PERVAPORIZATION AND VAPER PERMEATION BEHAVIOR OF WATER AND 2-PROPANOL IN WATER-SELECTIVE MEMBRANES

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Key Words: Pervaporation, Vapor Permeation, Water-Selective Membrane, Solubility, Diffusion Coefficient

The pervaporation (PV) behavior of water and 2-propanol mixtures is compared with vapor permeation (VP) behavior using three types of water-selective composite or asymmetric membranes with different materials in their skin layers, i.e., membranes of polyion complex with polyacrylic acid (PIC-PAAc), polyion complex with partially hydrolyzed polyacrylonitrile (PIC-PAN), and polyparabanic acid (PPAc). From solubility measurements of water-2-propanol mixtures in dense membranes at 356 K, it is found that in liquid phase experiments PIC-PAAc and PIC-PAN membranes show higher solubility of water than PPAc membrane, although no significant difference in solubilities of water vapor among the three membranes is observed in vapor phase experiments. In permeation experiments at 356 K, the PV water fluxes through the three membranes are higher than those for VP if the mole fractions of 2-propanol in the feed solution (x_{2p}) are below 0.90. Using PIC-PAAc and PIC-PAN membranes, higher fluxes of 2-propanol are obtained for PV at less than x_{2p}=0.6 as compared with those for VP. However, remarkable differences in 2-propanol fluxes are not observed between PV and VP using a PPAc membrane.

Based on the solution-diffusion theory and taking account of water solubility in the membranes, the fluxes of water and 2-propanol for both PV and VP are analyzed for PIC-PAAc, PIC-PAN and PPAc membranes. Approximate coincidence in the estimated values of diffusion coefficients without swelling and the swelling parameters for water and 2-propanol, which indicated their diffusivities in the membranes, are obtained for PV and VP using the respective membranes.

Introduction

Membrane separation processes for azeotropic liquid-liquid mixtures using the pervaporation (PV) and vapor permeation (VP) have attracted attention as alternative techniques, since they are regarded to have promise as new energy-saving processes. Recently, PV and VP techniques using water-selective membranes have been applied to produce dehydrated alcohols and to remove water from organic solvents in commercial applications in the chemical industry (Sander and Soukup, 1988; Rautenbach and Blumenroth, 1990).

Kataoka et al. (1991) compared the fluxes of water and ethanol in PV with those in VP using membranes with different swelling properties towards water. They demonstrated that the differences in the permeation fluxes between PV and VP are significant in the case of the highly water-swollen cellulose acetate membrane. Scheil-Mann et al. (1995) reported that for water-2-propanol mixtures, total permeation flux is higher for VP compared to VP, while selectivity is lower below about 0.9 of weight fraction of 2-propanol in the feed solution when a polyvinylalcohol-polyacrylonitrile composite membrane is used.

In the present study, the permeation behaviors of water and 2-propanol in the PV experiments are compared with those in the VP experiments using three types of water-selective composite or asymmetric membranes, which incorporated of different materials in the skin layers, i.e., membranes of polyion complex with polyacrylic acid (PIC-PAAc), polyion complex with partially hydrolyzed polyacrylonitrile (PIC-PAN) and polyparabanic acid (PPAc). The solubilities of water and 2-propanol in the matrices of membranes (skin layer materials) are determined in the liquid and vapor phases of mixtures of water and

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Table 1  Selected specifications of membranes

<table>
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<tr>
<th>Membrane</th>
<th>Composite</th>
<th>Asymmetric</th>
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<tr>
<td></td>
<td>PIC-PAAc</td>
<td>Partially hydrolyzed PAN</td>
</tr>
<tr>
<td>Material</td>
<td>PAAc/PES</td>
<td>0.48</td>
</tr>
<tr>
<td>Number of carboxyl groups</td>
<td>[kmol·m⁻³]</td>
<td>0.22</td>
</tr>
<tr>
<td>Total thickness</td>
<td>[µm]</td>
<td>41</td>
</tr>
<tr>
<td>Skin layer thickness³</td>
<td>[µm]</td>
<td>0.2</td>
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</table>

³Thickness of skin layer was measured by SEM observation

2-propanol. The permeation fluxes through the composite or asymmetric membranes are determined using liquid and vapor mixtures of water and 2-propanol as feeds.

