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Application of Pervaporation and Vapor Permeation Processes to Separate Aqueous Ethanol Solution through Chemically Modified Nylon 4 Membranes

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ABSTRACT

The pervaporation performance of a nylon 4 membrane, chemically grafted by *N,N*-dimethylaminoethyl methacrylate (DMAEM), DMAEM-*g*-N4, was studied by measurement of the permeation ratio and the pervaporation separation index. It was found that the water permselectivity and permeation rate for the chemically modified Nylon 4 membrane were higher than those of the unmodified Nylon 4 membrane. Optimum pervaporation results, a separation factor of 28.3, and a permeation rate of 439 $g/m^2{\cdot}h$, were obtained when the degree of grafting was 12.7%. It was also found that all the permeation ratios at low temperature were less than unity. In addition, compared with pervaporation, vapor permeation effectively increases the permselectivity of water.

Key Words. Pervaporation; Vapor permeation; PSI value; Nylon 4; Membrane

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INTRODUCTION

The pervaporation technique is one of the potential methods to effectively separate azeotropic mixtures, heat-sensitive compounds, and isomers. Increasing the hydrophilicity of a membrane by incorporating hydrophilic moieties into the membrane matrix is an effective method to fabricate membranes with better pervaporation performance. Yoshikawa et al. reported that water can selectively permeate through synthetic polymer membranes having imide groups (1), *N*-substituted imide groups (2), carboxylic acid moieties (3), and ester groups (4), from aqueous alcohol or acetic acid solutions because of the hydrogen-bonding interaction. The high permselectivity of water through these membranes is possibly because the high hydrophilicity of the pendant groups increases the affinity of the membranes for water. However, because organic feed mixtures are directly in contact with polymer membranes in the pervaporation process, the physical and chemical properties of the membranes are often influenced by the feed mixtures through the effects of swelling or shrinking. Vapor permeation, a membrane separation technique, was proposed by Uragami et al. and Okamoto et al. (5–7) to improve the disadvantages of pervaporation. In this vapor permeation technique, the feed solution is vaporized first and then permeated through the membrane. Thus, the swelling or shrinking of polymer membranes due to the feed solutions can be prevented. In this paper, pervaporation and vapor permeation separation of water from water/ethanol solution was performed by using chemically modified nylon 4 membranes of which the hydrophilic ester group is introduced to enhance the affinity for water molecules. The effects of the degree of grafting and feed temperature on pervaporation performance of the prepared membranes were investigated.

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EXPERIMENTAL

Materials

The nylon 4 synthesis procedure was carried out as described in Ref. 8. The molecular weight of the samples, measured by a Cannon Fenske viscometer with *m*-cresol as the solvent at 25°C, was 25,000–30,000. *N*,*N*-Dimethylaminoethyl methacrylate (DMAEM) and 2,2-azobis (2-methylpyropionitrile) (AIBN) were purified before being used. Water was deionized and distilled.

Grafting Procedure

An ampule containing DMAEM (2–12 vol%), AIBN, and nylon 4 polymer solution (10 g/100 mL formic acid) was degassed by three freeze–pump–thaw cycles and sealed off under a high vacuum (10^{-4} torr). The sealed tube was then placed in a constant temperature bath at 80°C for 3 hours while agitating. The reaction mixture was poured into a large amount of methanol, allowed to stand at room temperature, and then dried at 80°C in vacuum. After extraction of the homopolymer for 72 hours using a Soxhlet with water, the degree and efficiency of grafting DMAEM onto nylon 4 were calculated according to the following equations:

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

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

where A is the weight of grafted nylon 4 (after extraction), B is the weight of nylon 4 before grafting, and C is the weight of the crude grafted nylon 4.

Membrane Preparation

The membrane of DMAEM-*g*-N4 was prepared from a casting solution by dissolving the grafted copolymer in formic acid. The detailed procedure can be found in a previous article (8). The measured membrane thickness was in the 15–25 μm range.

