Modified Free-Volume Model for Pervaporation of Water/Ethanol Mixtures Through Membranes Containing Hydrophilic Groups or Ions

HYO JIN KIM,[1] WON HO JO,[1,*] and YONG SOO KANG[2]

[1]Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, South Korea; [2]Division of Polymer Science and Engineering, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

SYNOPSIS

The free-volume model for pervaporation has been modified by considering the polar path, in order to apply the model to membranes containing hydrophilic groups. The free-volume parameters were determined by inverse gas chromatography. For the polyacrylonitrile (PAN) membrane, the transport mechanism could be analyzed only by the free-volume model; however, for a membrane containing a hydrophilic moiety, the transport properties could be interpreted by the modified model. In water/ethanol mixtures, ethanol transports through the membrane matrix, while water permeates through the polar pathways consisting of polar groups or ions and water molecules as well as through the membrane matrix. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The pervaporation through a moderately swelling membrane was analyzed as a solution–diffusion process, on the assumption that the diffusion coefficient of the permeant is a function of its concentration. Single-component permeation through a homogeneous polymeric membrane can be satisfactorily described by Fick's law with a concentration-dependent diffusion coefficient, as has been studied by several authors.[1-3] Free-volume theory also showed good agreement with experiment.[4]

For the transport of a binary mixture through the homogeneous membrane, several theories have been developed. Fels[5] modified the free-volume model to include contributions of both penetrants to the total free volume. Greenlaw et al.[6] reported a linear relationship between the concentrations of permeants and their diffusion coefficients. These treatments were found to hold only for mixtures of nonpolar solvents which behave almost ideally, but not for polar mixtures such as water–ethanol. When

a liquid mixture permeates through a swollen membrane, there will be a coupling of fluxes. The permeation of a component of the binary mixture may be affected not only by the presence of itself but also by the movement of the other component. In polymers below their glass transition temperatures, the thermal motions of the chain segments are very restricted. When low molecular weight components are dissolved in such polymers, the mobility of the chains increases. In the case of a binary mixture, both components will exert a plasticizing effect on the segmental motions, and thus the mobilities of both permeants will be enhanced by the combined plasticizing action. This phenomenon becomes more significant for polar solvent mixtures. Therefore, in a model description for the permeation of liquid mixtures by pervaporation, coupling phenomena have to be taken into account. Brun et al.[7] proposed a six-coefficient exponential model, which is an extension of Long's model[8] to the case of binary mixtures. Mulder and Smolders[9] developed a modified sorption–diffusion model, which describes transport and concentration profiles of water and ethanol in homogeneous membranes. They investigated polymer–liquid and liquid–liquid interactions in detail by swelling exper-

iments in order to determine the Flory–Huggins interaction parameters.

Although numerous theories have been reported, no model has been developed that can satisfactorily describe the transport of polar mixtures through the membrane containing hydrophilic groups. In this article, we simply modified the free-volume model originally developed by Yeom and Huang[10] by taking into account a polar path, in order to interpret a transport mechanism for a membrane containing a hydrophilic moiety. The free-volume parameters for the model were determined from inverse gas chromatographic data. The model predictions for flux and selectivity were compared with experimental data.

THEORY

Free-volume Model for Pervaporation

Recently, Yeom and Huang[10] successfully developed a pervaporation transport model based on the Fu-

jita's free-volume theory.[11] The steady-state permeation of a single component through a membrane can be described by Fick's first law as

$$J_i = -D_i \frac{dC_i}{dx} \qquad (1)$$

where J_i is the flux of single component i; D_i, the concentration-dependent diffusion coefficient of component i in the polymer fixed frame of reference; and dC_i/dx, the concentration gradient across the membrane. Fujita introduced a thermodynamic diffusion coefficient of component i, $(D_T)_i$, which is related to the diffusion coefficient, D_i, by eq. (2):

$$(D_T)_i = D_i \frac{\partial \ln \phi_i}{\partial \ln a_i} \qquad (2)$$

In eq. (2), ϕ_i is the volume fraction of component i in the membrane, and a_i, the chemical activity of
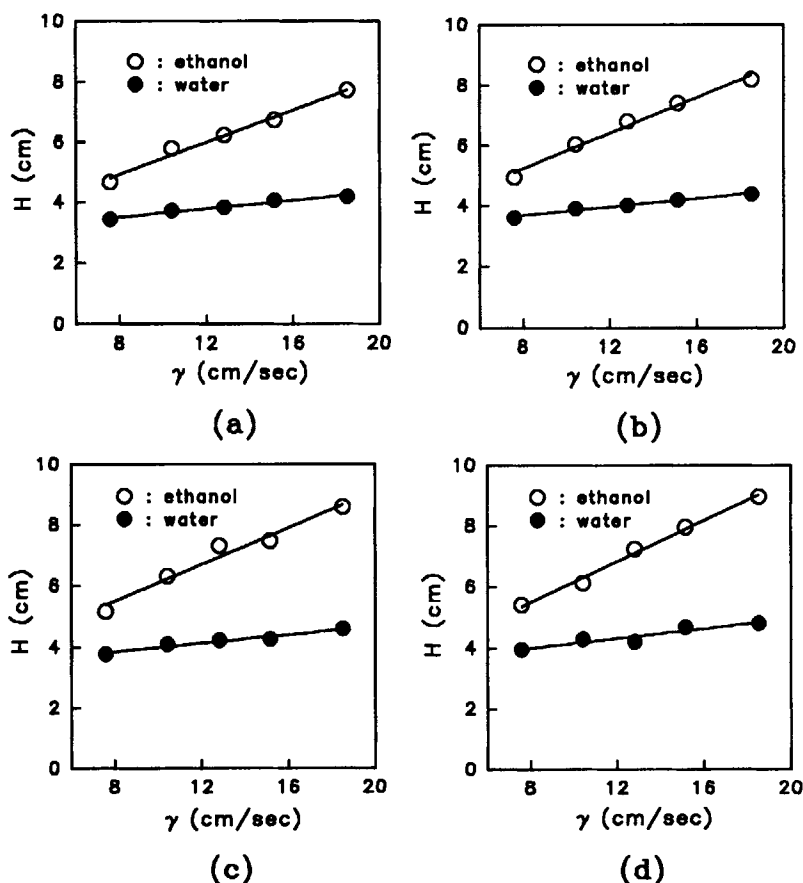

Figure 1 Plots of the theoretical plate height vs. the linear velocity of the carrier gas at 30°C. The polymers coated on the column-packing material are (a) PAN, (b) poly(AN-co-AA) (8.5 mol % AA), (c) Poly(AN-co-AA) (8.5 mol % AA)/poly(AN-co-VP) (10 mol % VP) blend (50/50 by weight), and (d) poly(AN-co-AA) (Na) (8.2 mol % AA).

