Application and Development of Synthetic Polymer Membranes. VI. Pervaporation of Aqueous Ethanol Solution through Quaternized Poly[3-(N',N'-dimethyl)aminopropylacrylamide-co-acrylonitrile] Membranes

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SYNOPSIS

Membranes obtained from polymers, quaternized poly[3-(N',N'-dimethyl)aminopropy-lacrylamide-co-acrylonitrile]s, showed selective separation of water from aqueous ethanol solution by pervaporation. The separation factor toward water reached over 15,000. Membrane performance showed a good correlation to membrane polarity. Differential scanning calorimetric melting endotherms of the water-swollen membranes were studied to clarify the state of water in the membranes. The results suggested that there are two states of water in the membrane: bound and free. The higher the fraction of bound water in the membrane, clearly, the more preferentially was water permeated.

INTRODUCTION

The energy problem, of which a typical example is an exhaustion of fossil fuel, is one of the most serious problems to be solved immediately. It is our duty to conquer this important and inevitable problem. There exist two ways to find a solution to this fatal problem: One way is to utilize biomass energy,[1-3] which is a clean and a regenerable energy; the other is to make use directly of solar energy,[4-8] which is also a clean and inexhaustible energy. Turning our eyes on utilization of biomass energy, the production of ethanol, which is regarded as not only an energy resource but also a chemical raw material,[9] by fermentation of biomasses will be in the near future an important and indispensable industrial process.

As to formation of ethanol via fermentation of biomasses, the liquid product is an aqueous solution containing around 5 wt % ethanol, which is separated by distillation to give 95.6 wt % ethanol. This

distillation process is an energy-intensive step that accounts for a large portion of the cost of ethanol production from biomasses. In this process, the pervaporation technique is expected to be an economical and energy-saving alternative process for water–ethanol separation.[10]

There are two ways to separate an aqueous ethanol solution by pervaporation: One way is for ethanol to be preferentially separated through membranes,[11-28] whereas the other is for water to be selectively removed through membranes.[21,29-54] Water-permeable membranes are expected to be applicable to the separation (removal) of water from other aqueous organic liquids, such as acetic acid, acetone, and butanols, which are water-miscible and produced by fermentation of biomasses.

On the basis of this idea, the authors have studied novel membrane materials for the separation of water from aqueous ethanol solutions, especially water–ethanol mixtures, by a pervaporation technique.[21,42-54] As a strategy for preparation of novel membrane materials, incorporation of a fixed carrier (functional moiety), which may cause a strong interaction toward the separated substrate, into membranes has been adopted. As a specific interaction toward water, there exists both hydrogen-bonding

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interaction and Coulombic (electrostatic) interaction. Synthetic polymer membranes having imide groups,[42,43,45] N-substituted imide groups,[46] carboxylic acid moieties,[21,44,54] or N-substituted imide groups and ester groups,[47,48] selectively permeated water from aqueous ethanol (alcohol) or acetic acid solution by using the hydrogen-bonding interaction. Those containing pyridinium moieties,[49–51] or ammonium groups,[52,53] preferentially removed water from the aqueous ethanol solution by using the Coulombic interaction. Separation of water from the water–ethanol solution in terms of Coulombic interaction was also attempted through ion-exchange membranes.[37,39,41] There was also another attempt made of pervaporation of water through a partially quaternized poly(4-vinylpyridine) membrane.[55]

In the present article, attention is focused on the selective separation of water from an aqueous ethanol solution in terms of the Coulombic interaction. Membranes having ammonium moieties as cationic charge sites, e.g., quaternized poly[3-(N',N'-dimethyl)aminopropylacrylamide-co-acrylonitrile] membranes, were prepared, and selective separation of water–ethanol mixtures through the present membranes were investigated. As to water-permeable membranes, it is anticipated that the state of the water in the membrane exerts a strong influence on the membrane performance. There are many reports on the state of water in the membrane and in the polymer.[56–80] However, there has been no attempt, except our preliminary study,[53] to investigate the state of water in the membrane employed for pervaporation. The relation between the state of water in the membrane and its membrane performance might be one of the most promising indices for the development of novel membranes like solubility parameter[81] or membrane polarity.[43,52,82] On the basis of this idea, we also investigated the relationship between membrane performance and the state of water in the membrane.

EXPERIMENTAL

Materials

Acrylonitrile (AN),[83] 2,2'-azobis(2-methylpropionitrile) (AIBN),[84] and N,N-dimethylformamide[83] were purified by the usual methods. 3-(N',N'-dimethyl)aminopropylacrylamide (DMAPAA), which was kindly provided by Kohjin Co., halides (RX), and ethanol were used without further purification. Deionized water was employed.

Syntheses of Membrane Materials

Poly[3-(N',N'-dimethyl)aminopropylacrylamide-co-acrylonitrile] (**1, 5, 13, 17, 21**, and **31**; Scheme 1), with a mol fraction of the DMAPAA unit of 0.025, 0.035, 0.036, 0.060, 0.063, or 0.068, was synthesized by the usual radical copolymerization of DMAPAA and AN initiated by AIBN at 45°C with shaking. Quaternized polymers were prepared by the reaction of polymers **1, 5, 13, 17, 21**, or **31** and the corresponding halide in DMF solution at 30°C. The chemical composition of the obtained polymers was determined by elemental analysis. The results are summarized in Tables I and II.