Pervaporation and Vapor Permeation Measurement

A traditional pervaporation process (9) was used. In pervaporation, the feed solution is in direct contact with the membrane. The effective area was 10.2 cm^2. The permeation rate was determined by measuring the weight of permeate. The compositions of the feed solution and the permeate were measured by gas chromatography (G.C. China Chromatography 8700 T). The vapor permeation experiment was carried out by using the same apparatus as for pervaporation, except that the feed solution was not in contact with the membrane. The feed solution was first vaporized and then permeated through the membrane. It should be noted that to prevent the feed liquid from being in contact with the membrane, we turned the permeation cell upside down as shown in Scheme 1(b) and carefully adjusted the flow rate of the feed. In addition, to verify that the liquid feed was not in contact with the membrane, we attached a filter paper to the membrane surface facing the feed solution. After the vapor permeation experiment, we found that the filter paper remained dry, confirming that the liquid feed was not in direct contact with the membrane. The separation factor was determined by

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where X_A, X_B and Y_A, Y_B are the weight fractions of A and B in the feed and

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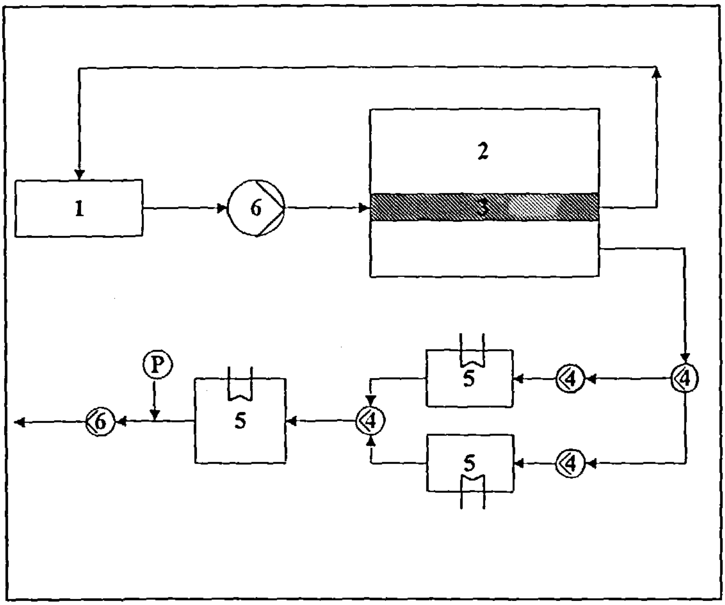

1: Feed.
2: Permeation cell.
3: Membrane.
4: Teflon cock.
5: Cooled trap.
6: Circulation pump.
7: Vacuum gauge.

(a) Pervaporation (b) Vapor permeation

SCHEME 1

the permeate (A being the more permeative species), respectively. In vapor permeation, X_A and X_B are the weight fractions of water and alcohol vapors in the feed, and Y_A and Y_B are the weight fractions of water and alcohol in the permeate.

THEORY

For a binary mixture, the total permeation ratio (θ_t), a measure of the deviation of the actual total permeation rate (Q_t) from the ideal total permeation rate (Q_t°), describes the interaction between polymer and permeates (10):

$$\theta_t = Q_t/Q_t^\circ$$

The ideal permeation rate is the permeation rate in the ideal situation where the permeation of each component is independent of the existence of other components in the feed mixture. For an ideal binary mixture, the permeation rate can be expressed in terms of the permeation rates of pure components as follows:

$$Q_t^\circ = X_1Q_1^\circ + X_2Q_2^\circ$$

where X_1 and X_2 are the weight fractions of water and ethanol, respectively, in the feed mixture, and Q_1° and Q_2° are the permeation rates of pure water and ethanol, respectively.

RESULTS AND DISCUSSION

Effect of Monomer Concentration on the Process of Chemical Grafting

Table 1 shows the effect of monomer concentration on the grafting process. It can be seen that the degree of grafting increases with increasing monomer

TABLE 1
Effect of Monomer Concentration on Degree of Grafting and Grafting Efficiency[a]

Monomer concentration (vol%)	Degree of grafting (%)	Grafting efficiency (%)
2	5.0	26.5
4	7.6	25.4
6	12.7	25.3
8	18.5	24.5
10	17.0	24.0
12	14.8	23.4

[a] Grafting time: 3 hours. Polymer concentration: 10 g nylon 4/100 mL formic acid.

