

The Behavior of Solute Organic Compounds and Water in Poly(dimethylsiloxane)

S. MISHIMA,¹ T. NAKAGAWA²

¹ Kanagawa Environmental Research Center, 842, Nakaharashimojyuku, Hiratsuka 254-0072, Japan

² Department of Industrial Chemistry, Meiji University, Higasi-mita, Tamaku, Kawasaki 214-0033, Japan

Received 7 May 1999; accepted 15 November 1999

ABSTRACT: The properties of an aqueous solution are interesting depending on its application. Their characteristics are mainly a result of a hydrophobic interaction. The permeation behavior, particularly for an aqueous solution with a hydrophilic solute, is affected by the hydration of water to the solute. In case of an aqueous solution of organic compounds, generally, the water molecule adjacent to the solute become less mobile than in the pure water due to hydration. The hydration may affect the diffusivity of solute molecules during permeation. In this study, we investigated the pervaporation through a poly(dimethylsiloxane (PDMS) membrane and the hydration effect on the solution-diffusion mechanism for various organic compounds. When the concentration of the solution was over the concentration calculated by the number of water molecules adjacent to a solute molecule, the hydration number, the water molecules hydrate to several solute molecules, and the motion of the water molecules was prevented. During pervaporation, the solute was concentrated in the PDMS membrane and the diffusion of water molecules was prevented. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1304–1311, 2000

Key words: hydration; sorption; diffusion; organic compounds; pervaporation

INTRODUCTION

The permeation behavior, particularly for an aqueous solution with a hydrophilic solute, is affected by the hydration of water to the solute.

The physicochemical properties of an aqueous solution is interesting depending on its application and has been extensively studied.^{1–14} Their properties are mainly due to a hydrophobic interaction.

Water molecules are always moving. The motion of water molecules in an aqueous solution containing a solute is affected by the water and solute interaction, and differ from that in pure water. This interaction (the water hydration of a

solute) is important for the kinetic properties of a solution. The transitional motion of water molecules in a diluted aqueous solution was considered in several reports.^{9,10}

For pure water, the water molecules exchange in the vicinity of each other almost immediately. The mean time in an equilibrium position is denoted as τ . The value of the activation energy of the exchange is denoted as E . In the case of an aqueous solution, the mean time that a water molecule is in the closest equilibrium position to the ion in the structure of the solution is denoted as τ_i . The value of the activation energy of the exchange of the closest molecules is denoted as $E + \delta E_i$. The following relation is then obtained^{9,10}:

$$\tau_i/\tau = \exp(\delta E_i/RT) \quad (1)$$

In the case that the solute is an organic compound, the interaction between water molecules

Correspondence to: T. Nakagawa.

Journal of Applied Polymer Science, Vol. 78, 1304–1311 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Physicochemical Properties of Solute Organic Compounds

Compound	Formula	Molecular Weight	Molecular Volume (cm ³ /mol)	Hydration Number of Water
Acrylonitrile	CH ₂ CHCN	53.06	65.83	
Isopropanol	CH ₃ CHOHCH ₃	60.09	76.42	17 ^{10,12}
Acetic acid	CH ₃ COOH	60.05	57.23	12 ^{10,12}
<i>n</i> -Butyl amine	CH ₃ (CH ₂) ₃ NH ₂	73.13	98.55	20 ^{10,12}

and a hydrophobic group or a hydrophilic group is as follows:

$$\delta E_i = \delta E_1 + \delta E_2 \quad (2)$$

The activation energy of the exchange of the water molecules connected to hydrophilic group is denoted as δE_1 . The activation energy of the exchange of the water molecules connected to hydrophilic group is denoted as δE_1 .

When $\delta E_i > 0$ is the magnitude of the ratio $\tau_i/\tau > 1$, i.e., the time that the water molecules connect in the vicinity of a solute molecule in the solution is longer than the time adjacent to the vicinity of a water molecule in pure water. The motion of the water molecules are prevented by the solute vicinity. When $\delta E_i < 0$ and the ratio $\tau_i/\tau < 1$, the water molecule adjacent to the solute becomes more mobile than in pure water. In the case of an aqueous solution of organic compounds, generally, the water molecules adjacent to the solute becomes less mobile than in pure water.