Preparation of Membranes

All membranes were obtained by casting from DMF solution (100 g dm^{-3}). The solution was poured onto a glass plate with an applicator, of which casting thickness was 0.254 mm, and the solvent was allowed to evaporate at 45°C for 4 h. The thickness of the membrane was 12–18 μm.

Determination of Membrane Polarity

An evaluation of membrane polarity was carried out in terms of Dimroth's solvent polarity value [E_T (25°C)].[85] Membrane polarities [E_T (25°C)] of these membranes were measured as described previously, using 1-octadecyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2H-benzopyran) as the indicator.[86] A 500 W xenon lamp was used as the light
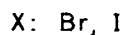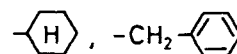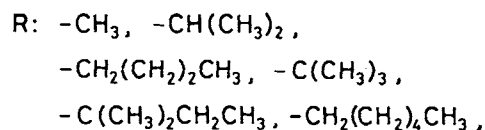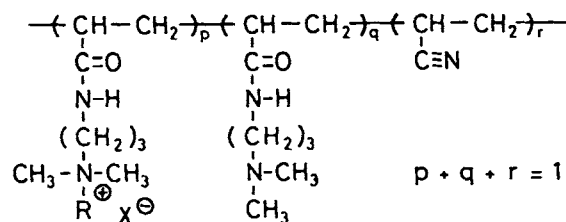
Scheme 1

Table I Results of Copolymerization[a]

Polymer		Monomer/g		AIBN (mg)	Time (h)	Yield (g)	Mol Fraction of DMAPAA in	
		DMAPAA	AN				Monomer	Polymer
1	025	0.97	16.1	25.4	50	14.9	0.020	0.025
5	035	1.47	16.1	25.6	46	16.5	0.030	0.035
13	036	1.47	16.1	25.6	50	14.6	0.030	0.036
17	060	2.50	16.1	26.2	50	14.1	0.050	0.060
21	063	2.49	16.1	26.2	46	16.0	0.050	0.063
31	068	3.55	16.1	26.8	46	16.9	0.070	0.068

[a] Polymerization temperature was 45°C; (AIBN)/(monomer) = 1/200 (mol/mol).

Table II Results of Quaternization of Parent Polymers[a]

	Polymer Membrane[b]	Amount of Parent Polymer (g)	Amount of RI (g)	Reaction Time (h)	Yield (g)	Unit mol fraction			Fraction of Quaternization
						p	q	r	
2	025-Me-025	1.0	0.43	50	0.82	0.025	0	0.975	1.000
3	025-Tb-008	0.5	0.33	50	0.48	0.008	0.017	0.975	0.320
4	025-Ch-011	0.5	0.38	50	0.31	0.011	0.014	0.975	0.440
6	035-Me-035	1.0	0.35	91	1.06	0.035	0	0.965	1.000
7	035-Ip-023	0.5	0.53	50	0.43	0.023	0.012	0.965	0.657
8	035-Tb-019	0.5	0.57	50	0.41	0.019	0.016	0.965	0.543
9	035-Am-007*	0.5	0.47	50	0.41	0.007	0.028	0.965	0.200
10	035-He-028	1.0	1.31	90	0.67	0.028	0.007	0.965	0.800
11	035-Ch-017	1.0	1.30	92	0.69	0.017	0.018	0.965	0.486
12	035-Bz-035*	1.0	0.62	88	1.05	0.035	0	0.965	1.000
14	036-Me-036	1.0	0.60	50	0.88	0.036	0	0.964	1.000
15	036-Tb-007	0.5	0.49	50	0.50	0.007	0.029	0.964	0.194
16	036-Ch-007	0.5	0.56	50	0.37	0.007	0.029	0.964	0.194
18	060-Me-060	1.0	0.96	50	0.96	0.060	0	0.940	1.000
19	060-Tb-007	0.5	0.79	50	0.51	0.007	0.053	0.940	0.117
20	060-Ch-014	0.5	0.90	50	0.26	0.014	0.046	0.940	0.233
22	063-Me-063	1.0	0.66	91	1.17	0.063	0	0.937	1.000
23	063-Ip-019	0.5	0.90	50	0.43	0.019	0.044	0.937	0.302
24	063-Bu-054	1.0	1.29	88	1.20	0.054	0.009	0.937	0.857
25	063-Tb-015	0.5	0.97	50	0.37	0.015	0.048	0.937	0.238
26	063-Am-001*	0.5	0.80	50	0.41	0.001	0.062	0.937	0.016
27	063-He-055	1.0	2.24	90	0.98	0.055	0.008	0.937	0.873
28	063-Ch-006*	1.0	1.14	91	0.92	0.006	0.057	0.937	0.095
29	063-Ch-028	1.0	2.22	92	0.81	0.028	0.035	0.937	0.444
30	063-Bz-028*	1.0	1.20	88	1.05	0.028	0.035	0.937	0.444
32	068-Me-068	1.0	0.96	91	1.18	0.068	0	0.932	1.000
33	068-Bu-068	1.0	1.86	88	1.28	0.068	0	0.932	1.000
34	068-He-063	1.0	2.41	90	0.81	0.063	0.005	0.932	0.926
35	068-Ch-011*	1.0	1.65	91	0.90	0.011	0.057	0.932	0.162
36	068-Ch-031	1.0	2.38	92	0.80	0.031	0.037	0.932	0.456
37	068-Bz-068*	1.0	1.73	88	1.04	0.068	0	0.932	1.000

