide (DMAc), and DMF. The pure organic liquid except DMAc and DMF was supplied first, followed by the organics of decreasing concentration. The pressure of the permeate side was 0.5-2 Torr. The flux J_1 was determined by the weight increase (mostly 0.1-0.2 g) in the trap for a given time. The weight increase and the composition of the permeate was checked several times by exchanging the cold trap. Close values were averaged to give the station-

ary overall permeability P [$=J_1 \times \Delta x$ (g m)/(m^2 h)] and permeate concentration. The solute permeability Ps was estimated from P and the permeate composition, and denoted by a dimension of mol m/ m^2 h. The permeate concentration was determined with a total organic carbon analyzer Shimazu TOC-500. For aqueous ethanol feed, Yanaco batch type apparatus GTR-12L was also used with a gas chromatographic analysis of the permeate. Separation factor for water $\alpha(H_2O)$ was expressed by the following equation

$$\alpha(H_2O) = (Y_w/Y_s)/(X_w/X_s).$$

where X and Y are the weight fractions of the feed and permeate, respectively, and the subscripts w and s denote water and organic solute, respectively.

Deviation coefficient or permeation ratio ϵ to represent the nonideality or the degree of the influence of one component on the other one in PV of binary mixtures was determined according to the following equations:[15,16]

$$\epsilon_i = J_i/(X_i J_i^0)$$

$$\epsilon_j = J_j/(X_j J_j^0)$$

where subscripts i and j denote the species of feed component, J is flux for the feed of composition X_i and X_j, J^0 is flux of pure component, and X is mol fraction in feed.

Oxygen and nitrogen permeability coefficients were measured in the same manner as described before.[17]

Measurements

^{1}H-NMR spectra were recorded with a JEOL JNM-PMX60 at 60 MHz with TMS as an internal stan-
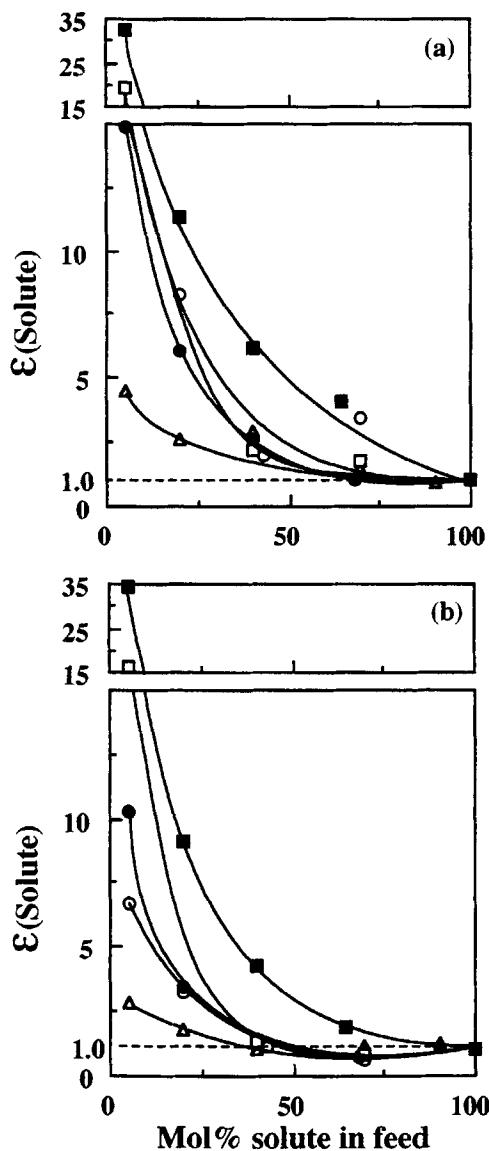
Figure 3 Deviation coefficients of solute ε(solute) vs. feed composition. Membrane: (a) MP38, (b) MP39 complexed. △: EtOH; ○: n-PrOH; ●: i-PrOH; □: s-BuOH; ■: t-BuOH.

dard. Tensile strength of membranes was measured with TOM-5 instrument of Minebea Co.

Thermal analysis was conducted with a differential scanning calorimeter DSC-50 of Shimadzu Seisakusho Co. Ltd. at a heating rate of 10°C/min.

Swelling degree was defined as the ratio of net weight increase to the weight of the membrane dried under reduced pressure of a few Torr for 24 h after equilibration with the solution at room temperature for more than 24 h. Water content is wt % of water in a wet membrane whose superficial water was blotted.

Viscosity of polymer solutions was measured for 0.5 wt % solution at 25°C and expressed as inherent viscosity $\eta_i(dL/g) = \ln \eta_r/C$, where η_r, is relative viscosity and C is concentration of the solution (g/dL).

