

# Specialty Polymeric Membranes 3. Pervaporation Separation of Acetic Acid/Water Mixtures Through Polymeric Membranes Having a Pyridine Moiety as a Side Group

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## SYNOPSIS

Pervaporation of an acetic acid/water mixture was studied through synthetic polymeric membranes made from poly(1-butyl methacrylate), poly(2-ethylhexyl methacrylate), polystyrene, and copolymers of 4-vinylpyridine and styrene, whose mole fraction of 4-vinylpyridine was 0.028 or 0.050. Permselectivities through polystyrene and poly(4-vinylpyridine-*co*-styrene) (mole fraction of 4-vinylpyridine, 0.050) are discussed based on the solution-diffusion theory. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Much effort has been devoted to developing novel membrane materials for the selective separation of ethanol from its aqueous solutions in connection with the effective production of biomass energy.<sup>1</sup> From the point of saving of both energy and production costs, most organic liquid mixtures, which have been separated by distillation until today, could be fractionated by pervaporation. However, there has been no reliable membrane materials, except polydimethylsiloxane membrane in the selective separation of organic compounds from aqueous solutions, to separate a specific organic compound with high efficiency.

Since 1985,<sup>3</sup> attention has been focused on the pervaporation separation of acetic acid/water solutions because acetic acid is one of the most important organic intermediates in the chemical industry<sup>3</sup> and one of the top fifty in chemicals production.<sup>4</sup> So far, several articles have dealt with the pervaporation of aqueous acetic acid solution.<sup>2,5-10</sup> Among these, only one has reported the selective permeation of acetic acid through the commercially available polydimethylsiloxane membrane produced by General Electric Company.<sup>8</sup> In continuation of

our studies on the development of novel organic permeable membranes from common polymer materials,<sup>11-14</sup> we report the pervaporation of acetic acid/water mixture through polymeric membranes bearing a pyridine moiety as a side group.

## STRATEGY OF MEMBRANE MATERIAL DESIGN

According to the solution-diffusion theory, the permselectivity of a pervaporation membrane must be given by the product of two determining quantities, i.e., solubility and diffusivity. Solubility is based on the chemical nature of both permeant and membrane material, while diffusivity is based on both molecular weight and shape of the permeant. In general, it seems to be difficult to attain selectivity by controlling the diffusivity since molecular weights and shapes of permeants consisting in the liquid mixture are not so different. On the other hand, the solubility of permeant could be theoretically controlled from null to infinite. By introducing functional moieties or chemical species, which was named a fixed carrier,<sup>15</sup> and can recognize and transport (or permeate) the specific substrate with high efficiency, one can make it possible to separate such a specific permeant in preference to other components. A pyridine moiety was chosen as a fixed carrier for acetic acid in order to make use of acid-base interactions as recognizing interaction.

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Selection of a membrane material, forming the membrane matrix is another important subject to be considered. Because the membrane matrix determines the environment of the whole membrane and especially that for the vicinity of a fixed carrier it might exhibit a cooperative effect in the interaction between a fixed carrier and a substrate.

## EXPERIMENTAL

### Materials

4-Vinylpyridine (4VP), 1-butyl methacrylate (BMA), 2-ethylhexyl methacrylate (2EHMA), styrene (ST), and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purified in the usual manner. Chloroform, toluene, acetic acid, and distilled water were used without purification. Membrane materials, such as poly(1-butyl methacrylate) (PBMA), poly(2-ethylhexyl methacrylate) (P2EHMA), polystyrene (PST), and copolymers of ST and 4VP (4VP/ST-028 and 4VP/ST-050) with the mole fraction of 4VP units of 0.028 and 0.050, respectively, were synthesized by the usual radical polymerization initiated by AIBN at 45°C with shaking. The chemical composition of the polymers thus prepared were determined by elemental analysis. The results are summarized in Table I.

