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Specialty polymeric membranes

4. Pervaporation separation of acetic acid/water mixtures through modified polybutadiene membranes

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SUMMARY

Pervaporation of acetic acid/water mixture was investigated through uncrosslinked and crosslinked polybutadiene membranes. Crosslinked polybutadiene membrane permeated acetic acid in preference to water indicating that polybutadiene must be a candidate for a permselective membrane material for acetic acid separation from its aqueous solution.

INTRODUCTION

Pervaporation has been recognized as a promising membrane separation process, which might lead to energy saving and the effective separation of liquid mixtures.[1] It may emerge in chemical industries as stand-alone and hybrid system with distillation in the near future. Especially, both selective separation of water from aqueous watermiscible organic liquid solutions and that of ethanol from ethanol/water mixtures have been intensively investigated by using the pervaporation technique.[2,3] Acetic acid is one of the most important organic intermediates in the chemical industry[4] and one of the top fifty chemicals produced.[5] Separation of acetic acid/water mixtures is one of the systems for prime energy-saving candidates.[6] Dehydration of acetic acid/water mixtures by pervaporation has been studied since 1985.[7-17] On the other hand, preferential pervaporation of acetic acid can be also found.[18]

The authors investigated new membrane materials for selective pervaporation of acetic acid from its aqueous mixtures in continuation of our studies on the development of novel organic permeable membranes from common polymer materials.[19-23] In order to obtain acetic acid permselective membrane materials, following two strategies were deduced from the previous paper[17] : (1) Introduction of a fixed carrier, which shows high affinity towards acetic acid molecules, into the membrane. (2) Adoption of a more hydrophobic membrane matrix. The former leads to an increase in solubility selectivity towards acetic acid. The latter causes a decrease in water solubility for the membrane, that is, such a membrane material can repel water molecules. The present paper deals with development of pervaporation membrane materials for the selective separation of acetic acid following the strategy (2): polybutadiene was chosen as a membrane material because of the hydrophobic character of polybutadiene, and their membrane performance was investigated.

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EXPERIMENTAL

Materials

Polybutadiene (cis) (**PB**) was purchased from Aldrich Chemical Company, Inc. and used without further purification. Bis(1-methyl-1-phenylethyl)peroxide (**DCP**) was recrystallized from ethanol; mp 43.5 - 45.0°C. Acetic acid, distilled water, toluene, and benzene were used without purification.

Preparation of Membranes

PB membranes were prepared as follows: 30cm^3 of a toluene solution, which concentration was 66.7gdm^{-3}, was poured into a flat laboratory dish (12.6cm diameter) and the solvent was allowed to evaporate at 45°C for 24h. The thickness of the membrane was ca. 150μm. Crosslinked **PB** membranes were prepared as follows: first a **PB** membrane containing **DCP**, which consisted of 100 parts of **PB** and 1 part of **DCP**, was prepared from toluene solution in the same way as for the preparation of **PB** membranes. Then the formed membrane was heated at 150°C for 1h so that crosslinks were introduced into the membrane. The crosslinking density was determined to be 0.57mol dm^{-3} using the Flory-Rehner equation.[24,25] Benzene was used as a solvent for the evaluation of the crosslinking density. For the **PB**/benzene system, the Flory solvent-polymer interaction parameter χ_1 is given to be 0.314.[26]

Pervaporation

Pervaporation of aqueous acetic acid mixtures was carried out through the present membranes as described previously[22] at the constant operating temperature of 25°C. The membrane area in contact with liquid was 9.9cm^2. The downstream pressure was in the range of 380 to 450Pa (2.9 - 3.4mmHg).