RESULTS AND DISCUSSION

Polycondensation

The results of polycondensation of PDCL with each of five dihydrazides are summarized in Table I. The polymer that displayed the highest viscosity and film-forming property was MP. The polymers IPP and TPP were soluble in formic acid alone but did not form any film that was strong enough for separating operation. The polymer OP was insoluble in ordinary solvents. The polymer OBSP was soluble in DMF, DMSO, and hexamethylphosphoramide (HMPA), but did not form a strong film probably because of a lower viscosity. Changes in the reaction
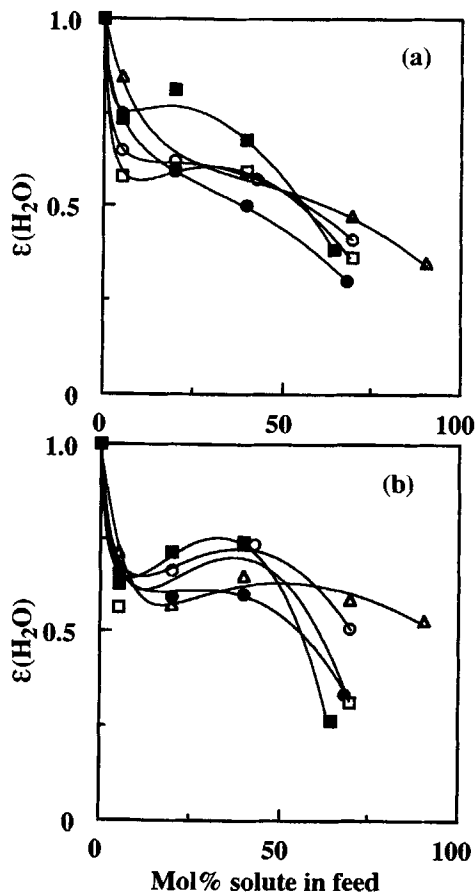
Figure 4 Deviation coefficients of water ε(H_2O) vs. feed composition. Membrane: (a) MP38, (b) MP39 complexed. △: EtOH; ○: n-PrOH; ●: i-PrOH; □: s-BuOH; ■: t-BuOH.
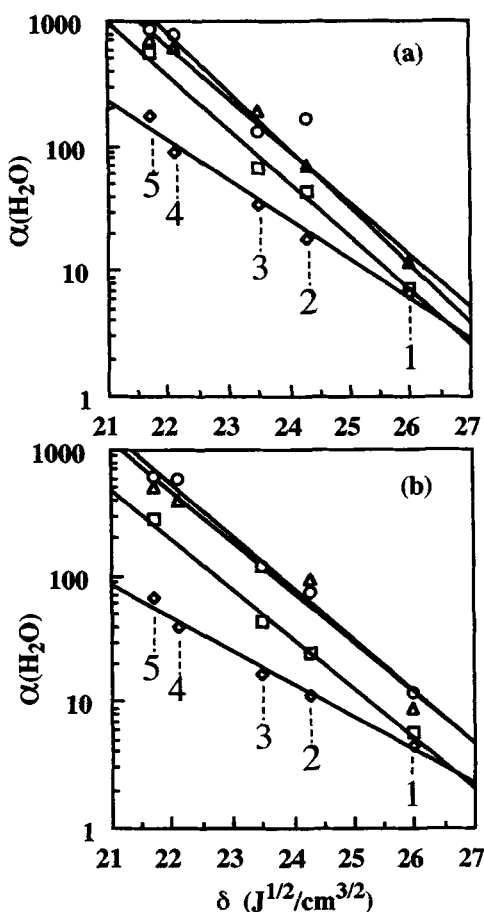
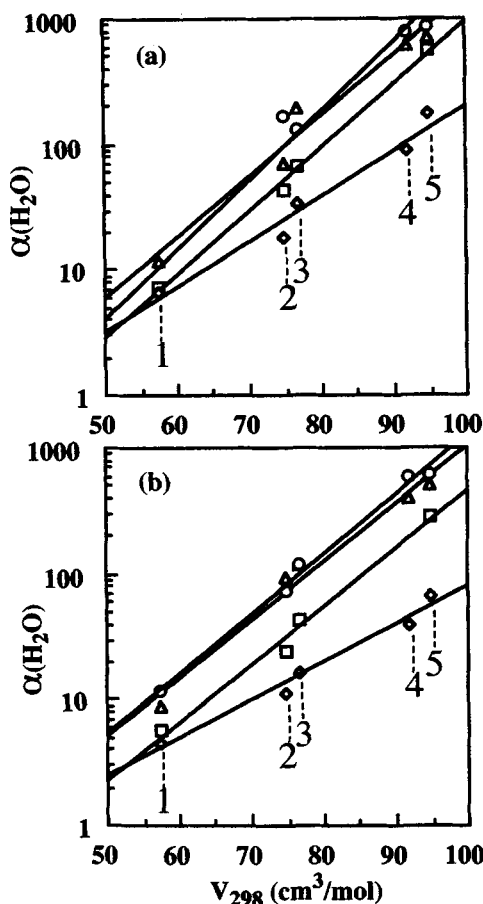**Figure 5**   Separation factor of water $\alpha(H_2O)$ vs. solubility parameter (δ). Membrane: (a) MP38, (b) MP39 complexed. △: 70 mol %; ○: 40 mol %; □: 20 mol %; ◇: 5 mol % solute in feed. 1: EtOH; 2: n-PrOH; 3: i-PrOH; 4: s-BuOH; 5: t-BuOH.

temperature up to 70°C and time fairly longer than 2 h did not give any η_i value considerably higher than 0.1. Because OBSP possesses hydrophilic groups of SO_2, films of OBSP are likely to be water permselective. Thus, copolycondensation between OBSH and MDH was carried out to give the results shown in Table II. Yields are quite similar to each other but η_i gradually increases as the OBSH content decreases or MDH increases. The difference between No. 11 and No. 12 is great, indicating that the addition of a small amount of OBSH to MDH appreciably reduces the chain length of the copolycondensate. The polymer 11 could form a film, although it was readily broken by a weak bending force. A smaller reactivity of OBSH than of MDH probably stems from a weaker basicity of H_2NNH— adjacent to —SO_2— than that adjacent to —CO—, because Hammett substituent constant of CH_3SO_2—(para) is 0.72, while that of

CH_3CO— (para) is 0.502,[18] implying that a stronger electron-withdrawing character of —SO_2— renders H_2NNH— a weaker base.

As the most reactive of the five dihydrazides were MDH, the conditions for MDH–PDCL polycondensation such as pressure, reaction temperature, and time were studied in some details. The results are tabulated in Table III. In general, a small difference is observed, depending on the conditions. It can be summarized from Table III that the conditions favorable for the formation of a higher molecular weight are 40°C for reaction temperature, 120 Torr for pressure, and 1–2 h for reaction time. Therefore, the polycondensates used for membranes were prepared under those conditions (MP35 and MP37 ~ 39).

DSC analysis of the polymers showed no apparent glass transition but clear decomposition at 272–279°C.