### Preparation of Membranes

PBMA membrane was prepared as follows: 10 cm<sup>3</sup> of a chloroform solution (25 g dm<sup>-3</sup>) was poured into a flat laboratory dish (8.6-cm diameter) and the solvent allowed to evaporate at 25°C for 24 h. The thickness of the membrane was about 35 μm. Other membranes from P2EHMA, PST, 4VP/ST-028, and 4VP/ST-050 were prepared as follows: 5

cm<sup>3</sup> of a polymer solution (50 g dm<sup>-3</sup>) was poured into a flat laboratory dish (8.6-cm diameter) and the solvent allowed to evaporate at 25°C for 24 h. Chloroform was used as a solvent for P2EHMA, and toluene was adopted as a solvent for PST, 4VP/ST-028, and 4VP/ST-050. The P2EHMA membrane was about 20-μm thick, and those from PST, 4VP/ST-028, and 4VP/ST-050 ranged from 35 to 40 μm in thickness.

### Pervaporation

Pervaporation of aqueous acetic acid mixtures was carried out through the present membranes as described previously<sup>14</sup> at the constant operating temperature of 25°C. The membrane area in contact with the liquid was 9.9 cm<sup>2</sup>. The downstream pressure was in the range of 380 to 450 Pa (2.9–3.4 mmHg).

The separation analysis was carried out on a Shimadzu GC-8A gas chromatograph with a 2.0 m-long column packed with polyethylene glycol 20M on Chromosorb W (AW-DMCS).

The separation factor  $\alpha$  is defined as

$$\alpha = (Y_{\text{acetic acid}}/Y_{\text{water}})/(X_{\text{acetic acid}}/X_{\text{water}}) \quad (1)$$

where  $X_i$ 's and  $Y_i$ 's are the weight fractions of the component  $i$  in the feed and in the permeate, respectively.

### Measurement of Degree of Swelling

After being dried to constant weight a membrane sample was immersed in an acetic acid/water mixture at 25°C. When the sorption equilibrium was reached, the sample was weighed rapidly after blotted free of adhering surface liquid. The degree of

**Table I** Results of Copolymerization

Polymer	Monomer				AIBN <sup>a</sup> (mg)	Time (day)	Yield (g)	Mol fraction of 4VP in	
	BMA (g)	2EHMA (g)	ST (g)	4VP (g)				Monomer	Polymer
PBMA	12.80	—	—	—	74	4	12.3	—	—
P2EHMA	—	15.87	—	—	66	4	15.2	—	—
PST	—	—	12.50	—	98	4	12.0	—	—
4VP/ST-028	—	—	12.19	0.32	98	4	11.9	0.025	0.028
4VP/ST-050	—	—	11.87	0.63	98	4	11.9	0.050	0.050

Polymerization temperature, 45°C.

<sup>a</sup> (AIBN)/(monomer) = 1/200 (mol/mol).

swelling for membranes was defined by

degree of swelling (%)

$$= 100 \times (W_s - W_d) / W_d \quad (2)$$

where  $W_d$  and  $W_s$  denote the weight of the sample in both the dry and swollen state, respectively. After the measurement of swelling, the sample was dried again to determine the weight of the dry sample so that the weight loss of the sample was scarcely observed before and after the swelling study.

### Evaluation of Solubility Selectivity

A membrane sample, prepared in the same way as described for the measurement of degree of swelling, was transferred to the apparatus shown in Figure 1. The apparatus was connected to a vacuum line. After the container was locally cooled with liquid nitrogen, the entire apparatus was completely evacuated. Then, the container that held the swollen membrane sample was heated to purge the swelling solution from the sample while the manifold was kept cool to trap the solution in it. The composition of the collected liquid was analyzed by gas chromatography in the same way for the composition analysis of pervaporation.