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concentration up to 8 vol% whereas, beyond this concentration, the degree of grafting decreases. These results might be due to the fact that homopolymerization is more favored at high monomer concentration than grafting polymerization, evidenced by the observation that the grafting efficiency decreases with increasing monomer concentration as shown in Table 1. Similar results were observed by Nishioka et al. (11).

Effect of the Degree of Grafting on Pervaporation Performance

The effect of the degree of grafting on the permeation rate and the separation factor for pervaporation of 90 wt% aqueous ethanol solution through chemically modified nylon 4 membrane is shown in Table 2. The permeation rate increases as the degree of grafting increases for the DMAEM-*g*-N4 membrane. These results can be explained from the viewpoint of the hydrophilicity of the chemically modified nylon 4 membrane. Hydrophilicity of the DMAEM-*g*-N4 membrane increases with an increasing degree of grafting, evidenced by data from experiments of the water contact angle. A larger contact angle indicates less hydrophilicity, suggesting that less DMAEM is grafted. Table 2 also shows that the contact angle of the ungrafted nylon 4 membrane is 78°, higher than that of the chemically modified nylon 4 membrane. This result confirms that the hydrophilicity increases as more DMAEM monomers are grafted onto the nylon 4 backbone. The hydrogen-bonding interaction between modified nylon 4 membrane and water molecules in the feed solution is stronger than that between the unmodified membrane and water, resulting in higher permselectivity of water for the modified nylon 4 membrane. The product of the total permeation rate and the separation factor is defined as the pervaporation separation index (PSI), a measure of the sepa-

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TABLE 2
Effect of Degree of Grafting on Pervaporation Performances of Chemically Modified Nylon 4 Membranes[a]

Degree of grafting (%)	Separation factor (α)	Permeation rate ($g/m^2 \cdot h$)	Contact angle (degrees)
0	4	350	78
5.0	13.7	385	73
7.6	18.2	417	70
12.7	28.3	439	66
18.5	17.5	688	58

[a] 90 wt% aqueous ethanol solution. Operation temperature: 25°C. Operation pressure: 2 mmHg. Membrane thickness: 25 μm.

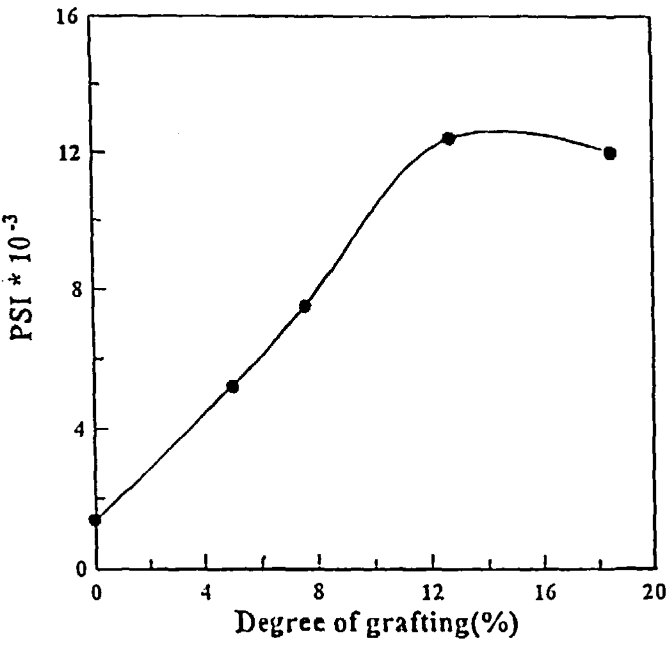

FIG. 1 Effect of degree of grafting on the PSI value for the 90 wt% feed aqueous ethanol solution permeating through the DMAEM-*g*-N4 membrane.