Figure 6   Separation factor of water $\alpha(H_2O)$ vs. molar volume (V_{298}). Membrane: (a) MP38, (b) MP39 complexed. △: 70 mol %; ○: 40 mol %; □: 20 mol %; ◇: 5 mol % solute in feed. 1: EtOH; 2: n-PrOH; 3: i-PrOH; 4: s-BuOH; 5: t-BuOH.
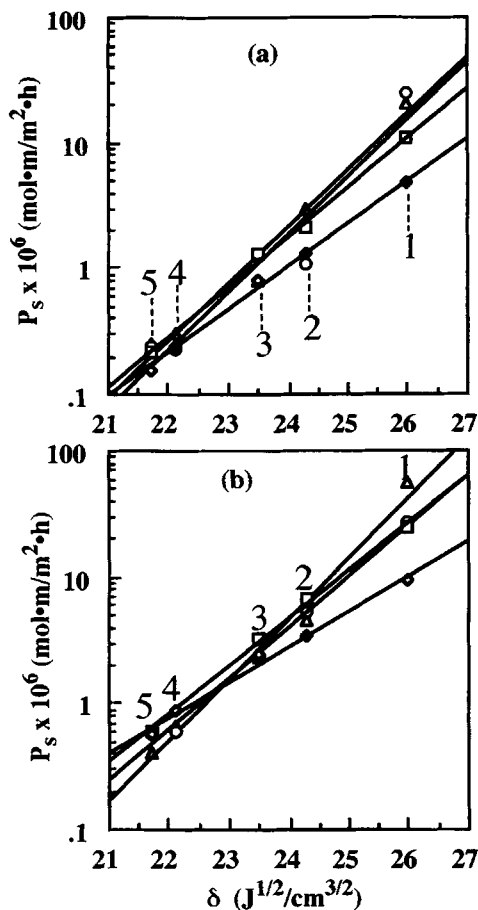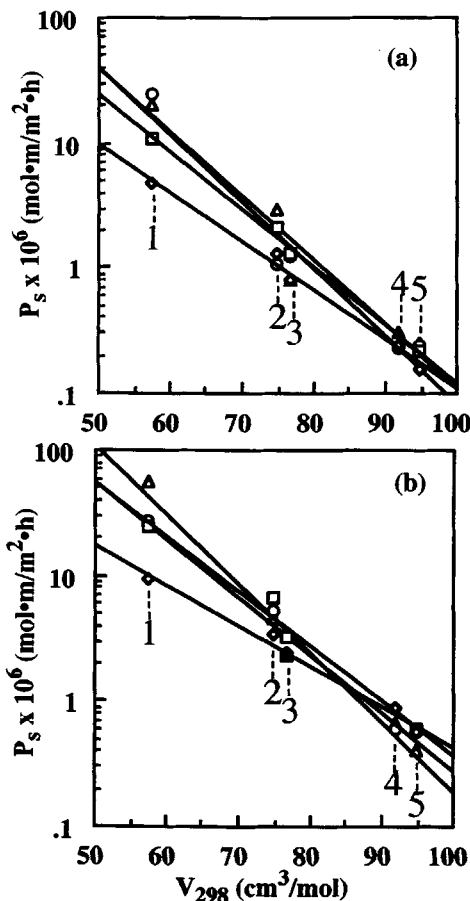
Figure 7 Permeation coefficient of solute P_s vs. volubility parameter (δ). Membrane: (a) MP38, (b) MP39 complexed. △: 70 mol %; ○: 40 mol %; □: 20 mol %; ◇: 5 mol % solute in feed. 1: EtOH; 2: n-PrOH; 3: i-PrOH; 4: s-BuOH; 5: t-BuOH.

Separation Properties of Membranes

Because MP alone gave self-supporting tough films that were endurable against a high pressure of 7.85 MPa (80 kg/cm²) and bending force, separation performance was investigated principally for MP membranes. Some of the performance data obtained in reverse osmosis are listed in Table IV. Flux J_1 and rejection R for NaCl are not high. Addition of LiCl to the casting solution on casting enhanced the flux though R remained unimproved. R of $CoCl_2$, on the contrary, was improved to a great extent because of the capture by the complexation of $CoCl_2$ with the membrane and subsequent Donnan exclusion of the charged membrane.[12,19] Although a great difference in R of MP4–24 appears to be effective to separate each solute, the R difference is likely to be diminished in view of the fact that when a mixture of NaCl and $CoCl_2$ was fed, the R difference for a

poly(allylamine) derivative membrane was reduced to about one-fourth of the difference in the R of individual permeation.[14] It can be summarized that MP polymer itself gives a reverse osmosis membrane of low R values like 74.5% for NaCl in case of no additive.

The copolycondensates of OBSH and MDH with PDCL had such a small viscosity, as shown in Table II, that they yielded only weak membranes. Therefore, a blend membrane of Nos. 2 and 12 in Table II was made by casting on cellophane. The cellophane support was necessary because a self-supporting membrane without cellophane was still too weak to resist the pressure and bending force. Because MP is hydrophilic due to its polar character and blend polymer contains hydrophilic SO_2 groups, the blend membrane was anticipated to preferentially separate water from an aqueous organic solution. Table V summarizes the results of separation factor and individual permeabilities in PV against

Figure 8 Permeation coefficient of solute P_s vs. molar volume (V_{298}). Membrane: (a) MP38, (b) MP39 complexed. △: 70 mol %; ○: 40 mol %; □: 20 mol %; ◇: 5 mol % solute in feed. 1: EtOH; 2: n-PrOH; 3: i-PrOH; 4: s-BuOH; 5: t-BuOH.
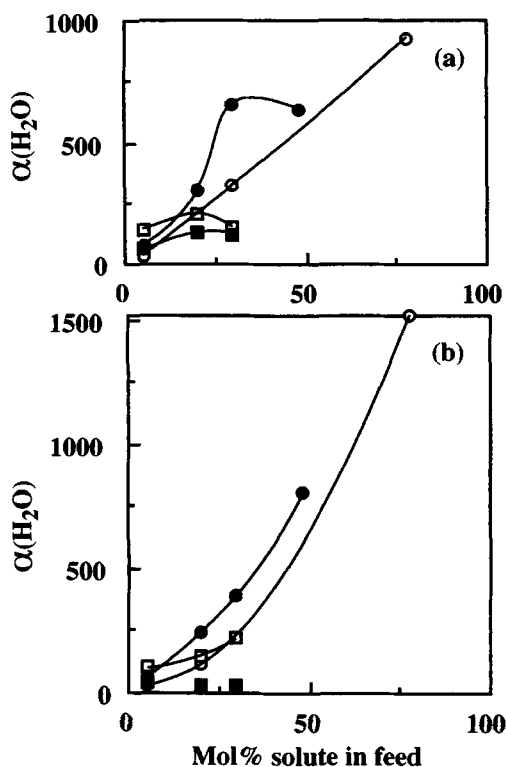
Figure 9 Separate factor of water $\alpha(H_2O)$ vs. feed composition. Membrane: (a) MP37, (b) MP38 complexed. O: THF; ●: DOX; □: DMAc; ■: DMF.