Based on the solution-diffusion theory considering water solubility in the membranes, the permeation fluxes of water and 2-propanol through the membranes in both the PV and VP processes are analyzed using experimental data.

1. Experimental

1.1 Preparation of membranes

Composite or asymmetric membranes used in the permeation experiments were prepared as follows. PIC-PAAc composite membrane Polyacrylic acid (PAAc) with molecular weight of 4,000,000 was purchased from Scientific Polymer Products Inc. An aqueous solution containing 0.3 wt% PAAc and 0.03 wt% ethylene glycol diglyceride ether (EGDE) was spread over a polyethersulfone (PES) ultrafiltration membrane (DUS-40, 41 µm in thickness, Daice Chemical Industries Ltd.). The membrane was dried at 293 K for 10 minutes. The casting and drying procedures were repeated three times. After the membrane was dried, it was immersed in an aqueous solution of 2 wt% polycation (PCA-107, a polymer with quaternized ammonium ion) at room temperature for 12 hours to form an ion complex on the membrane surface. This polycation, PCA-107, was synthesized according to the method of Karakane et al. (1991).

PIC-PAN composite membrane A polycrylonitrile (PAN) ultrafiltration membrane (DUY-H, 59 µm in thickness, Daice Chemical Industries Ltd.) was partially hydrolyzed in 1 kmol·m⁻³ NaOH aqueous solution at 353 K for 50 minutes. The membrane was rinsed sufficiently with deionized water, and then an ion complex was allowed to form on its surface via the same method as that used to prepare the PIC-PAAc composite membrane.

PPAc asymmetric membrane Polypararbanic acid (PPAc) purchased from Töhnen Chemical Co. was dissolved in N,N-dimethylformamide (DMF) at a concentration of 18 wt% PPAc. The solution was cast onto a glass plate and coagulated in water at 293 K. The resultant membrane was dried at 373 K for 12 hours, followed by annealing at 553 K for 12 hours.

Dense membranes composed of the skin layer materials were used to evaluate the solubilities of water and 2-propanol in the membranes. These membranes were separately prepared as follows.

PIC-PAAc dense membrane An aqueous solution containing 2 wt% PAAc and 0.2 wt% EGDE was cast onto a glass plate. Then water was evaporated at 353 K for 12 hours. The ion complex was allowed to form in the same manner as that in the case of the PIC-PAAc composite membrane.

PIC-PAN dense membrane 18 wt% of PAN (PAN-B, Daice Chemical Industries, Ltd.) dissolved in DMF solution was prepared, and the solution was cast onto a glass plate. Then the solvent was evaporated at 353 K for 12 hours. The resultant membrane was partially hydrolyzed in 1 kmol·m⁻³ NaOH aqueous solution at 353 K for 50 minutes. The ion complex was allowed to form on this membrane through a procedure similar to that used in the preparation of the PIC-PAN composite membrane.

PPAc dense membrane 18 wt% of PPAc dissolved in DMF solution was prepared, and the solution was cast onto a glass plate. Then the solvent was evaporated at 373 K for 12 hours, followed by annealing at 553 K for 12 hours.

Some specifications of the composite or asymmetric membranes used in the present study are shown in Table 1. The thickness of the skin layer was estimated through scanning electron micrograph (SEM). The numbers of carboxyl groups in the PIC-PAAc and PIC-PAN membranes were determined by the acid-base titration method (Fisher and Kunin, 1955).

1.2 Permeation experiments

Pervaporation experiment The apparatus used in the PV experiment is shown in Fig. 1. Each membrane, with effective area of 1.3×10⁻³ m², was set at the bottom of a stainless steel cell (2×10⁻⁴ m³ in volume) with a water-jacket maintained at 356 K by circulating thermostatted water. The face of the skin layer of each membrane was in contact with the feed solution. A 0.2×10⁻³ m² feed solution with mole fraction of 2-propanol, x₁₉, of 0.07 to 0.94 was
the experimental conditions employed in this study, the equilibrium between liquid and vapor phases was attained by employing a temperature of 356 K, which was close to the boiling points of a solution of \( x_{1p} = 0.07 - 0.94 \). The collection of the permeates was carried out using the same method as those in the PV experiment.