Hydrogen-bond formation of water molecules in aqueous solutions is thought to form clusters with an "ice-like" structure that are stabilized by the presence of a hydrophobic group. The hydrophobic effect of a methylene group was evaluated on the basis of the quantitative assessment of the hydrophobic effect from the standard free energy, enthalpy, and entropy of solution.⁷ On the other hand, the hydrogen-bonding ability of a polar solute was also studied.⁷ The hydration number of water molecules is what can be packed around the partition function for the hydrocarbon solution. The hydration number of water molecules will depend on the solute conformation and the assumed water structure. The hydration number is also related to the surface area of the solute that passes through the centers of the water molecules which can be affixed to the solute.^{11,12} The bulk water is the water molecules that are not adjacent to the solute and have no interaction.⁹

For permeate transport, the solution-diffusion mechanism is important. The hydrophobicity is closely concerned with the solubility of the organic compounds.¹⁵⁻²¹ Also, the molecular volume is closely concerned with the diffusivity of the organic compounds.¹⁵⁻²¹ The hydration may effect the diffusivity of the solute molecules during permeation.

Polydimethylsiloxane (PDMS) is well known as an excellent polymer membrane material due to its high permeability to gases and liquids. The permeate molecules permeate quickly in rubbery membranes like PDMS, and the permselectivity was not so affected by the diffusivity. Solubility significantly affects the permselectivity during pervaporation through a hydrophobic rubbery membrane. Furthermore, the relationships between hydration and permeation of various organic compounds during pervaporation in a PDMS membrane can be considered.

In this study, we investigated the pervaporation through a PDMS membrane and the hydration effect on the solution-diffusion mechanism for various organic compounds.

EXPERIMENTAL

Materials

Commercial PDMS membranes (Fuji Systems Corporation), 50 μm thick, were used throughout this work. Isopropanol, acrylonitrile, acetic acid, and *n*-butyl amine (special grade, Wako Pure Chemical Industries, Ltd.) were used as received. The physicochemical properties of the solutes used in this study are shown in Table I.

Pervaporation Experiment

The pervaporation experiments were performed in a previous study^{22,23} using the continuous-feed type method at 25°C. The feed solution was cir-

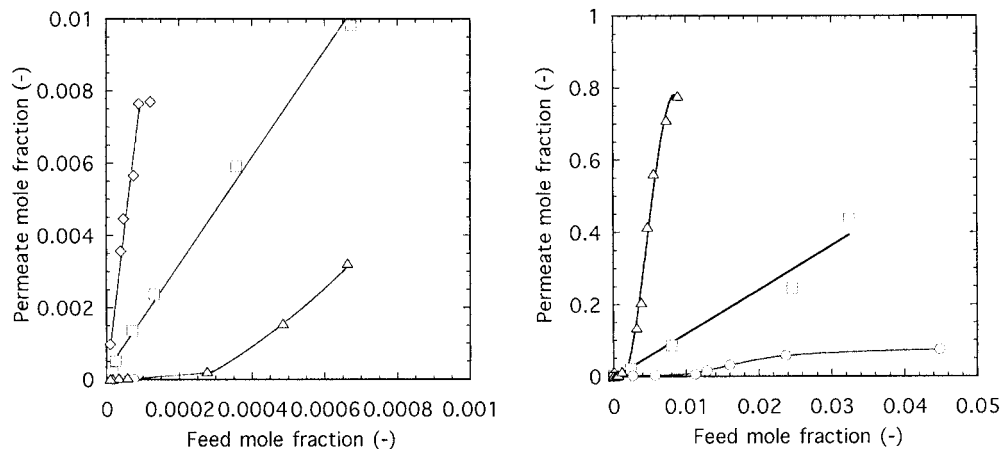


Figure 1 Relationship between solute concentration in feed and permeation during pervaporation: (□) isopropanol, (◇) acrylonitrile, (○) acetic acid, and (△) *n*-butyl amine.

culated through the cell and the feed tank. The effective membrane area in the cell was 19.6 cm². The pressure at the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (−196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux (J), was obtained using eq. (3):

$$J = Q/At \quad (3)$$

where Q is the amount permeated during the experimental time interval t and A is the effective surface area. The solute flux was calculated from the total flux and the permeate composition.

The concentration of solute in the feed and permeate solution was determined by gas chromatography using a free induction decay detector. The enrichment factor β_{pv} was calculated as

$$\beta_{pv} = Y/X \quad (4)$$

where X and Y denote the concentration of solute in the feed and permeate solution, respectively.