Table I Diffusion Coefficients of Pure Ethanol at Zero Concentration at Various Temperatures[a]

Polymer	30°C	40°C	50°C	60°C
PAN	0.812	1.099	1.471	1.967
Poly(An-co-AA)	1.460	2.074	2.647	3.518
Poly(AN-co-AA)/poly(AN-co-VP)	4.472	6.220	8.548	11.111
Poly(An-co-AA) (Na)	1.054	1.428	1.918	2.754

[a] 10^{-9} cm²/s.

component i in the membrane which can be calculated by Flory–Huggins thermodynamics.

Equation (2) represents that the thermodynamic diffusion coefficient consists of a diffusive term, D_i, and a thermodynamic term, $\partial \ln \phi_i / \partial \ln a_i$. The thermodynamic diffusion coefficient of component i at zero concentration, $(D_T)_{io}$, can be written as

$$(D_T)_{io} = RTA_{di}\exp\left\{\frac{-B_i}{f(0, T)}\right\} \quad (3)$$

where A_{di}, B_i are constants characteristic of the given polymer–penetrant pair and $f(0, T)$ is the free-volume of the polymer itself. In the case of binary liquid permeation, the thermodynamic diffusion coefficient of component 1 can be expressed as

$$(D_T)_1$$

$$= RTA_{d1}\exp\left\{\frac{-B_1}{f(0, T) + \beta_1(T)\phi_1 + \beta_2(T)\phi_2}\right\} \quad (4)$$

where β_i, a proportionality constant relating to the amount free volume, is increased by the diffusing species. The thermodynamic term of eq. (2) can be predicted by Flory–Huggins thermodynamics. Combining eqs. (1)–(4) and integrating with boundary conditions at an isothermal state, we can calculate the total flux by

$$\int_0^l J_i dx = \rho_i \int_0^{\phi_{io}} (D_T)_i \frac{\partial \ln a_i}{\partial \ln \phi_i} d\phi_i \quad (5)$$

where l is the membrane thickness, and ϕ_{io}, the concentration of component i at the interface between the membrane and the feed mixture.

Modified Model for Pervaporation

Several authors[12,13] indicated that the mechanism of water transport through a membrane containing polar moieties such as acid, base group, and ion is not easily explained by random solution and diffusion through the polymer matrix. Rather, the transport through highly water-selective continuous paths (channels) within the membrane is probably responsible for the observation of the low activation energy and high fluxes. Therefore, the free-volume model[10] is modified for the membrane containing polar moieties by taking into account a polar path. To develop the modified free-volume theory, two assumptions are made: First, ethanol cannot interact or permeate through this highly water selective path, and, second, the diffusion coefficient of water in this path is constant, i.e., it is independent of water concentration. The flux of water, J_1, can be expressed as

$$J_1 = kJ_{1p} + (1 - k)J_{1m} \quad (6)$$

Table II Diffusion Coefficients of Pure Water at Zero Concentration at Various Temperatures[a]

Polymer	30°C	40°C	50°C	60°C
PAN	3.361	3.974	4.675	5.456
Poly(AN-co-AA)	3.540	4.188	4.630	5.787
Poly(AN-co-AA)/poly(An-co-VP)	5.408	6.126	7.504	8.777
Poly(AN-co-AA) (Na)	5.439	6.027	7.556	8.843

[a] 10^{-9} cm²/s.

where k is the surface area fraction of polar paths in the membrane, and J_{1p} and J_{1m}, the flux of water through the polar pathway and through the membrane matrix, respectively. The fraction of polar paths, k, can be regarded as a surface area fraction of the polar component, which will be explained in more detail in the Results and Discussion section. J_{1p} and J_{1m} can be expressed as

$$J_{1p} = \rho_1 D_{1p} \frac{\partial \phi_1}{\partial x} \qquad (7)$$

and

$$J_{1m} = \rho_1 D_{1m} \frac{\partial \phi_1}{\partial x} \qquad (8)$$

where D_{1p} and D_{1m} are the diffusion coefficients of water in the polar pathway and in the membrane matrix, respectively. Substitution of eqs. (7) and (8) into eq. (6) gives

$$J_1 = k\rho_1 D_{1p} \frac{\partial \phi_1}{\partial x} + (1 - k)\rho_1 D_{1m} \frac{\partial \phi_1}{\partial x} \qquad (9)$$

Integrating eq. (9) over the membrane thickness gives

$$\int_0^l J_1 dx = \int_0^{\phi_{1p}} \rho_1 k D_{1p} d\phi_1$$
$$+ \int_0^{\phi_{1m}} \rho_1 (1 - k) D_{1m} d\phi_1 \qquad (10)$$

Therefore, the flux of water and ethanol of the system, J_1 and J_2, can be expressed as

$$J_1 = \frac{\rho_1}{l} \left\{ \int_0^{\phi_{1p}} k D_{1p} d\phi_1 + \int_0^{\phi_{1m}} (1 - k) D_{1m} d\phi_1 \right\} \qquad (11)$$

and

$$J_2 = (1 - k) \frac{\rho_2}{l} \int_0^{\phi_{2m}} D_{2m} d\phi_2 \qquad (12)$$

where ϕ_{1p} is the concentration of water in the polar pathway at the membrane surface, and ϕ_{1m} and ϕ_{2m}, the concentrations of water and ethanol in the membrane matrix, respectively, at the interface between the feed mixture and the membrane. The selectivity, $\alpha_{1/2}$, can be calculated by

$$\alpha_{1/2} = \frac{J_1/J_2}{c_{1f}/c_{2f}} \qquad (13)$$

where c_{1f} and c_{2f} are the wt % of water and ethanol in feed mixture, respectively.

