

# Polyvinyl Alcohol/Polysulfone (PVA/PSF) Hollow Fiber Composite Membranes for Pervaporation Separation of Ethanol/Water Solution

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**ABSTRACT:** Polysulfone (PSF) hollow fiber membranes were spun by phase-inversion method from 29 wt % solids of 29 : 65 : 6 PSF/NMP/glycerol and 29 : 64 : 7 PSF/DMAc/glycol using 93.5 : 6.5 NMP/water and 94.5 : 5.5 DMAc/water as bore fluids, respectively, while the external coagulant was water. Polyvinyl alcohol/polysulfone (PVA/PSF) hollow fiber composite membranes were prepared after PSF hollow fiber membranes were coated using different PVA aqueous solutions, which were composed of PVA, fatty alcohol polyoxyethylene ether (AEO<sub>9</sub>), maleic acid (MAC), and water. Two coating methods (dip coating and vacuum coating) and different heat treatments were discussed. The effects of hollow fiber membrane treatment methods, membrane structures, ethanol solution temperatures, and MAC/PVA ratios on the pervaporation performance of 95 wt % ethanol/water solution were studied. Using the vacuum-coating method, the suitable MAC/PVA ratio was 0.3 for the

preparation of PVA/PSF hollow fiber composite membrane with the sponge-like membrane structure. Its pervaporation performance was as follows: separation factor ( $\alpha$ ) was 185 while permeation flux ( $J$ ) was 30g/m<sup>2</sup>·h at 50°C. Based on the experimental results, it was found that separation factor ( $\alpha$ ) of PVA/PSF composite membrane with single finger-void membrane structure was higher than that with the sponge-like membrane structure. Therefore, single finger-void membrane structure as the supported membrane was more suitable than sponge-like membrane structure for the preparation of PVA/PSF hollow fiber composite membrane. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 247–254, 2005

**Key words:** pervaporation; phase inversion; polysulfone; hollow fiber membrane; separation factor; poly(vinyl alcohol)

## INTRODUCTION

Pervaporation is an energy efficient combination of membrane permeation and evaporation. It often has the advantages for the separation of constant-boiling azeotropes because of the low temperatures and pressures in pervaporation. Pervaporation is also used for the dehydration of organic solvents and the removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for separation of heat-sensitive products. Pervaporation is used for breaking azeotropes, dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol removal, and wastewater purification.<sup>1–20</sup>

Generally, many researchers prepared flat sheet composite membranes for the dehydration of ethanol–water mixtures by the pervaporation process.<sup>1–17</sup> For example, Karakane et al.<sup>1</sup> studied the separation of polyion complexes (PIC) consisting of polyacrylic acid

and a polycation. Toutianoush et al.<sup>2,3</sup> also studied the composite membranes with an ultrathin polyelectrolyte separation layer on their use for alcohol/water separation under pervaporation conditions. If a poly(vinyl amine)/poly(vinyl sulfate) separation layer was used for ethanol/water pervaporation, a separation factor up to 700 was found, while the flux was about 0.5 kg/m<sup>2</sup>·h. Chen et al.<sup>4</sup> investigated the pervaporation separation of ethanol/water mixtures utilizing composite membranes prepared by coating a thin film of a polystyrenesulfonate (PSS) across the surface of a microporous alumina support membrane (Al<sub>2</sub>O<sub>3</sub>). Poly(vinyl alcohol)–polyacrylamide interpenetrating polymer network membranes (PVA–PAAM IPN) both unsupported and supported on polyethersulfone (PES) ultrafiltration membranes were prepared and investigated with regard to the pervaporation of water–ethanol mixtures by Ruckenstein and Liang.<sup>5</sup> Yanagishita et al.<sup>7</sup> investigated the preparation of polyimide pervaporation membranes for the separation of aqueous ethanol solutions. They concluded that the pervaporation performance of this asymmetric polyimide membrane was not only governed by the molecular structure of the membrane, but also the