RESULTS AND DISCUSSION

Pervaporation for Various Aqueous Solution

The pervaporation properties of various solute aqueous solution were determined in this study.

The relationships between the solute concentration in the feed and permeate are shown in Figure 1. The permeate concentrations of isopro-

panol and acrylonitrile, which are not dissociable, were increased with feed concentration. The relationship was linear. The permeate concentration of acetic acid and *n*-butyl amine, which are dissociable, were significantly increased with feed concentration.

The relationships between the feed solute concentration and the enrichment factor (β_{pv}) are shown in Figure 2. The enrichment factors of isopropanol and acrylonitrile were constant with feed concentration. The enrichment factors of acetic acid and *n*-butyl amine were below 1 at a low feed concentration; however, for a high feed concentration, they were significantly increased with feed concentration.

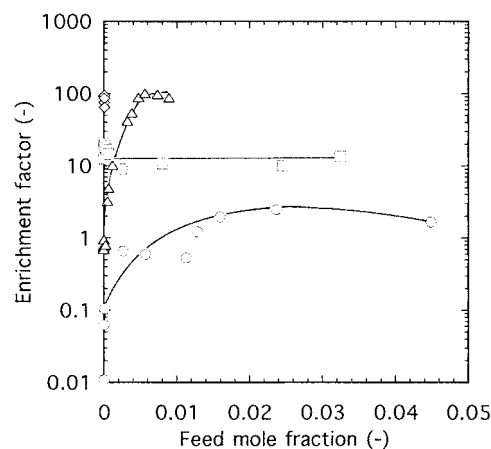


Figure 2 Effect of feed concentration on the enrichment factor (β_{pv}) during pervaporation: (□) isopropanol, (◇) acrylonitrile, (○) acetic acid, and (△) *n*-butyl amine.

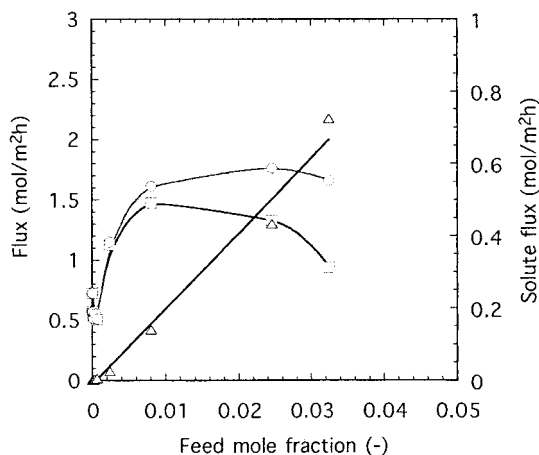


Figure 3 Effect of feed concentration on flux for isopropanol-water mixtures during pervaporation: (□) water flux, (○) total flux, and (△) isopropanol flux.

Flux for Aqueous Solution with Nondissociate Solute

The flux as a function of the feed isopropanol concentration is shown in Figure 3 for the aqueous isopropanol solution. The isopropanol flux was increased with increasing feed concentration. The water flux increased until the maximum at a feed isopropanol mole fraction of 0.01 and then decreased with increasing feed concentration.

The liquid water has a distribution of hydrogen-bond clusters and space.^{13,14} The organic compounds dissolve in the space of the liquid water. The water molecules hydrate the solute molecules. The motion of the water molecules are prevented in the vicinity of the solute.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed isopropanol concentration is shown in Figure 4. The water flux increased until a maximum at the feed isopropanol mole fraction of 0.01 because the water diffusion was promoted by hydration. However, in the high feed concentration, mole fraction > 0.01, the isopropanol solution was concentrated in the PDMS membrane and the permeate concentration was over 0.08 mole fraction. The hydration number for various solutes is shown in Table I. The hydration number of water molecules on isopropanol is 17. The 0.059 mole fraction describes that 17 water molecules per one isopropanol molecule exist. In the 0.059 mole fraction, almost all water molecules are involved in hydration. When the concentration is over the 0.059 mole fraction, one water molecule is adjacent to several solute molecules and the motion of the water molecules is prevented. Hence, it is