1.3 Solubility measurements

To measure the solubilities of water and 2-propanol in the liquid phase, a dense membrane was soaked in a liquid mixture of water and 2-propanol (\( x_{1p} = 0.07 - 0.94 \)) at 356 K for 8 hours. To measure the solubilities in the vapor phase, a dense membrane was suspended in vapor equilibrated with a liquid mixture of water and 2-propanol (\( x_{1p} = 0.07 - 0.94 \)) at 356 K for 8 hours. Subsequently, the membrane was taken out of the liquid or vapor phase and weighed immediately after its surface was wiped with paper. The mole concentrations of water and 2-propanol per unit volume of the membranes were determined by the desorption method described previously (Hamada et al., 1996). The volume of each membrane was obtained from the product of area and thickness of the membrane.

1.4 Analysis

The mole fractions of water and 2-propanol in the mixtures were determined by means of gas chromatography (GC14-A, Shimadzu Corp.) equipped with a column containing Porapack Q (Water Associates, Inc.).

2. Results and Discussion

2.1 Solubilities of water and 2-propanol in the membranes

The mole concentrations of water, \( C_{w} \), and 2-propanol, \( C_{p} \), in the dense membranes of PIC-PAAc, PIC-PAN, and PPAAc were determined by the solubility experiments in liquid and vapor phases. In the experiment in the liquid phase, \( C_{w} \) and \( C_{p} \) values are plotted against mole fractions of water and 2-propanol multiplied by activity coefficients in the liquid phase. In the case of the experiment in the vapor phase, the plots of \( C_{w} \) and \( C_{p} \) values against mole fractions of water and 2-propanol multiplied by activity coefficients in the liquid phase are employed assuming that the vapor phase is in equilibrium with the liquid phase. Figure 3 shows the semi-logarithm plots of \( C_{w} \) values against \( y_{w}x_{1w} \) values in solution for the respective membranes. Figure 4 shows the semi-logarithm plots of \( C_{p} \) values against \( y_{p}x_{1p} \) values in solution for the membranes. The activity coefficients, \( y_{w} \) and \( y_{p} \), are calculated by the Wilson equation (Kagaku Kogaku Binran, 1988). The values of \( C_{w} \) and \( C_{p} \) in all membranes from the liquid phase are larger than those in the vapor phase, and they increase as the mole fractions of 2-propanol in the solution...
Fig. 3 Plots of $C_w$ values against $y_w x_{1w}$ values in solution in solubility measurements using PIC-PAAC, PIC-PAN and PPAC dense membranes kept in liquid and vapor phases.

Fig. 4 Plots of $C_e$ values against $y_p x_{1p}$ values in solution in solubility measurements using PIC-PAAC, PIC-PAN and PPAC dense membranes kept in liquid and vapor phases.

dense membranes become more hydrophilic through the formation of ion complex between carboxyl anion and polycation in the membranes. According to Kurokawa et al. (1980), the formation of polyelectrolyte complex between polyanion and polycation endowed a polymer matrix with a high adsorptive capacity for water. Secondly, the physical properties of the respective polymers are different. PAAC and PAN, the main materials of PIC-PAAC and PIC-PAN dense membranes, are aliphatic polymers with glass transition temperatures, $T_g$, of 379 and 398 K, respectively (Polymer Handbook, 1989). On the other hand, PPAC is an aromatic polymer with $T_g$ of about 550 K (Polymer Handbook, 1989). At the temperature used in this study, 356 K, it is considered that more amorphous regions exist in PIC-PAAC and PIC-PAN dense membranes, which facilitates higher solubility of water and 2-propanol than a PPAC dense membrane.

2.2 Effects of feed concentration and permeation side pressure on fluxes of water and 2-propanol in PV and VP

The effects of feed concentration ($x_{1p}$) on the fluxes of water, $J_w$, and 2-propanol, $J_p$, in both the PV and VP experiments are examined. Figures 5, 6 and 7 show the results obtained for PIC-PAAC and PIC-PAN composite membranes and PPAC asymmetric membrane, respectively. For all the membranes tested, when the values of $x_{1p}$ are less than 0.9, $J_w$ values in the PV experiments are larger than those in the VP experiments, and the differences in $J_w$ values between PV and VP experiments for PIC-PAAC and PIC-PAN composite membranes are larger than those for PPAC asymmetric membrane. On the other hand, using PIC-PAAC and PIC-PAN composite
membranes, larger values of $J_p$ are observed in the PV experiments at less than $x_{1p}=0.6$, as compared with those in the VP experiments. However, there is no significant difference in $J_p$ values between PV and VP experiments using the PPAc membrane. As seen in the cases of PIC-PAAc and PIC-PAN membranes, these differences in permeation fluxes between PV and VP are reported for other membranes with high swelling degrees for water, that is, high hydrophilicity, such as membranes of cellulose acetate (Kataoka et al., 1991), polyvinylalcohol-polyacryronitrile composite (Will and Lichtenhalter, 1992) and cellophane (Suematsu et al., 1989) in separation of mixtures of water and ethanol or water and 2-propanol.

