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Dehydration of Acetic Acid/Water Mixture by Pervaporation through a Chemically Modified Poly(4-methyl-1-pentene) Membrane

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ABSTRACT

Dehydration of a water–acetic acid mixture by pervaporation through a modified poly(4-methyl-1-pentene) (TPX) membrane chemically grafted onto glycidyl methacrylate (TPX-*g*-PGMA) was investigated. Sulfonation was also used to improve the separation performance of the TPX-*g*-PGMA membrane. Investigations focused on the effects of feed compositions, feed temperature, degree of grafting, and downstream pressure. Compared with pure TPX membrane, the TPX-*g*-PGMA membrane and the sulfonated TPX-*g*-PGMA membrane (TPX-*g*-PGMAS) effectively improved pervaporation performances. Optimum pervaporation results were obtained using a TPX-*g*-PGMAS membrane with 13.7% degrees of grafting, giving a separation factor of 73 and a permeation rate of 125 g/m^2·h for an 84 wt% aqueous acetic acid solution.

Key Words. Pervaporation; Sulfonation; Chemical grafting; Glycidyl methacrylate; Poly(4-methyl-1-pentene)

INTRODUCTION

Acetic acid is an important commodity product of the chemical industry. End-product production is almost always accompanied by waste and/or recycling streams containing acetic acid/water mixtures. Therefore, the

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separation of acetic acid solutions is of interest to the chemical industry. Straight distillation consumes too much energy. Due to the closeness of water and acetic acid boiling points, large numbers of trays and a high reflux ratio are necessary to obtain glacial acetic acid. From an energy-saving standpoint, pervaporation can be a useful alternative for acetic acid/water separation.

Many experimental attempts have been made to prepare high-performance pervaporation membranes for separating acetic acid solutions (1–8). For example, Nguyen et al. (1) investigated using blends of hydrophilic polymer to separate acetic acid solutions. Poly(4-methyl-1-pentene) (TPX) is a highly chemical-resistant and mechanically strong polymer. This makes the polymer suitable for use as a membrane material for the dehydration of acetic acid, where chemical resistance of the membrane material is a necessary requirement. Lai et al. reported using a modified TPX membrane for gas separation and pervaporation separation (9–14).

In this article we report an attempt to separate water from acetic acid/water mixtures using chemically modified TPX membranes to increase ester groups or ionic sites and to enhance the affinity for water molecules through pervaporation techniques. The effects of feed temperature, feed composition, and degree of grafting on the pervaporation performances of prepared membranes were investigated. Comparisons between unsulfonated modified TPX membranes and sulfonated modified TPX membranes in pervaporation separations were also made.

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EXPERIMENTAL

Materials

Poly(4-methyl-1-pentene) (TPX, MX-002), supplied by the Mitsui Co., and cyclohexene, supplied by the Merck Co., were used as grafting and casting solvents, respectively. Glycidyl methacrylate (GMA) and benzoyl peroxide (BPO) were purified before used. Methanol was used as the precipitation agent, and water was deionized and distilled. All other reagent-grade chemicals were used directly without further purification.

Synthesis of TPX-*g*-PGMAS

Glycidyl methacrylate (2–10 vol%, GMA/cyclohexene), BPO, and 5 wt% TPX in cyclohexene solution were added to an ampule using a mechanical stirrer, then degassed through three freeze–pump–thaw cycles and sealed off under high vacuum ($<10^{-4}$ torr). The sealed tube was then placed in a constant temperature bath at 85°C for 3 hours and agitated. The degree and efficiency of grafting GMA onto TPX following the extraction of homopolymers for 72 hours using a Soxhlet with methanol were calculated according to:

$$\text{Degree of grafting (\%)} = (A - B)/B \times 100$$

$$\text{Grafting efficiency (\%)} = (A - B)/(C - B) \times 100$$

where A = weight of grafted TPX (after extraction with methanol)
B = weight of TPX before grafting
C = weight of the crude grafted TPX

Membrane Preparation

Membranes of pure TPX and TPX-*g*-PGMA were prepared from a grafted copolymer casting solution in cyclohexene solvent. The clear solution obtained was cast on a glass plate using a Gardner knife. The liquid film was then evaporated to dryness in a well-ventilated oven at 90°C for 40 minutes. The glass plate with the membrane was then immersed in water at 4°C for 2 hours. The membrane was 15–25 μm thick.