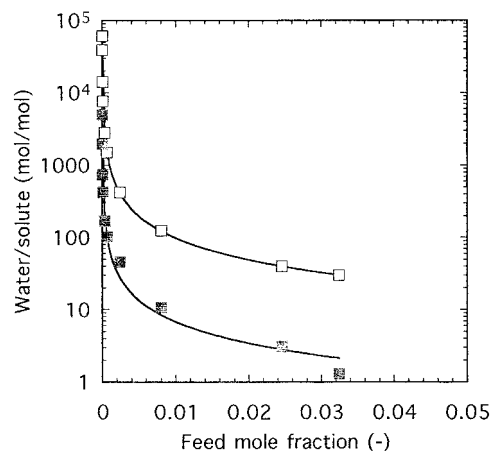


Figure 4 Relationship between feed isopropanol concentration and water molecular number/isopropanol molecular number in feed or permeate solution: (□) in feed and (■) in permeate.

considered that when the feed mole fraction is greater than 0.01, the isopropanol solution was concentrated in the PDMS membrane and the diffusion of water molecules was prevented.

The total flux increased until a maximum at the feed isopropanol mole fraction of 0.01 and then decreased with increasing feed concentration due to the effect of water flux.

The flux as a function of the feed acrylonitrile concentration is shown in Figure 5 for the acrylonitrile solution. The acrylonitrile flux was increased with increasing feed concentration. The water and total flux were constant with low feed concentrations.

Flux for Aqueous Solution of Dissociate Solute

The flux as a function of the feed acetic acid concentration is shown in Figure 6 for the aqueous

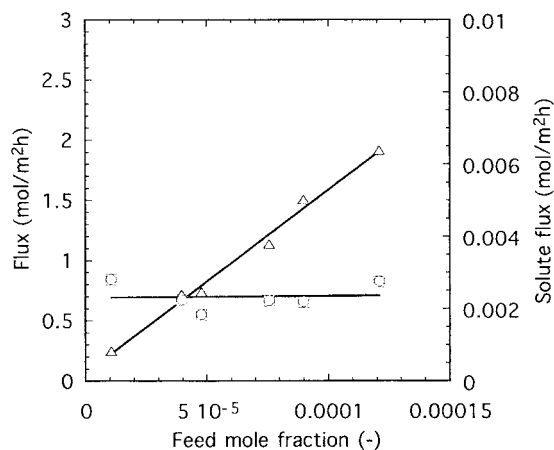


Figure 5 Effect of feed concentration on flux for acrylonitrile-water mixtures during pervaporation: (□) water flux, (○) total flux, and (△) acrylonitrile flux.

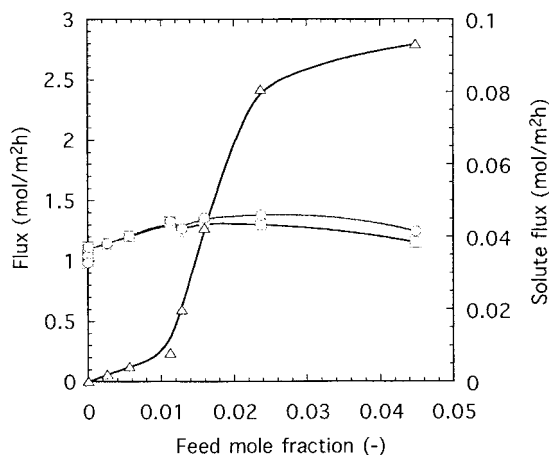


Figure 6 Effect of feed concentration on flux for acetic acid-water mixtures during pervaporation: (□) water flux, (○) total flux, and (△) acetic acid flux.

acetic acid solution. The water flux increased until the maximum feed acetic acid mole fraction of 0.025 and then decreased with increasing feed concentration.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed acetic acid concentration is shown in Figure 7. The water flux increased until the maximum at a feed acetic acid mole fraction of 0.025 because the hydration promoted water diffusion. When the feed concentration was over 0.025 mole fraction, the acetic acid solution was concentrated in the PDMS membrane and the permeate concentration was over 0.06 mole fraction. The hydration numbers for various solutes are shown in

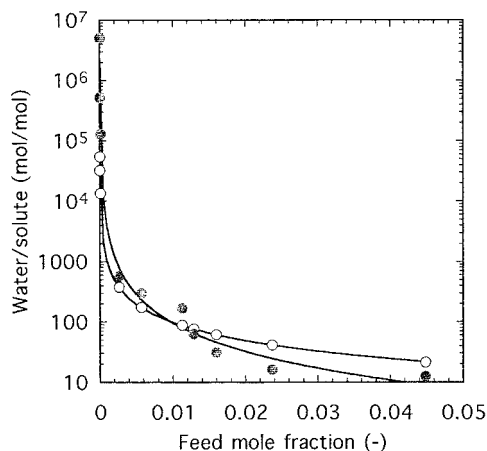


Figure 7 Relationship between feed acetic acid concentration and water molecular number/acetic acid molecular number in feed or permeate solution: (○) in feed and (●) in permeate.