OBSH content in the blend polymer. The OBSH content is the calculated one based on 67 mol % of No. 2 in Table II, because of no great variation between the yields of Nos. 2 and 12 in Table II. As the OBSH content increases, $P(H_2O)$ and $P(EtOH)$ decrease and α rather increases, indicating that phenylene groups dominate permeabilities more strongly than SO_2 groups. OBSH moieties are characteristic of α higher than that of MP (OBM-1). Of these membranes, the most water permeable is OBM-1 that contains no OBSH. Moreover, OBM-1 does not have so much lower value of α and has a high tensile strength of 3–4 kg/cm², which corresponds to about 2.5–3.4 times stronger than cellulose acetate membrane, with water content of 22–25 wt %. Hence, PV performance of MP membranes in preferential separation of water from aqueous organic solutions was studied in some details in the following section.

In oxygen–nitrogen (air) permeation, MP35 membrane ($\Delta x = 41.7$ μm) prepared by the frame-casting method showed $\alpha(O_2/N_2)$ of 2.3 and $P(O_2)$ [(cm s(STP) cm)/(cm² s cmHg)] of 7.9 × 10⁻¹² and in the addition of 10 mol % $CoCl_2$ to MP35 membrane ($\Delta x = 30.6$ μm), $\alpha(O_2/N_2)$ of 1.07 and

$P(O_2)$ of 2.5 ×10⁻¹¹. These values indicate that MP membranes are not useful for the separation of oxygen from air even in the presence of cobalt complexes.

Pervaporation through MP Membranes

In our previous study on the permeation of various organic solutions through Schiff base membrane of poly(allylamine) we demonstrated that the permeation results could be separately discussed based on the class of the organic solute, e.g., alcohols and aprotic solutes.[12] A similar treatment was employed in the discussion of reverse osmosis results.[20,21] Therefore, we summarized the results of PV according to the class of the organic solute, i.e., alcohols and aprotic solutes, and discussed on the basis of the properties of organics that govern the performance: affinity to the membrane polymer, swelling ability, molecular size (molar volume), and vapor pressure. $CoCl_2$-complexed membranes containing 10.0 mol % $CoCl_2$ based on the repeat unit were used for comparison throughout the following study.
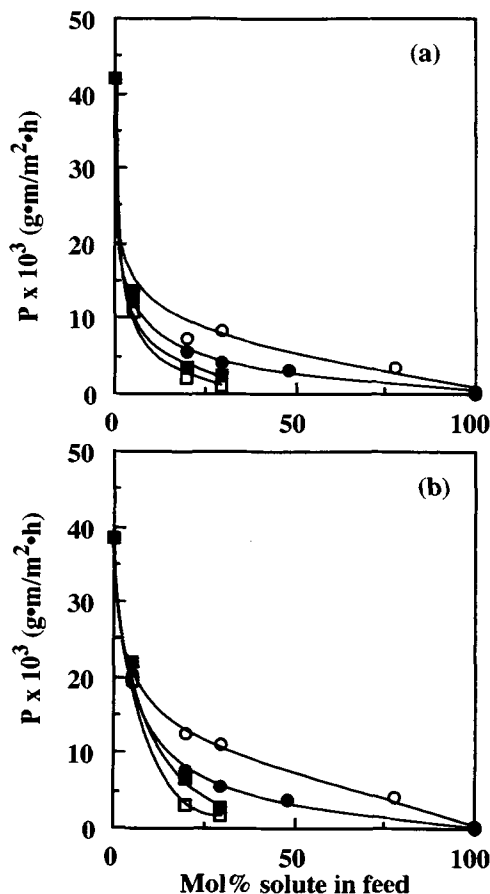
Figure 10 Overall permeation coefficient P vs. feed composition. Membrane: (a) MP37, (b) MP38 complexed. O: THF; ●: DOX; □: DMAc; ■: DMF.
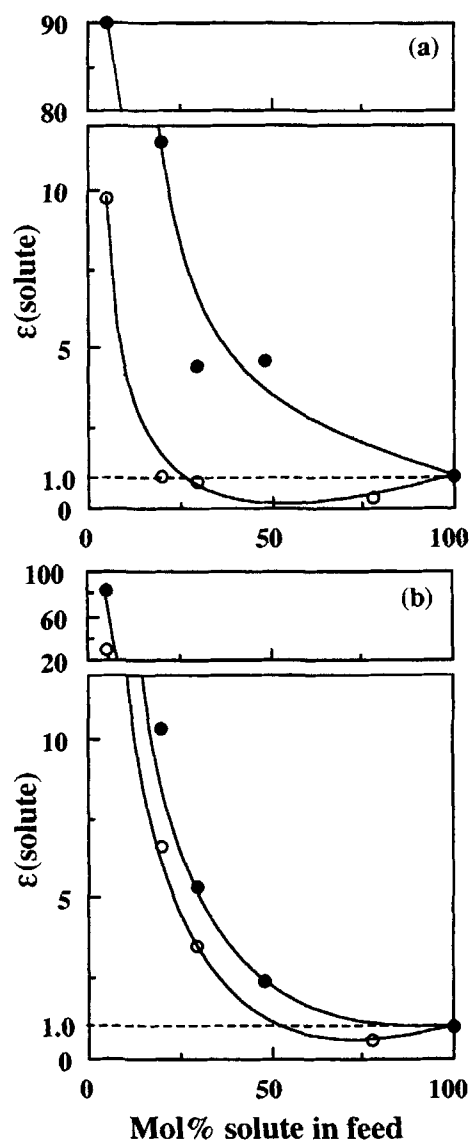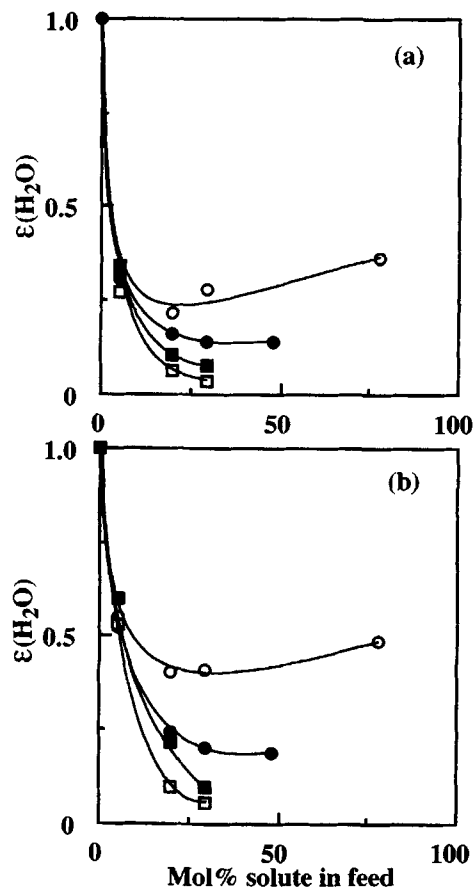
Figure 11 Deviation coefficients of solute ε(solute) vs. feed composition. Membrane: (a) MP37, (b) MP38 complexed. O: THF; ●: DOX.

