

# Poly(vinyl alcohol)/Chitosan Blend Membranes for Pervaporation of Benzene/Cyclohexane Mixtures

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Received 16 March 2005; accepted 1 September 2005

DOI 10.1002/app.23158

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(vinyl alcohol)/chitosan (PVA/CS) blend membranes were prepared by mixing the two polymeric homogeneous solutions. The interaction between PVA and chitosan arising from hydrogen bond was analyzed through intrinsic viscosity determination and Fourier transform infrared (FTIR) spectra, and there existed an incompatibility region in the blend membranes when chitosan content was 50 wt %. X-ray diffraction (XRD) showed that the crystalline structure of PVA and chitosan was disrupted through blending. The incompatibility of two polymers and disrupted crystalline structure led to a less compact structure. The blend membranes were used to pervaporative separation of benzene/cyclohexane (Bz/Chx) mixtures. The effects of chitosan content in blend membranes, weight fraction of benzene in feed, and operating temperature on separation

performance of Bz/Chx mixtures were investigated. Compared with pure PVA and pure chitosan membranes, blend membranes showed much higher permeation flux and slightly higher benzene permselectivity. As the weight fraction of benzene in feed increased, separation factor decreased but total permeation flux increased. And it was observed that total permeation flux increased and separation factor decreased with increasing operating temperature. The total permeation flux of blend membrane with 50 wt % chitosan was 51.41 g/(m<sup>2</sup> h) and separation factor was 49.9 for Bz/Chx mixtures with 50 wt % of benzene at 323 K. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 167–173, 2006

**Key words:** pervaporation; poly(vinyl alcohol); chitosan; blend membrane; benzene/cyclohexane mixtures

## INTRODUCTION

Benzene and cyclohexane are both important chemicals for their versatile applications, and high purity is often required. Since cyclohexane is usually produced by hydrogenation of benzene, separating Bz/Chx mixtures becomes a routine task in petrochemical industry. However, separation of Bz/Chx mixture is very difficult because the difference in boiling points and Lennard–Jones collision diameters of benzene and cyclohexane are only 0.6 K and 0.08 nm. The current dominating separation methods, azeotropic distillation and extractive distillation, suffer from the complexity and high cost of removing the third component from distillate or residue.<sup>1</sup> Recently, pervaporation as a novel, efficient, and low-energy separation technique has attracted considerable research interests.<sup>2–5</sup> Unlike distillation process, pervaporation relies on the difference in sorption and diffusion properties of components in membranes.

Benzene, which has  $\pi$ -electron clouds, shows a stronger interaction with the polar or hydrophilic polymeric materials than cyclohexane. Therefore, various polar and hydrophilic membrane materials, such as polyacrylonitrile,<sup>6</sup> polyurethanes,<sup>7</sup> acetyl cellulose,<sup>2</sup> poly(vinyl chloride),<sup>8</sup> and poly(vinyl alcohol)<sup>9</sup> were employed to separate Bz/Chx mixtures. Among them, PVA has been used as a preferred material because of its high hydrophilicity, good chemical stability, facile membrane-forming property, and low cost. However, because of the close packing of polymer chains caused by intermolecular and intramolecular hydrogen bonding,<sup>10</sup> homogeneous PVA membrane often shows low permeation flux.<sup>9</sup> To improve permeation flux of PVA membrane, chemically and physically modified PVA membranes had been introduced. Yamasaki et al.<sup>9</sup> found that total permeation flux and separation factor were 4.2 g/(m<sup>2</sup> h) and 10 of asymmetric PVA membranes compared with 3.5 g/(m<sup>2</sup> h) and 3 of homogeneous PVA membranes for Bz/Chx mixtures with 80 wt % benzene. Bryant et al.<sup>11</sup> prepared PVA membranes filled with Ag (I) ions as the carrier for separation of 8/2 (v/v) Bz/Chx mixtures. Total permeation flux was 30.8 g/(m<sup>2</sup> h) and separation factor was 60. Pandey et al.<sup>12</sup> prepared chemically modified PVA (PVAc) and found that permeation flux increased from 24.8 g/(m<sup>2</sup> h) of PVA membranes to 47.0 g/(m<sup>2</sup> h) of PVAc membranes for pure benzene. However,

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Contract grant sponsor: SINOPEC Corp. Funding; contract grant number: X503029.