Determination of Free-volume Parameters

The free-volume data of the pure water were obtained from the literature.[14] The density of ethanol was given as a function of temperature in the form of a Taylor expansion.[15] The T_g of the membranes were determined to be about 105°C by differential scanning calorimetry (DSC). Therefore, the free-volume parameters, $\beta(T)$, $f(0, T)$, and $f(1, T)$, could be calculated by following the method of Yeom and Huang.[10]

The free-volume parameters of penetrants in the membrane have been often determined from diffusion coefficients which are measured by a vapor-sorption method. However, this method is time-consuming and requires extensive data analysis. In this work, inverse gas chromatography (IGC) was used to determine permeant diffusion coefficients. IGC has been well established as a means of studying interactions between polymers and volatile solutes. Van Deemter et al.[16] related the peak broadening in a gas chromatographic column to column properties through eq. (12):

$$H = C_1 + \frac{C_2}{\gamma} + C_3 \gamma \qquad (14)$$

where H is the theoretical plate height; γ, the linear velocity of the carrier gas; and C_1, C_2, and C_3, constants independent of γ. Whereas C_1 and C_2 are related to instrument performance and gas-phase spreading, C_3 depends on a number of factors including the diffusion coefficient of the probe molecule in the stationary phase. The constant C_3 is given by

$$C_3 = \frac{8}{\pi^2} \frac{d^2}{D_i} \frac{K}{(1 + K)^2} \qquad (15)$$

where D_i is the diffusion coefficient of the probe molecule, and d, the thickness of the stationary phase (the polymer film coated on the packing material) calculated by the equation

$$d = \frac{1}{3} w \left(\frac{\rho_B}{\rho_P} \right) \bar{r} \qquad (16)$$

In eq. (14), w is the coverage ratio of polymer to packing; $\bar{r}$, the average radius of beads; and ρ_B and ρ_P, the density of the bead and polymer, respectively. IGC is applicable only to solutes at infinite dilution to avoid concentration dependence of the diffusion coefficient. Thus, D_i in eq. (15) can be regarded as the diffusion coefficient of the probe molecule at zero concentration (D_{io}). K is the partition ratio given by

$$K = \frac{t_r - t_n}{t_n} \qquad (17)$$

where t_r and t_n are the retention time to peak maximum of the probe molecule and a noninteracting material such as air. The determination of D_{io} involves the measurement of H at several relatively high flow rates, where the term C_2/γ is usually negligible.[17] The slope obtained from a plot of H vs. γ enables one to calculate D_{io}, since K is known in these experiments. The plate height, H, is determined from the eluted peaks displayed on a chart record by

$$H = \frac{L_c}{5.54}\left(\frac{W_{1/2}}{t_r}\right)^2 \qquad (18)$$

where L_c is the column length, and $W_{1/2}$, the peak width at half the peak height.

Determination of Binary Compositions of Permeants in Membrane

To obtain the flux of the permeating component in eqs. (5), (11), and (12), the boundary conditions should be determined. Mulder et al.[18] suggested a simple equation of preferential sorption for a pervaporation membrane, assuming that a thermodynamic equilibrium exists between the membrane surface and the liquid feed mixture. In the case of highly water selective polymers which are slightly swollen, the equation can be written as

$$\ln\frac{\phi_1}{\phi_2} - \ln\frac{v_{1f}}{v_{2f}}$$

$$= (L-1)\ln\frac{\phi_1}{v_{2f}} - g_{12}(u_2)(\phi_2 - \phi_1)$$

$$- g_{12}(v_{2f})(v_{1f} - v_{2f}) - \phi_3(\chi_{13} - L\chi_{23})$$

$$+ u_1\phi_2\frac{\partial g_{12}}{\partial u_1} - v_{1f}v_{2f}\frac{\partial g_{12}}{\partial v_{2f}} \qquad (19)$$

where v_{if} is the volume fraction of each component in the feed; L, the ratio of molar volume (V_1/V_2); u_i, the volume fraction of component i in the membrane with respect to the liquid part; g_{ij}, the concentration-dependent binary interaction parameter between component i and j; and χ_{ij}, Flory–Huggins interaction parameter which is independent of the concentration at small amount of sorption. Therefore, once the total sorption of the feed mixture into the membrane is determined, the sorption of each component in the membrane can be predicted from eq. (19). Finally, this makes it possible to predict the individual fluxes with varying feed concentration, if the values of g_{12}, χ_{13}, and χ_{23} are properly determined. It was reported that the values of χ_{13} and χ_{23} could be easily determined by the sorption experiment and that the value of g_{12} could be calculated from the excess free energy of mixing of water and ethanol by

$$g_{12}(v_{2f}) = 0.9820 - 1.3483v_{2f} + 4.15v_{2f}^2$$

$$- 3.316v_{2f}^3 + 0.8897v_{2f}^4 \qquad (20)$$

where v_{2f} is the volume fraction of ethanol in the feed, and for the liquid mixture in the polymer membrane, v_{2f} has to be replaced by u_2.

EXPERIMENTAL

Materials, Membrane Preparation, Sorption, and Pervaporation

The polymer materials, poly(acrylonitrile) (PAN), poly(acrylonitrile-co-acrylic acid) [poly(AN-co-AA)], poly(acrylonitrile-co-vinyl pyridine) [poly(AN-co-VP)] and sodium salt of poly(acrylonitrile-co-acrylic acid) [poly(AN-co-AA)(Na)], used in this study were synthesized in our laboratory. Poly(ethylene oxide) was purchased from Aldrich Co. The preparation of the membranes, sorption measurement, and pervaporation procedure are described in detail elsewhere.[19,20]

Inverse Gas Chromatography (IGC)

The column-packing material was prepared by the soaking method.[21] The polymers were dissolved in DMF and then were coated onto a supporting material, Chromosorb W of 60–80 mesh. The support was washed by acid and treated with dimethyldichlorosilane. The coated supports were packed into 1 m-long stainless columns, 0.14 cm inner diameter. The columns were conditioned in the oven
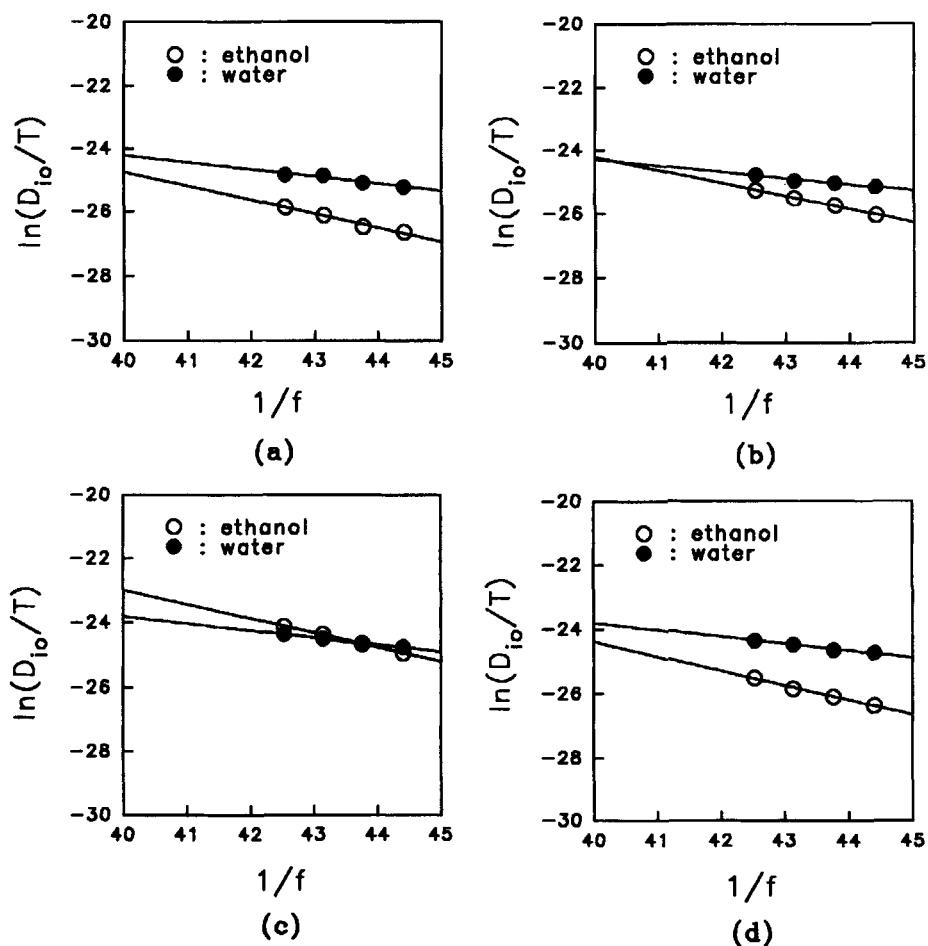
Figure 2   Relationship between the free volume and the diffusion coefficients of water and ethanol at zero concentration: (a) PAN; (b) poly(AN-co-AA) (8.5 mol % AA); (c) poly(AN-co-AA) (8.5 mol % AA)/poly(AN-co-VP) (10 mol % VP) blend (50/50 by weight); (d) poly(AN-co-AA) (Na) (8.2 mol % AA). The experiment was carried out at 30, 40, 50, and 60°C.