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TABLE I  
Composition and Experimental Parameters of Spinning PSF Hollow Fiber Membranes

Support Membrane	A	B
Dope solution composition	PSF/NMP/glycerol 29 : 65 : 6	PSF/DMAc/glycol 29 : 64 : 7
Bore fluid composition	NMP/H <sub>2</sub> O (93.5 : 6.5)	DMAc/H <sub>2</sub> O (94.5 : 5.5)
Bore flow rate (ml/min)	0.3	0.4
Dope pressure (MPa)	0.7	0.8
External coagulant	Water	Water
Coagulant temperature (°C)	20	20

fine structure of the membrane. Besides, their membranes exhibited a separation factor  $\alpha$  (H<sub>2</sub>O/EtOH) = 900 with a flux of 1.0 kg/m<sup>2</sup>·h for an aqueous 95 wt % ethanol solution at 90°C. Kim et al.<sup>8</sup> described the preparation of polyimide composite membranes by interfacial polymerization/thermal imidization method and their dehydration performance by pervaporation.

The dip-coating method has been widely used for the fabrication of pervaporation composite membranes. Lee et al.<sup>14</sup> investigated a composite membrane of polyacrylic acid (PAA) dip-coated asymmetric polycarbonate (PC) membrane for the purpose of separating aqueous alcohol solution by the use of the pervaporation technique. Page et al.<sup>15</sup> reported the separation of organic/water mixtures by the pervaporation process using polydimethylsiloxane dip-coated polyetherimide (PEI) membranes. Zhu and Chen<sup>16</sup> prepared a composite catalytic membrane with a crosslinked PVA dense active layer coated on a porous ceramic plate support using a novel method and evaluated it with a pervaporation setup for the separation of several organic aqueous mixtures. Lang et al.<sup>17</sup> studied thin-film composite membranes by coating porous polysulfone (PSF) membranes with a PVA layer and further crosslinking its surface.

Recently, a hollow fiber composite membrane was developed for the separation of ethanol–water solutions and the VOCs recovery by the pervaporation process.<sup>18–20</sup> Wang and Jiang<sup>18</sup> prepared polyacrylonitrile (PAN) hollow fiber by a dry–wet spinning method. The separation factor of 90 wt % ethanol–water mixtures at 48°C was 60 ~ 70 while the permeation rate was 70 ~ 80g/(m<sup>2</sup>·h). Using EPDM as the selective top layer on a microporous polyetherimide hollow fiber, hollow fiber composite membranes were prepared by Borges et al.<sup>19</sup> The separation and recovery of VOCs from surfactant-concentrating aqueous solutions by a composite hollow fiber membrane-based pervaporation process was studied by Abou-Nemeh et al.<sup>20</sup> The process employed hydrophobic microporous polypropylene hollow fibers having a thin plasma polymerized silicone (PDMS) coating on the outside diameter, trichloroethylene (TCE) as the model contaminant, and sodium dodecyl sulfate (SDS) as the surfactant.

Therefore, hollow fiber composite membrane for pervaporation separation of ethanol/water solution was seldom investigated previously. In this case, PVA is one kind of strong hydrophilic material that is suitable for the separation of water and ethanol mixture by the pervaporation process. Different composite membranes consisting of two different asymmetric PSF hollow fiber substrates and a thick PVA layer were prepared to investigate the effects of substrate hollow fiber membrane structure, membrane treatment methods, MAC/PVA ratio, and ethanol solution temperature on the pervaporation performances for the separation of 95 wt % aqueous ethanol solution.

## EXPERIMENTAL

### Materials

Polysulfone in powder form was obtained from Shuguang Chemical Company (People's Republic of China) and used as a membrane material. Reagent grade *N*-methyl-2-pyrrolidone (NMP >> 98%) and *N,N*-dimethylacetamide (DMAc) used as solvents, glycerol and glycol used as a nonsolvent additives (NSA), and PVA (75,000~79,000 *M<sub>w</sub>*), maleic acid (MAC), and fatty alcohol polyoxyethylene ether (AEO<sub>9</sub>) used as a coating materials were obtained from Shanghai Chemical Agent Company (People's Republic of China).