[a] Quarternization was carried out at 30°C in DMF solution; the concentration of polymer in DMF solution was 40–50 g dm^{-3}.
[b] Me, methyl; Ip, isopropyl; Bu, butyl; Tb, tert-butyl; Am, 1,1-dimethylpropyl; He, hexyl; Ch, cyclohexyl; Bz, benzyl; *, counteranion is Br$^-$; counteranion for no asterisk, I$^-$.

source. The membrane was illuminated with UV light using a Corning color filter no. 7-54. Absorption spectra were measured with a Shimadzu UV-365 UV-VIS-NIR recording spectrophotometer.

Measurement of Fluorescence Spectrum

The membrane sample for the measurement of the fluorescence spectrum was prepared from the DMF solution containing magnesium 1-anilino-8-naphthalenesulfonate (ANS), having a concentration of 1.0×10^{-5} mol dm^{-3}. The membrane was prepared as described above in Preparation of Membranes. Fluorescence spectra were recorded with a Shimadzu RF-540 spectrophotometer at ambient temperature. The excitation wavelength was 350 nm, and both the excitation and emission slits were set at 5 nm.

Water Content

The water content was measured as follows: After the membrane was dried *in vacuo* at 56°C over 6 h to the constant weight, the dried membrane sample, the weight of which was W_d, was immersed in deionized water at 30°C for 1 week. After the swelling equilibrium was attained, the membrane sample was weighed immediately after blotting the free surface water. The water content W_t was defined by

$$W_t = (W_s - W_d)/W_d \qquad (1)$$

where W_s and W_d denote the weights of water-swollen and dry membrane, respectively.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimeter used was a Seiko I & E DSC 10 and SSC/580 thermal controller. A membrane sample of about 10–30 mg, which was prepared in the same way as described for the measurement of the water content, was transferred to the Pt sample pan that was hermetically sealed to prevent evaporation. The sample was cooled down to −30°C by using liquid nitrogen and then heated slowly at a scanning rate of 5°C min^{-1} up to 20°C.

Pervaporation

Pervaporation of the water–ethanol mixture was carried out through the present membranes as described previously.[27] The membrane area in contact with liquid was 10.5 cm^2. The downstream pressure was maintained around 400 Pa (3.0 Torr).

The separation analysis was carried out on a Shimadzu GC-8A gas chromatograph with a 3.1 m-long column packed with polyethylene glycol 6000 on Shimalite TPA.

The separation factor toward water, α, is defined as

$$\alpha = (Y_{Water}/Y_{Ethanol})/(X_{Water}/X_{Ethanol}) \qquad (2)$$

where the Y_i's are the weight fractions of permeates and the X_i's those of feeds, respectively.

RESULTS AND DISCUSSION

Separation of the Water–Ethanol Mixture by Pervaporation through the Present Membranes

As an example of the pervaporation results, Figure 1 shows the results from the 035-Me-035 membrane, where the separation factor (α) and the total flux (J) were plotted as a function of the weight fraction of water in the feed. Figure 1 clearly shows that the
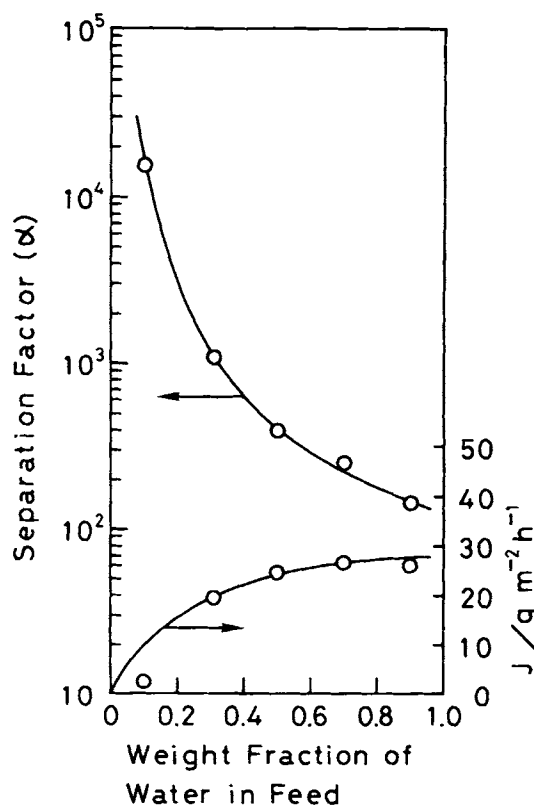

Figure 1 Effect of feed composition on separation factor (α) and flux (J) through the 035-Me-035 (6) membrane. Downstream pressure, 400 Pa [3.0 Torr]; operating temp, 30°C.