Table 2 shows the values of total permeation fluxes, $J_T$, and separation factors, $\alpha_{PV}$ and $\alpha_{VP}$, in the PV and VP experiments, respectively, by using PIC-PAAc, PIC-PAN and PPAc membranes. The values of $\alpha_{PV}$ and $\alpha_{VP}$ are defined by the following equations, respectively.

$$\alpha_{PV} = \frac{J_u/J_p}{x_{1w}/x_{1p}}$$  \hspace{1cm} (1-a)

$$\alpha_{VP} = \frac{J_u/J_p}{y_{1w}/y_{1p}}$$  \hspace{1cm} (1-b)

The values of $y_{1w}$ and $y_{1p}$ in Eq. (1-b) are obtained from those of $x_{1w}$ and $x_{1p}$, respectively, by using the data on vapor-liquid equilibrium for the mixtures of water and 2-propanol at 356 K and 101.3 kPa (Wilson and Simons, 1952).

For PIC-PAAc and PIC-PAN membranes, $\alpha_{PV}$ values are larger than $\alpha_{VP}$ values at the high value of $x_{1p}=0.94$, although the $\alpha_{PV}$ value is somewhat smaller than the $\alpha_{VP}$ value for the PPAc membrane at $x_{1p}=0.94$.

The effects of permeation side pressure, $p_2$, on $J_u$
and $J_p$ values in both the PV and VP experiments at $x_{1p}=0.94$ are shown in Fig. 8(a) and (b). As shown in Fig. 8(a), for all the membranes, $J_w$ values in both the PV and VP experiments decrease linearly as $p_2$ increases, and the differences in $J_w$ values between PV and VP experiments decrease as $p_2$ increases. As shown in Fig. 8(b), however, clear dependencies of $J_p$ values on $p_2$ are not observed in the PV and VP experiments for all the membranes under the experimental conditions employed in this study. Also the $J_p$ values in both experiments are almost the same for each membrane.

2.3 Permeation equations of water and 2-propanol through the membranes

From the results of both the PV and VP experiments, fluxes of water and 2-propanol in PIC-PAAc and PIC-PAN composite membranes and PPAC asymmetric membrane are analyzed using mass transfer equations. The mass transfer equations are derived based on the following assumptions.

1. In both the PV and VP experiments, mass transfers of water and 2-propanol in the membrane obey the solution-diffusion theory.

2. The changes in thickness of the skin layer during the PV and VP experiments are ignored.

3. The distribution coefficients of each component at the feed side are the same as those at the permeation side according to Kataoka et al. (1991).

4. In the VP experiment, the feed vapor phase is in equilibrium with the liquid phase.

From assumption (1), the permeation flux of component $i$ at a steady state is represented as follows.

$$J_i = -D_i \frac{dC_i}{dz} \quad (i = w, p) \quad (2)$$

As seen in Figs. 3 and 4, the mole concentrations of water in the membranes were much higher than those of 2-propanol in the membranes under the conditions in the present study. Therefore, it was postulated that the concentrations of water in the membranes affect the diffusion coefficients of water and 2-propanol. The dependencies of diffusion coefficients of water and 2-propanol on water concentration in the membrane are assumed to be expressed by an exponential formula proposed by Nguyen (1987) as follows.

$$D_i = D_{i0} \exp(A_iC_w) \quad (i = w, p) \quad (3)$$

where $D_{i0}$ is diffusion coefficient without swelling and $A_i$ is swelling parameter.