Contract grant sponsors: CNPC Innovation Fund, Cross-century Young Talent Program from the Ministry of Education, People's Republic of China.

only few reports on PVA blend membranes for Bz/Chx mixtures pervaporative separation can be found. Park et al.<sup>13</sup> prepared PVA/poly(allyl amine) blend membrane, which showed separation factor of 11.0 and permeation flux of 20.6 g/(m<sup>2</sup> h) for 50 wt % Bz/Chx mixtures.

In fact, blending is the most versatile and the least expensive way of preparing membranes with new desirable pervaporative separation performance.<sup>14</sup> Chitosan may become one of the most commonly used blending material for following reasons: chitosan is an abundant natural polymer and can be easily obtained by alkaline deacetylation of chitin; as a cationic polysaccharide, chitosan has some desirable properties such as high hydrophilicity, good chemical resistance, biodegradability, and good membrane-forming property.<sup>15</sup> As a rigid polymer, chitosan has a large free volume and allowing easy segmental mobility in glassy state, which results in high permeability. However, chitosan exhibits low selectivity because of significant swelling in Bz/Chx mixtures.

In this study, PVA/CS blend membranes were prepared aiming at obtaining high permeability and selectivity simultaneously for pervaporative separation of Bz/Chx mixtures. The compatibility of PVA/CS and crystalline structure of their blend membranes was examined. Furthermore, the effect of blend composition in membranes, feed concentration, and feed temperature on the permselectivity has been investigated.

## EXPERIMENTAL

### Materials

PVA (degree of polymerization was 1750 ± 50, degree of hydrolysis was 95%) was supplied by Tianjin Yuanli Chemical Co. (Tianjin, China), chitosan (deacetylation was 91.05%) was purchased from Yuhuan Sea Biochemical Co., Ltd. (Zhejiang, China), benzene and cyclohexane were purchased from Tianjin Jiangtian Chemicals Ltd. (Tianjin, China). All chemicals were used without further purification. Double distilled water was used throughout this study.

### Preparation of PVA/CS blend membranes

PVA was dissolved in distilled water and stirred at 363 K for 1 h to obtain 5 wt % PVA solution. Chitosan solution (2.5 wt %) was prepared by dissolving chitosan in 2 wt % acetic acid solution and stirring at 353 K for 1 h. The casting solution was prepared by uniformly mixing together the two solutions with a given ratio, and then cast onto a glass plate with the aid of a casting knife and dried at room temperature for 24 h. The mass ratio of PVA to chitosan was varied as 10/0, 8/2, 5/5, 2/8, and 0/10, and the resulting blend mem-

branes were designated as a, b, c, d, and e, respectively. The thickness of dry membranes was about 50 μm.

### Intrinsic viscosity determination

Solutions of PVA, chitosan, and their blends in acetic acid solution were prepared at 353 K for 2 h, and then filtered. Viscosity measurement was made with an Ubbelohde dilution viscometer at 298.00 ± 0.05 K. The pass times were recorded with an accuracy of ± 0.01 s. Extrapolation procedure from data obtained for four concentrations of solutions was used to evaluate intrinsic viscosity.

### Membrane characterization

The interaction between PVA and chitosan was confirmed using FTIR spectrometer (Nicolet, 5DX). FTIR spectra were recorded in the range of 4000–400 cm<sup>-1</sup>. Morphology of the membranes was investigated at room temperature using a Rigaku D/max advanced wide-angle X-ray diffractometer. The X-ray source was nickel-filtered Cu Kα radiation (40 kV, 200 mA). The dried membranes of uniform thickness (about 50 μm) were mounted on a sample holder and scanned in the reflection mode at an angle 2θ over a range from 3 to 50° at a speed of 0.02°/s.