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ration ability of the membrane. Figure 1 shows the effect of the degree of grafting on the pervaporation separation index for 90 wt% aqueous ethanol solution through the DMAEM-*g*-N4 membrane. The optimum pervaporation performance was obtained by the DMAEM-*g*-N4 membrane with a 12.7% degree of grafting: a separation factor of 28.3, a permeation rate of 439 g/m^2·h, and 1.2 × 10^4 PSI. Furthermore, compared with the pervaporation performances of various modified nylon 4 membranes listed in Table 3 (12–15), the chemically grafted membrane (DMAEM-*g*-N4) showed a significant improvement.

Vapor Permeation

The performances of aqueous ethanol solutions through the DMAEM-*g*-N4 membrane with a 12.7% degree of grafting by pervaporation and vapor permeation are shown in Table 4. Water molecules are predominately permeated through the grafted membranes in both methods. It is also shown in Table 4 that the permeation rate increases with a decrease of the ethanol

TABLE 3
Pervaporation Performances of Nylon 4 Membranes Modified by Different Methods

Membrane	Separation factor (α)	Permeation rate (g/m²·h)	Pervaporation separation index (PSI)	Ref.
Unmodified Nylon 4	4.0	350	1,400	This work
DMAEMA-*g*-N4	28.3	439	12,000	This work
PHEMA-*g*-N4[a]	97.6	194	18,900	12
PVA-*p*-N4[b]	13.5	420	5,600	13
PVA-homo-*g*-N4[c]	7.3	691	5,000	14
PVA-hetero-*g*-N4[d]	13.9	358	4,900	15

[a] Chemical grafting with a 104.3% degree of grafting.
[b] Plasma deposition, 10 W/20 min.
[c] ^{60}Co γ-ray irradiation homografting with a 42.2% degree of grafting.
[d] ^{60}Co γ-ray irradiation heterografting with a 21.2% degree of grafting.

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concentration in the feed solution. In addition, the permeation rate of vapor permeation is much lower than that of pervaporation. This phenomenon might be due to the fact that the membrane is in direct contact with the feed solution and swollen for the pervaporation process but is not in contact with the liquid feed for the vapor permeation process. Thus, the diffusivity of the permeating species in vapor permeation is lower than that in pervaporation because the swelling effect caused by the liquid feed is less obvious in vapor permeation. In addition, the separation factors of DMAEM-*g*-N4 membranes in vapor

TABLE 4
Comparison of the Permeation Rate and Separation Factor of the DMAEM-*g*-N4 Membrane Between Pervaporation and Vapor Permeation[a]

Ethanol concentration (wt%)	Pervaporation		Vapor permeation	
	Permeation rate (g/m²·h)	Separation factor (α)	Permeation rate (g/m²·h)	Separation factor (α)
90 (90.8)[b]	439	28.3 (31)[c]	85	193.1 (211.7)[c]
70 (77.3)	624	17.0 (24.8)	92	114.2 (166.6)
50 (67.7)	663	6.3 (13.2)	92	48.3 (101.2)
30 (60.4)	718	3.3 (11.7)	113	24.5 (87.1)
10 (43.9)	767	2.4 (16.9)	127	18.7 (131.7)

[a] Operation temperature, 25°C.
[b] Estimation from vapor–liquid equilibrium data.
[c] Based on feed vapor.

permeation are much higher than those in pervaporation, suggesting that the vapor permeation method is effective in increasing the water permselectivity for the aqueous ethanol solution.

Effect of Temperature on Pervaporation Performance

The effects of temperature and feed composition on the total permeation rate are shown in Fig. 2. The total permeation rate increases with increasing temperature and decreasing ethanol concentration of the feed solution. According to the free volume theory (16), the random thermal motion of polymer chains in the amorphous region produces free volume. As temperature increases, the frequency and amplitude of the chain jumping increase and the resulting free volume becomes larger, and therefore permeation of the permeating molecules and the associated molecules through the DMAEM-*g*-N4 membrane becomes easier, resulting in an increase of the total permeation rate. In addition, the plasticizing effects of the permeates and the interaction between permeates and polymer can be used to explain further the above experimental observation. As the temperature increases, the interaction becomes weaker, so the plasticizing effect becomes more important. However, the strong interaction at low temperatures can reduce the plasticizing effect (16). The data from swelling experiments also support the above deduction:

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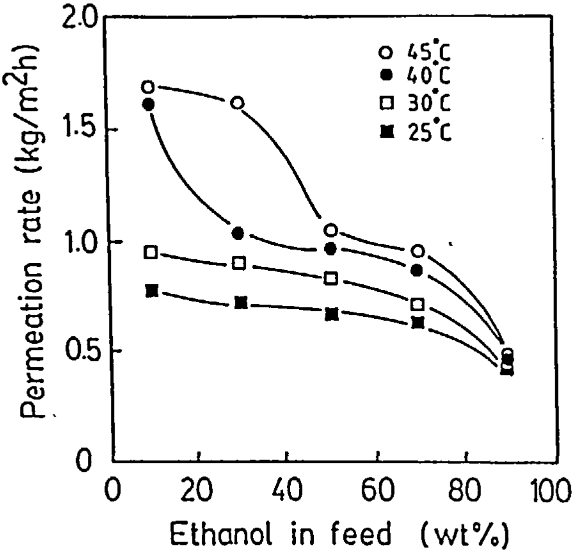

FIG. 2 Effect of temperature and feed composition on the total permeation rate.

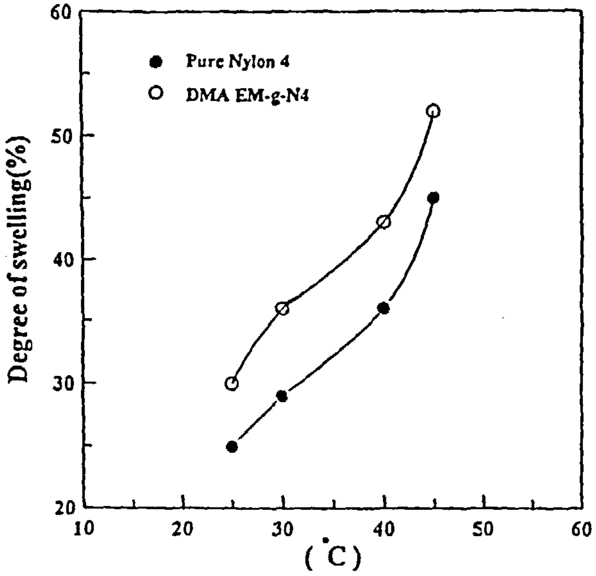

FIG. 3 Effect of temperature of the feed on the degree of swelling.

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the degree of swelling of membranes increases with increasing temperature for both modified and unmodified nylon 4 membranes, as shown in Fig. 3. Figure 3 also indicates that the degree of swelling of the DMAEM-*g*-N4 membrane with a degree of grafting of 12.7% is higher than that of the unmodified nylon 4 membrane, suggesting that the interaction between the water molecules in the feed and the pendant group of DMAEM-*g*-N4 is higher than that between water and the unmodified membrane.

Permeation Ratio (θ) and Pervaporation Separation Index (PSI)

For the pervaporation of binary mixtures, the pervaporation ratio (θ_t) is defined as the ratio of the actual permeation rate (Q) to its ideal permeation rate (Q°) by Huang et al. (10, 17). When the feed alcohol solution exhibits an ideal permeation behavior, the permeation ratio should be equal to 1. The value of the permeation ratio may be higher or lower than 1 for nonideal permeation. If the permeation ratio of a system is higher than 1, the system can be said to exhibit a "permeation enhancement effect," while a value lower than 1 indicates a "permeation depression effect." The product of the total permeation rate and the separation factor is the pervaporation separation