From assumption (2), the boundary conditions are as follows.

$$C_i = C_{i1} \quad \text{at} \quad z = 0 \quad (i = w, p) \quad (4-a)$$

$$C_i = C_{i2} \quad \text{at} \quad z = \delta \quad (i = w, p) \quad (4-b)$$

The following equations concerning fluxes of water and 2-propanol can be obtained by integrating Eq. (2) with Eqs. (3), (4-a) and (4-b).

$$J_w = \frac{D_{w0}}{\delta A_w} \left\{ \exp(A_wC_{w1}) - \exp(A_wC_{w2}) \right\} \quad (5)$$

$$J_p = \frac{D_{p0}}{\delta A_w M} \left[ \exp(A_wC_{w1}) - \exp(NC_{1w}) + MN(C_{2p} - C_{1p}) \right]^\frac{A_s}{N} \quad (6)$$

where $M=J_w D_{w0}/J_p D_{p0}$ and $N=A_w-A_p$.

According to assumptions (3) and (4), the equilibriums at the surfaces of the membrane at the feed and permeation sides in PV and VP are attained as follows.

At the feed side, the equilibrium relationship can be described as

$$C_{i1} = K_i/\gamma_i x_{i1} \quad (i = w, p; j = PV, VP) \quad (7)$$

At the permeation side, the equilibrium can be described as
Table 3  Estimated values of $a_w$, $a_p$, $b_w$ and $b_p$

<table>
<thead>
<tr>
<th>Dense membrane</th>
<th>PIC-PAAc</th>
<th>PIC-PAN</th>
<th>PPAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid phase</td>
<td></td>
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</tr>
<tr>
<td>$a_w \times 10^2$ [mol·m$^{-2}$]</td>
<td>7.31</td>
<td>4.25</td>
<td>9.77</td>
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<tr>
<td>$a_p \times 10^2$ [mol·m$^{-2}$]</td>
<td>5.95</td>
<td>1.60</td>
<td>2.73</td>
</tr>
<tr>
<td>$b_w$</td>
<td>2.73</td>
<td>2.47</td>
<td>0.96</td>
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<tr>
<td>$b_p$</td>
<td>-7.30</td>
<td>-6.49</td>
<td>-4.20</td>
</tr>
<tr>
<td>Vapor phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_w \times 10^2$ [mol·m$^{-2}$]</td>
<td>4.93</td>
<td>3.55</td>
<td>10.1</td>
</tr>
<tr>
<td>$a_p \times 10^2$ [mol·m$^{-2}$]</td>
<td>1.93</td>
<td>1.23</td>
<td>0.78</td>
</tr>
<tr>
<td>$b_w$</td>
<td>1.52</td>
<td>1.62</td>
<td>0.85</td>
</tr>
<tr>
<td>$b_p$</td>
<td>-4.55</td>
<td>-4.19</td>
<td>-3.06</td>
</tr>
</tbody>
</table>

$$C_{vj} = K_{vj} \frac{p_{vij} \exp \left( \frac{v(p_{vij} - p_{ij})}{RT} \right)}{p_{vij}} (i = w, p; j = PV, VP) \quad (8)$$

In the present study, from the results shown in Figs. 3 and 4, $K_{wv}$, $K_{wv}$, $K_{pv}$, $K_{pv}$ and $K_{pv}$ values for both the liquid and vapor phases are expressed by the following experimental equation.

$$K_{vj} = \frac{a \exp(b_v x_{ij})}{(i = w, p; j = PV, VP)} \quad (9)$$

where $0.19 \leq \gamma_{wv} \gamma_{wp} \leq 0.97$ and $0.19 \leq \gamma_{pv} \gamma_{vp} \leq 0.95$.

The parameter values, $a_w$, $a_p$, $b_w$ and $b_p$ for PV and VP are determined by the least-squares method using the data of $C_{we}$ and $C_{pe}$ against $\gamma_{wv} x_{1w}$ and $\gamma_{pv} x_{1p}$ shown in Figs. 3 and 4. These values are indicated in Table 3. The correlation coefficients are in the ranges of 0.889 – 0.996 and 0.865 – 0.981 for the data shown in Figs. 3 and 4, respectively. Some data deviate from the fitted lines for the PIC-PAAc and PIC-PAN dense membranes. These deviations may be caused by the difficulty in measurement of very low solubility of 2-propanol in the membranes. When analysing the experimental data via the solution-diffusion theory, it is assumed that the value of $\exp\left(\frac{v(p_{vij} - p_{ij})}{RT}\right)=1$ in Eq. (8), mol fractions of water in permeates, $x_{2w}=1$, and those of 2-propanol in permeates, $x_{2p}=0$, and that $C_{we}$ and $C_{pe}$ values obtained from the solubility measurements are equal to $C_{1w}$ and $C_{1p}$ values, respectively. By substituting Eqs. (7), (8) and (9) for Eqs. (5) and (6), water and 2-propanol fluxes in both the PV and VP are represented, respectively, as follows.