selective separation of water was attained through the present membrane. As can be seen in Table III, the whole membranes studied permeated water more preferentially than did ethanol. As shown in Figure

1, the values of α turned out to be over 15,000 when the weight fraction of water in the feed was 0.10. From the separation factors shown in Figure 1, most of the flux was due to water permeation. Actually,

Table III   Membrane Properties, State of the Water, and Membrane Performance of Synthetic Polymer Membranes

Polymer Membrane[a]		Membrane Polarity (kcal mol^{-1})	λ^F_{max} (nm)	W_t^b	W_b^c	Fraction of Bound Water	Separation Factor $(\alpha)^d$	Flux^d (g m^{-2} h^{-1})
1	025	50.7	404	0.18	0.18	1.00	189	17
2	025-Me-025	51.4	452	0.13	0.13	1.00	504	19
3	025-Tb-008	52.2	454	0.12	0.12	1.00	1104	15
4	025-Ch-011	48.1	428	0.08	0.08	1.00	575	13
5	035	49.9	444	0.14	0.14	1.00	226	20
6	035-Me-035	52.9	463	0.11	0.11	1.00	398	25
7	035-Ip-023	51.4	447	0.12	0.12	1.00	370	20
8	035-Tb-019	51.4	460	0.10	0.10	1.00	440	19
9	035-Am-007*	52.2	457	0.13	0.13	1.00	336	18
10	035-He-028	49.2	451	0.37	0.37	1.00	184	20
11	035-Ch-017	52.5	461	0.16	0.16	1.00	528	20
12	035-Bz-035*	50.7	446	0.15	0.15	1.00	50	80
13	036	50.3	418	0.13	0.13	1.00	227	24
14	036-Me-036	52.5	461	0.13	0.13	1.00	853	25
15	036-Tb-007	51.8	455	0.11	0.11	1.00	747	24
16	036-Ch-007	49.2	429	0.13	0.13	1.00	396	15
17	060	47.7	440	0.17	0.17	1.00	107	47
18	060-Me-060	52.2	469	0.16	0.16	1.00	55	96
19	060-Tb-007	49.2	462	0.13	0.13	1.00	136	84
20	060-Ch-014	49.9	445	0.15	0.15	1.00	236	58
21	063	47.7	442	0.18	0.16	0.89	93	45
22	063-Me-063	49.9	457	0.17	0.17	1.00	103	140
23	063-Ip-019	48.4	459	0.16	0.16	1.00	165	62
24	063-Bu-054	47.7	447	0.19	0.10	0.53	30	82
25	063-Tb-015	47.7	462	0.18	0.18	1.00	150	66
26	063-Am-001*	47.7	465	0.21	0.21	1.00	109	69
27	063-He-055	48.4	455	0.15	0.15	1.00	33	77
28	063-Ch-006*	49.2	459	0.21	0.20	0.95	52	54
29	063-Ch-028	51.4	463	0.15	0.15	1.00	102	71
30	063-Bz-028*	51.4	462	0.14	0.14	1.00	306	19
31	068	45.5	444	0.34	0.22	0.65	29	132
32	068-Me-068	47.0	452	1.00	0.41	0.41	9.1	393
33	068-Bu-068	45.8	470	0.44	0.15	0.34	11	159
34	068-He-063	47.0	461	0.13	0.13	1.00	12	227
35	068-Ch-011*	45.8	399	0.46	0.27	0.59	24	80
36	068-Ch-031	47.7	389	0.26	0.16	0.62	25	154
37	068-Bz-068*	45.8	453	0.81	0.15	0.19	50	132

[a] Me, methyl; Ip, isopropyl; Bu, butyl; Tb, tert-butyl; Am, 1,1-dimethylpropyl; He, hexyl; Ch, cyclohexyl; Bz, benzyl; *, counteranion is Br$^-$; counteranion for no asterisk, I$^-$.
[b] Water content: g H_2O/g membrane.
[c] Bound water in membrane, g H_2O/g membrane.
[d] Downstream pressure, 400 Pa (3.0 Torr); operating temp except **35** and **37**, 30°C; operating temp for **35** and **37**, 25°C; weight fraction of water in feed, ca. 0.5.

all weight fractions of water in permeate for the 035-Me-035 membrane were over 0.997.

From the profile of total flux shown in Figure 1, water might have permeated through the 035-Me-035 membrane by a carrier-mediated mechanism. To ascertain this, we separated the observed fluxes into their respective water and ethanol fluxes, so that they can be plotted against its feed concentration as previously proposed.[21,22,27,28,46-50,54] These separated fluxes are shown in Figure 2.