### Preparation of asymmetric PSF hollow fiber membranes and PVA/PSF hollow fiber composite membranes

At room temperature, PSF hollow fiber membranes were spun using the dry/wet-spinning method, described elsewhere.<sup>21–25</sup> The spinneret has an outer diameter of 900  $\mu$ m and an inner diameter of 500  $\mu$ m. Table I summarizes composition and the spinning conditions of the fabricated PSF hollow fiber membranes. The ratio of dope flow rate to bore fluid rate was constant in all spinning processes. All nascent fibers were not drawn (no extension), which means that the take-up velocity of the hollow fiber membrane was nearly the same as the falling velocity in the coagulation bath. The coagulation bath and bore fluid

TABLE II  
PVA/PSF Hollow Fiber Composite Membrane Preparation Conditions

Membrane no.	Support membrane	Treatment method	The coating solution PVA/MAC/AEO <sub>9</sub> (wt %)	Heat treatment	
				Temperature (°C)	Time (min)
1	A	Dip-coated	4.1/0.2/0.3	100	90
2	A	Vacuum-coated	4.1/0.2/0.3	100	90
3	A	Vacuum-coated	4.0/0.6/0.8	130	120
4	A	Vacuum-coated	4.0/0.8/0.8	130	120
5	A	Vacuum-coated	4.0/1.2/0.8	130	120
6	A	Vacuum-coated	4.0/1.6/0.8	130	120
7	A	Vacuum-coated	4.9/0.4/0.2	130	120
8	B	Vacuum-coated	4.9/0.4/0.2	130	120
9	B	Dip-coated	4.9/0.4/0.2	130	120

were maintained at room temperature. The fabricated hollow fibers were stored in the water bath for 24 h to remove the residual DMAc and NMP. After this period, the fibers were posttreated, kept in a 60 wt % glycerol aqueous solution for another 24 h to prevent the collapse of porous structures, and then kept in the water at room temperature to remove the glycerol.

For the preparation of the coating solution, PVA was dissolved in water at 90°C with agitation to become PVA aqueous solution. After cooling the PVA aqueous solution to room temperature, MAC was mixed with the PVA solution as well as AEO<sub>9</sub>, which was supposed to decrease the solution interfacial tension with PSF hollow fiber surface until the coating solution became homogeneous. Finally, PSF hollow fiber membranes were coated by two methods, immersion in the coating solution for 30 s (dip-coating method) or immersion in the coating solution while keeping the inner side of the hollow fiber membranes under vacuum pressure for 30 s (vacuum-coating method). The PVA-coated PSF hollow fiber composite membranes then were dried at room temperature. The final PVA/PSF hollow fiber composite membranes were obtained after heat treatment in an oven at different temperatures and times as shown in Table II.

### Pervaporation process of ethanol/water separation

Figure 1 illustrates the schematic diagram of the pervaporation apparatus used in this case. 95/5 (wt/wt) ethanol/water was used as a feed composition. Therefore, the hollow fiber membrane cell has three modules; each module consisted of 8 fibers with lengths of 25 cm. The two ends of the hollow fiber bundles were glued using a thermoset epoxy resin. The permeate side was maintained at a vacuum pressure (98.3 kPa) using a vacuum pump. The ethanol/water mixture in the feed tank was kept in a water bath at a constant temperature of 50°C using a temperature controller. After each 4 h (running steady state), the permeate vapor sample was collected after condensation in a

cold trap using liquid nitrogen. Permeation flux ( $J$ , g/m<sup>2</sup>·h) of hollow fiber membranes was obtained as follows:

$$J = \frac{W}{t \times A} \quad (1)$$

Where  $W$  = total amount of permeate (g),  $t$  = experimental time interval (h), and  $A$  = hollow fiber membranes outer surface area (m<sup>2</sup>).

