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Chemically Modified Poly(4-methyl-1-pentene) Membrane for Pervaporation Separation of Acetic Acid–Water Mixtures

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ABSTRACT: The membranes of pure poly(4-methyl-1-pentene) (TPX) and the 4-vinylpyridine (4-VP) modified TPX membranes, TPX/P4-VP, were prepared for pervaporation. The introduction of high hydrophilic 4-VP monomer into the TPX matrix was done by free radical polymerization to form the TPX/P4-VP membrane. The separation factor and the permeation rate of TPX/P4-VP membranes are higher than those of the unmodified TPX membranes for pervaporation of aqueous acetic acid solution. FTIR spectra and water permeation behavior were utilized to study the permeation mechanism of aqueous acetic acid solution through the TPX/P4-VP membranes. A good relationship was obtained between the feed water concentration and water permeation rate by applying the Michaelis–Menten equation.

KEY WORDS TPX / Acetic Acid–Water Mixture / Poly(4-methyl-1-pentene) / 4-Vinylpyridine / Pervaporation /

The membrane separation technique is considered for the separation of organic mixtures, such as the azeotropic and close boiling point mixtures or structural isomers. Recently, most efforts on pervaporation have focused on water/ethanol separation.[1-3] Nevertheless, among the organic liquids, acetic acid is an important commodity product in the chemical industry. Therefore, much attention has been directed to the separation of the acetic acid–water mixture by pervaporation.[4]

So far, membrane materials, such as polyimide,[5] poly(4-vinylpyrine-*co*-acrylonitrile),[6] poly(vinyl alcohol),[7] poly(acrylic acid-*co*-acrylonitrile),[4] etc., were effectively used for the dehydration of the acetic acid–water mixtures by pervaporation. We reported previously that the performance of TPX membranes for the acetic acid/water separation can be improved using TPX/Ethylene vinylacetate membranes.[8] Yoshikawa *et al.*[9] examined two special interactions assuming a fixed carrier mechanism, that is, hydrogen bonding and coulombic interaction. Thus, the objective of this article is to utilize the TPX/P4-VP membrane which possesses high chemical resistance, hydrophilicity, and mechanical strength for the dehydration of acetic acid by pervaporation. The hydrogen-bonding interaction between the pyridine moiety of membrane and carboxylic acid in the feed is discussed. In addition, the permeation mechanism of aqueous acetic acid solution through modified TPX membranes was characterized by FTIR spectra and water permeation behavior.

EXPERIMENTAL

Material

4-Vinylpyridine (4-VP), cyclohexene, and chloroform were purchased from Merck Company. TPX (MX-002) was supplied by Mitsui Company in Japan. The initiator, dibenzoylperoxide (BPO), was purified by traditional methods and the 4-VP monomer was distilled under reduced pressure in vacuum.

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Synthesis

TPX/P4-VP was synthesized as follows: 1.0 g of TPX polymer and 20 ml of cyclohexene were placed in an ampule, and then dissolved at 50°C for 24 h with stirring. The 0.4 ml mixture of 4-VP monomer and BPO initiator (5 ml/0.06 g) was sealed in an ampule after dissolving entirely. Then the mixture solution was degassed by three freeze-pump-thaw cycles and sealed off under high vacuum pump. Polymerization was carried out at 80°C for 2 h by shaking. The product TPX/P4-VP was collected by precipitating in excess acetone solution. P4-VP content in the products was measured by the weight method.

Membrane Preparation

The pure TPX membrane and TPX/P4-VP membrane were prepared as described previously.[10] The thickness of membrane was in the range of 19—25 μm.

Apparatus and Measurements

Permeation of aqueous acetic acid–water solution was carried out through a membrane by ordinary pervaporation technique.[8,10] In pervaporation the feed solution is in contact with the membrane, whereas the effective area is 10.2 cm^2. The permeate was collected in a trap cooled by liquid nitrogen and the permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions and permeates were analyzed by gas chromatography (GC, China chromatography 8700T). The separation factor was calculated from the following equation:

$$\alpha = \frac{Y_{\text{water}}/Y_{\text{acetic acid}}}{X_{\text{water}}/X_{\text{acetic acid}}}$$

where X_{water}, $X_{\text{acetic acid}}$, and Y_{water}, $Y_{\text{acetic acid}}$ are the weight fractions in the feed and permeate, respectively.