of the chromatograph for at least 6 h above 80°C. Measurements were made on a Varian Model 6000 gas chromatograph equipped with a thermal conductivity detector. Dried helium was used as a carrier gas. The flow rate was controlled by a pre-cision needle valve and was measured by a soap bubble flowmeter. The inlet and outlet pressures were frequently measured by a mercury manometer. Air was used as a marker for retention time. Ethanol, one of the probes, was reagent grade.

Table III   Free-volume Parameters of Penetrants in the Membranes[a]

Membrane	Water		Ethanol	
	B_i	$RA_{di} \times 10^7$	B_i	$RA_{di} \times 10^4$
PAN	0.210	1.245	0.421	3.567
Poly(AN-co-AA)	0.211	1.370	0.419	5.799
Poly(AN-co-AA)/poly(AN-co-VP)	0.208	1.832	0.421	19.400
Poly(AN-co-AA) (Na)	0.209	1.926	0.422	4.783

[a] RA_{di}: cm^2/s K.

Water was distilled before use. The sample was injected into the chromatographic column in volumes less than 0.5 μL.

RESULTS AND DISCUSSION

Sorption and Diffusion Experiments

Diffusion coefficients of water and ethanol at zero concentration in the polymers are determined from the slopes in Figure 1, according to eqs. (14) and (15). In Tables I and II, the diffusion coefficients of ethanol and water at zero concentration are summarized for various operating temperatures. Diffusion coefficients are of the same order of magnitude for all polymers, and the diffusion coefficient increases with temperature, indicating that at zero concentration of penetrants the diffusion depends not only on the thermal motion of polymer chain

Table IV   Diffusion Activation Energy for Water and Ethanol Through the Membranes

	E_a (kcal/mol)	
Membrane	Water	Ethanol
PAN	3.250	5.925
Poly(AN-co-AA)	3.160	5.805
Poly(AN-co-AA)/poly(AN-co-VP)	3.324	6.138
Poly(AN-co-AA) (Na)	3.379	6.381

but also on penetrants, which increases the free volume of the system. In fact, according to the free-volume theory, the diffusivity of a penetrant at zero concentration through a membrane is a function of the size and shape of the penetrant. In other words, the molecules with a smaller molecular size permeate faster. As can be seen in Tables I and II, water molecules diffuse faster than does ethanol except for
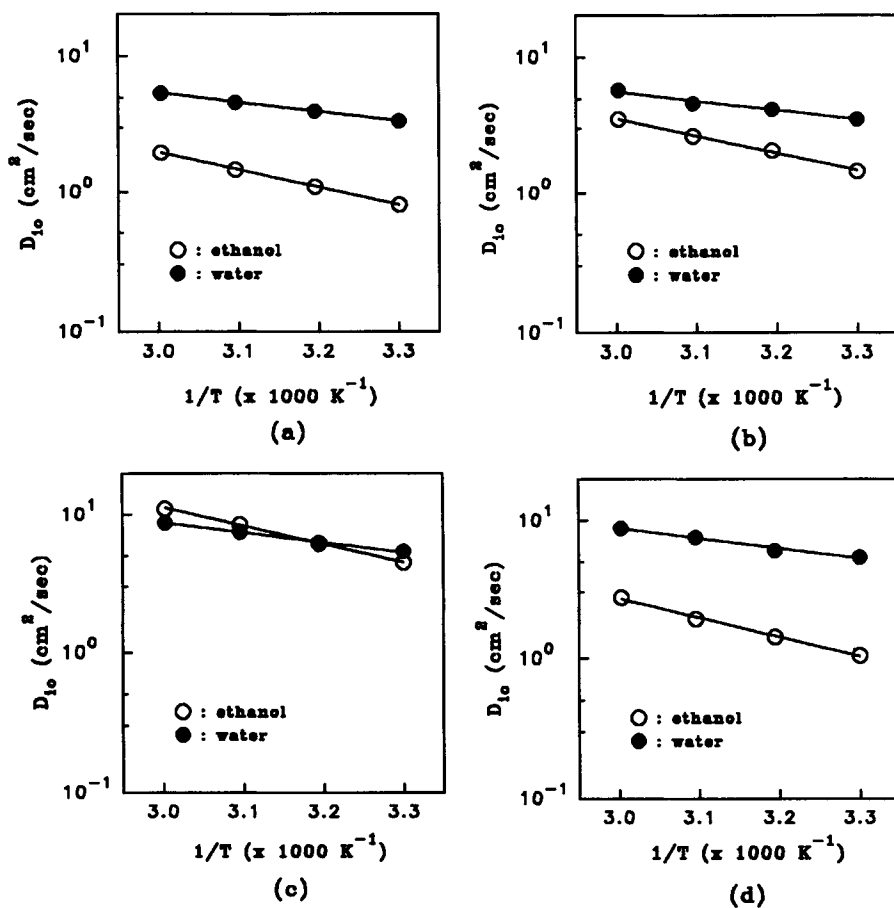

Figure 3   The effect of the operating temperature on the diffusion coefficient of water and ethanol at zero concentration: (a) PAN; (b) poly(AN-co-AA) (8.5 mol % AA); (c) poly(AN-co-AA) (8.5 mol % AA)/poly(AN-co-VP) (10 mol % VP) blend (50/50 by weight); (d) poly(AN-co-AA) (Na) (8.2 mol % AA).