The relationship between water flux and water concentration $(C_{H,0})$ in the feed is shown in Figure 2(a). This profile is of a typical Michaelis–Menten type. In other words, the flux approaches an asymptotic limit as the concentration in the feed increases. This result strongly supports a carrier-mediated mechanism for water permeation through the 035-Me-035 membrane. In the present case, however, a carrier, an ammonium moiety, was immobilized in the membrane. The water flux noted in Figure 2(a) may be represented by the following equation:

$$J_H = (D/l)(KC_0C_{H,0})/(1 + KC_{H,0}) \qquad (3)$$

In this equation, D is the diffusion coefficient in the membrane for water, l is the membrane thickness, K denotes the complex formation constant between fixed carrier and water, C_0 denotes the carrier concentration in the membrane, and $C_{H,0}$ is the water concentration in the feed. Values of the constants in eq. (3) may be estimated. A Lineweaver–Burk analysis[87] gave values of D and K in eq. (3). Obtained values were as follows: $D = 4.23 \times 10^{-8}$ m^2 h^{-1}; $K = 1.00 \times 10^{-4}$ m^3 mol^{-1}. Other relationships between each component–flux and feed concentra-

tion of the present membranes except the 063 and 068-Me-068 membranes gave similar profiles as shown in Figure 2(a). In the water permeation through the 063 and 068-Me-068 membranes, the relationship obeys the Henry-type equation; that is, these relationships are straight lines that pass through the origin.

On the other hand, the ethanol flux dependence on its feed concentration $(C_{E,0})$ was more complicated, having a maximum flux value. This profile suggests that ethanol permeation through the present membranes was affected by not only by the internal concentration of ethanol but also by that of water. Other relationships between ethanol fluxes and ethanol concentrations in the feed gave similar profiles, as shown in Figure 2(b).

Relationship between Membrane Polarity and Membrane Performance

It is important to systematize membrane performance, since the systematization so-obtained might be effective to the molecular design of novel membrane materials. On the basis of this idea, we proposed that membrane polarity is one of the most promising parameters for use in the development of membranes for separation of water–ethanol mixtures by making use of the hydrogen-bonding interaction[43,82] or the Coulombic interaction.[52] In the present article, the relationship between the separation factor toward water and the membrane polarity was investigated. Obtained results are summarized in Table III and Figure 3.

Figure 3 shows the relationship between the separation factor and the membrane polarity. The sep-
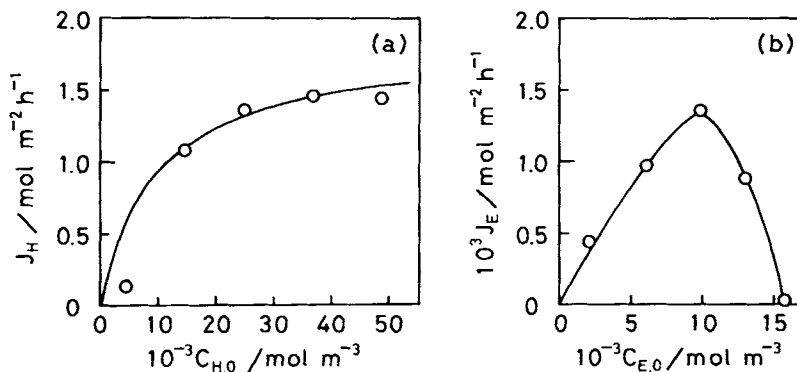

Figure 2 Effect of water (a) and ethanol (b) concentration on their fluxes in water–ethanol pervaporation through the 035-Me-035 (6) membrane. Downstream pressure, 400 Pa (3.0 Torr); operating temp, 30°C; the solid line in (a) is the calculated line, using the values $D = 4.23 \times 10^{-8}$ m^2 h^{-1}; $K = 1.00 \times 10^{-4}$ m^3 mol^{-1}; $C_0 = 5.68 \times 10^2$ mol m^{-3}; and $l = 1.3 \times 10^{-5}$ m.
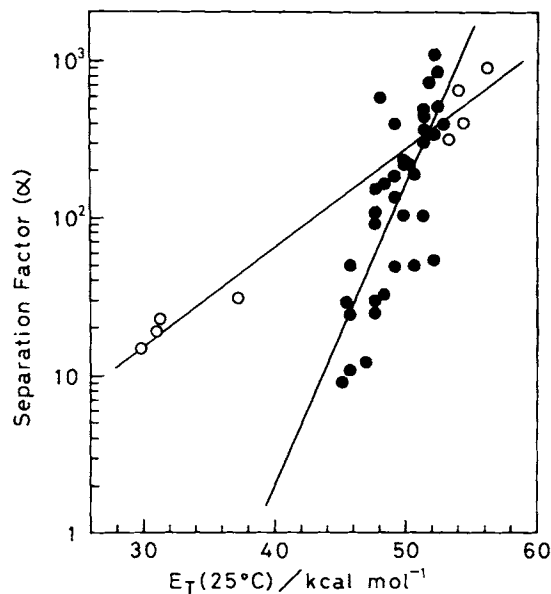
Figure 3 Relationship between separation factor (α) and membrane polarity. ($\bullet$) Present data: downstream pressure 400 Pa (3.0 Torr); operating temp except membranes **35** and **37**, 30°C; operating temp for membranes **35** and **37**, 25°C; weight fraction of water in feed, ca. 0.5. ($\bigcirc$) Cited from Ref. 82.

aration factors of the present membranes are correlated to the membrane polarity, though plots are dispersed. The correlation coefficient for the present relationship was determined to be 0.739. The relationship for the present membrane was different from the previously reported relationship by making use of a hydrogen-bonding interaction.[43,82]

The following two factors are anticipated as dominant factors for the difference between the relationship obtained in the present study and that previously reported[43,82]: (1) the difference in interaction, which is employed as a specific interaction to separate the water–ethanol mixtures, namely, the present membranes separate the aqueous ethanol solution by making use of the Coulombic interaction, whereas those previously reported[43,82] separate by making use of the hydrogen-bonding interaction; and (2) the difference in the operating temperature. The present studies were carried out at 30°C, whereas the previous pervaporation experiments were done at 15°C. The latter difference is, however, thought to give less influence over the membrane performance compared with the former factor.