The following equation was used to calculate the effective area of each module:

$$A = n\pi d_o l \quad (2)$$

where  $n$  = number of hollow fiber membranes in the cell,  $d_o$  = the average outer diameter (o.d.) of hollow fiber membranes, and  $l$  = the effective membrane length in the module.

The compositions of the feed solutions and permeates were analyzed using a gas chromatograph (G.C. China Chromatography GC7890 T) with a column filled with a 401 packed, at a temperature of 120°C.

The separation factor ( $\alpha$ ) is defined by

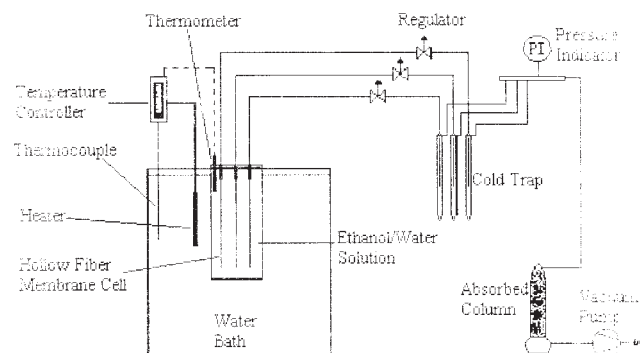


Figure 1 Schematic diagram of pervaporation process apparatus.

**TABLE III**  
**Pervaporation Performance of Different PVA/PSF Composite Membranes at 50°C**

Membrane no.	Support membrane	Treatment method	Separation factor ( $\alpha$ )	Permeation flux. $J$ (g/m <sup>2</sup> · h)	$PSI^a$ (g/m <sup>2</sup> · h)
1	A	Dip-coated	43	60	2580
2	A	Vacuum-coated	50	72	3600
3	A	Vacuum-coated	65	46	2990
4	A	Vacuum-coated	105	34	3570
5	A	Vacuum-coated	185	30	5550
6	A	Vacuum-coated	365	14	5110
7	A	Vacuum-coated	34	70	2380
8	B	Vacuum-coated	93	60	5580
9	B	Dip-coated	74	66	4884

<sup>a</sup> Pervaporation separation index,  $PSI = \alpha \times J$  (g/m<sup>2</sup> · h).

$$\alpha = \frac{(Y_W/Y_E)_{\text{permeate}}}{(X_W/X_E)_{\text{feed}}} \quad (3)$$

Where  $Y_W$ ,  $Y_E$ ,  $X_W$ , and  $X_E$  are the weight fraction of the water and ethanol in permeates and feed solution, respectively.

#### Membrane morphology of PSF hollow fiber membranes

Inner and outer diameters of hollow fibers were measured by means of an optical microscope. Membrane morphology was examined by using a scanning electron microscope (SEM; JEOL Model JSM-6360 LV, Tokyo, Japan). The cross section of hollow fibers for the SEM was prepared after breaking the membranes in liquid nitrogen to avoid destroying the structure of the cross sections of hollow fibers.

## RESULTS AND DISCUSSION

#### Effect of treatment methods on pervaporation performance of different PVA/PSF hollow fiber composite membranes

A typical method was used to fabricate hollow fiber composite membranes: the supported hollow fiber membrane was immersed into the coating polymer solution and then dried (dip-coating method). However, it was difficult for the coating polymer solution to spread on the hollow fiber surface because of the low surface tension of polymer. One method used was adding surfactant while another method used was keeping the inner side of hollow fiber membrane under vacuum pressure while immersing the outer side of hollow fiber membrane in the coating polymer solution (vacuum-coating method). As shown in Table III, the effect of the treatment methods of PVA/PSF hollow fiber membranes on pervaporation performance for the separation of 95 wt % ethanol/water solution at 50°C is investigated. In Table III, the separation factor ( $\alpha$ ) of membrane 2 using the vacuum-

coating method is higher than that of membrane 1 using the dip-coating method, while a higher permeation flux ( $J$ ) also is obtained. This might be due to the fact that the coating solution will adsorb and spread on supported hollow fiber membrane under vacuum with good uniformity, which leads to the decrease of top layer faults and therefore the separation factor is higher. Based on experimental results, the vacuum-coating method is used as the main method for the preparation of hollow fiber composite membrane.