Table V   Flory–Huggins Interaction Parameters Between Pure Liquid and Membranes

Membrane	χ_{13}	χ_{23}
PAN	2.06	3.79
Poly(AN-co-AA)	2.03	3.70
Poly(AN-co-AA)/PEO	1.98	3.72
Poly(AN-co-AA)/poly(AN-co-VP)	1.89	3.75
Poly(AN-co-AA) (Na)	1.83	3.71

the poly(AN-co-AA)/poly(AN-co-VP) blend membrane.

The change of diffusion coefficients at zero concentration with temperature can be predicted from eq. (3). Thus, the free-volume parameters, B_i and

A_{di}, of water and ethanol can be calculated from the slope and intercept of the plot of ln D_{io}/T vs. $1/f(0, T)$. In Figure 2, for all polymers, the slope of ethanol is larger than that of water, indicating that the value of B_i for ethanol is higher than for water. As the free volume of the system linearly depends on temperature, the slope of Figure 2 can be regarded as the activation energy of penetrant for diffusion through the membrane. Thus, it indicates that activation energy is larger for diffusion of ethanol than for diffusion of water.

In Table III, the free-volume parameters determined by the IGC method are summarized. As mentioned above, the B_i value of water is smaller than that of ethanol because water has a smaller diffusional size. From the slope of Figure 3, the activation
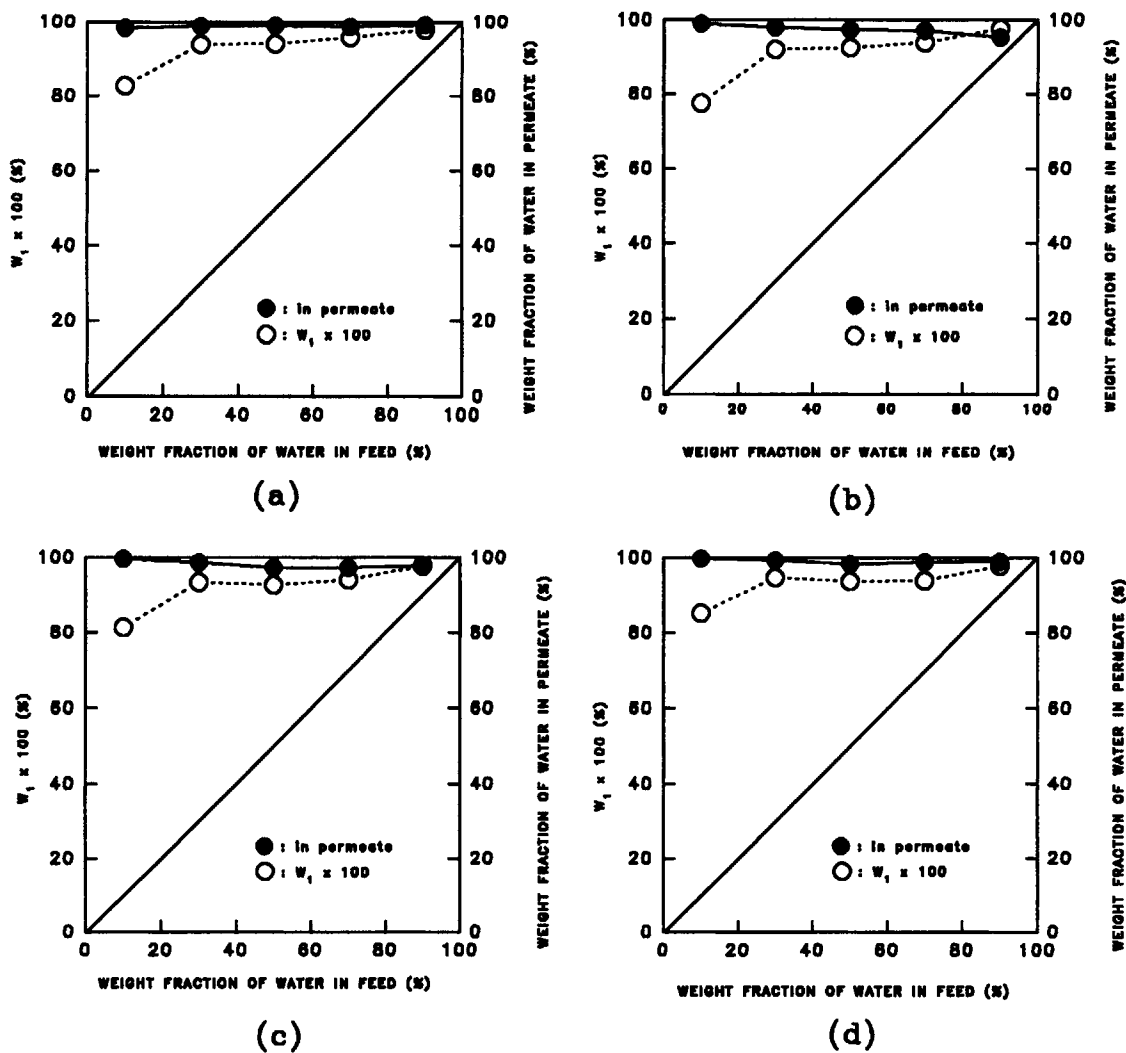

Figure 4   Plots of the calculated composition of water in membrane with respect to the liquid part (w_1) and in permeate against the feed composition at 30°C: (a) PAN; (b) poly(AN-co-AA); (c) poly(AN-co-AA)/poly(AN-co-VP); (d) poly(AN-co-AA) (Na).
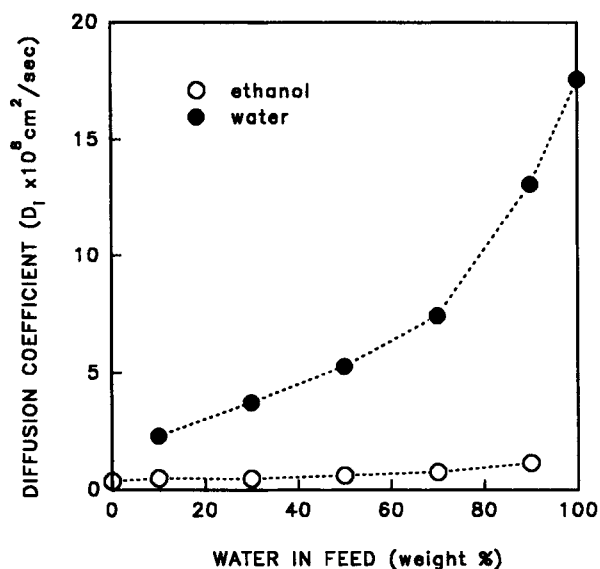
Figure 5 The calculated diffusion coefficients of penetrants through PAN membrane on the upstream side of the membrane as a function of the water content in water/ethanol feed mixture at 30°C.

energies for diffusion at zero concentration can be calculated and are summarized in Table IV. As described above, the value of B_i is closely related to the activation energy for diffusion.