The clean and dried membrane with known weight (W_d) was immersed in feed acetic acid solution at room temprature for 24 h to reach equilibrium swelling. This membrane was rapidly removed, blotted, and weighed. The weight (W_w) of the solvent-swollen membrane was obtained.[11] The swelling ratio was calculated as follows:

$$\text{Swelling ratio} = \frac{W_w}{W_d}$$

RESULTS AND DISCUSSION

FTIR Spectra

Recently, several studies report that the pervaporation separation process has good performance if the complex between the function group moiety in the membrane and permeant in the feed is strongly bound in the membrane and if there is a continuous supply fixed complex sites from the feed.[6] Therefore, in order to confirmed the formation of an *in-situ* complex between the pyridine moeity in the TPX/P4-VP membrane and carboxylic acid in the feed, FTIR analysis was made.

The infrared spectra of 4-vinylpyridine modified TPX membranes were dipped in 90 wt% aqueous acetic acid–water solution for one day at 25°C, and dried at 25°C for 72 h, as shown in Figure 1. From Figure 1(c), the stretching vibration of a carbonyl (C=O) peak appears at 1730 cm^{-1} and characteristic pyridine ring peaks disappear at 1600—1665 cm^{-1}. This phenomenon is attributed to the formation of the complex wight strong hydrogen-bonding interaction between the pyridine moiety in the membrane and acetic acid in the feed. This was also observed by Leet *et al.*[6]

Effects of Feed Acetic Acid Concentration on Swelling of Membrane

The effects of acetic acid concentration on the swelling of TPX and TPX/P4-VP membranes are shown in Figure 2. The swelling of TPX membrane decreased with acetic acid concentration. TPX is a nonpolar material, and its swelling in water is small. However, the acetic ion is more polar than the water