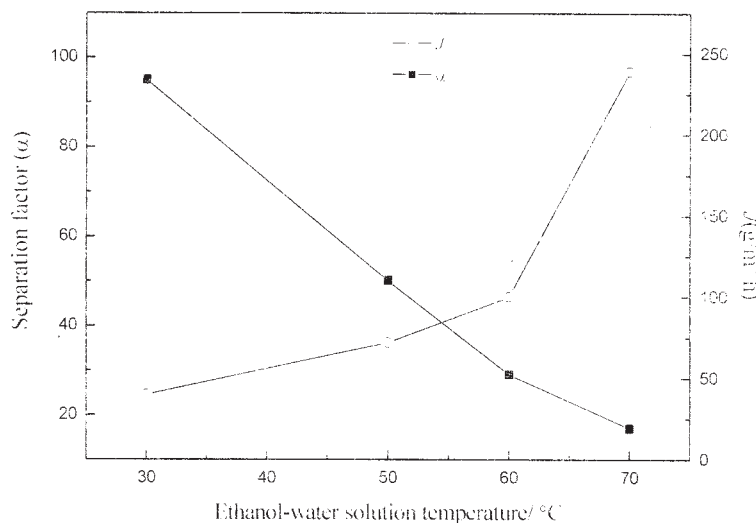
#### Effect of ethanol–water solution temperature on pervaporation performance of PVA/PSF hollow fiber composite membrane

The effect of the ethanol–water solution temperature on the pervaporation performance of the PVA/PSF hollow fiber composite membrane (membrane 2) for 95 wt % ethanol/water solution is shown in Figure 2. In Figure 2, with an increase of ethanol/water solution temperature, the separation factor ( $\alpha$ ) decreases while the permeation flux ( $J$ ) of the PVA/PSF composite membrane increases. The activation energy ( $\Delta E_a$ ) of the PVA/PSF hollow fiber composite membrane for 95 wt % ethanol/water solution is also calculated on the basis of the Arrhenius equation as shown in Figure 3. The relationship between permeation flux and ethanol–water solution temperature is defined as follows:

$$\ln J = \ln J_0 - \frac{\Delta E_a}{RT} = 17.44 - \frac{3.5 \times 10^3}{RT} \quad (4)$$

The activation energy ( $\Delta E_a = 35$  KJ/mol) of PVA/PSF hollow composite membrane (membrane 2) is shown in Figure 3. In this case, the higher PVA concentration in the coated solution forms the thicker top layer of the PVA/PSF hollow fiber composite membrane. This result is the agreement with that reported by Lee et al.<sup>14</sup>

Figure 4 shows that the pervaporation separation index ( $PSI$ ) decreases with the increase of the ethanol solution temperature from 30 to 60°C. As seen in

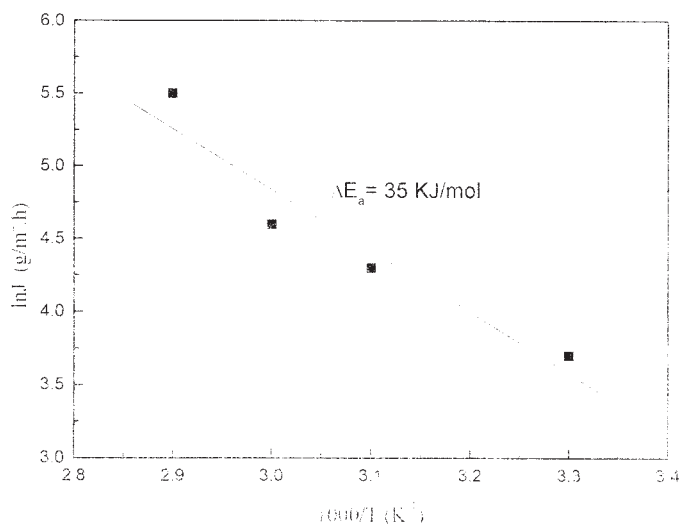


**Figure 2** Effect of ethanol–water solution temperature on pervaporation performance of PVA/PSF hollow fiber composite membrane 2.