Fluorescence Spectra of Membranes

Making use of multiple relationships between membrane performance and membrane property is ex-

pected to make it easy to design molecular structures of membrane materials for the separation of the aqueous ethanol solution. Fluorescence spectra of magnesium 1-anilino-8-naphthalenesulfonate (ANS) in membrane might give us hydrophobicity in the vicinity of the fixed carrier. ANS has been employed extensively as a hydrophobic probe to evaluate the microenvironment.

We investigated the relationship between membrane performance and the emission maximum, λ_{max}^{F}, of the present membrane. The obtained relationships for each membrane are shown in Figure 4. There seems to be a certain relationship for each membrane family, that is, the relationship for each membrane family was maximum. Figure 4 suggests that such a hydrophobic parameter might also be applicable to the index for development of new membrane materials for water–ethanol separation as the membrane polarity; these were, however, preliminary results. Studies on the relationship between membrane performance and membrane property, such as membrane polarity or hydrophobicity of the membrane, may open the door to the development of novel membrane materials.

State of Water in the Membrane

In reverse osmosis, it was suggested that the state of water in the membrane played an important role for the selective permeation of water.[66,88] In pervaporation for the selective separation of water, it is also anticipated that the state of water in the membrane shows a serious effect on membrane performance. From this point of view, we have started to investigate the state of water in the present membranes.[53]

We first investigated the relationship between the water content, W_t, and the separation factor. The relationship is shown in Figure 5. The separation factor increases with decreasing water content against the expectation that the selectivity toward water increases as the amount of water in the membrane increases.