Pervaporation of Aqueous Alcohol Solutions

PV results are shown in Figures 1–4. Figure 1 shows that α tends to increase as the concentration and carbon number of alcohols increase. Figure 2 shows decreasing tendencies of P with an increasing alcohol concentration, and also shows the independence of the class of the alcohol, which is because the major part of the permeate is comprised of water. The complexation by the addition of CoCl₂ to the membrane increased P in comparison between Figures 2(a) and (b), which usually occurs due to the increased polarity in common with the results in the previous report,[12] but the presence of CoCl₂ gave no marked effect on α in Figure 1(b) compared with

Figure 1(a) except for butanols. The lowering of α for butanols and also for propanols to some extent at about 70 mol % can be ascribed to an increased permeation of alcohols by the shrinkage of membranes, which is apparent from the decrease in swelling degree shown in Table VI, e.g., from 30.0% and 27.5% at 50 mol % to 19.1% and 18.8% at 70 mol % for sec-butanol and t-butanol, respectively.

The deviation coefficient ε of solute was higher than unity, especially in the dilute feed and in the case of the solute of a larger carbon number, as shown in Figure 3, which means that the permeation rate of the solutes was increased by coupling with water. However, in the higher region of feed concentration, the permeation of ethanol and propanols tended to be blocked to a small extent by the coupling with water. On the contrary, ε of water was less than unity over the whole range of feed concentration, as shown in Figure 4, clearly indicating the decrease in the rate of water permeation as the results of coupling with an organic solute. The decreasing ε of water with an increasing alcohol con-

Figure 12 Deviation coefficients of water ε(H₂O) vs. feed composition. Membrane: (a) MP37, (b) MP38 complexed. O: THF; ●: DOX; □: DMAc; ■: DMF.
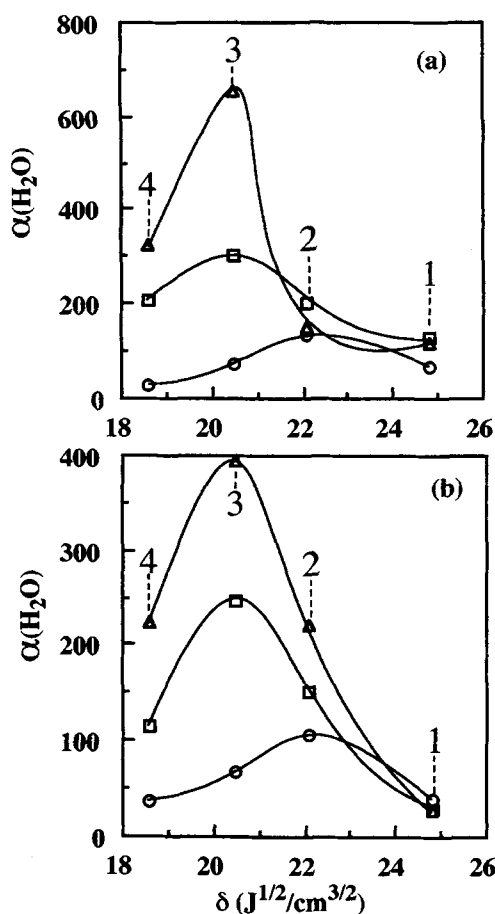
Figure 13 Separation factor $\alpha(H_2O)$ vs. solubility parameter (δ). Membrane: (a) MP37, (b) MP38 complexed. $\triangle$: 30 mol %; $\square$:20 mol %; $\bigcirc$: 5 mol % solute in feed. 1: DMF; 2: DMAc; 3: DOX; 4: THF.

centration just corresponds to the decreasing P in Figure 2. A high ϵ of solute at a dilute concentration in Figure 3 seems to indicate that water cluster formed by the preferential penetration of water in the membrane dissolves the solute, which favors for an increased permeation of the solute and concurrently retards water permeation.