$$J_w = \frac{D_{w0}}{\delta A_w} \left[ \exp\{A_w a_w \exp(b_w x_{1w})\} - \exp\left\{A_p a_p \exp(b_p x_{1p})\right\} \right] (10)$$

Table 4  Estimated values of $D_{w0}$, $D_{p0}$, $A_w$ and $A_p$ in PV and VP experiments

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PIC-PAAc</th>
<th>PIC-PAN</th>
<th>PPAC</th>
</tr>
</thead>
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<tr>
<td>PV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{w0} \times 10^{12}$ [m$^2$·s$^{-1}$]</td>
<td>4.97</td>
<td>9.02</td>
<td>4.13</td>
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<td>$D_{p0} \times 10^{13}$ [m$^2$·s$^{-1}$]</td>
<td>0.45</td>
<td>0.28</td>
<td>2.30</td>
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<tr>
<td>$A_w \times 10^4$ [m$^3$·mol$^{-1}$]</td>
<td>0.91</td>
<td>3.87</td>
<td>9.09</td>
</tr>
<tr>
<td>$A_p \times 10^4$ [m$^3$·mol$^{-1}$]</td>
<td>0.87</td>
<td>1.88</td>
<td>0.55</td>
</tr>
<tr>
<td>VP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{w0} \times 10^{12}$ [m$^2$·s$^{-1}$]</td>
<td>5.03</td>
<td>8.69</td>
<td>3.89</td>
</tr>
<tr>
<td>$D_{p0} \times 10^{13}$ [m$^2$·s$^{-1}$]</td>
<td>0.44</td>
<td>0.24</td>
<td>2.01</td>
</tr>
<tr>
<td>$A_w \times 10^4$ [m$^3$·mol$^{-1}$]</td>
<td>1.19</td>
<td>4.17</td>
<td>7.56</td>
</tr>
<tr>
<td>$A_p \times 10^4$ [m$^3$·mol$^{-1}$]</td>
<td>0.98</td>
<td>2.20</td>
<td>0.54</td>
</tr>
</tbody>
</table>

$$J_p = \frac{D_{p0}}{\delta A_w M} \left[ \exp\{A_w a_w \exp(b_w x_{1w})\} \right. - \left[\exp\{A_w a_w \exp(b_w x_{1w})\} \right] - MN(a_p \exp(b_p x_{1p})^N) \right] (11)$$

where $x_{1w} + x_{1p} = 1$.

The value of $p_{wv}$ in Eq. (10) was estimated from the Antoine equation (Kagaku Kogaku Rinran, 1988).

2.4 Estimation of diffusion coefficients without swelling and swelling parameters

The lines shown in Figs. 5, 6 and 7 are fitted values to the data of $J_w$ and $J_p$ values through the respective membranes in both the PV and VP experiments under various values of $x_{1p}$ in feed solution using Eqs. (10) and (11) by means of the least-squares method. The fitted values of parameters, $D_{w0}$, $D_{p0}$, $A_w$ and $A_p$, are shown in Table 4. Using Eqs. (10) and (11) with these parameters, the values of $J_w$ and $J_p$ are calculated under various permeation side pressures by assuming that $C_{we}$ and $C_{pe}$ do not depend on permeation side pressure. As indicated by the lines in Fig. 8(a) and (b), the calculated values are approximately in agreement with experimental data.

As shown in Table 4, the values of $D_{w0}$, $D_{p0}$, $A_w$ and $A_p$ in the PV experiment are close to those in the VP experiment for the respective membranes. These results may be supported by the fact that when a membrane is not swollen with water, the PV flux coincides with that of VP (Kataoka et al. 1991). The values of $A_p$ in the PV and VP experiments are larger than those of $A_w$ in both the experiments for respective membranes. The differences between $A_p$ and $A_w$ values in both the PV and VP experiments for PIC-PAAc and PIC-PAN composite membranes are larger than those for PPAC asymmetric membrane. As reported by Yoshikawa et al. (1987), the $D_{w0}$ values for 4-vinylpyridine-co-acrylonitrile membrane in PV
experiments with water-ethanol mixtures was 4.78×10^{-13} \text{ mol} \cdot \text{s}^{-1}. \ D_{00} \text{ values for all the membranes used in the present study are larger than the reported value for 4-vinylpyridine-co-acrylonitrile membrane. The highest value of } D_{00} \text{ and the lowest value of } D_{p0} \text{ in both the PV and VP experiments are observed for the PIC-PAN composite membrane. These results may be explained by the high hydrophilicity of the PIC-PAN composite membrane, since the PIC-PAN composite membrane possesses an ion complex formed between carboxyl group and polymer, and the number of carboxyl groups in PIC-PAN composite membrane is larger than that in PIC-PAAc composite membrane.}