Equation (18) was used to calculate the individual sorption data, ϕ_1 and ϕ_2. The Flory–Huggins interaction parameters determined from the sorption data are summarized in Table V. The calculated weight fractions of the binary liquid mixture in the ternary system are shown in Figure 4 with pervaporation results. Very high values for the preferential sorption of water are observed. This behavior could be expected because of the smaller molar volume of water and the much higher affinity between water and the membranes in comparison with between ethanol and the membranes. For all membranes used, the results of pervaporation are higher than those of sorption, indicating that the concentration of water in the permeate is higher than that in the membrane. Recently, Neel et al.[22,23] considered that the selective diffusion in a dry region of the membrane near the downstream plays a governing role in determining the overall selectivity, whereas Mulder et al.[18] interpreted the selectivity as a result of a preferential sorption of one component of a binary mixture on the swollen surface of the membrane at the upstream side. In this study, it is suggested that not only preferential sorption but also selective diffusion contribute to the selective transport if these results follow the solution–diffusion

model, which describes the flux of a component through a membrane as a function of both solubility and diffusivity.

Pervaporation of PAN Membrane

Both the free-volume model and the modified model were applied to the experimental data for pervaporation of a water and ethanol mixture through the membranes used in this study. For the PAN membrane, which is assumed to have no polar groups to interact specifically with water molecules, the transport of water and ethanol is analyzed by the free-volume model and represented in Figures 5 and 6. As shown in Figure 5, the diffusion coefficient of water at the upstream side of the PAN membrane, where the membrane surface is in contact with the liquid feed mixture, is larger than that of ethanol over the entire range of the feed composition. Especially, from the fact that the diffusion coefficient of ethanol slightly increases with the water content in the feed while the diffusion coefficient of water increases dramatically when the water content in the feed becomes higher, it is envisaged that the water molecules play a role as a plasticizer for the membrane, resulting in an increase of the diffusion coefficient of ethanol. Figure 6 shows the comparison of experimental data with the results from the free-volume model, when the model is applied to the per-
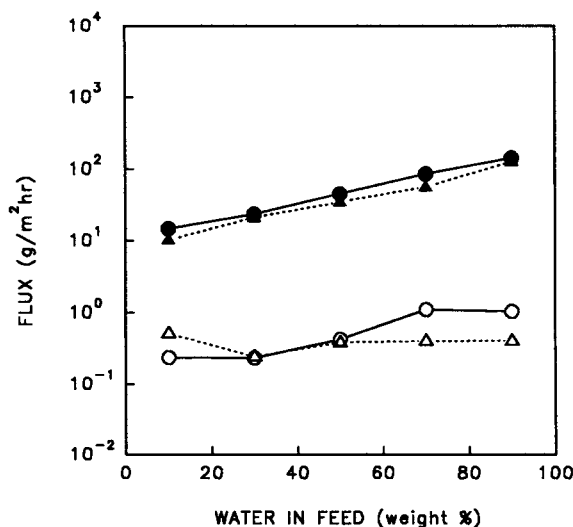

Figure 6 The experimental and calculated fluxes of permeating components through PAN membrane as a function of the water content in the water/ethanol feed mixture at 30°C: open and filled symbols denote the ethanol flux and water flux, respectively; circles and triangles represent the experiment and the free-volume model, respectively. The membrane thickness is 10 μm.
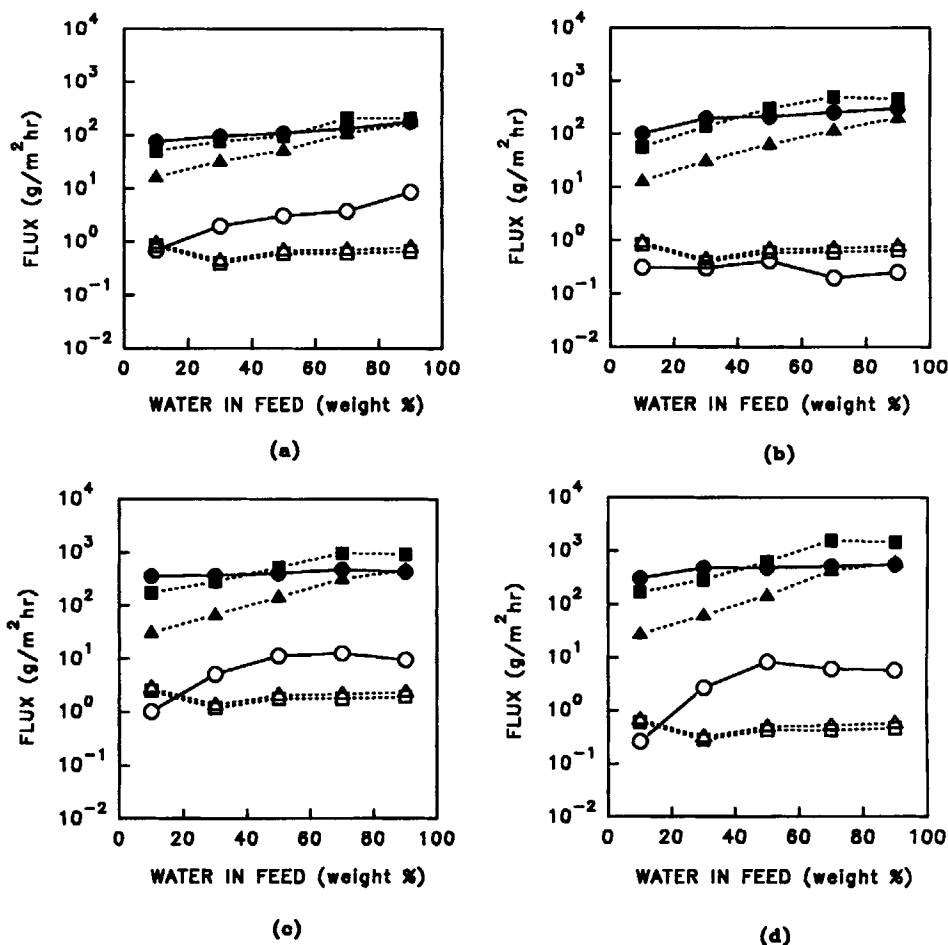
Figure 7   Comparison of the experimental fluxes with the model predictions of water and ethanol at 30°C: (a) poly(AN-co-AA); (b) poly(AN-co-AA)/PEO; (c) poly(AN-co-AA)/poly(AN-co-VP); (d) poly(AN-co-AA) (Na). Open and filled symbols denote the ethanol flux and water flux, respectively; circles, triangles, and squares represent the experiment, the free-volume, and the modified model, respectively. The membrane thickness is 10 μm.