The above PV results were attempted to relate some physicochemical parameters of solutes. In Figures 5 and 6, log α was correlated to solubility parameter δ and molar volume V_{298} at 298 K, respectively. Very close linear relationships were obtained by the method of least squares, i.e., the increase in log α with the decrease in δ and with the increase in V_{298} both in single and complexed membrane up to a high concentration of 70 mol % (85.7 wt % for ethanol, 88.6 wt % for propanols and 90.6 wt % for butanols). Figure 5 indicates that since δ of the membrane is calculated as 33.6 $(J/cm^3)^{1/2}$ according to the group contribution method,[22] ethanol (δ = 26.0) that has the highest affinity to membrane is the most penetrable into the membrane, eventually showing the lowest separation factor, i.e., the highest solute permeability, as shown in Figure 7, and the reverse is true for t-butanol. Figure 6 shows the difficulty in the permeation for the solute of a larger molecular size corresponding to a higher α value. Similar linear relationships showing completely opposite tendencies were observed in log P_s for alcohols, as shown in Figures 7 and 8. These facts suggest that α and P_s do not appreciably depend on the swelling degree of the membrane in various alcohols solution of the same con-

Table VII PV Performance of Membranes for Azeotrope Feeds

|	Bp[a] (°C)	V_{298}[b] (cm^3/mol)	δ[c] ($J^{1/2}/cm^{3/2}$)	Azeotrope Composition[a] (wt % (mol %))	MP[d] $\alpha(H_2O)$	MP[d] P^f	MP Complexed[e] $\alpha(H_2O)$	MP Complexed[e] P^f
EtOH	78.3	57.5	26.0	96.0 (90.4)	12.5	1.28	7.13	4.70
n-PrOH	97.2	74.7	24.3	71.7 (43.2)	171	4.33	72.4	9.22
i-PrOH	82.3	76.5	23.5	87.6 (68.0)	189	1.31	119	2.46
s-BuOH	99.6	91.7	22.1	73.2 (39.9)	775	4.68	581	9.59
t-BuOH	82.4	94.9	21.7	88.2 (64.6)	718	1.81	503	2.04
THF	66	81.2	18.6	93.3 (77.7)	927	3.41	1518	4.25
DOX	101.3	85.1	20.5	82.0 (48.2)	639	3.01	806	3.74

[a] Ref. 23.
[b] Molecular weight/density at 298 K(25°C).[23]
[c] Ref. 24.
[d] PM38 for alcohols and PM37 for THF and DOX.
[e] PM39 for alcohols and PM38 for THF and DOX.
[f] Overall permeability, 10^{-3} (g m)/(m^2 h).
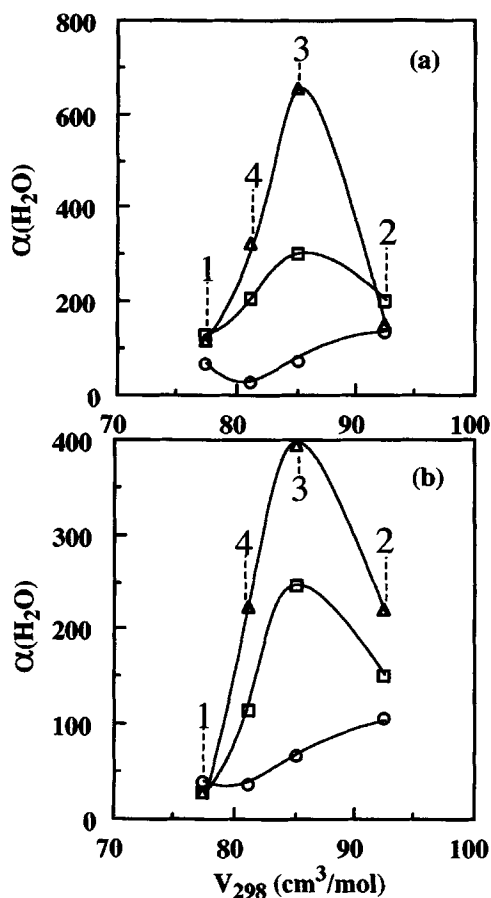
Figure 14 Separation factor of water $\alpha(H_2O)$ vs. molar volume (V_{298}). Membrane: (a) MP37, (b) MP38 complexed. $\triangle$: 30 mol %; $\square$:20 mol %; $\bigcirc$: 5 mol % solute in feed. 1: DMF; 2: DMAc; 3: DOX; 4: THF.

centration (Table VI), though the membrane generally tended to shrink in a higher concentration and swell in a lower one, indicating hydrophilicity.

In all those figures (Figs. 5–8), the slope of the lines shows a tendency to increase with increasing alcohol concentration of the feed, which may be caused by strengthening the difference of the solute with an increase in the concentration.

In summary, separation factor and permeability of alcohol depend both on the affinity to the membrane and their molecular size. Because the increasing order of δ is entirely parallel to the decreasing order of V_{298}, the predominance between the two factors in the influencing power on α and P_s is not distinct at present, but these results agree with those of our previous study of the alcohol permeation under pressure through the Schiff base membrane of poly(allylamine).[12] The complexed membranes, on the whole, showed a tendency to increase perme-

abilities and decrease α to a small extent compared with the uncomplexed membranes.