The solubility selectivity,  $S_S$ , is defined as

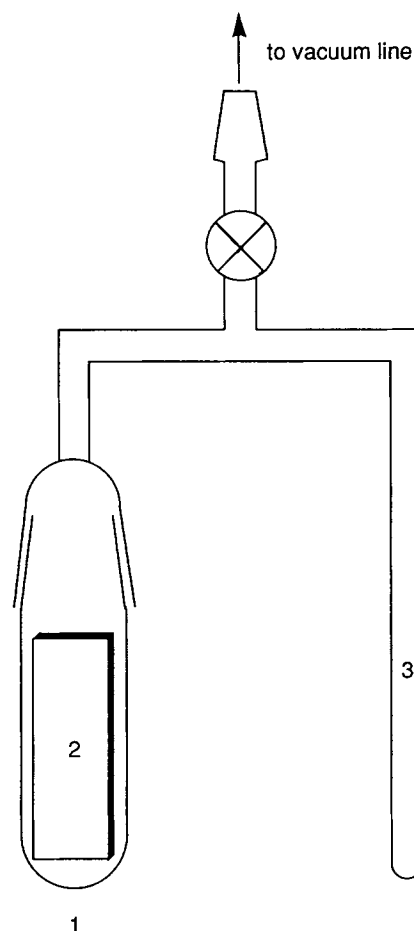
$$S_S = (Z_{\text{acetic acid}} / Z_{\text{water}}) / (X_{\text{acetic acid}} / X_{\text{water}}) \quad (3)$$

where  $X_i$ 's and  $Z_i$ 's are the weight fractions in the solution and in the membrane, respectively.

## RESULTS AND DISCUSSION

### Selection of Membrane Matrix

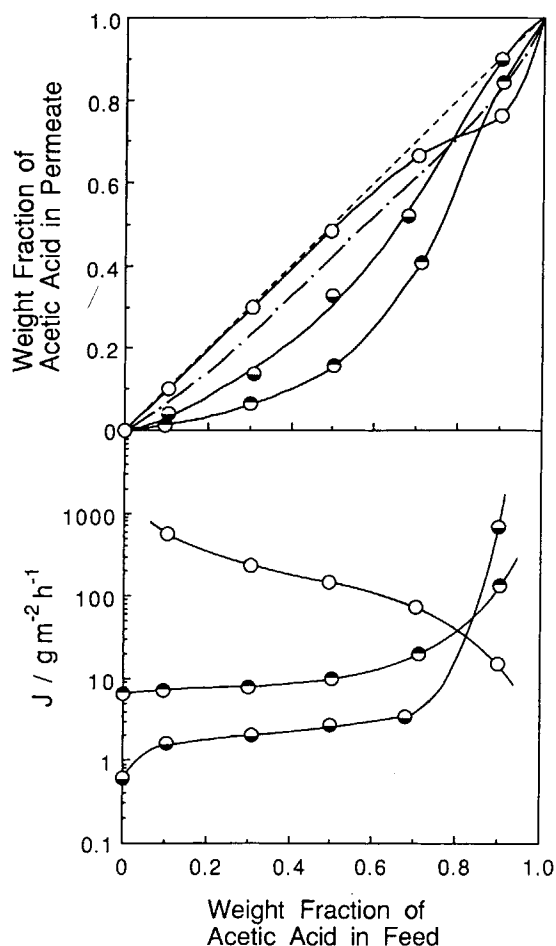
First a polymer material for the membrane matrix was selected. Selective separation of acetic acid from aqueous acetic acid mixture was attempted. This led to the conclusion that the membrane matrix should be hydrophobic. It is expected that a hydrophobic membrane matrix should have affinity to acetic acid but repel water. From this point of view, PBMA, P2EHMA, and PST were chosen and cast into the membranes for the pervaporation of acetic acid/water mixtures. The results are summarized in Figure 2. In addition, the vapor-liquid equilibrium curve for acetic acid/water system at 25°C<sup>16</sup> is also depicted in Figure 2. These three membranes did not show permselectivity toward acetic acid in the whole feed fraction range; in other words, the weight frac-



**Figure 1** Rough sketch of the apparatus for the determination of solubility selectivity. 1, container; 2, membrane; 3, manifold.

tion of acetic acid in permeate did not exceed the diagonal line shown in Figure 2. However, the weight fraction of acetic acid in the permeate for the PST membrane was slightly higher than that of the vapor-liquid equilibrium line, the weight fraction of acetic acid in the feed being less than around 0.8. The permselectivity toward acetic acid is on the order of PST > P2EHMA > PBMA.