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Sulfonation

The TPX-*g*-PGMA membrane was dipped into Na_2SO_3 (10% by weight) and $NaHSO_3$ (7% by weight) mixed solutions with a pH value of 6.5–6.7 (15, 16). Sulfonation was carried out at 70°C for 2 hours. The sulfonated membrane was washed with distilled water.

Characterization

The FT-IR spectra of the pure TPX membrane and the modified TPX membrane, ranging from 4000 to 500 cm^{-1}, were obtained using a Jasco FTIR-7000 spectrometer. The TPX-*g*-PGMA FT-IR spectrum showed a new absorption peak ν_{max} at 1730 cm^{-1} due to C=O stretching in the GMA. The TPX-*g*-PGMAS FT-IR spectrum showed a new absorption peak ν_{max} at 1081 cm^{-1} (SO_3^- Na^+ salt). Thermal analysis was conducted using a Perkin-Elmer Thermal Gravimetrical Analyzer, Model TGS-II. The structures of the prepared membranes were examined using a Hitachi Model S570 scanning electron microscope (SEM). The samples were coated with a 150 Å thick layer of gold.

Degree of Swelling

Modified TPX membranes were dipped into test tubes filled with various concentrations of aqueous acetic acid solution. Their degrees of swelling were assessed according to

$$\text{Degree of swelling (g/g)} = \frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}}$$

Apparatus and Pervaporation Measurements

Conventional pervaporation processes were used. Membrane areas of about 10.2 cm^2 were in contact with the liquid. Most of the experiments were conducted at 25°C. However, the effects of temperature were also studied in the 25–55°C range. The permeation rate was determined by measuring the weight of the permeate. The downstream pressure was maintained at 4 to 8 torr. The compositions of the feed solution and permeates were measured by gas chromatography (G. C., China chromatography 8700T). The separation factor (α) and permeation rate (J) are defined as follows.

$$\alpha_{H_2O/AA} = (Y_{H_2O}/Y_{AA})/(X_{H_2O}/X_{AA})$$

$$J = Q/At$$

where Y_{H_2O}, Y_{AA} and X_{H_2O}, X_{AA} are the weight fractions of water and acetic acid in the permeate and feed, respectively. Q, A, and, t represent the permeate weight (g), effective membrane area (m^2), and operating time (hours), respectively.

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RESULTS AND DISCUSSION

Effect of Monomer Concentration on the Chemical Grafting Process

To produce a high permeation rate, a hydrophilic monomer of glycidyl methyacrylate (GMA) was grafted onto a pure TPX membrane. An ampule containing glycidyl methacrylate, BPO, and TPX polymer solution was sealed under vacuum. The ampule was then placed in a constant-temperature bath at 85°C for 3 hours and agitated. Figure 1 shows that the degree of grafting increased with increasing monomer concentration. However, the grafting efficiency decreased gradually as the monomer concentration was increased, perhaps because an increase in GMA concentration results in an increase in the creation of free radicals and concomitant increases in the degree of grafting. In addition, the grafting efficiency decreased gradually, indicating that homopolymerization became predominant at higher monomer concentrations. In the FT-IR spectrum, the TPX-*g*-PGMA membrane showed a sharp peak at 1730 cm^{-1} due to C=O stretch-