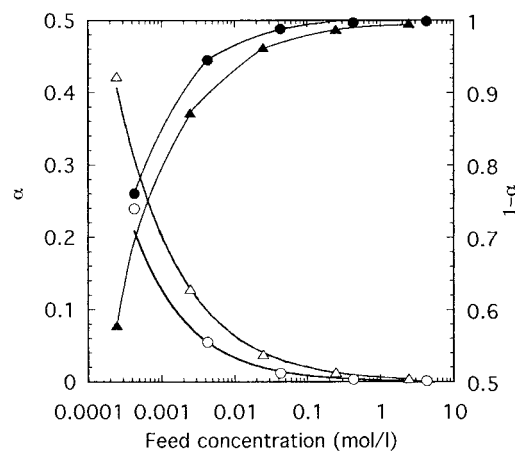


Figure 8 Relationship between feed solute concentration and the degree of dissociation (α) or $1-\alpha$ in feed: (○) α for acetic acid, (●) $1-\alpha$ for acetic acid, (△) α for *n*-butylamine, and (▲) $1-\alpha$ for *n*-butyl amine.

Table I. One acetic acid molecule was hydrated to 12 water molecules. Almost all water molecules were involved in hydration at the 0.077 mole fraction. When the concentration was over 0.077 mole fraction, one water molecule hydrates several solute molecules and the motion of the water molecules are prevented. When the feed acetic acid concentration was over 0.025 mole fraction, the acetic acid solution was enriched in the PDMS membrane and the diffusion of water molecules was prevented by hydration of the solute molecules.

The total flux increased until the maximum feed acetic acid mole fraction of 0.025 and then decreased with increasing feed concentration due to the effect of water flux.

The acetic acid flux was significantly increased with increasing feed concentration. During the permeation of the aqueous acetic acid solution, acetic acid, acetate ion, and water molecules penetrate through the membrane. The degree of dissociation as a function of the feed acetic acid concentration is shown in Figure 8. The proton or acetate ion as a function of the feed acetic acid concentration is shown in Figure 9. When the acetic acid mole fraction was below 0.01, the concentration of permeate solution was below 0.01 mole fraction and the degree of dissociation is high. Hence, the permeation of acetate ion controlled the total acetic acid permeation.

For the permeate transport, a solution-diffusion mechanism plays an important role. During the permeation of a dilute organic solution through the PDMS membrane, the permeate molecules quickly penetrate in a rubbery membrane

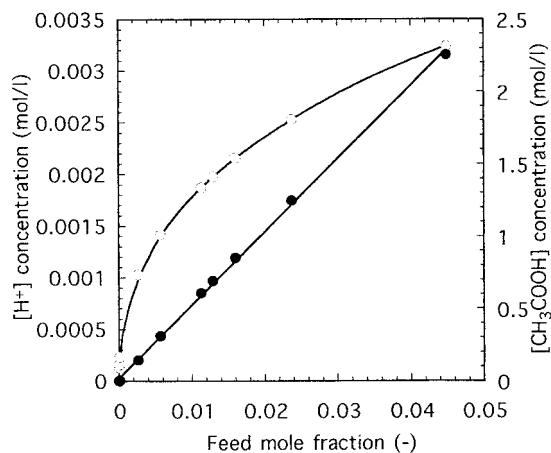


Figure 9 Relationship between feed acetic acid concentration and $[H^+]$ concentration or $[CH_3COOH]$ concentration: (○) $[H^+]$ and (●) $[CH_3COOH]$.

like PDMS. Hence, the solubility significantly affects the permselectivity. Therefore, the permselectivity of acetate ion was not very high. Furthermore, the diffusivity of water, which was a small molecule, was high. The enrichment factor of acetic acid was below 1 at a 0 ~ 0.01 feed mole fraction. At a 0.01 ~ 0.02 feed mole fraction, the concentration of permeate solution was over 0.01 mole fraction and the degree of dissociation is low. The acetic acid flux significantly increased with increasing feed concentration because the perme-

ation of acetic acid was almost the same as the total acetic acid permeation. Over a 0.025 feed mole fraction, the diffusivity of acetic acid was also prevented by hydration. The tentative illustration of the permeation through the PDMS membrane for solute–water mixture is shown in Figure 10. In the feed solution, water molecules were bulk water or hydrate water, but when the solution was concentrated in the membrane, bulk water is decreased and hydrate water was included—hence, the diffusivity of molecules was prevented.