Next we investigated the bound (nonfreezing) water in the membrane. As an example, in Figure 6, enthalpic heats of melting, ΔH, of freezable water in the 068-Ch-031 membrane using the area under the endothermic curve is plotted against water contents, W_t, which were varied in order to investigate the influence of water content on the state of water in the membrane. The data plot is indeed linear, with its slope approximately equal to 333.5 J g^{-1} (79.8 cal g^{-1}). The fact that the points should fall on a straight line with a slope equal to the heat of
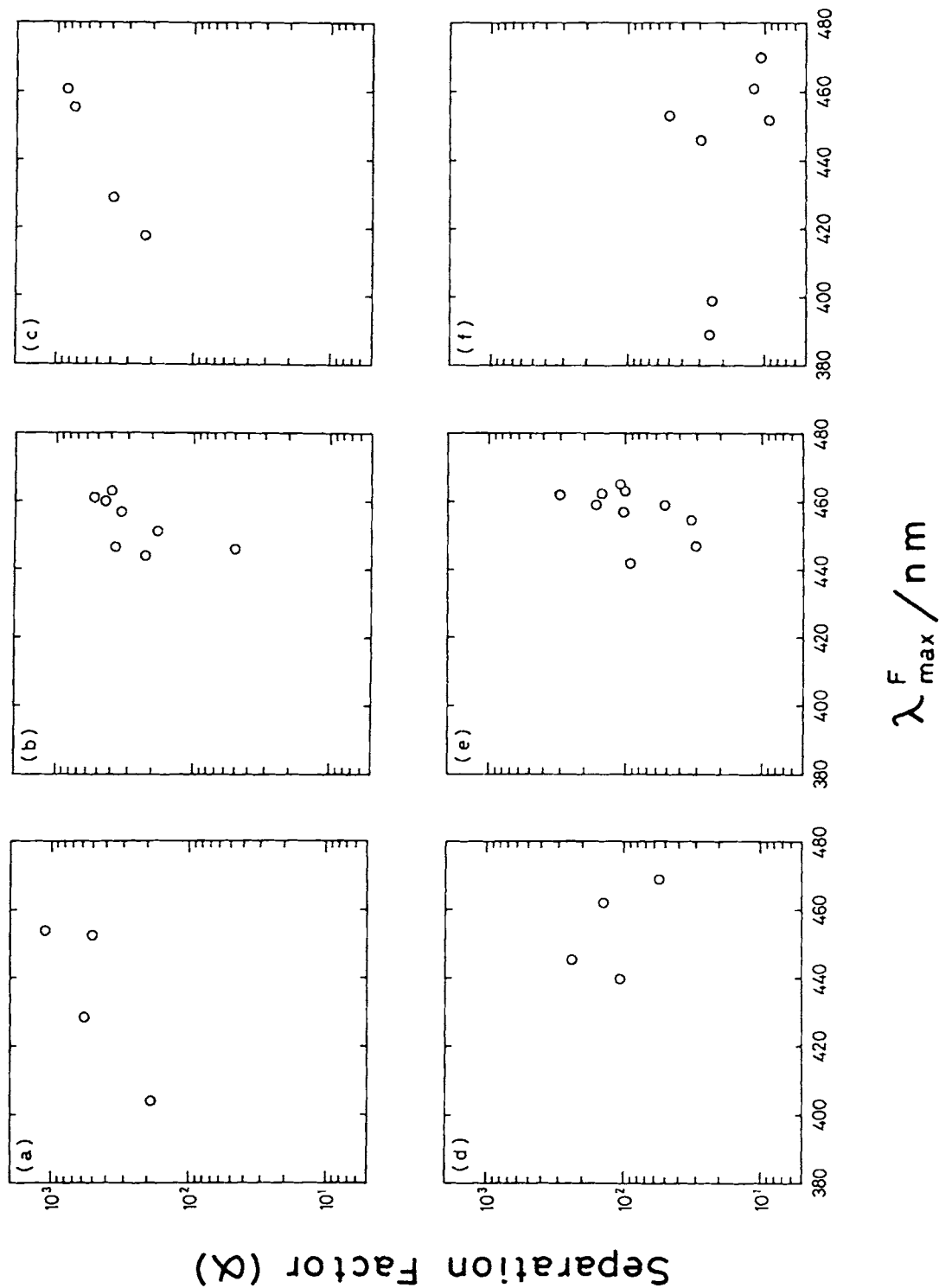
Figure 4 Relationship between separation factor (α) and fluorescence emission maximum (λ_{max}^{F}) of ANS in the membrane. Downstream pressure, 400 Pa (3.0 Torr); operating temp except membranes **35** and **37**, 30°C; operating temp for membranes **35** and **37**, 25°C; weight fraction of water in feed, ca. 0.5.
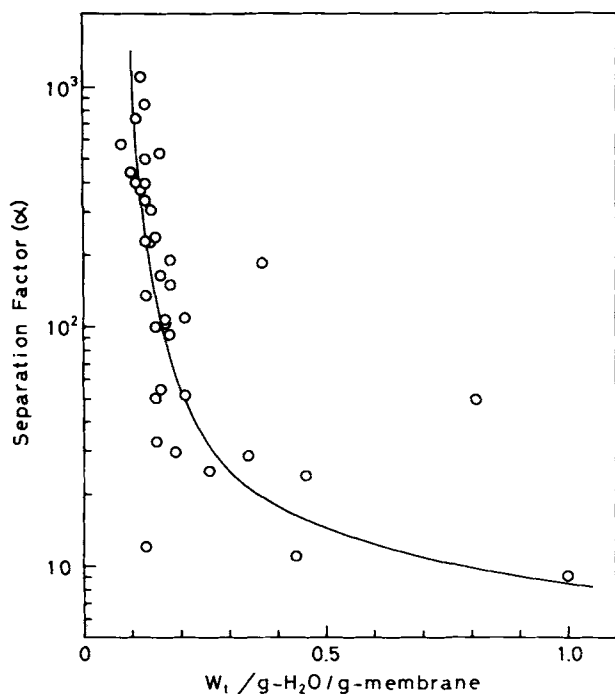
$$R_b = W_b / W_t \qquad (5)$$

Figure 5 Relationship between separation factor (α) and the total water content in the membrane (W_t). Downstream pressure, 400 Pa (3.0 Torr); operating temp except membranes **35** and **37**, 30°C; operating temp for membranes **35** and **37**, 25°C; weight fraction of water in feed, ca. 0.5.

Permselectivity toward water had an inclination to increase with an increasing fraction of bound water. This might be explained as follows: The solubility of ethanol in the bound water might be negligible or null, and the membrane with a high fraction of bound water had a high separation factor. The numerical values of the separation factors at the point where the fraction of bound water was unity for 28 kinds of membranes range from 10^2 to 10^3. Ethanol may be dissolved in the polymer matrix, that is, a small amount of ethanol permeated through these membranes by the solution–diffusion model via the polymer matrix. The difference in the magnitudes of solution and diffusion of ethanol for each membrane was the reason for such scattering of the separation factors.

This result suggests that the control of the state of water in the membrane at any rate is essential to the molecular design of novel membrane materials for selective separation of aqueous ethanol solution. An emergence of the membrane, which has high water content and in which all water molecules can be assigned to the bound water, will lead to a superior membrane for the selective separation of water from water–ethanol mixtures.
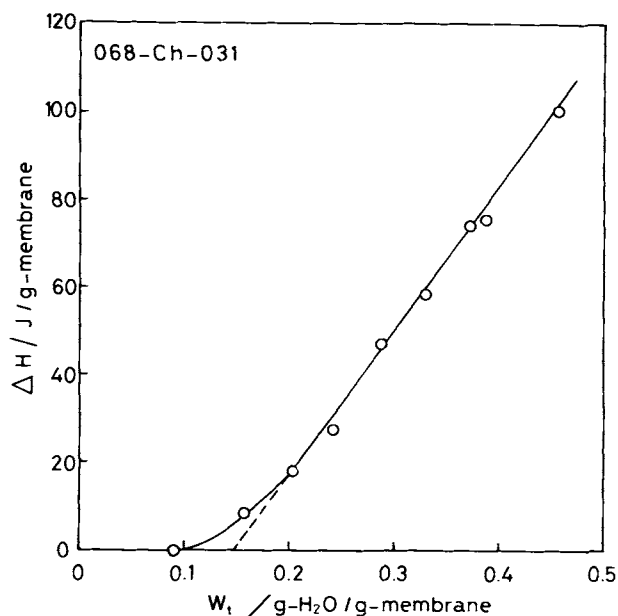
fusion of bulk water suggests that the data obtained here are accurate. Extraporation of $\Delta H = 0$ intercepts the water content axis at a point that is the total bound water content of that sample.