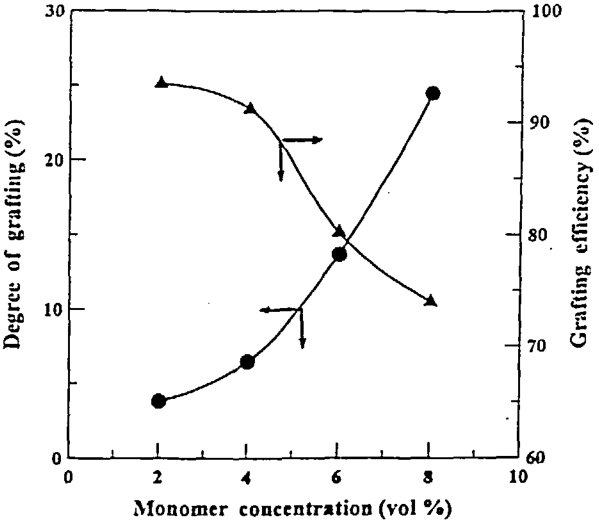

FIG. 1 Effect of monomer concentration on the degree of grafting and grafting efficiency: (●) degree of grafting, (▲) grafting efficiency.

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ing in the GMA, and the TPX-*g*-PGMAS membrane showed a new absorption peak at 1081 cm^{-1} (SO_3^- Na^+ salt). This indicates that the GMA monomer was successfully grafted onto the TPX backbone.

Thermal Characterization

The TG curves for thermal degradation of the pure TPX membrane and the TPX-*g*-PGMA membrane heated at 20°C/min in a nitrogen atmosphere are shown in Fig. 2, where it can be seen that thermal degradation of such polymers occurred in one stage in a nitrogen atmosphere. The maximum derivative temperature (T_{max}) of the TPX-*g*-PGMA membrane was higher than that of the pure TPX membrane. That is, the heat stability of the TPX-*g*-PGMA membrane was higher than that of the unmodified TPX membrane because the entanglement between the side chain (PGMA) and the TPX backbone resulted in an increase in thermal stability. Phase separations also occurred in the TPX-*g*-PGMA membrane when the degree of grafting was higher than 24.5%, resulting in a decrease in thermal degradation temperature. These phenomena might be due to a decrease in the