This difference in selectivity may be explained in terms of the solubility parameter<sup>17</sup> or the membrane polarity,<sup>18,19</sup> which was proposed as an index for the selection of pervaporation membrane materials. In the present study solubility parameters were adopted because of a lack of comprehensive knowledge of the membrane polarities of these polymers. The solubility parameter ( $\delta_{sp}$ ), consisting of the contributions of dispersion forces ( $\delta_d$ ), dipole forces ( $\delta_p$ ), and hydrogen bonding ( $\delta_h$ ), were calculated for each membrane, as in the literature.<sup>20-22</sup> The space dis-



**Figure 2** Effect of feed composition on the separation of acetic acid/water mixtures and flux through PST, P2EHMA, and PBMA membranes. Operating temp., 25°C; downstream pressure, 380–450 Pa (2.9–3.4 mmHg); (○) PST membrane; (●) P2EHMA membrane; (●) PBMA membrane; — · —, vapor-liquid equilibrium curve.

tance between acetic acid and membrane (DAM) and that between water and membrane (DWM) are defined by eqs. (4) and (5) with the following values:  $\delta_{d,A} = 14.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ,  $\delta_{p,A} = 7.98 \text{ J}^{1/2} \text{ cm}^{-3/2}$ , and  $\delta_{h,A} = 13.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$  for acetic acid<sup>20,21</sup>; and  $\delta_{d,W} = 19.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ,  $\delta_{p,W} = 17.8 \text{ J}^{1/2} \text{ cm}^{-3/2}$ , and  $\delta_{h,W} = 17.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$  for water.<sup>23</sup> The equations themselves are<sup>14</sup>:

$$\text{DAM} = [(\delta_d - \delta_{d,A})^2 + (\delta_p - \delta_{p,A})^2 + (\delta_h - \delta_{h,A})^2]^{1/2} \quad (4)$$

$$\text{DWM} = [(\delta_d - \delta_{d,W})^2 + (\delta_p - \delta_{p,W})^2 + (\delta_h - \delta_{h,W})^2]^{1/2}. \quad (5)$$

Estimated DAM and DWM for these three membranes are summarized in Table II. The tendency of the permselectivity toward acetic acid through these membranes correlated with the increase in DWM. The larger the space distance of  $\delta_{sp}$  between water and membrane became, the more the water molecule was repelled from the membrane material. As a result, the pervaporation selectivity was increased with the increase in DWM. The expectations with regard to permselectivity deduced from the order of DAM in Table II were opposite to both the observed permselectivity and the expectation from DWM. In the present study, the permselectivity can be explained by DWM but not by DAM.

The total flux values for PBMA and P2EHMA increased with the increase in acetic acid feed fraction. Especially the flux values increased drastically over the feed fraction of 0.7. On the other hand, the total flux value for PST decreased with the increase in acetic acid feed fraction.

Among these three polymeric materials, it can be said that PST is preferable as a membrane matrix. Hereafter, PST was used as a membrane matrix.