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 α is defined as

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

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 acetic acid/water mixture at 25°C. When the sorption equilibrium was reached, the sample was weighed rapidly after blotted free adhering liquid on its surface. The degree of swelling of membranes was defined by

$$\text{Degree of Swelling (\%)} = 100 \times (W_s - W_d) / W_d \qquad (2)$$

where W_d and W_s denote the weight of the sample in both 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 in the preceding paragraph of the measurement of degree of swelling, was used for the evaluation of solubility selectivity. The composition of liquid mixture sorbed in the membrane was determined as described previously.[17]

The solubility selectivity, S_S, is defined as

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

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

RESULTS AND DISCUSSION

Figure 1 shows the results of the pervaporation experiments for acetic acid/water mixtures through both uncrosslinked and crosslinked **PB** membranes, where weight fractions of acetic acid in permeate and total flux values, J, are plotted against weight fractions of acetic acid in feed. The vapor-liquid equilibrium curve for acetic acid/water system at 25°C[27] is also depicted in Figure 1. Observed data points for **PB** membrane locate along the diagonal line in the whole feed fraction range, while those for polystyrene (**PST**) membranes were below this line the weight fraction of acetic acid in feed being higher than 0.7.[17] This means that **PB** may be a candidate for membrane material, which shows permselectivity towards acetic acid, rather than **PST**. This tendency can be explained in terms of the solubility parameters as reported previously.[17] The space distance of solubility parameter between acetic acid and membrane (**DAM**) and that between water and membrane (**DWM**) can be estimated by eqs. (4) and (5)[17] with the following values: $\delta_{d,A} = 14.5 J^{1/2}cm^{-3/2}$, $\delta_{p,A} = 7.98 J^{1/2}cm^{-3/2}$, and $\delta_{h,A} = 13.5 J^{1/2}cm^{-3/2}$ for acetic acid[28,29]: and $\delta_{d,W} = 19.5 J^{1/2}cm^{-3/2}$, $\delta_{p,W} = 17.8 J^{1/2}cm^{-3/2}$, and $\delta_{h,W} = 17.6 J^{1/2}cm^{-3/2}$ for water.[30]

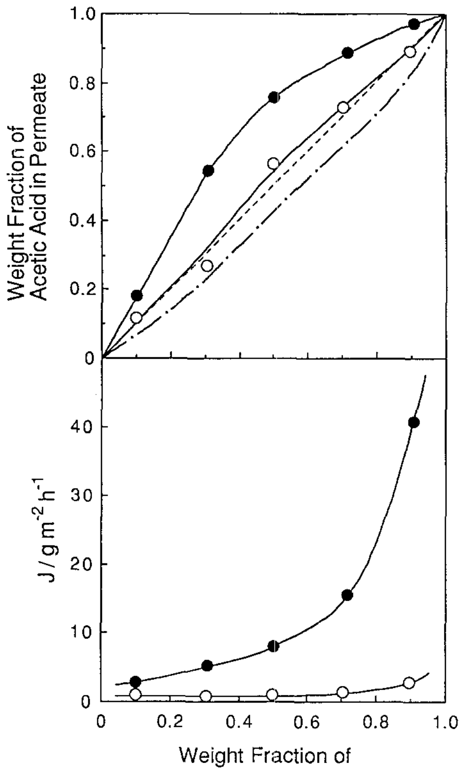

Figure 1 Effect of feed composition on the separation of acetic acid/water mixtures and flux through uncrosslinked and crosslinked PB membranes. (Operating temp., 25°C; downstream pressure, 380-450Pa (2.9-3.4mmHg); ○, uncrosslinked PB membrane; ●, crosslinked PB membrane; — · —, vapor-liquid equilibrium curve.)

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

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

Estimated **DAM** and **DWM** for **PB** are summarized in Table 1 together with those for **PST**. From Table 1, the permselectivity can be explained by **DWM** rather than by **DAM** like the separation of aqueous acetic acid mixtures with **PST** membrane.[17] In other words, the larger the space distance of the solubility parameters between water and membrane became, the more the water molecule was repelled from the membrane material.