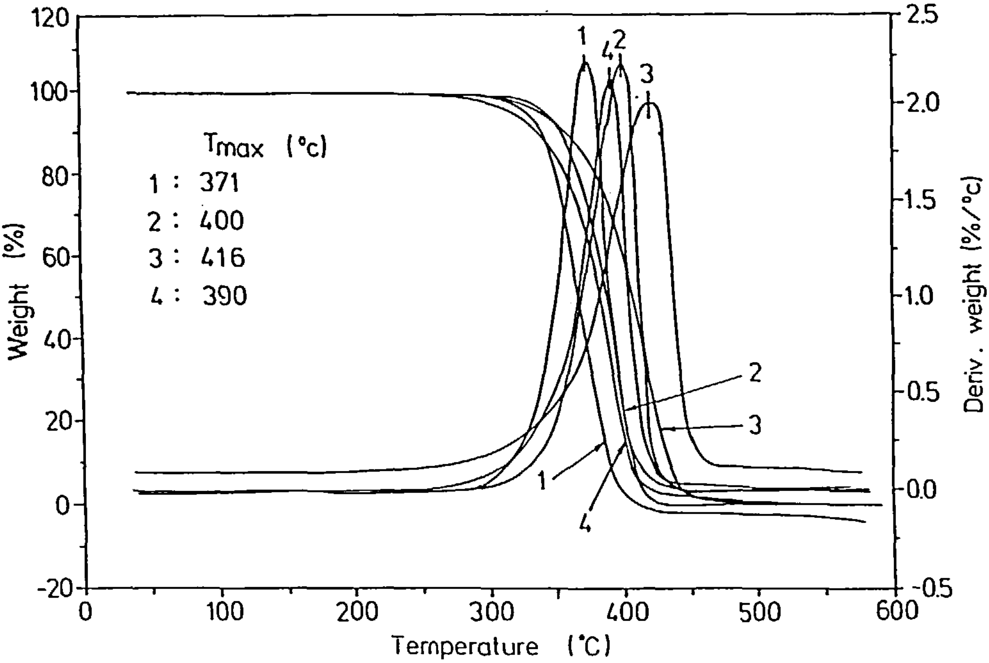

FIG. 2 TG curves for pure TPX and TPX-*g*-PGMA membrane: (1) pure TPX; (2)–(4) 3.8, 13.7, and 24.5 degrees of grafting of TPX-*g*-PGMA membrane, respectively.

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ability of poly(glycidyl methacrylate) to be incorporated into the TPX polymer matrix. SEM micrographs clearly confirm these results, as shown in Fig. 3.

Effect of the Degree of Grafting on Pervaporation Performance

Results of an investigation of the effect of the degree of membrane-grafting on pervaporation performance is presented in the pervaporation testing of the TPX-*g*-PGMAS membrane in an 84 wt% aqueous acetic acid solution (Table 1). This shows that the permeation rate increased and the separation factor reached a maximum and then decreased as the degree of grafting increased. This may be due to the fact that glycidyl methacrylate hydrophilic monomer was induced in the TPX polymer matrix, resulting in an increase in the hydrophilicity of the TPX-*g*-PGMAS membrane. Thus, the permeation rate increased as the degree of grafting increased.

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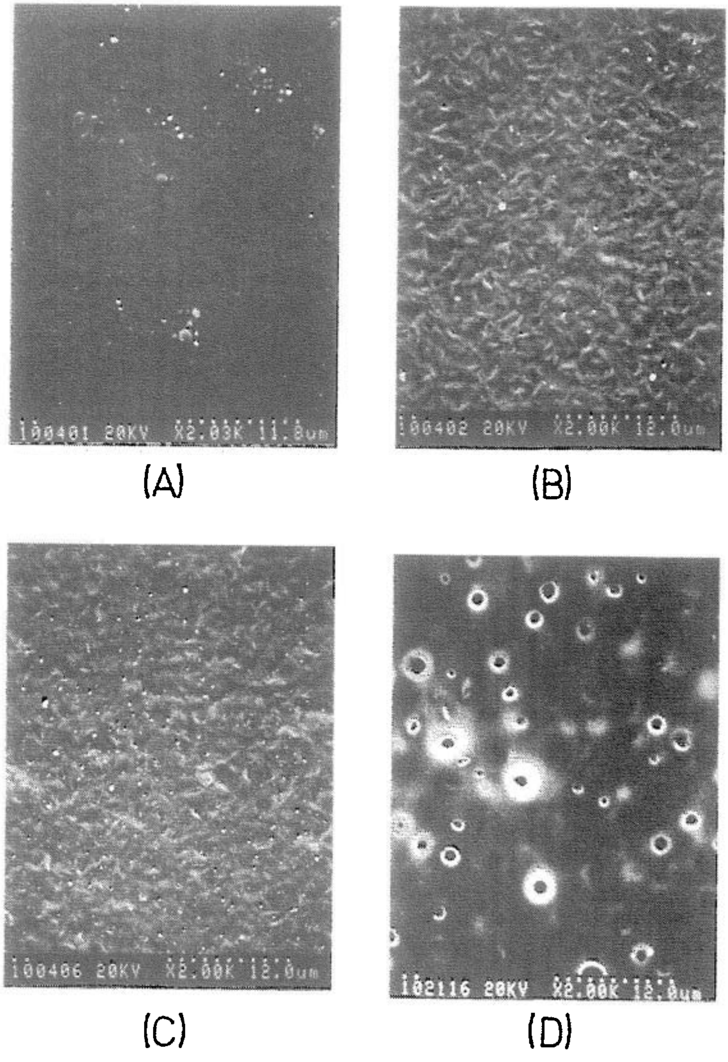

(A) (B)

(C) (D)

FIG. 3 SEM photograph surface views of TPX and TPX-*g*-PGMA membranes. (1) pure TPX; (2)–(4) 3.8, 13.7, and 24.5 degrees of grafting TPX-*g*-PGMA membrane, respectively.