Pervaporation of Aqueous Aprotic Organics Solutions

PV results are summarized as shown in Figures 9–12. The decreases in α of DMAc and DMF at 30 mol % [Fig. 9(a)] are due to the very high affinity of DMAc and DMF to MP polymer, because they themselves can dissolve the polymer and swelling degree considerably increased with an increase in their concentration on the contrary to the trend of other solutes (Table VI). Therefore, ϵ of DMAc and DMF could not be determined. The CoCl$_2$ complexed membranes in Figure 10(b) showed a tendency to increase P in comparison with Figure 10(a) similarly to the case of alcohols, while small decreases in α
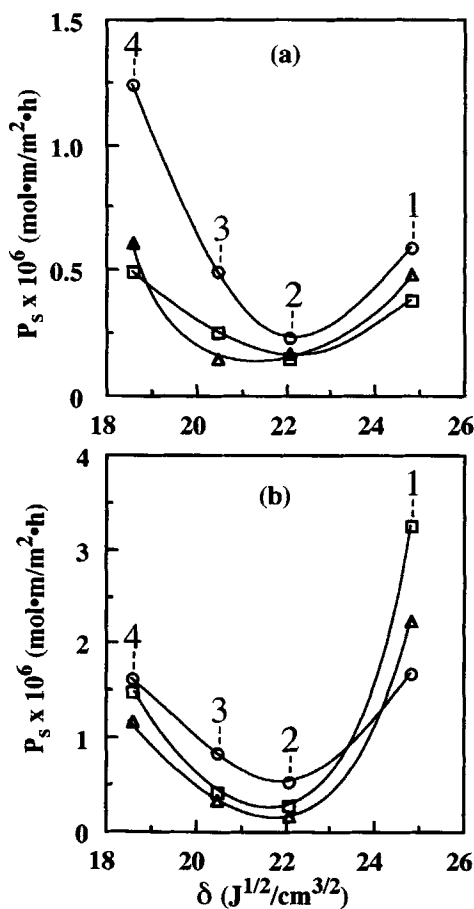
Figure 15 Permeation coefficient of solute P_s vs. solubility parameter (δ). Membrane: (a) MP37, (b) MP38 complexed. $\triangle$: 30 mol %; $\square$:20 mol %; $\bigcirc$: 5 mol % solute in feed. 1: DMF; 2: DMAc; 3: DOX; 4: THF.
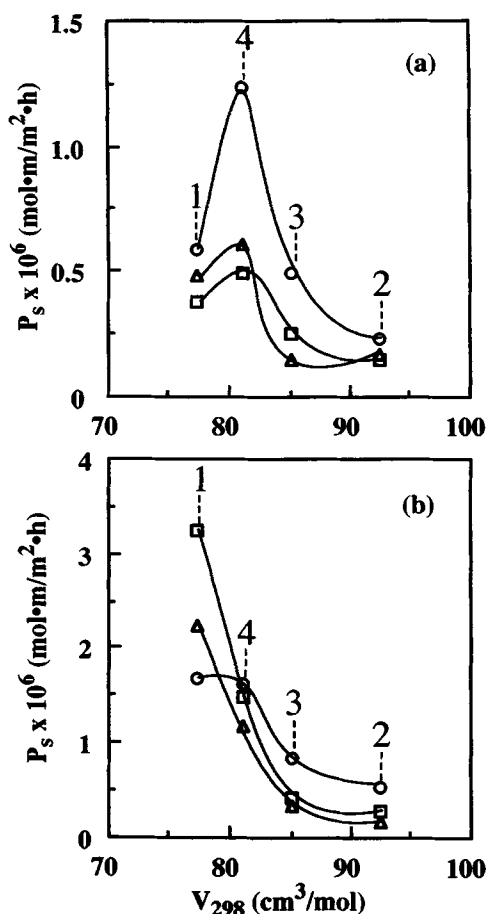
Figure 16 Permeation coefficient of solute P_s vs. molar volume (V_{298}). Membrane: (a) MP37, (b) MP38 complexed. $\triangle$: 30 mol %; $\square$: 20 mol %; $\bigcirc$: 5 mol % solute in feed. 1: DMF; 2: DMAc; 3: DOX; 4: THF.

were observed for the complexed membranes in feeds more dilute than 50 mol % (Fig. 9).

ϵ in the permeation of aprotic solutes showed a tendency similar to that of alcohols (Figs. 11 and 12). As is seen in Figure 11, ϵ of THF was less than

unity in the middle and higher region of the feed concentration. ϵ values of THF lower than those of DOX indicate that the THF permeation is facilitated by water to a smaller extent. In comparison between Figure 11(a) and (b), the increase in ϵ is more apparent in THF than in DOX. ϵ of water was more strongly affected than in alcohols (Fig. 12).

The relation of α and P_s to δ and V_{298} in the PV of aprotic solutes was shown in Figures 13-16. The decreasing tendency of α with an increase in δ among DOX, DMAc, and DMF except for THF in Figure 13 resembles the results for alcohols. The unexpectedly small value of α for THF probably stems, in part, from a swelling ability of THF higher than DOX at a given, particularly higher, concentration as shown in Table VI. The difference in relative volatility or boiling point is ruled out because it is assumed that the composition of the permeate in PV does not depend on the relative volatilities of the components but on the relative permeation rates through membrane, and, in reality, α for alcohols did not depend on boiling point at all, as listed in Table VII. A higher swelling ability of THF appears to bring about a higher permeability than that of DOX, as shown in Table VII. A higher overall permeability of THF in Table VII corresponds to a higher P_s value than that of DOX, as shown in Figure 15, a tendency opposite to that of alcohols (Fig. 7), while DMAc and DMF gave a relation parallel to that of alcohols. However, P_s of the four solutes vs. V_{298} exhibited a tendency for P_s to decrease with an increase in V_{298}, as shown in Figure 16(b). In Figure 16(a), on the other hand, lower values of P_s for DMF than those for THF in spite of a higher swelling ability of DMF than of THF seem peculiar, but the results for THF and DOX and those for DMAc and DMF may have to be discussed separately, because the latter two have a very strong affinity to the membrane polymer and the trend of P_s values between THF and DOX and between DMAc and DMF

Table VIII PV Performances in THF Separation

Membrane	Δx (μm)	THF in feed wt % (mol %)	α (H_2O)	J_1 [g/(m^2 h)]	$P \times 10^3$ [(g m)/(m^2 h)]	Ref.
Polytetrafluoroethylene Polyvinylpyrrolidone (PVPD)		94.3 (80.5)	18.4	940	-	25
Polyacrylonitrile (PAN) PVPD Blend	-	94.1 (79.7)	10.7	400	-	26
Composite PVA (Pervap 100)	-	90.0 (69.2)	24.3	450	-	27
MP37	28.4	93.3 (77.7)	927	120	3.41	This study
MP38 complexed	34.0	93.3 (77.7)	1518	125	4.25	This study

is similar to that of alcohols. The lowering tendency of the swelling degree (Table VI) of DMAc and DMF by the complexation with $CoCl_2$ may have realized a "normal" relation, as shown in Figure 16(b). Hence, the large difference in swelling power apparently gives a crucial influence on the permeation of aprotic solutes.