Table 1 Solubility parameter

	δ_{sp} $J^{1/2}cm^{-3/2}$	**DAM** $J^{1/2}cm^{-3/2}$	**DWM** $J^{1/2}cm^{-3/2}$
PB	16.2	15.8	25.3
PST	18.2	15.6	24.3

In the previous study[23], it was made clear that the introduction of crosslinks into the **PB** membrane improved its permselectivity towards alcohols and made it an alcohol permselective membrane. Therefore, we tried to modify **PB** using the crosslinking technique with **DCP**. As we expected, weight fractions of acetic acid in permeate for crosslinked **PB** membrane were exceeding both diagonal line and vapor-liquid equilibrium curve. The crosslinked **PB** membrane gave, strange to say, a higher flux value than uncrosslinked **PB** membranes. Similar results were observed in the separation of aqueous alcohol mixtures through uncrosslinked and crosslinked **PB** membranes.[23] We would like to discuss this later.

The relationship between the composition of the liquid mixture sorbed in the membrane and the feed composition for uncrosslinked **PB** membrane is shown in Figure 2 and that for crosslinked PB membrane in Figure 3. Weight fractions of acetic acid in uncrosslinked **PB** membrane were slightly lower than the diagonal line and also locate below those in permeate of pervaporation. In the crosslinked **PB** membrane system, weight fractions of acetic acid in membrane were apparently higher than the diagonal line, though those were lower than weight fractions of acetic acid in permeate of pervaporation. Introduction of crosslinks into **PB** membrane led to an increase in affinity of membrane towards acetic acid and to the suppression of swelling by feed solutions. From swelling behavior shown in Figures 2 and 3, and flux values in Figure 1, high flux value for crosslinked **PB** membrane might be due to the drastic increase in diffusivity for both permeants by the modification of membranes. The increase in diffusivity caused by the introduction of crosslinks was opposed to our expectation.[31] From this, we speculated that the nature itself of **PB** in modified membrane was changed from that of unmodified **PB** membrane. As a result, diffusivities of permeant in the modified **PB** membrane became higher than those in the unmodified **PB** membrane.

Using pervaporation and sorption data, solubility selectivity (S_S) and diffusivity selectivity (S_D) can be evaluated. Diffusivity selectivity is given by[17]

$$S_D = \alpha / S_S \ (= D_{acetic\ acid}/D_{water}) \qquad (6)$$

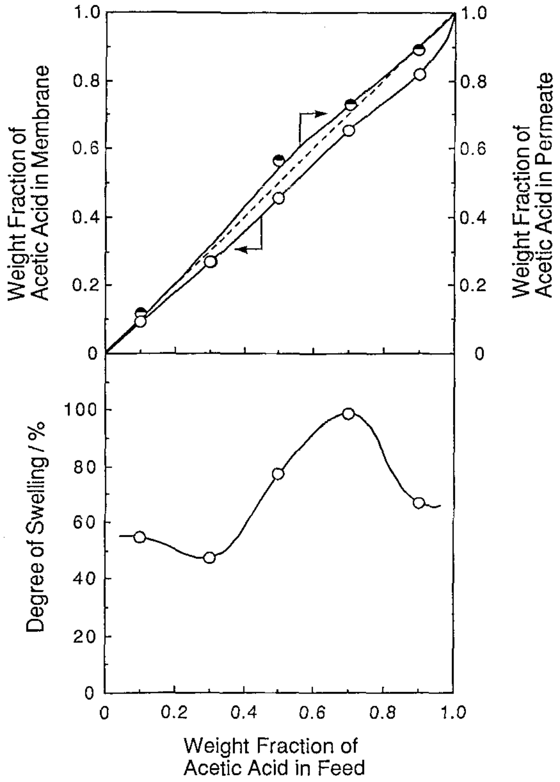

Figure 2 Effect of acetic acid feed concentration on the concentration of solution sorbed in uncrosslinked PB membranes and on the degree of swelling. (Operating temp., 25°C; downstream pressure, 380-450Pa (2.9-3.4mmHg).)