TABLE 1
Effect of Degree of Grafting on Pervaporation Performances[a]

Degree of grafting (%)	Permeation rate ($g/m^2 \cdot h$)	Separation factor	PSI value
0	57.1	43	2451
3.8	69.3	56	3881
13.7	125	73	7125
24.5	200	19	3800

[a] 84 wt% acetic acid aqueous solution. Operating temperature 25°C. PSI = permeation rate product separation factor.

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Meanwhile, the hydrogen-bonding interaction between the TPX-*g*-PGMAS membrane and the water molecules in the feed solution became stronger, resulting in a higher water permselectively than that of the unmodified TPX membrane. The separation factor increased with the degree of grafting up to 13.7% and then decreased, perhaps because the compatibility of the polymer solution decreased when the degree of grafting exceeded 13.7%. This was verified by scanning electron microscopy (SEM), as shown in Fig. 3. The optimum pervaporation results were obtained using a TPX-*g*-PGMAS membrane with a 13.7% degree of grafting giving a separation factor of 73, a permeation rate of 125 $g/m^2 \cdot h$, and a PSI value of 7125. Compared with the pervaporation performances of the literature results listed in Table 2, the chemically modified membrane (TPX-*g*-PGMAS) showed a significant improvement.

TABLE 2
Performances of Polymer Membranes for the Dehydration of Acetic Acid by Pervaporation[a]

Membrane	Feed (wt%)	Separation factor	Permeation rate ($g/m^2 \cdot h$)	Reference
TPX-*g*-PGMAS	84	125	73	This work
PVA/PAA	90	17.5	300	1
Nylon 6/PAA	75.5	69.5	43	4
TPX/P4-VP	90	807	68	13
PVA	84	210	80	17
Nafion 324	80	4	1700	18
PAA-*co*-PAN	80	180	2.5	19

[a] PAA = poly(acrylic acid), P4-VP = poly(4-vinylpyridine), PVA = poly(vinyl alcohol), PAN = polyacrylonitrile, Nafion = polytetrafluoroethylene-SO_3^-.

Effect of Downstream Pressure on the Pervaporation Performance

Figure 4 shows the effect of downstream pressure on the pervaporation performances of pure TPX and modified TPX membranes with a 13.7% degree of grafting on an 84 wt% aqueous acetic acid solution. The permeation rates were more independent of downstream pressure at pressures lower than 10 mmHg. However, the permeation rate decreased sharply at pressures above 20 mmHg. Since downstream pressures above 20 mmHg are comparable with the vapor pressure at 25°C with 20 mmHg and 23.7 mmHg for acetic acid and water, respectively, the evaporation of the permeates from the downstream membrane surface should be suppressed at downstream pressures higher than 20 mmHg. This suggests that a reasonable downstream pressure should be lower than 20 mmHg.

Effect of the Feed Concentration on Pervaporation Performance

Figure 5 shows the effect of the feed composition on the separation factor and the permeation rate of unmodified TPX membrane, TPX-*g*-