### Swelling measurements and sorption experiments

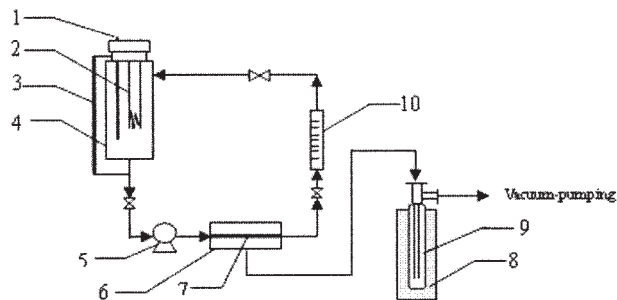
The dried membrane with known weight was immersed into Bz/Chx mixtures with 50 wt % benzene at 323 K for 30 h. When the sample kept constant weight, it was carefully blotted between filter papers to remove surface liquid, and then weighted quickly to measure the weight of the swollen membrane. All experiments were repeated at least three times, and the results were averaged. The degree of swelling (DS) for the membrane is defined by

$$DS = \frac{w_s - w_d}{w_d} \times 100\% \quad (1)$$

where  $w_d$  and  $w_s$  are the weights of dry and swollen membranes, respectively.

In the sorption experiments, the liquid sorbed in membranes was recovered in a liquid nitrogen trap by desorbing the equilibrated sample in the purge-and-trap apparatus. The compositions of Bz/Chx in membranes and in feed were determined by gas chromatography. The sorption selectivity,  $\alpha_{\text{sorp,Bz/Chx}}$ , can be expressed as

$$\alpha_{\text{sorp,Bz/Chx}} = \frac{(M_{\text{Bz}}/M_{\text{Chx}})}{(F_{\text{Bz}}/F_{\text{Chx}})} \quad (2)$$



**Figure 1** Experimental setup for pervaporation: 1. thermocouple, 2. heater, 3. liquidometer, 4. feed tank, 5. recycle pump, 6. membrane cell, 7. membrane, 8. liquid nitrogen trap, 9. permeator, and 10. rotor flow meter.

where  $F_{Bz}$  and  $F_{Chx}$  are weight fractions of benzene and cyclohexane in feed solution and  $M_{Bz}$  and  $M_{Chx}$  are those in membranes, respectively.

According to Solution-Diffusion mechanism, diffusivity selectivity ( $\alpha_{diff,Bz/Cxh}$ ) could be calculated from eq. (3),

$$\alpha_{diff,Bz/Chx} = \alpha_{PV,Bz/Chx} / \alpha_{sorp,Bz/Chx} \quad (3)$$

### Pervaporation experiment

The pervaporation experimental setup is shown in Figure 1. Pervaporation experiments were performed on P-28 membrane module (CM-Celfa AG Company, Switzerland). The effective area of membrane was 28.0 cm<sup>2</sup> and downstream pressure was kept below 0.3 kPa. After a steady state (about 2 h) was obtained, the permeate was collected in the cold trap immersed in liquid nitrogen. The compositions of benzene and cyclohexane were determined by gas chromatography (Agilent 6820) on the condition that detector temperature and column temperature were 423 K and 333 K, respectively. The evaluation of pervaporative separation performance was carried out by using two parameters, i.e., permeation flux ( $J$ ) and separation factor ( $\alpha$ ).  $J$  was calculated from the eq. (4),

$$J = \frac{w}{A \times t} \quad (4)$$

where  $w$  is the weight of permeate, g;  $A$  is the effective area of membrane, m<sup>2</sup>; and  $t$  is the time, h.  $\alpha$  was calculated from eq. (5),

$$\alpha_{PV,Bz/Chx} = \frac{(P_{Bz}/P_{Chx})}{(F_{Bz}/F_{Chx})} \quad (5)$$

where  $P_{Bz}$  and  $P_{Chx}$  are the concentrations of benzene and cyclohexane in permeate, and  $F_{Bz}$  and  $F_{Chx}$  are the

concentrations of benzene and cyclohexane in feed, respectively.