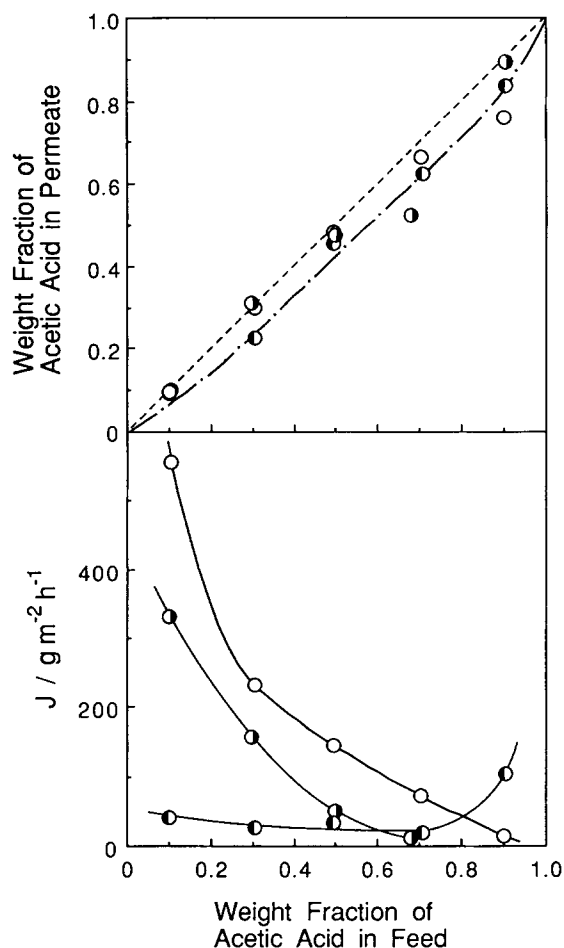
#### Pervaporation Through 4VP/ST Membranes

Figure 3 indicates the results of the pervaporation through PST, 4VP/ST-028, and 4VP/ST-050, where weight fractions of acetic acid in the permeate and total fluxes are plotted against the weight fractions of acetic acid in feed. Unexpectedly, a prominent improvement of the permselectivity toward acetic acid was scarcely attained by the introduction of a pyridine moiety into the PST membrane matrix.

It was reported that water molecules are permeated in preference to ethanol through hydrophobic polymeric membranes, such as poly(vinyl chloride),<sup>24</sup> polystyrene,<sup>25</sup> and poly(vinyl *p*-tert-butylbenzoate)<sup>26</sup> even though ethanol was preferentially incorporated into them. In the present study, the same phenomenon could be anticipated. Based on this, the composition of acetic acid/water mixtures adsorbed in PST and 4VP/ST-050 were investigated. The results are shown in Figure 4. Acetic acid

**Table II** Solubility Parameters

	$\delta_{sp}$ ( $\text{J}^{1/2} \text{ cm}^{-3/2}$ )	DAM ( $\text{J}^{1/2} \text{ cm}^{-3/2}$ )	DWM ( $\text{J}^{1/2} \text{ cm}^{-3/2}$ )
PBMA	18.0	7.96	18.1
P2EHMA	17.3	9.59	19.7
PST	18.2	15.6	24.3

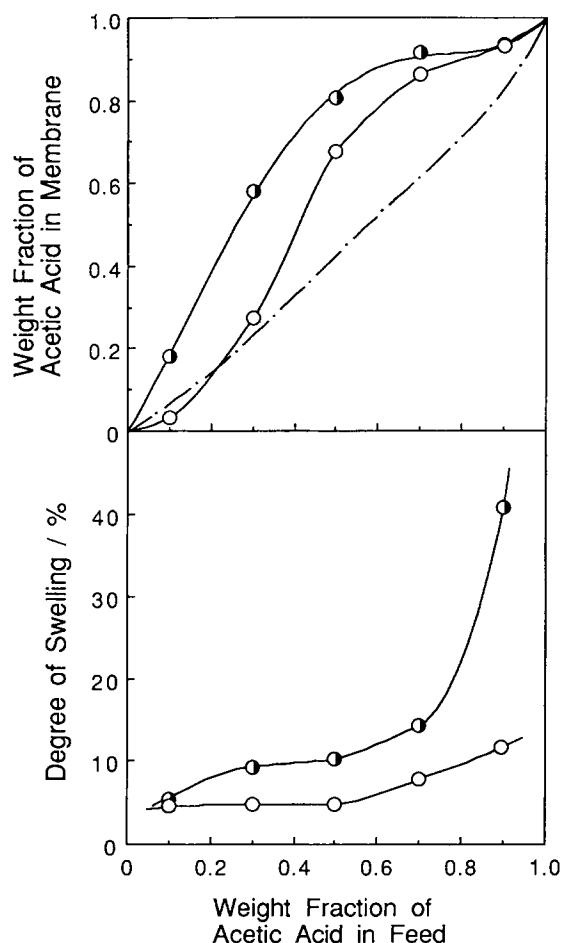


**Figure 3** Effect of feed composition on the separation of acetic acid/water mixtures and flux through 4VP/ST-050, 4VP/ST-028, and PST membranes. Operating temp., 25°C; downstream pressure, 380–450 Pa (2.9–3.4 mmHg); (○) PST membrane; (●) 4VP/ST-028 membrane; (●) 4VP/ST-050 membrane; — · —, vapor–liquid equilibrium curve.