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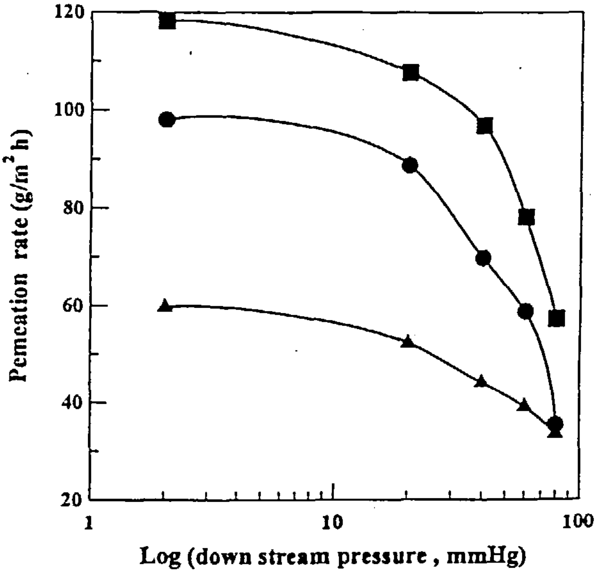

FIG. 4 Effect of downstream pressure on permeation rate: (▲) pure TPX membrane, (●) TPX-*g*-PGMA membrane, (■) TPX-*g*-PGMAS membrane.

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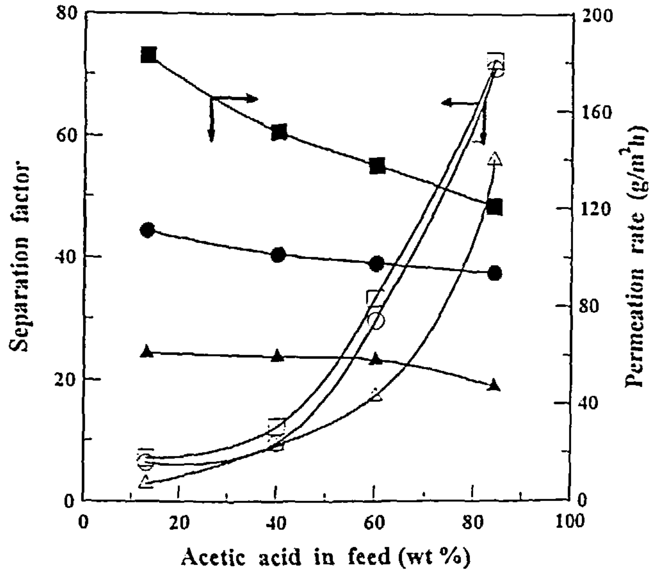

FIG. 5 Effect of feed composition on pervaporation performance: (△, ▲) pure TPX membrane, (○, ●) TPX-*g*-PGMA membrane, (□, ■) TPX-*g*-PGMAS membrane.

PGMA membrane, and TPX-*g*-PGMAS membrane. For all of the above membranes, permeation rates decreased as the acetic acid feed concentrations were increased, but their separation factors increased. The degrees of swelling decreased as the acetic acid feed concentrations increased for these membranes, as shown in Fig. 6. These results correspond well with the results of the pervaporation performance study of the modified TPX and unmodified TPX membranes, as indicated in Fig. 5. The pervaporation performances of the TPX-*g*-PGMA and TPX-*g*-PGMAS membranes were higher than that of the unmodified TPX membrane, perhaps because the polymer (PGMA or PGMAS) grafted onto the TPX backbone increased the hydrogen-bonding potentials between the feed solutions and the modified TPX membranes. Thus, the permeation rates and separation factors obtained for both modified TPX membranes were higher than that of the unmodified TPX membrane. Furthermore, the pervaporation performance of the TPX-*g*-PGMAS membrane was better than that of the TPX-*g*-PGMA membrane. This may be because sulfonation improved the hydro-