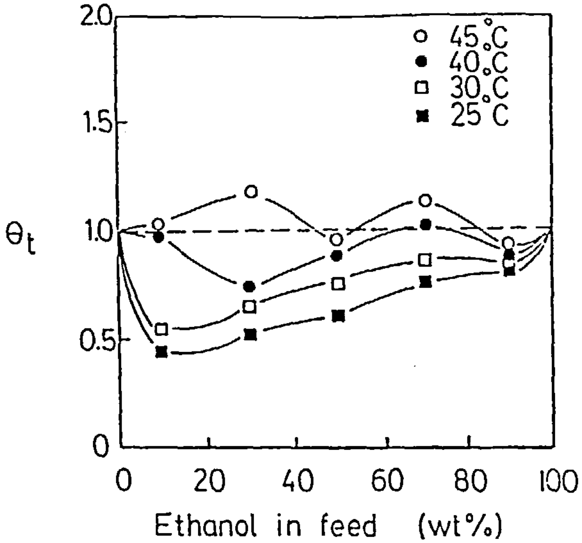

FIG. 4 Effect of feed ethanol concentration on the total permeation ratio at different temperatures.

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index (PSI), a measure of the separation ability of a membrane. Figure 4 shows the total permeation ratio versus the feed composition with varying temperature for the DMAEM-*g*-N4 membrane. All θ_t values are less than 1 at low temperatures, indicating the existence of interactions between the permeates and the DMAEM-*g*-N4 membrane. Therefore, the interaction effect dominates over the plasticizing effect on the polymer membrane, so the permeation rate is smaller than the ideal permeation rate. However, when the operation temperature is high, the plasticizing effect of the permeates becomes dominant and results in permeation enhancement. Thus, the permeation ratio θ_t approaches 1 or exceeds 1 at higher operation temperatures. Figure 5 shows the effects of temperature and feed composition on the pervaporation separation index for the DMAEM-*g*-N4 membrane. The PSI value increases with increasing ethanol concentration in the feed solution at 25 and 40°C. This is because the separation factor is higher at higher ethanol concentrations in the feed (Table 4). Furthermore, the PSI value decreases rapidly for a 90 wt% aqueous ethanol solution at 40°C. This is because the separation factor of the aqueous ethanol solution through the DMAEM-*g*-N4 membrane decreases rapidly, but the permeation rate increases slowly at 40°C feed solution. Thus, the PSI value decreases rapidly for an ethanol concentration of 90 wt%.

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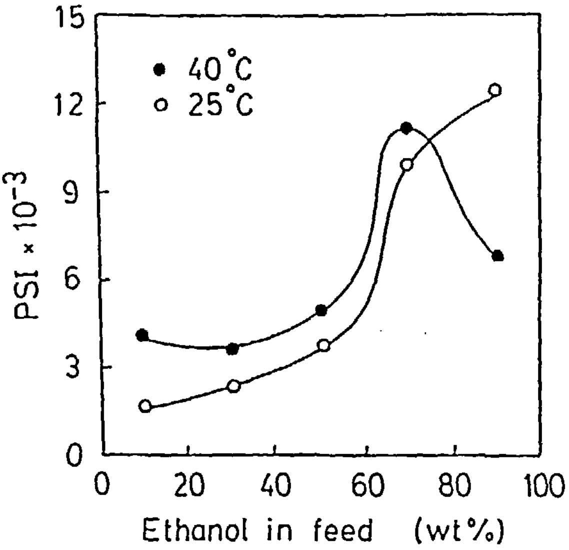

FIG. 5 Effect of temperature and feed ethanol concentration on PSI value for the DMAEM-*g*-N4 membrane with 12.7% degree of grafting.

CONCLUSION

The pervaporation performance of the modified nylon 4 (DMAEM-*g*-N4) membrane is significantly improved compared to that of the unmodified nylon 4 membrane. The optimum separation performance is obtained when the degree of grafting of the DMAEM-*g*-N4 membrane is 12.7%. The optimum results for separation factor, permeation rate, and PSI value are 28.3, 439 $g/m^2 \cdot h$, and 1.2×10^4, respectively. It was found that both the interaction between permeant and membrane and the plasticizing effect of permeant on membrane could significantly alter the permeation and separation properties of the prepared membranes. Compared with the pervaporation process, the vapor permeation process can significantly increase the separation factor, along with decreasing the permeation rate. The PSI value increases with increasing feed solution temperature. All the permeation ratios (θ_t) are less than 1 at low temperature. In addition, it was observed that the degree of swelling increases with increasing temperature of the aqueous alcohol solution.

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