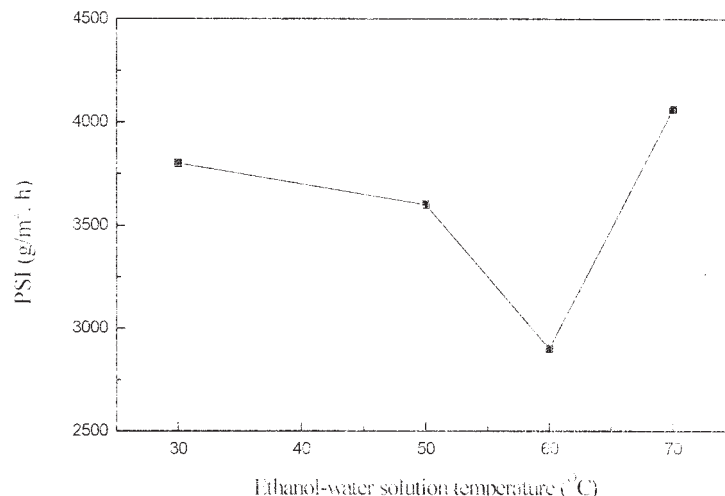
Figure 2, the decrease of separation factor ( $\alpha$ ) is faster than the increase of permeation flux ( $J$ ). After 60°C, the separation factor ( $\alpha$ ) decreases very slowly but the permeation flux ( $J$ ) increases more rapidly. Therefore, the *PSI* increases as seen in Figure 4. The reason is as follows: as the ethanol solution temperature increases to some degree, the membrane matrix swells to a critical state so that water and ethanol could freely permeate through the top layer of the PVA/PSF hollow fiber composite membrane (membrane 2). There should be different critical temperatures for different composite membranes with different swelling ability. The operation temperature was fixed at 50°C while the effect of the other factor was investigated.

#### Effect of MAC/PVA ratio on pervaporation performance of PVA/PSF composite membrane

In this case, the influence of the MAC/PVA ratio in the PVA-coated solution on the separation factor ( $\alpha$ ) and permeation flux ( $J$ ) of PVA/PSF hollow fiber composite membrane (membrane 2) at 50°C ethanol solution temperature is shown in Figure 5. With an increase in the MAC/PVA ratio, the separation factor ( $\alpha$ ) increases while the permeation flux ( $J$ ) decreases. Because of the many reactions between MAC and PVA, this results in an increase of the crosslinking density of the PVA top layer of the PVA/PSF hollow fiber composite membrane. Therefore, the chain mo-



**Figure 3** The activation energy required for pervaporation permeation of 95 wt % ethanol–water solution through PVA/PSF hollow fiber composite membrane 2.