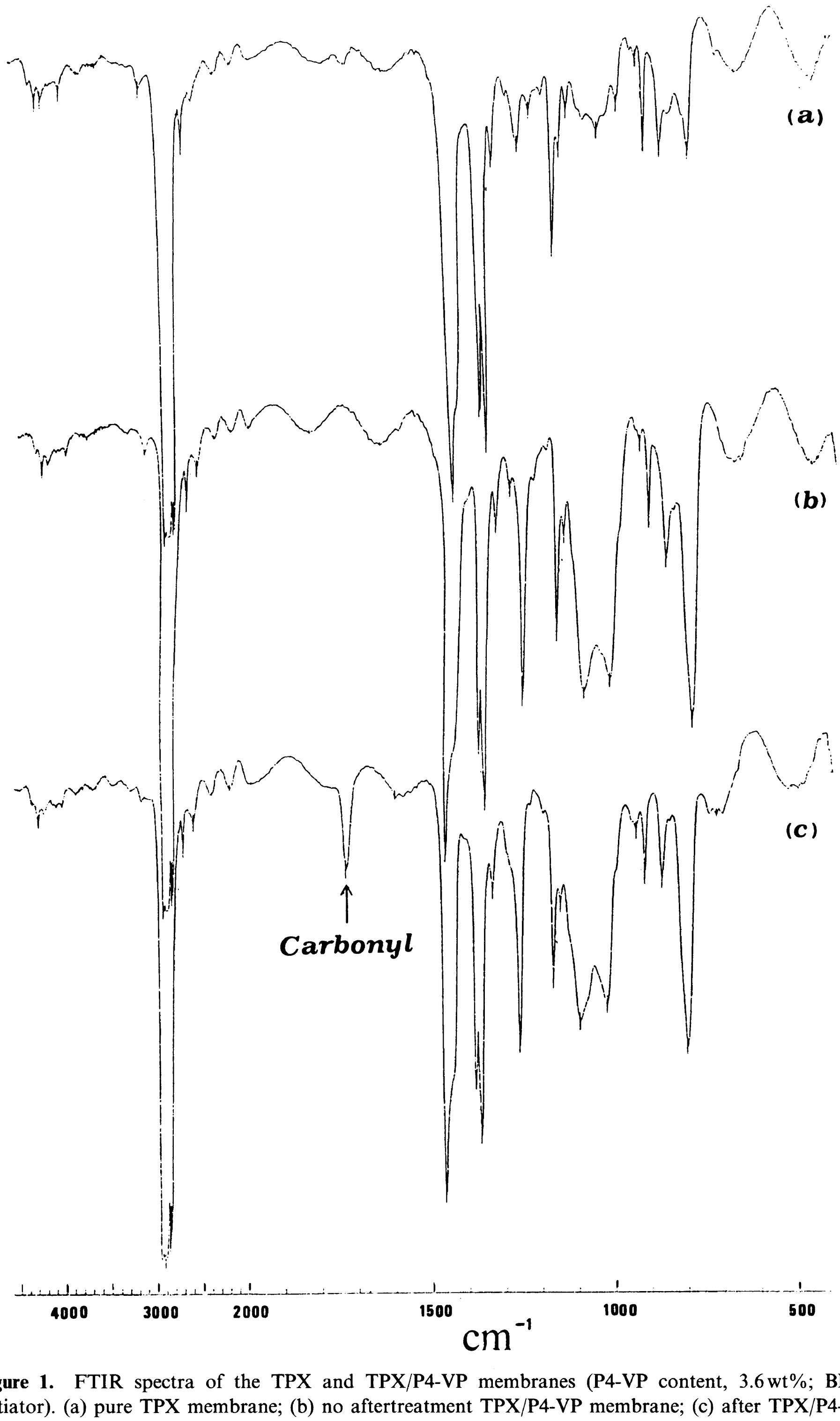

Figure 1. FTIR spectra of the TPX and TPX/P4-VP membranes (P4-VP content, 3.6 wt%; BPO, initiator). (a) pure TPX membrane; (b) no aftertreatment TPX/P4-VP membrane; (c) after TPX/P4-VP membrane immersion in acetic acid–water solution for 24 h and drying at 25°C for 72 h.

molecule. Increase of acetate concentration further decreased the swelling of the nonpolar membrane.

Opposite swelling was observed for the TPX/P4-VP membrane. As shown in Figure 2, the TPX/P4-VP membrane swelled as acetic acid concentration increased. The TPX/P4-VP membrane is more polar than TPX. A polar solvent (acetic acid) should swell a polar membrane. But TPX/P4-VP cannot be considered as hydrophilic membrane. We consider the further swelling of this membrane by increasing acetic acid to possibly arise from the formation of a complex between acetic acid and the pyridine group on the membrane.

Feed Concentration Effects

It is shown in Table I that the selectivity of TPX membrane on water increased with acetic acid concentration. When compared with the results from a swelling experiment, it become clear that pore size of the membrane controlled the selectivity. As acetic acid concentration increased, the membrane shrinked and therefore pore size reduced the diffusivity of water and acetic acid. Since acetic acid is a larger molecule, the effect of reducing pore size on toral permeation rate is much more for acetic acid than for water molecule. As a result, the total permeation rate decreased and the selectivity of water over acetic acid increased.

The same argument does not hold for the TPX/P4-VP membrane. Both swelling and membrane selectivity increased as acetic acid concentration increased. Furthermore, the swelling of membrane did not facilitate total permeation. This may also indicate acetic acid complexation with the pyridine group on membrane. Although the adsorption of acetic acid swelled the membrane, it did not increase pore size. The adsorbed acetic acid was assumed to occupy a certain space, causing decrease in pore volume. This is supported by decrease of total permeation. As effective pore size decreases, the reduction of diffusivity is much greater for a larger molecule (acetic acid)

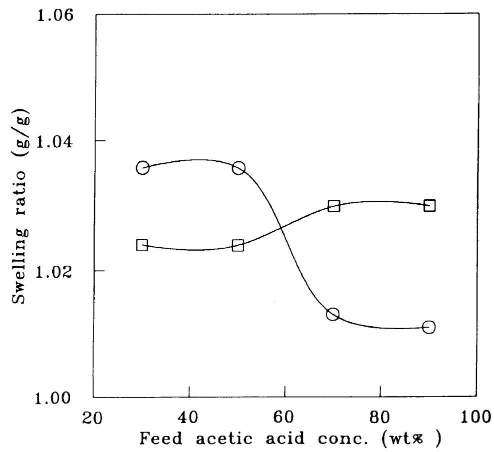

Figure 2. Degrees of swelling at various feed acetic acid concentrations for TPX (○) and TPX/P4-VP (□) membranes.