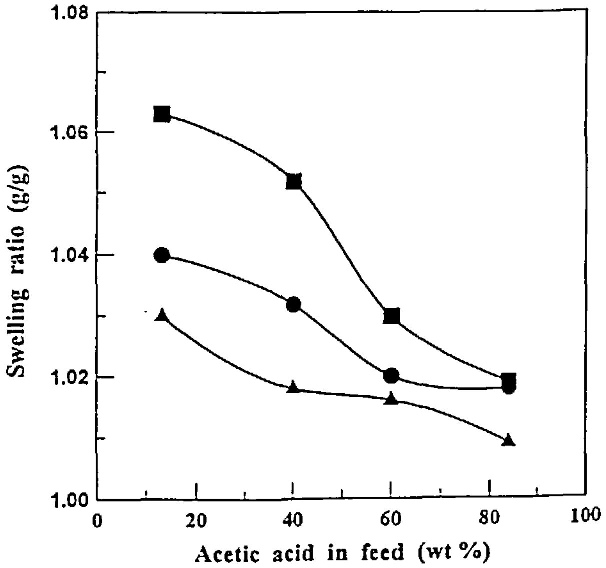

FIG. 6 Effect of feed composition on the degree of membrane swelling: (▲) pure TPX membrane, (●) TPX-*g*-PGMA membrane, (■) TPX-*g*-PGMAS membrane.

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philicity of the TPX-*g*-PGMAS membranes, and the hydrogen-bonding interaction between an ionized group (SO_3^- Na^+) and the water molecules in the feed solution was higher than for the unsulfonated membrane (TPX-*g*-PGMA).

Effect of Composition of the Adsorbed and Permeated with TPX-*g*-PGMAS Membrane

In order to investigate the effects of solubility and diffusivity on membrane permselectivity, sorption experiments were made. Figure 7 shows that the acetic acid concentration in the membrane was higher than that in the permeate of the TPX-*g*-PGMAS membrane for acetic acid feed concentration in the 13–84 wt% range. The permeate and sorption composition curves lie under the diagonal line, indicating that water molecules were selectively dissolved into the TPX-*g*-PGMAS membrane, which contained the hydrophilic ionized group (SO_3^- Na^+) and the hydroxyl group (—OH), and were also predominantly diffused through the membranes.

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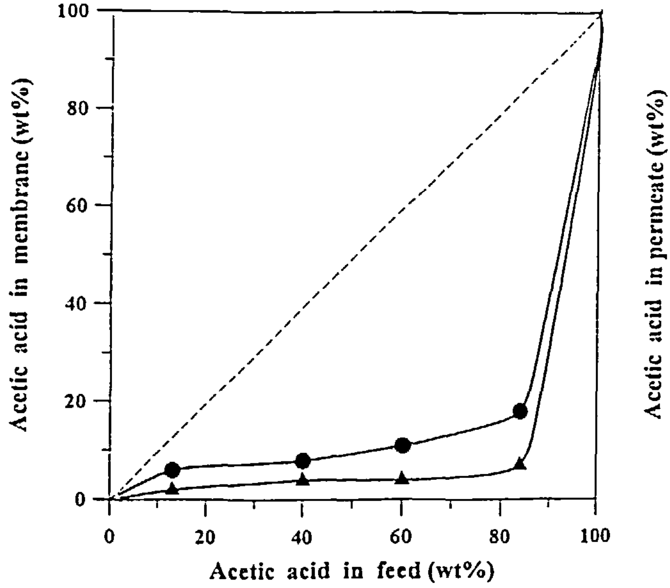

FIG. 7 Effect of feed composition on the composition of the solution adsorbed and permeated with TPX-*g*-PGMAS membrane: (▲) permeate, (●) adsorbate.

Effect of Feed Temperature on Pervaporation Performance

The activation energy required for permeation of an 84 wt% aqueous acetic acid solution through the modified TPX and unmodified TPX membranes can be obtained from the permeation rate temperature curve shown in Fig. 8. As shown, the permeation rate increased with increasing feed solution temperature. Higher feed temperatures, caused by an increase in membrane chain mobility and swelling of the membrane matrix, resulted in the higher permeation rates observed. The activation energies were calculated according to an Arrhenius plot. The activation energies of unmodified TPX, TPX-*g*-PGMA, and TPX-*g*-PGMAS membranes were 3.0, 1.8, and 1.6 kcal/mol, respectively.