The bound (nonfreezing) water content, W_b, and the free (freezing or bulk) water content, W_f, were estimated and are plotted against the total water content, W_t, in Figure 7. The amount of free water, W_f, was estimated from the difference in the water content and the amount of bound water:

$$W_f = W_t - W_b \qquad (4)$$

All water molecules absorbed in the 068-Ch-031 membrane exist as bound water at water contents lower than around 0.1. The amount of bound water, W_b, increases with increasing the total water content, W_t, approaching around 0.15 asymptotically.

In Figure 8, the separation factors toward water are plotted against their fractions of bound water, R_b, which is defined by eq. (5):

Figure 6 Water content dependence of the heat of melting of freezing water, ΔH, in the 068-Ch-031 membrane.
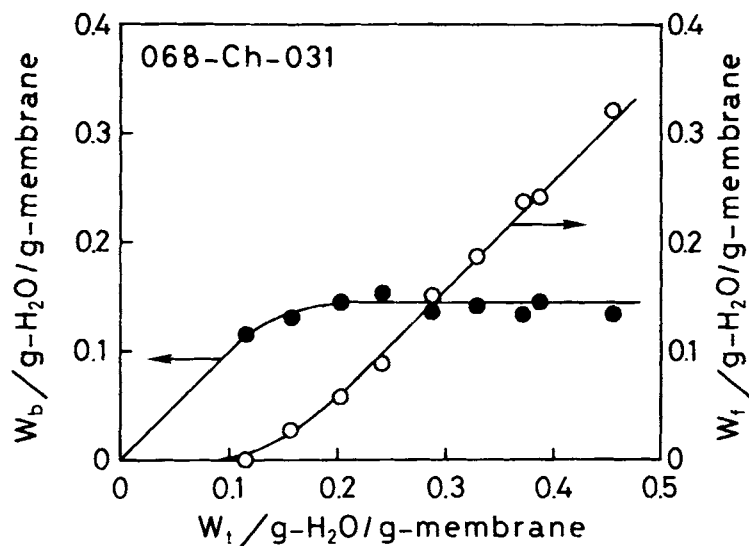
Figure 7   Water content dependence of bound and free water content in the 068-Ch-031 membrane. (●) Bound water; (○) free water.

CONCLUSION

Membranes obtained from polymers having a cationic charge site, quaternized poly[3-(N',N'-di-
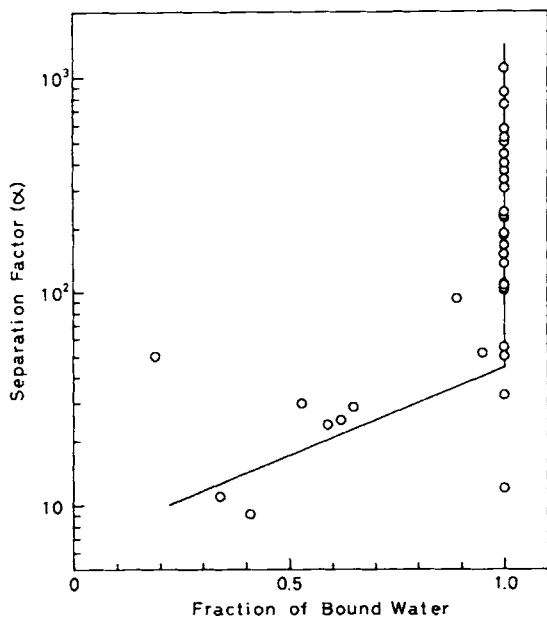

Figure 8   Relationship between separation factor (α) and fraction of bound water in the membrane (R_b). Downstream pressure, 400 Pa (3.0 Torr); operating temp except membranes **35** and **37**, 30°C; operating temp for membranes **35** and **37**, 25°C; weight fraction of water in feed, ca. 0.5.

methyl)aminopropylacrylamide-co-acrylonitrile]s, preferentially permeated water from the aqueous ethanol solution by pervaporation. The separation factor toward water reached over 15,000. Membrane performance and the separation factor showed a good correlation to membrane polarity, which was evaluated using 1-octadecyl-3,3-dimethyl-6'-nitro-spiro(indoline-2,2'-2H-benzopyran) as an indicator. The state of water in the membrane was investigated by differential scanning calorimetry. Clearly, there were two states of water in the membrane: bound and free. Permselectivity toward water increased with an increasing fraction of bound water in the membrane. This result suggested that the control of the state of water in the membrane is an indispensable way to reach a superior membrane material for selective separation of water from aqueous ethanol solution.

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