was preferentially incorporated into both membranes from aqueous acetic acid mixtures (Fig. 4). Especially weight fractions of acetic acid in 4VP/ST-050 membrane were higher than not only those for PST membrane but also for the vapor–liquid equilibrium curve at 25°C in the whole feed fraction range. The degree of swelling increased with the increase in weight fraction of acetic acid in feed. As expected, the degree of swelling for 4VP/ST-050 was higher than that for PST. Both curves tended to increase with the increase in feed fraction from the feed fraction of around 0.7. This increase tendency for the 4VP/ST-050 membrane was prominent. This might be due to the specific interaction between acetic acid and the pyridine moieties in the

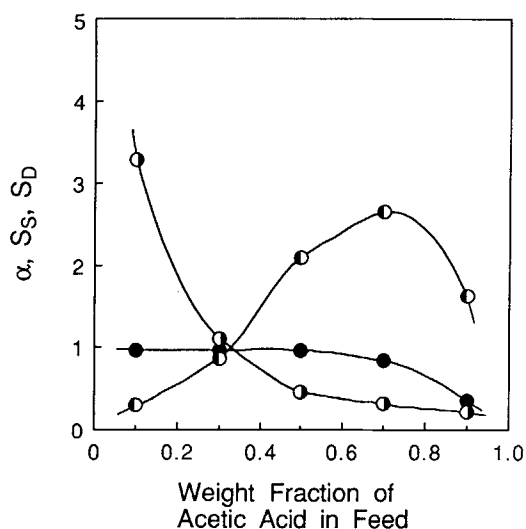
membrane; that is, an acid–base interaction between permeant and membrane material. From flux values for PST and 4VP/ST-050 membranes shown in Figure 3 and swelling behavior for these membranes in Figure 4, low flux value for 4VP/ST-050 membrane might be due to the decrease in diffusivity for both permeants by the introduction of pyridine moiety into the PST membrane.

Using the data shown in Figure 4, we evaluate the solubility selectivity,  $S_S$ . Diffusivity selectivity,  $S_D$ , can be estimated using both separation factor,  $\alpha$ , and  $S_S$  (see Appendix).  $\alpha$ ,  $S_S$ , and  $S_D$ , for PST and 4VP/ST-050 membranes are shown in Figures 5 and 6, respectively. The solubility selectivity toward acetic acid was increased by the introduction of pyridine moieties into the membrane and that was over unity in the whole composition range. This

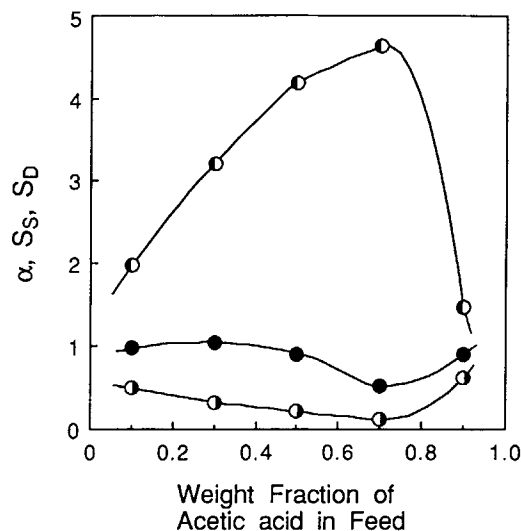


**Figure 4** Effect of acetic acid feed concentration on the concentration of solution sorbed in PST and 4VP/ST-050 membranes and on the degree of swelling. Operating temp., 25°C; (●) 4VP/ST-050 membrane; (○) PST membrane; — · —, vapor–liquid equilibrium curve.