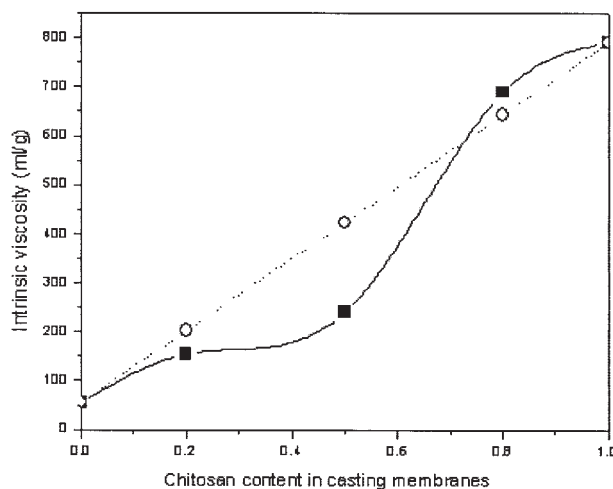
## RESULTS AND DISCUSSION

### Viscosity determination

Viscometry is a common method to investigate polymer compatibility because of its simplicity and reliability. Theoretically, the increase of intrinsic viscosity may result from expanding of the polymer coils caused by attractive interaction between the chains of two different polymers in solution, i.e., it is larger than that calculated according to the additivity law, and vice versa for the case of repulsive interaction. The intrinsic viscosity represents the effective hydrodynamic volume of a polymer molecule in solution.<sup>16-18</sup> Therefore, the change of intrinsic viscosity can be an indication of polymer chain expanding or shrinking. Figure 2 shows intrinsic viscosity values of PVA/CS blends with various weight fraction of chitosan in acetic acid buffer solution at 298.0 K. It can be observed that the intrinsic viscosity values of the most PVA/CS blends were not equal to the values simply derived from the additivity law. Positive deviation was observed when chitosan content was larger than 0.7, which reflected the expanding of both PVA and chitosan coil dimensions due to the strong intermolecular interaction or compatibility, and the negative deviation was observed when chitosan content was around 0.5, which reflected the shrinking of both PVA and chitosan coil dimensions due to the weak intermolecular interaction or incompatibility.

### FTIR spectra

FTIR spectrum is a useful technique for characterization of specific intermolecular interactions be-



**Figure 2** Intrinsic viscosity of PVA/CS blends.

tween the groups in different polymer molecules and conformational changes occurring in compatible blend systems.<sup>19</sup> These intermolecular interactions refer to mainly hydrogen bonding interaction, and result in either frequency shifting or band broadening of specific functional groups. The FTIR spectra of PVA/CS blend membranes are shown in Figure 3. The pure PVA membrane [Fig. 3(a)] showed characteristic bands at  $3340\text{ cm}^{-1}$  (characteristic of the O—H stretch) and at  $1088\text{ cm}^{-1}$  (characteristic of the C—O stretch).<sup>15</sup> The characteristic bands of chitosan membrane were located at  $3320\text{ cm}^{-1}$  for stretching band of O—H group overlapping with N—H stretching band, and  $1649\text{ cm}^{-1}$ ,  $1552\text{ cm}^{-1}$  for amide I and II, respectively.<sup>20</sup> The band intensity of hydroxyl group for the blend membranes was stronger than that for PVA and chitosan membranes. Such results might be caused by the association or dissociation of hydrogen bonding between hydroxyl group of PVA and hydroxyl group, amidogen group of chitosan. Moreover, the O—H stretching band of PVA near  $3340\text{ cm}^{-1}$  broadened and shifted towards higher frequency regions, with the increase of chitosan content, and the wavenumber of hydroxyl group in membrane depressed linearly with decrease of chitosan content, then dramatically went up at the region of chitosan content from 0.3 to 0.7, and again decreased linearly with decrease of chitosan content, as shown in Figure 4. It indicated that an immiscibility region existed in PVA/CS blend membranes. Meanwhile, C—O stretching band moved to lower frequency regions with increasing chitosan content, which indicated hydrogen bonding between O—H of PVA and C—O—C of chitosan.