The flux as a function of the feed *n*-butyl amine concentration is shown in Figure 11 for the *n*-butylamine acid solution. The water flux increased until a maximum at the feed *n*-butylamine mole fraction of 0.0015 and then decreased with increasing feed concentration.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed *n*-butyl amine concentration is shown in Figure 12. The water flux increased until a maximum feed *n*-butyl amine mole fraction of 0.0015 because the hydration promoted water diffusion. However, at the high feed concentration, mole fraction > 0.0015, the *n*-butyl amine solution was concentrated in the PDMS membrane and the permeate concentration was over 0.05 mole fraction. The hydration numbers for various solutes are shown in Table I. The hydration number of

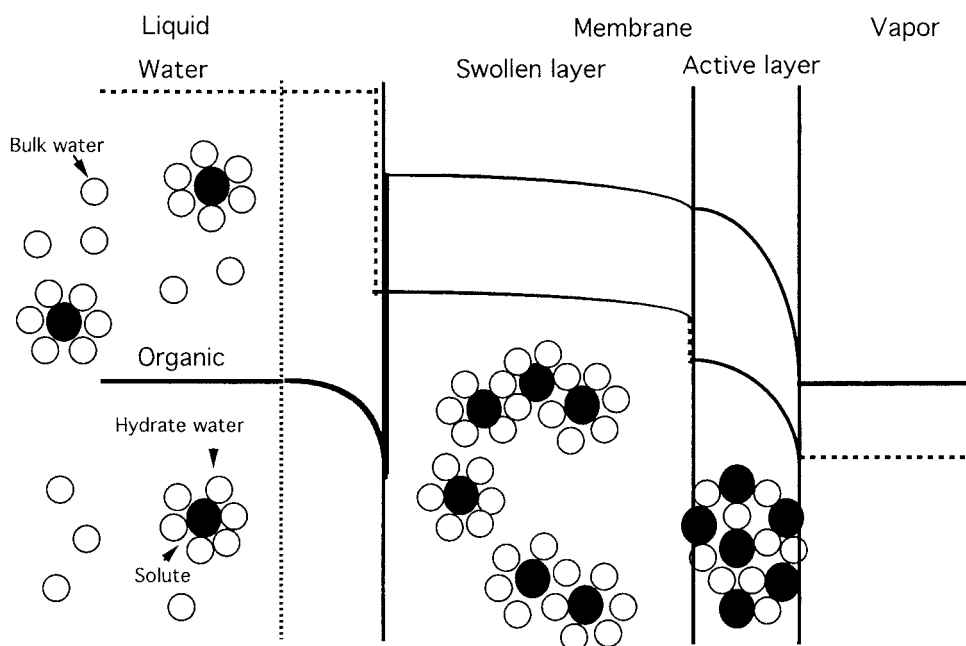


Figure 10 Tentative illustration of the permeation through the PDMS membrane for solute–water mixture.

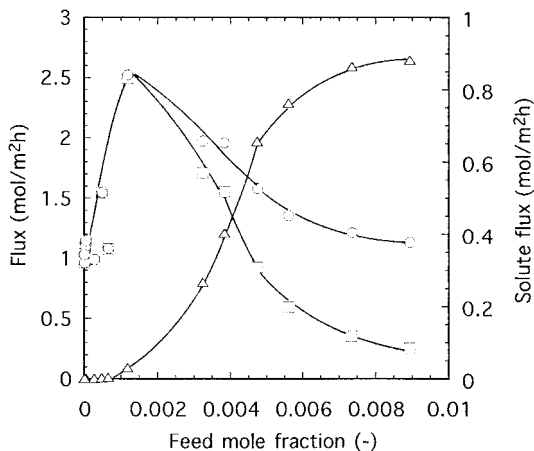


Figure 11 Effect of feed concentration on flux for *n*-butylamine–water mixtures during pervaporation: (□) water flux, (○) total flux, and (△) *n*-butyl amine flux.

water molecules on *n*-butyl amine is 20. Almost all water molecules are involved in hydration at the 0.048 mole fraction. When the concentrations are over 0.048 mole fraction, the water molecules hydrate to several solute molecules and the motion of the water molecules are prevented. Hence, it is considered that over a 0.0015 feed mole fraction, the *n*-butyl amine solution was concentrated in the PDMS membrane and the diffusion of water molecules was prevented.