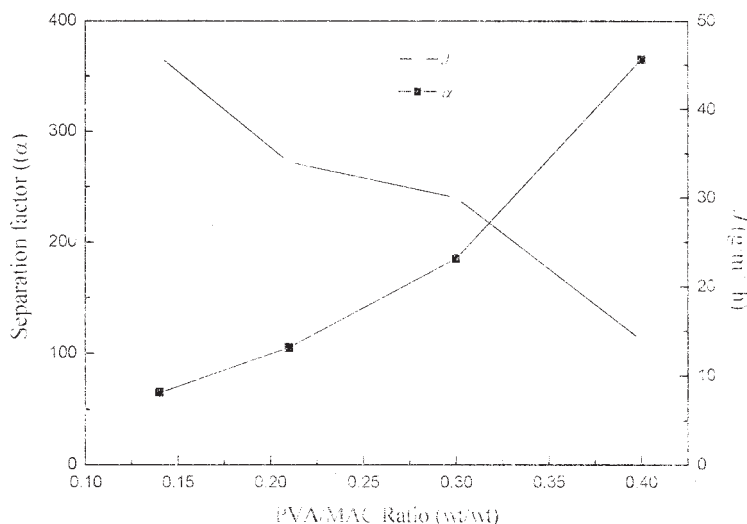


**Figure 4** Effect of ethanol–water solution temperature on pervaporation separation index (*PSI*) of PVA/PSF hollow fiber composite membrane 2.

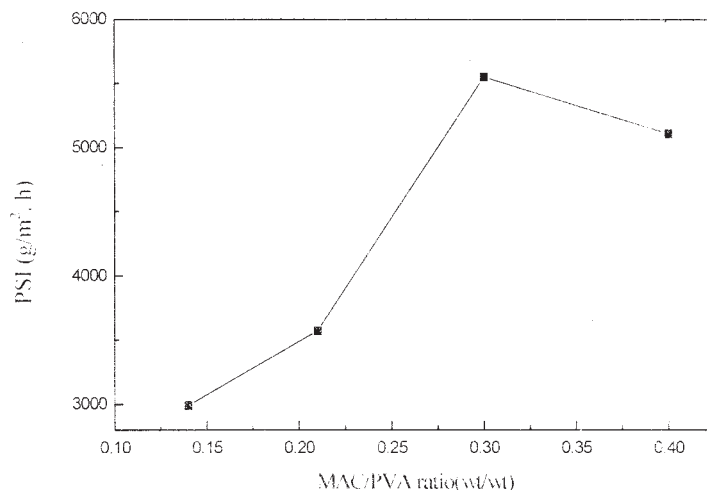
bility and swelling ability of PVA decreases. The separation factor ( $\alpha$ ) increases while permeation flux ( $J$ ) decreases. Figure 6 also shows that the *PSI* increases with an increase of MAC/PVA ratio in the PVA-coated solution up to 0.3 and then decreases. This illustrates that the separation factor ( $\alpha$ ) increases faster than the decrease of permeation flux ( $J$ ) as the ratio of MAC/PVA is less than 0.3. However, the decrease of permeation flux ( $J$ ) is predominant, as the ratio of MAC/PVA is over 0.3. Based on the above experimental results, the suitable MAC/PVA ratio is 0.3 for the preparation of PVA/PSF hollow fiber composite membrane with separation factor ( $\alpha = 185$ ) and permeation flux ( $J = 30\text{g}/\text{m}^2\cdot\text{h}$ ).

#### Effect of membrane structure on pervaporation performance of different PVA/PSF hollow fiber composite membranes

To compare the effect of the membrane structures on the separation factor ( $\alpha$ ) and permeation flux ( $J$ ) of the PVA/PSF hollow fiber composite membrane, two types of PSF hollow fiber membranes were fabricated, as shown in Table I. Figure 7 shows the cross-sectional structures of two kinds of supported PSF hollow fiber membranes. In Figure 7, membrane A, fabricated from PSF/NMP/glycerol (29 : 65 : 6) dope solution, has a sponge-like structure, while membrane B, fabricated from PSF/DMAc/glycol (29 : 64 : 7) dope solution, has



**Figure 5** Effect of MAC/PVA ratio in PVA-coated solution on pervaporation performance of PVA/PSF hollow fiber composite membrane (support membrane A, vacuum-coated).