is due to the specific interaction between acetic acid and a fixed carrier, pyridine moiety, in 4VP/ST-050 membrane. Permselectivity toward acetic acid for 4VP/ST-050 was, however, not improved in comparison with PST membrane. This might be due to low diffusivity selectivity of 4VPST-050 membrane (Fig. 6).  $S_D$  for acetic acid in the 4VP/ST-050 was below unity in the whole feed composition.  $S_D$  for PST membrane also gave a similar tendency as observed for the 4VP/ST-050 membrane except in the low feed composition range. The results of Figures 5 and 6 might be explained as follows comparing the pervaporation of aqueous ethanol solution through the hydrophobic membranes.<sup>24-26</sup> The acetic acid molecules are incorporated into the membrane in preference to water molecules. However, it is difficult for acetic acid molecules to migrate from the upstream side to the downstream side because of the relatively strong interaction between acetic acid and the membrane material. An especially strong interaction can be expected for an acetic acid/4VP/ST-050 membrane system. On the other hand, it is difficult for water molecules to be incorporated into these membranes because of the hydrophobic nature of PST and 4VP/ST-050 membranes. Water molecules incorporated into the membrane, however, might diffuse through it with ease because of the weak interaction between water and the membrane material. Water molecules might also migrate through the membrane faster than acetic acid mol-



**Figure 5** Effect of acetic acid feed concentration on separation factor ( $\alpha$ ), solubility selectivity ( $S_S$ ), and diffusivity selectivity ( $S_D$ ) of PST membrane. Operating temp., 25°C; downstream pressure, 380–450 Pa (2.9–3.4 mmHg); (●)  $\alpha$ ; (○)  $S_S$ ; (◐)  $S_D$ .



**Figure 6** Effect of acetic acid feed concentration on separation factor ( $\alpha$ ), solubility selectivity ( $S_S$ ), and diffusivity selectivity ( $S_D$ ) of 4VP/ST-050 membrane. Operating temp., 25°C; downstream pressure, 380–450 Pa (2.9–3.4 mmHg); (●)  $\alpha$ ; (○)  $S_S$ ; (◐)  $S_D$ .

ecules due to the difference in molecular size between acetic acid and water. As a result, permselectivity toward acetic acid was not attained by the polymeric membranes having a pyridine moiety as a fixed carrier. The following two methods to attain acetic acid permselective pervaporation membranes are: 1. introduction of other amine moiety, with a  $pK_a$  value which is much higher than that of the pyridine moiety, into the membrane. This leads to an increase in solubility selectivity toward acetic acid. (2) Adoption of a more hydrophobic membrane matrix, such as polymers consisting of fluorocarbons or siloxanes, in lieu of PST. This causes a decrease in water solubility for the obtained membrane, that is, such a membrane material can prevent water molecules from being incorporated into the membrane.

## APPENDIX

Obeying the solution–diffusion theory, separation factor for the present study can be given by<sup>27</sup>

$$\alpha = P_{\text{acetic acid}}/P_{\text{water}} \quad (\text{A1})$$

where  $P_{\text{acetic acid}}$  and  $P_{\text{water}}$  denote the permeability coefficients for acetic acid and water, respectively. Solubility selectivity,  $S_S$ , can be led to the derivation of eq. (A2) from eq. (3):

$$S_S = S_{\text{acetic acid}}/S_{\text{water}} \quad (\text{A2})$$

where  $S_{\text{acetic acid}}$  and  $S_{\text{water}}$  are the solubility coefficients of acetic acid and water, respectively. From eq. (A1) and (A2), diffusivity selectivity,  $S_D$ , is given by

$$S_D = \alpha/S_S (= D_{\text{acetic acid}}/D_{\text{water}}) \quad (\text{A3})$$

where  $D_{\text{acetic acid}}$  and  $D_{\text{water}}$  are the diffusivity coefficients of acetic acid and water, respectively.

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