vaporation performance of the PAN membrane. The water and ethanol fluxes from the model are very close to the experimental data. This suggests that, although PAN carries nitrile groups which may specifically interact with water molecules, the transport of water is due mainly to the creation of free volume resulting from the thermal motion and self- or cross-plasticizing action of the penetrants. This means that the dipole interaction between the nitrile group and water, which had been proven to exist by several authors,[24,25] has little effect on the permeation of water; however, structural effects, such as the rigidity of the polymer chain and the plasticizing action of water, rather play a significant role in permeating of water. For the permeation of ethanol, it is also assumed that the specific interaction between ethanol and the membrane does not exist, and thus

the transport is interpreted only by the free-volume model.

Influence of Hydrophilic Groups on Pervaporation

For membranes containing hydrophilic groups, the transport of permeants is analyzed by the modified model and represented in Figure 7. The parameters in eqs. (11) and (12) were estimated from the sorption experiments. As shown in Figure 4, water is sorbed mainly into the membrane, resulting from the smaller molar volume of water and the much higher affinity between water and the membrane in comparison with the affinity between ethanol and the membrane. Since it is considered that the polar moiety is related to swelling, the surface area frac-

Table VI   Surface Area Fraction of Polar Pathways and Diffusion Coefficients of Water in the Polar Pathways

Membrane	k^a	D_{1p} (cm²/s)		
		This Study	Literature	Ref.
PAN	0.0000	0.00	—	
Poly(AN-co-AA)	0.1006	3.33×10^{-6}	2.278×10^{-8}	13
Poly(AN-co-AA)/PEO	0.0911	7.86×10^{-6}	—	
Poly(AN-co-AA)/poly(AN-co-VP)	0.1052	6.55×10^{-6}	—	
Poly(AN-co-AA) (Na)	0.0983	8.10×10^{-6}	1.070×10^{-6}	26
			2.400×10^{-6}	27

ᵃ Surface area fraction of polar groups.
ᵇ cm²/s.

tion of the polar pathway, k, is assumed to be the same as $m^{2/3}$ where m is the swelling ratio. The swelling ratio is defined as the amount of the sorbent at equilibrium sorption divided by the dry weight of the membrane. The water concentration in the membrane matrix, ϕ_{1s}, is calculated from the Flory–Huggins thermodynamics, and the water concentration in polar pathways, ϕ_{1p}, is estimated from m and ϕ_{1s} in the PAN membrane. Figure 7(a) compares the fluxes of water and ethanol through the poly(AN-co-AA) membrane determined from experiment with predictions from two models. The diffusion coefficient of water was obtained by fitting

Figure 8 The experimental and calculated selectivity for PAN membrane as a function of the water content in the water/ethanol feed mixture at 30°C: filled and open symbols denote the selectivity determined from experiment and the free-volume model, respectively.

eq. (11) to the experimental data. The value was estimated to be 3.33×10^{-6} cm²/s.

The transport of water through membranes, containing hydrophilic groups such as carboxylic acid or vinyl pyridine, was widely investigated by Yoshikawa et al.[13] They suggested that for the membrane containing carboxylic acid groups in particular water molecules might be able to permeate by a so-called push–pull mechanism. They also estimated the diffusion coefficient of water through the membrane containing the carboxylic acid group to be 2.278×10^{-8} cm²/s by assuming that the water molecules permeate by direct hydrogen bonding between water molecules and carboxylic acid. The value is considerably smaller than that estimated from the modified free-volume model. This difference could be explained by considering multilayers of water molecules. Water molecules hydrogen-bonded with carboxylic acid in the first layer could hardly diffuse, while excess water molecules, forming successively multiple layers on the first layer, transport very easily, resulting in high values of the diffusion coefficient. Hence, the transport of water through the membrane containing hydrophilic functional groups cannot be explained by a simple diffusion mechanism of the free-volume theory.