The total flux increased until a maximum at the feed *n*-butyl amine mole fraction of 0.0015 and then decreased with increasing feed concentration due to the effect of water flux. The *n*-butyl

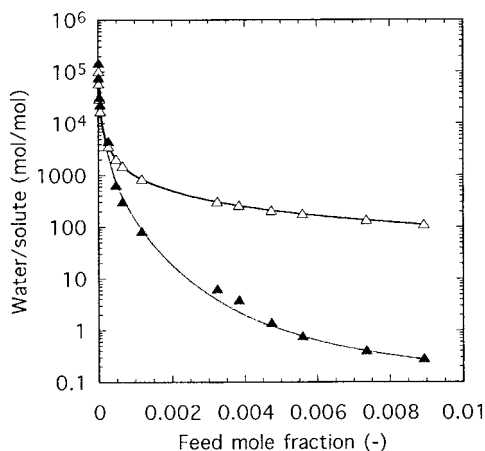


Figure 12 Relationship between feed *n*-butyl amine concentration and water molecular number/*n*-butyl amine molecular number in feed or permeate solution: (△) in feed and (▲) in permeate.

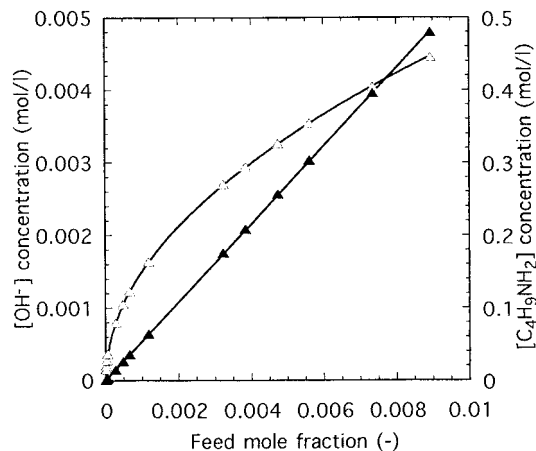


Figure 13 Relationship between feed *n*-butyl amine concentration and $[\text{OH}^-]$ concentration or $[\text{C}_4\text{H}_9\text{NH}_2]$ concentration: (△) $[\text{OH}^-]$ and (▲) $[\text{C}_4\text{H}_9\text{NH}_2]$.

amine flux was significantly increased with increasing feed concentration.

For the permeation of an aqueous *n*-butyl amine solution, *n*-butyl amine, *n*-butyl ammonium ion, and water molecules are penetrates. The degree of dissociation as a function of the feed *n*-butyl amine concentration is shown in Figure 8. The hydroxy or *n*-butyl ammonium ion as a function of the feed *n*-butyl amine concentration is shown in Figure 13. Below a *n*-butyl amine mole fraction of 0.0015, the concentration of permeate solution was below a 0.02 mole fraction. Hence, the degree of dissociation is high and the permeation of the *n*-butyl ammonium ion affected the total *n*-butyl amine permeation.

The solubility of the *n*-butyl ammonium ion is not very high and the diffusivity of water, which is a small molecule, is high. Therefore, the permselectivity of the *n*-butyl ammonium ion is not very high. The enrichment factor of *n*-butyl amine was low at a $0 < 0.0015$ feed mole fraction. At a $0.0015 \sim 0.008$ feed mole fraction, the *n*-butyl amine flux significantly increased with increasing feed concentration. When the *n*-butyl amine mole fraction was $0.0015 \sim 0.008$, the concentration of the permeate solution was over 0.02 mole fraction. Hence, the degree of dissociation is low and the permeation of *n*-butyl amine was almost the same as the total *n*-butyl amine permeation. Over a 0.008 feed mole fraction, the diffusivity of *n*-butyl amine was also prevented by hydration.

CONCLUSIONS

In this study, we investigated the pervaporation through a PDMS membrane and the hydration

effect on the solution-diffusion mechanism for various organic compounds.