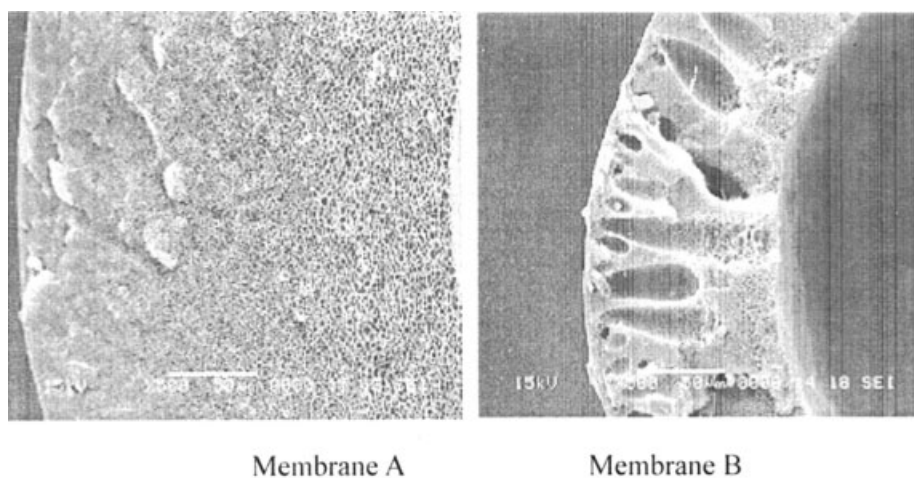


**Figure 6** Effect of MAC/PVA ratio in PVA-coated solution on pervaporation separation index (*PSI*) of PVA/PSF hollow fiber composite membrane (support membrane A, vacuum-coated).

a finger-void structure. Table III gives the pervaporation performance of different PVA/PSF hollow fiber composite membranes using membranes A and B as the supported membrane. Membrane 7 was made from supported membrane A while membranes 8 and 9 were made from supported membrane B. As seen in Table III, the separation factor ( $\alpha$ ) of membranes 8 and 9 using the vacuum-coating or dip-coating method is greater than that of membrane 7 using the vacuum-coating method while the permeation fluxes of membranes 8 and 9 seem to be unchanged in comparison with that of membrane 8. Therefore, single finger-void membrane structure as the supported membrane is more suitable than the sponge-like membrane structure for the preparation of PVA/PSF hollow fiber composite membrane. Attention will be paid to the single finger-void membrane structure as the supported membrane in future research.

## CONCLUSIONS

Polysulfone hollow fiber membranes were spun by phase-inversion method from 29 wt % solids of 29 : 65 : 6 PSF/NMP/glycerol and 29 : 64 : 7 PSF/DMAc/glycol using 93.5 : 6.5 NMP/water and 94.5 : 5.5 DMAc/water as a bore fluid, respectively, while the external coagulant was water. Polyvinyl alcohol/polysulfone hollow fiber composite membranes were prepared after PSF hollow fiber membranes were coated using PVA aqueous solution, which was composed of PVA, water, MAC, and AEO<sub>9</sub>. The investigation was conducted to evaluate the effects of membrane treatment methods, supported PSF hollow fiber membrane structures, ethanol solution temperatures, and MAC/PVA ratio on the pervaporation performances for the separation of 95 wt % aqueous ethanol solution. From the experimental results, it was concluded that the



**Figure 7** SEM cross-sectional structures of PSF hollow fibers wet spun from different dope solutions using different bore fluid composition: (membrane A) PSF/NMP/glycerol; (membrane B) PSF/DMAc/glycol (original magnification  $\times 500$ ).

suitable preparation method of PVA/PSF hollow fiber composite membranes with the sponge-like membrane structure was the vacuum-coating method while the suitable operation conditions were as follows: MAC/PVA ratio 0.3 and operation temperature 50°C. In this way, a better pervaporation performance ( $\alpha = 185$ ;  $J = 30\text{g/m}^2\cdot\text{h}$  at 50°C) for the separation of 95 wt % aqueous ethanol solution was obtained. Single finger-void membrane structure as the supported membrane was more suitable than sponge-like membrane structure for the preparation of PVA/PSF hollow fiber composite membrane.

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