Table I. Effects of feed acetic acid concentration on pervaporation[a]

Feed acetic acid concentration	TPX[b]		TPX/P4-VP[b]	
wt%	α	Q / $\mathrm{g\,m^{-2}\,h^{-1}}$	α	Q / $\mathrm{g\,m^{-2}\,h^{-1}}$
90	60	40	807	68
70	24	58	169	74
50	8	86	26	84
30	7	87	11	85

[a] Operation temperature, 25°C. [b] 5 wt% TPX membrane; solvent evaporation temperature, 50°C. 2.5 wt% TPX/P4-VP membrane; solvent evaporation temperature, 50°C.

than a smallar molecule (water). Therefore, the selectivity of water over acetic increases with acetic acid concentration.

As shown in Table I, a separation factor of 807 and 68 $\mathrm{g\,m^{-2}\,h^{-1}}$ permeation through the TPX/P4-VP membrane for dehydration of 90 wt% aqueous acetic acid solution were obtained. Compared to the pervaporation of pure TPX membrane, which has a separation of 60 and permeation of 40 $\mathrm{g\,m^{-2}\,h^{-1}}$ for 90 wt% aqueous acetic acid solution, the TPX/P4-VP membrane has a significantly larger separation factor and permeation, pos-

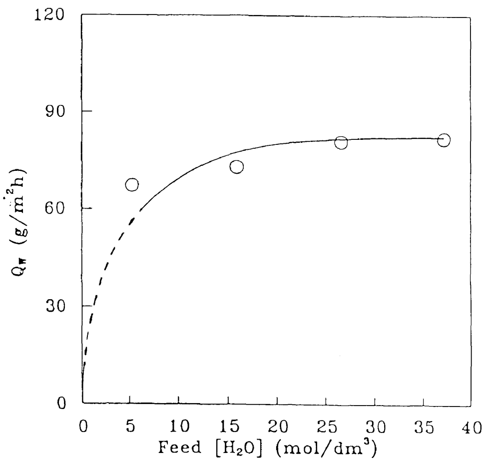

Figure 3. Effects of feed water concentration on flux in acetic acid–water pervaporation through the TPX/P4-VP membrane (average thickness of the TPX/P4-VP membranes was 22 μm).

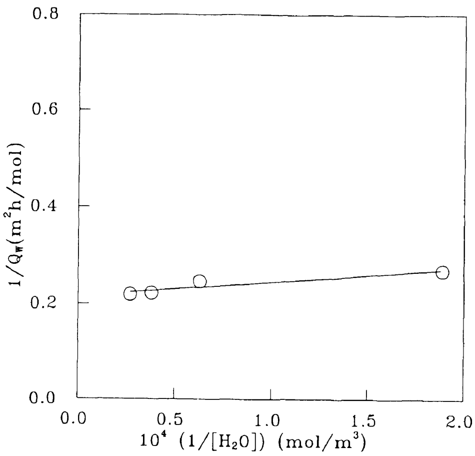

Figure 4. Relationship between reciprocal of water flux and reciprocal of feed water concentration through the TPX/P4-VP membrane.

sibly since the hydrophilic component (P4-VP) in the TPX/P4-VP membrane increases the hydrogen-bonding interaction and formation of an *in-situ* complex between the pyridine moiety and acetic acid molecules.

Lee and Yoshikawa *et al.* reported,[6,12] that water permeation to approach an asymptotic limit as water concentration in the feed increases. Water permeation behavior exhibits a typical Michaelis–Menten-type profile. In other words, this result supports a carrier-mediated mechanism for water permeation through the membrane. The relationship between water permeation through the TPX/P4-VP membrane and water concentration is displayed in Figure 3. The Michaelis–Menten type profile is in good agreement with water permeation through the TPX/P4-VP membrane.