**Conclusion**

The permeation behaviors of water and 2-propanol in PV were compared with those in VP using three types of water-selective composite or asymmetric membranes, and the following results are obtained.

1) From the solubility measurements using the dense membranes of PIC-PAAc, PIC-PAN and PPAC, the solubilities (mole concentrations) of water and 2-propanol in the respective membranes from liquid phase are larger than those from the vapor phase. The differences in the solubilities of water and 2-propanol between the liquid and vapor phases for PIC-PAAc and PIC-PAN membranes become larger than those for the PPAC membrane at lower mole fractions of 2-propanol in solution.

2) In permeation experiments using composite or asymmetric PIC-PAAc, PIC-PAN and PPAC membranes, when the mole fractions of 2-propanol in the feed solution were less than 0.9, water fluxes for PV were always larger than those for VP. For PIC-PAAc and PIC-PAN membranes, higher fluxes of 2-propanol were obtained for PV, as compared with those for VP. A significant difference in 2-propanol flux is not observed between PV and VP using the PPAC membrane.

3) The fluxes of water and 2-propanol for PV and VP are expressed based on the solution-diffusion theory by considering water solubilities of PIC-PAAc, PIC-PAN and PPAC membranes. It is found that the values of diffusion coefficients without swelling, and also the swelling parameters for water and 2-propanol in PV approximately agree with those for VP for the respective membranes. These results indicate that the differences in permeation fluxes of water and 2-propanol between PV and VP are attributable to the differences in solubilities of water and 2-propanol into the membranes from liquid and vapor phases.

**Nomenclature**

\[ A_i \] = swelling parameter for component \( i \) [\text{m}^3 \cdot \text{mol}^{-1}]

\[ a_i \] = parameter for component \( i \) in Eq. (9) [\text{mol} \cdot \text{m}^{-3}]

\[ b_i \] = parameter for component \( i \) in Eq. (9) [\text{]}]

\[ C_i \] = mole concentration of component \( i \) in membrane [\text{mol} \cdot \text{m}^{-3}]

\[ C_n \] = mole concentration of component \( i \) in membrane obtained from solubility measurement [\text{mol} \cdot \text{m}^{-3}]

\[ D_i \] = diffusion coefficient of component \( i \) [\text{m}^2 \cdot \text{s}^{-1}]

\[ D_0 \] = diffusion coefficient of component \( i \) without swelling [\text{m}^2 \cdot \text{s}^{-1}]

\[ J_i \] = permeation flux of component \( i \) [\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]

\[ J_T \] = total permeation flux, \( J_0 + J_p \) [\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]

\[ K_{i} \] = distribution coefficient of component \( i \) [\text{mol} \cdot \text{m}^{-3}]

\[ M \] = \( J_0 D_{00}/J_T D_{0} \) in Eq. (6) [\text{]}]

\[ N \] = \( A_n - A_p \) in Eq. (6) [\text{mol} \cdot \text{m}^{-2}]

\[ p \] = pressure [\text{Pa}]

\[ p_{vi} \] = saturation vapor pressure of component \( i \) [\text{Pa}]

\[ R \] = gas constant [\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]

\[ T \] = temperature [\text{K}]

\[ T_g \] = glass transition temperature [\text{K}]

\[ v \] = molar volume [\text{m}^3 \cdot \text{mol}^{-1}]

\[ x_i \] = mole fraction of component \( i \) in solution [\text{]}]

\[ y_i \] = mole fraction of component \( i \) in vapor [\text{]}]

\[ z \] = distance from feed side in membrane [\text{m}]

\[ a_i \] = separation factor [\text{]}]

\[ \delta \] = membrane thickness of dense layer [\text{m}]

\[ \gamma \] = activity coefficient in solution [\text{]}]

**Literature Cited**