Figure 7(b) compares the fluxes from experiment with those from models for the poly(AN-co-AA)/PEO blend membrane. In this case, D_{1p} was calculated as 7.86×10^{-6} cm²/s, which is higher than for the poly(AN-co-AA) membrane alone. This can be attributed to the strong plasticizing action of PEO causing water molecules to permeate more easily. This result indicates that the diffusion coefficient of water becomes higher through the blend membrane if the additive polymer is very water selective and highly plasticizable, although its content is relatively small.
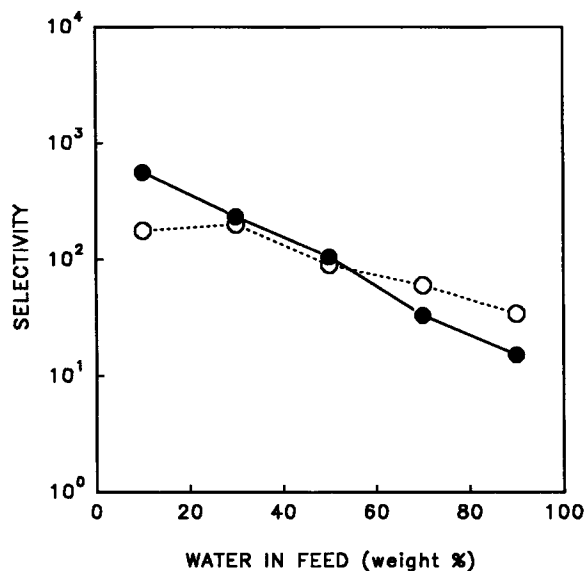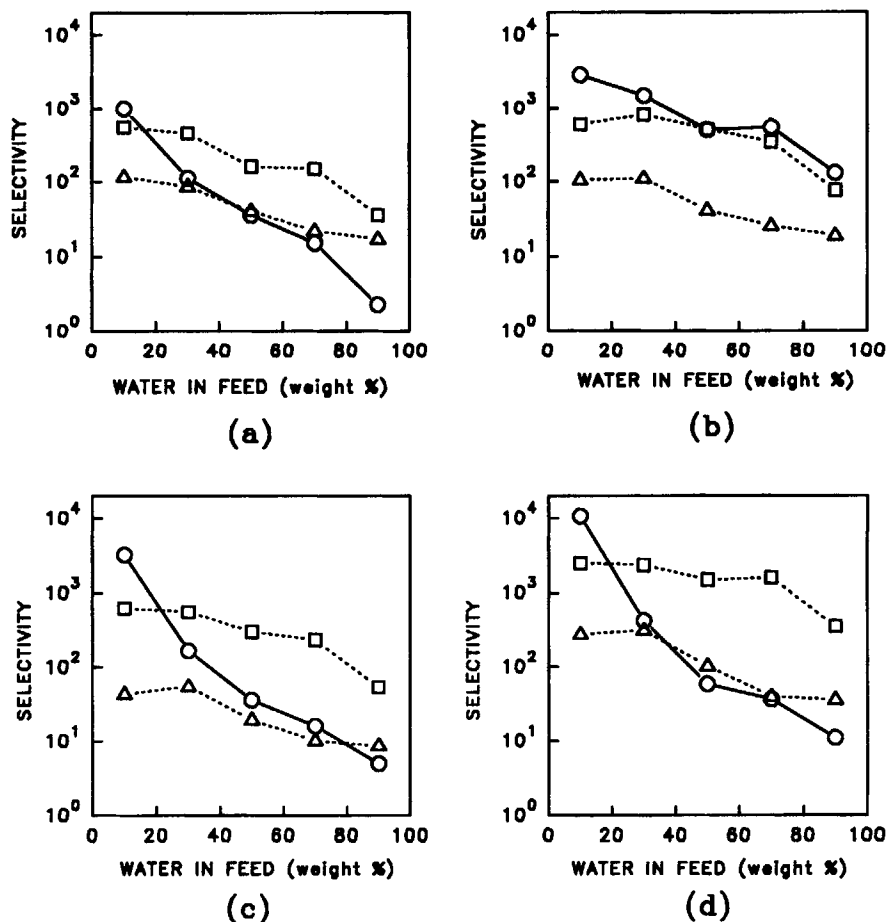
Figure 9 Comparison of the experimental selectivity with the model predictions of water/ethanol mixtures at 30°C: (a) poly(AN-co-AA); (b) poly(AN-co-AA)/PEO; (c) poly(AN-co-AA)/poly(AN-co-VP); (d) poly(AN-co-AA) (Na). Circles, triangles, and squares denote the selectivity determined from experiment, the free-volume, and the modified model, respectively.

Figure 7(c) represents the flux of the permeating component through the poly(AN-co-AA)/poly(AN-co-VP) membrane. An important factor in this system is that the membrane carries ionic moieties as reported in our previous article.[19] The calculated diffusion coefficient of water in ionic pathways, D_{1p}, is 6.55×10^{-6} cm^2/s.

There have been many efforts to elucidate the behavior of water within the hydrated ionic shell. Gierke[12] suggested a model of ion clustering for Nafion membranes. They suggested that short channels connecting adjacent clusters are responsible for the transport of ion or water through the membrane. Cabasso and Lin[26] studied in detail the pervaporation separation of water/ethanol mixtures by Nafion membranes and analyzed the transport mechanism with this short channels model. They computed the diffusion coefficient of water from pervaporation

data with various counterions. For the membrane of the sodium-substituted form, they reported that the mean value of the diffusion coefficient of water is about 1.23×10^{-6} cm^2/s. Meanwhile, Volino et al.[27] examined water mobility in a water-soaked Nafion membrane by a high-resolution neutron quasi-elastic study. They calculated the diffusion coefficient of water within the ionic cluster for various counterions. Table VI lists the diffusion coefficients of water determined from the modified model and the values from the literature. The diffusion coefficients from the modified model are comparable to those from the literature, showing the same order of magnitude. This suggests that the water transport in this system is explained by the transport mechanism through polar pathways developed by a hydrophilic functional group or an ionic site with water molecules.

The flux of water and ethanol through poly-(AN-*co*-AA) (Na) is shown in Figure 7(d). The transport of water shows the same behavior as in Figure 7(c). In this system, the diffusion coefficient of water through the ionic pathways was calculated as 8.10×10^{-6} cm^2/s. The mechanism of water transport could be explained in the same way as in the case of the poly(AN-*co*-AA)/poly(AN-*co*-VP) membrane. The deviations in the ethanol flux between experimental data and model-calculated data might arise from both a very small flux of ethanol and some inaccuracies in swelling experiments.

An interesting phenomenon to be pointed out is that the modified model overestimates the water flux when the concentration of water in feed mixture is relatively high (> 50 wt %). In this case, the free-volume model seems to predict the flux more precisely. It is believed from this fact that in the region of low water concentration the membrane hardly swells, maintaining an almost dry state, so that the flux through the polar pathways is much higher than through the membrane matrix. However, in the region of high water concentration, by the stronger plasticizing action of water than by ethanol, the membrane swells enough so that the increase in the free volume of the system has a more significant effect on the transport of water.

The results of model studies on the selectivity of the membranes are presented in Figures 8 and 9. As compared with the result of flux, the differences between calculated selectivity and experiment are relatively large. This may result from the fact that the selectivity is very sensitive to the ethanol flux. For the PAN membrane, the selectivity could be examined effectively by the free-volume model. In case of membranes containing the hydrophilic moiety, the modified model seems to overestimate the selectivity over most parts of the feed range. This may come from the difference between the ethanol fluxes from the experiment and theoretically calculated values. However, when the water content in the feed mixture is low (< 10 wt %), the modified model predicts results more precisely than does the free-volume model. This can be explained by the same mechanism as described for the flux.

CONCLUSIONS

The transport mechanism of a membrane, containing functional groups capable of interacting with water, was investigated for pervaporation of water/ethanol mixture by modeling. The experimental data were interpreted by both the free-volume model and the modified model. The diffusion coefficients of two permeants at zero concentration and free-volume parameters could be successfully determined with IGC. For the PAN membrane, the transport mechanism of two permeants could be analyzed only by the free-volume model, whereas for membranes containing hydrophilic groups, the modified model should be adopted to interpret more successfully the transport of water through the membranes. These results indicate that ethanol transports through the membrane matrix while water permeates through the hydrophilic polar pathways composed of polar groups or ions and water molecules as well as through the membrane matrix. Especially when the membrane was under a low swollen state, i.e., at a low concentration of water in the feed, it was believed that the transport of water through the polar pathways plays a more significant role in determining overall transport of water through the membrane.

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