In this case, the diffusion coefficient of the TPX/P4-VP membrane for water and interaction coefficient of water with the complex carrier were calculated from the Lineweaver–Burk equation shown in Figure 4. From Figure 4, the diffusion coefficient of the TPX/P4-VP membrane for water $= 1.01 \times 10^{-4}/[C]_0$ $\text{mol m}^{-1}\,\text{h}^{-1}$ and interaction coefficient of water with the complex carrier $= 7.72 \times 10^{-4}$ $\text{mol}^{-1}\,\text{m}^3$ were obtained $[C]_0$ denotes the carrier concentration in the membrane.

Feed Temperature Effects

The effects of feed temperature on pervaporation for the permeation of a 90 wt% aqueous acetic acid solution through pure TPX and TPX/P4-VP membranes are shown in Figures 5 and 6. Total permeation increased and the separation factor decreased with feed temprature. The free volume theory[13] and interaction between permeant and polymer can explain the above. When the feed temperature increases, free volume becomes large and activity of permeating molecules increases. Therefore, individual molecules of permeants more easily penetrate through membranes. This results in the increase of total permeation. However, interactions between permeating molecules and polymer decrease with feed temperature, resulting in decrease of the separation factor of aqueous acetic acid solution.

It should be noted that the total permeation rate and separation factor of the TPX/P4-VP membrane were higher than those of the pure TPX membrane, possibly since the complex carrier enchances interactions between the permeant and membrane. According to

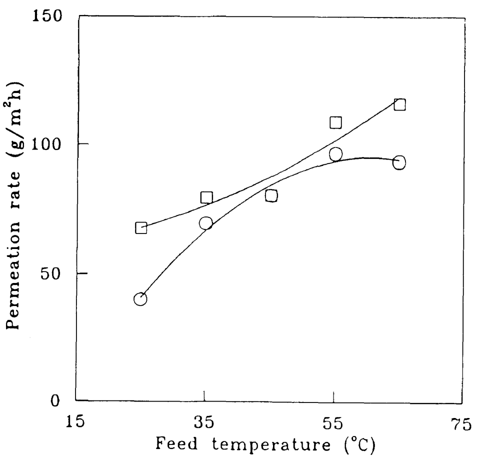

Figure 5. Effects of feed temperature on permeation for the separation of a 90 wt% acetic acid–water mixture solution. (○) TPX membrane; (□) TPX/P4-VP membrane.

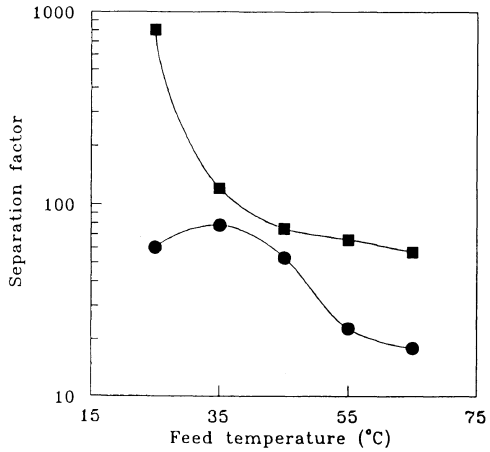

Figure 6. Effects of feed temperature on the separation factor for separation 90 wt% acetic acid–water mixture solution. (●) TPX membrane; (■) TPX/P4-VP membrane.

catalytic transport mechanism,[6] a functional group, *i.e.*, 4-vinylpyridine, in the membrane forms a complex with a permeant, *i.e.*, acetic acid, as a newly-formed complex carrier. This newly-formed complex carrier plays a transport role owing to strong interaction with water. Total permeation and the separation factor of the TPX/P4-VP membrane containing a pyridine thus increase.

CONCLUSIONS

Dehydration of acetic acid/water mixtures by pervaporation through the TPX/P4-VP membrane effectively improve pervaporation. A separation factor of 807 and permeation of $68\,g\,m^{-2}\,h^{-1}$ can be obtained for a 90 wt% feed acetic acid solution through the TPX/P4-VP membrane. A good relationship was obtained between feed water concentration and water permeation by applying the Michaelis–Menten equation.

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