Consequently, it can be summarized that in PV of aprotic organics the solute of higher affinity (higher δ) to the membrane and of smaller molecular size substantially more readily permeates and lowers α value, but the difference in swelling power exhibits more decisive effect than does the difference in δ.

Table VII also shows the results of the separation for azeotropes. Fairly high values of α were obtained, and the complexed membrane in this study was found to be effective for separating azeotropic mixtures, in particular, for propanols, butanols and THF.

Few reports are available on THF separation by PV. The PV performances reported are tabulated in Table VIII, together with our results. When MP37 is compared with the PAN–PVPD blend and composite PVA, α of MP37 is about 40 to 90 times higher, although the flux is one-fourth to one-third. A little thicker $CoCl_2$ complexed membrane of MP38 appears to extraordinarily enhance α while the flux remains comparable with that of the uncomplexed MP37. Therefore, the MP membrane may be useful for the single-step separation of water from aqueous THF of a high concentration.

CONCLUSIONS

From the discussion described above, the following conclusions can be drawn.

1. In the preparation of poly(acylhydrazone) by polycondensation of PDCL and each of five dihydrazides, MDH yielded a soluble polycondensate MP of the longest chain length. Other dihydrazides only gave insoluble or hardly soluble polycondensates of shorter chain length.

2. The optimum synthetic conditions of MP are 40°C, 120 Torr, and 1–2 h.

3. MP readily formed a film that can be used for a permeation membrane. MP blends with the copolycondensate of MDH and OBSH with PDCL were also available for the separation membrane when a support was used, although water permeability was lower than that of MP.

4. MP showed low permeabilities for oxygen and nitrogen, but was worthy of a PV membrane rather than a reverse osmosis membrane.

5. In PV for aqueous alcohols through an MP membrane, $\alpha(H_2O)$ and P_s were dominated by molecular size and δ. For aqueous aprotic organics solutions, swelling power and molecular size of the organics in the feed were more crucial than δ.

6. In the separation of mixture feed of azeotrope composition and concentrated solutions, MP membranes exhibited considerably higher values of $\alpha(H_2O)$ and was very useful, especially for propanols, butanols, and THF.

7. Complexation of the membrane with $CoCl_2$ was effective for the enhancement of water permeability, and for the separation of azeotropes and concentrated solutions.

REFERENCES

1. G. F. D'Alelio, F. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci., Chem.*, **A1**, 1161, 1251 (1967).
2. D. Whorle, *Forschr. Hochpolym.-Forsch.*, **10**, 35 (1972).
3. R. H. Michel and W. A. Murphy, *J. Appl. Polym. Sci.*, **7**, 617 (1963).
4. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and P. N. Griskova, *Dokrady, Akad. Nauk SSSR*, **149**, 602 (1963).
5. G. F. D'Alelio, J. V. Crivello, T. R. Dehner, and R. K. Schoenig, *J. Macromol. Sci., Chem.*, **A1**, 1331 (1967).
6. J. Idris Jones, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C2**, 303 (1968).
7. E. Oikawa and S. Kambara, *Bull. Chem. Soc. Jpn.*, **37**, 1849 (1964).
8. A. B. Padias and H. K. Hall, Jr., *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 1675 (1986).
9. E. Oikawa, K. Mori, and G. Saito, *Bull. Chem. Soc. Jpn.*, **39**, 1182 (1966).
10. T. Aoki, Y. Yamamoto, K.-H. Shin, and E. Oikawa, *Makromol. Chem. Rapid Commun.*, **13**, 525 (1992).
11. E. Oikawa, K. Hibi, N. Sakazume, H. Endo, T. Honda, and T. Aoki, *Desalination*, **94**, 25 (1993).
12. E. Oikawa, M. Soyama, and T. Aoki, *Polymer*, **35**, 2153 (1994).
13. G. Chesea, G. Marangoni, and B. Pitteri, *Reactive Polym.*, **12**, 219 (1990).
14. E. Oikawa, K. Katoh, and K. Yahata, *Sep. Sci. Technol.*, **25**, 45 (1990).
15. R. Y. M. Huang and V. J. C. Lin, *J. Appl. Polym. Sci.*, **12**, 2615 (1968).
16. E. Drioli, S. Zhang, and A. Basile, *J. Membr. Sci.*, **81**, 43 (1993).

17. T. Aoki, H. Nakahara, Y. Hayakawa, M. Kokai, and E. Oikawa, *J. Polym. Sci., Part A: Polym. Chem.,* **32,** 849 (1994).
18. D. H. McDaniel and H. C. Brown, *J. Org. Chem.,* **23,** 420 (1958).
19. E. Oikawa and Y. Yahata, *Polym. Bull.,* **17,** 315 (1987).
20. T. Matsuura, M. E. Bendas, J. M. Dickson, and S. Sourirajan, *J. Appl. Polym. Sci.,* **18,** 2829 (1974).
21. J. M. Dickson, T. Matsuura, P. Blais, and S. Sourirajan, *ibid,* **19,** 801 (1975).
22. D. W. Van Krevelen, *Properties of Polymers,* 3rd Ed., Elsevier, Amsterdam, 1990.
23. J. A. Riddick and W. B. Bunger, *Organic Solvents,* 3rd Ed., Wiley- Interscience, New York, 1970.
24. J. Brandrup and E. H. Immergut, *Polymer Handbook,* 3rd Ed., Wiley-Interscience, New York, 1989.
25. J. Neel, Q. T. Nguyen, R. Clement, and L. LeBlanc, *J. Membr. Sci.,* **15,** 43 (1983).
26. Q. T. Nguyen, L. LeBlanc, and J. Neel, *ibid,* **22,** 245 (1985).
27. J. Mencarini, Jr., R. Coppola, and C. C. Slater, *Sep. Sci. Technol.,* **29,** 465 (1994).