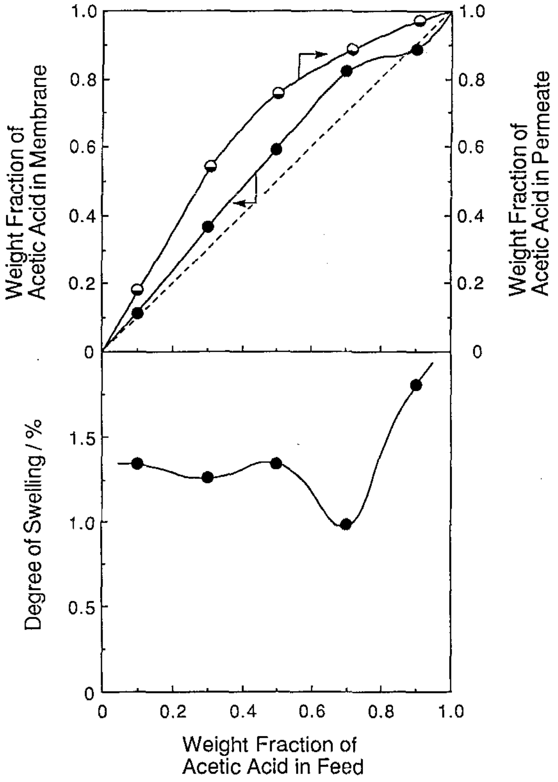

Figure 3 Effect of acetic acid feed concentration on the concentration of solution sorbed in crosslinked PB membranes and on the degree of swelling. (Operating temp., 25°C; downstream pressure, 380-450Pa (2.9-3.4mmHg).)

where $D_{acetic\ acid}$ and D_{water} are the diffusivity coefficients of acetic acid and water, respectively. Separation factor, solubility selectivity, and diffusivity selectivity for the uncrosslinked and crosslinked **PB** membranes are shown in Figure 4 as a function of weight fraction of acetic acid in feed. In general, the hydrophobic membrane material showed high affinity towards organics, but diffusivity of those were low compared with that of water.[17,32-34] Hydrophobic polymeric membranes, as a result, tended to give permselectivity towards water, even though they consisted of hydrophobic polymers.[17, 32-34]

In the present study, introduction of crosslinks into **PB** membrane brought about the increase in both solubility selectivity and diffusivity selectivity towards acetic acid molecules. Therefore, crosslinked **PB** membrane showed permselectivity towards acetic acid. As further extensions of this kind of study, it is necessary to explain the effect of the introduction of crosslinks on membrane performance in molecular level.

CONCLUSIONS

Crosslinked polybutadiene membranes permeated acetic acid from aqueous its solutions by pervaporation. It was made clear that permselectivity towards acetic acid was caused by both the increase in solubility and diffusivity selectivities, which were originated in the introduction of crosslinks into polybutadiene membranes. The obtained results suggested that crosslinked polybutadiene can be used as a pervaporation membrane material for selective separation of acetic acid from aqueous its mixtures.

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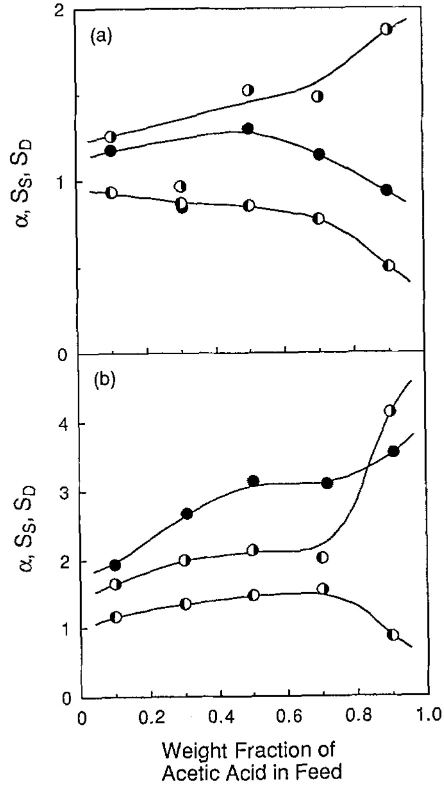

Figure 4 Effect of acetic acid feed concentration on separation factor (α), solubility selectivity (S_S), and diffusivity selectivity (S_D) of uncrosslinked (a) and crosslinked (b) PB membranes. (Operating temp., 25°C; downstream pressure, 380-450Pa (2.9-3.4mmHg); ●, α; ◐, S_S; ◑, S_D.)

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