The water molecule adjacent to the solute becomes less mobile in aqueous solutions of organic compounds than in the pure water due to the hydration. The liquid water has a distribution of hydrogen-bond clusters and space. The organic compounds dissolve in the space of the liquid water. The water molecules hydrate the solute molecules. The motion of the water molecules are prevented in the solute vicinity.

The water flux increased until a maximum at a low feed solute concentration because the hydration promoted water diffusion. However, at the high feed concentration, solute was concentrated in the PDMS membrane and permeate. Almost all water molecules are concerned with hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number. When the actual concentration was over this concentration, the water molecules hydrate to several solute molecules and the motion of the water molecules is prevented. During pervaporation, the solute was concentrated in the PDMS membrane and the diffusion of water molecules was prevented.

The permeation of the aqueous solution of dissociated solute included more interesting phenomena.

For permeate transport, a solution-diffusion mechanism is important. The permselectivity of ions is not very high. Furthermore, the diffusivity of water, which is a small molecule, is high.

When the dissociate solute mole fraction was a low, the concentration of permeate solution was a low mole fraction and the degree of dissociation is high. Hence, the permeation of organic ions affected the total dissociate solute permeation. The enrichment factor of dissociated compounds was low in the solution with a high degree of dissociation. At the high feed concentration, the solution was concentrated in the membrane and the degree of dissociation is low. The solute flux significantly increased with increasing feed concentration because the permeation of solute itself became the total solute permeation, until hydration prevents diffusion. The diffusivity of solute and water molecules are prevented by hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number.

The authors are grateful to the Fuji Systems Corporation for providing the PDMS membranes.

REFERENCES

- Geiger, A.; Stillinger, F. H.; Rahman, A. *J Chem Phys* 1979, 70, 4185.
- Nakanishi, K.; Ikari, K.; Okazaki, S.; Touhara, H. *J Chem Phys* 1984, 80, 1656.
- Desneyers, J. E.; Arel, M.; Perron, G.; Jobicoeur, C. *J Phys Chem* 1969, 73, 3346.
- Tanaka, H.; Touhara, H.; Nakanishi, K.; Watanabe, N. *J Chem Phys* 1984, 80, 5170.
- Kuharski, R. A.; Rossky, P. J. *J Am Chem Soc* 1984, 106, 5786.
- Franks, F. *J Chem Soc Faraday I* 1977, 73, 830.
- Nishi, N.; Yamamoto, K. *J Am Chem Soc* 1987, 109, 7353.
- Coker, D. F.; Miller, R. E.; Watts, R. O. *J Chem Phys* 1985, 82, 3554.
- Samoilov, O. Ya. *Disc Faraday Soc* 1957, 24, 141.
- Uedaira, H. *mizu no bunshi kougaku*; in Japan, Kodansha Co. Ltd., Tokyo, 1998.
- Hermann, R. B. *J Phys Chem* 1972, 76, 2754.
- Hermann, R. B. *J Phys Chem* 1975, 79, 163.
- Frank, H. S.; Quist, A. S. *J Chem Phys* 1961, 34, 604.
- Narten, A. H.; Danford, M. D.; Levy, H. A. *Disc Faraday Soc* 1967, 43, 97.
- Chandak, M. V.; Lin, Y. S.; Ji, W.; Higgins, R. J. *J Membrane Sci* 1997, 133, 231.
- Sun, Y.; Lin, C.; Chen, Y.; Wu, C. *J Membrane Sci* 1997, 134, 117.
- Takaba, H.; Koshita, R.; Mizukami, K.; Oumi, Y.; Ito, N.; Kubo, M.; Fahmi, A.; Miyamoto, A. *J Membrane Sci* 1997, 134, 127.
- Lau, W. W. Y.; Finlayson, J.; Dickson, J. M.; Jiang, J.; Brook, M. A. *J Membrane Sci* 1997, 134, 209.
- Watson, J. M.; Baron, M. G. *J Membrane Sci* 1996, 110, 47.
- Dotremont, C.; Brabants, B.; Geeroms, K.; Mewis, J.; Vandecasteele, C. *J Membrane Sci* 1995, 104, 109.
- Goethaert, S.; Dotremont, C.; Kuijpers, M.; Michels, M.; Vandecasteele, C. *J Membrane Sci* 1993, 78, 135.
- Mishima, S.; Nakagawa, T. *J Appl Polym Sci* 1999, 71, 273.
- Mishima, S.; Nakagawa, T. *J Appl Polym Sci*, in press.