The lower activation energy required by the sulfonated TPX-*g*-PGMA membrane can be explained by its having a higher hydrophilicity than the TPX-*g*-PGMA and pure TPX membranes. Figure 9 also shows that the separation factor peaks at about 35°C feed temperature for a 84 wt% aqueous acetic acid solution passing through modified TPX and unmodified

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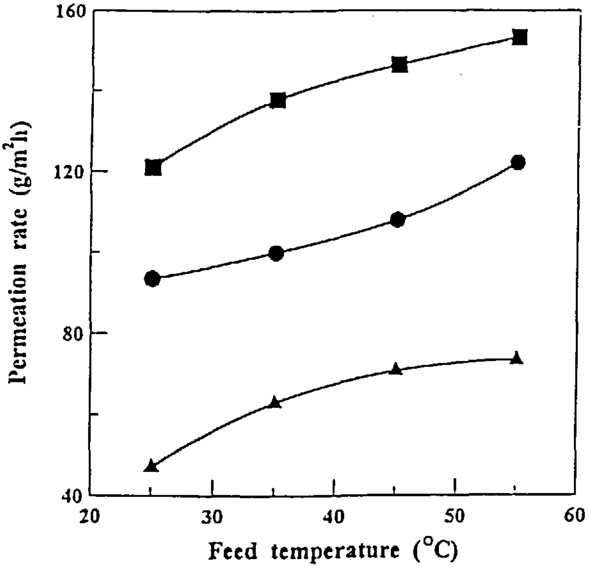

FIG. 8 Effect of feed temperature on permeation rate: (▲) pure TPX membrane, (●) TPX-*g*-PGMA membrane (■), TPX-*g*-PGMAS membrane.

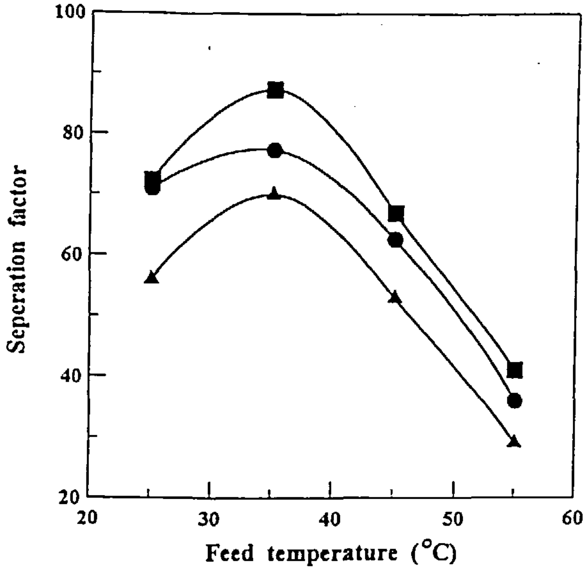

FIG. 9 Effect of feed temperature on separation factor: (▲) pure TPX membrane, (●) TPX-*g*-PGMA membrane, (■) TPX-*g*-PGMAS membrane.

TPX membranes, perhaps because the free volume in the amorphous regions increased as the feed solution temperature increased, resulting in an increase in permeating molecule activity. Thus, the separation factor increased with increasing feed temperatures up to 35°C. The decrease of the separation factor at temperatures higher than 35°C is attributed to the plasticizing effect of the permeates and the interaction between the permeates and the polymer.

CONCLUSION

TPX-*g*-PGMA and TPX-*g*-PGMAS membranes are water-selective polymers that dehydrate aqueous acetic acid solutions. We found the pervaporation performances of modified TPX membranes (TPX-*g*-PGMA and TPX-*g*-PGMAS) were higher than that of an unmodified TPX membrane. TPX-*g*-PGMA membranes with 13.7% degrees of grafting gave the best separation factor and permeation rate results, e.g., 73 and 125 g/m^2·h, respectively. The heat stability of TPX-*g*-PGMA membrane was higher than that of unmodified TPX membrane.

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