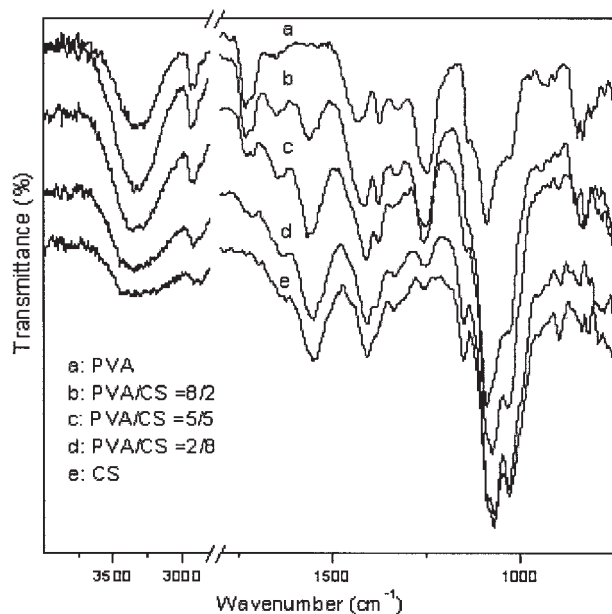


Figure 3 FTIR spectra of PVA/CS blend membranes.

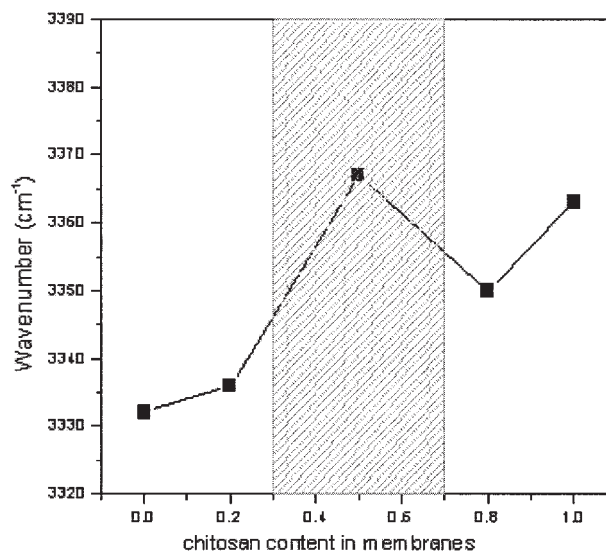


Figure 4 Shifting of hydroxyl group wavenumber with chitosan content in membranes.

#### X-ray diffraction

Figure 5 shows the XRD spectra of various membranes. As shown in Figure 5(a), one peak at  $2\theta = 19.3^\circ$  appeared, corresponding to the mixture of 101 and 200 plane of PVA semicrystalline in pure PVA membrane.<sup>21</sup> This peak broadened and shifted from  $19.3^\circ$  to  $19.9^\circ$  when chitosan content increased from 0 to 80 wt %, and disappeared in pure chitosan membrane [Fig. 5(e)]. Similarly, when PVA content in membranes increased, the peaks of chitosan around  $10^\circ$  and  $15^\circ$  disappeared gradually, and the small sharp peaks lessened. It illustrated that the crystallinity of PVA membrane was influenced by chitosan content in the

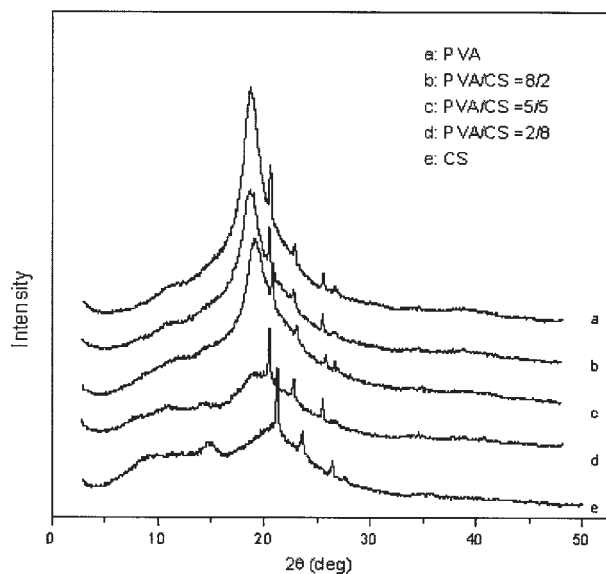
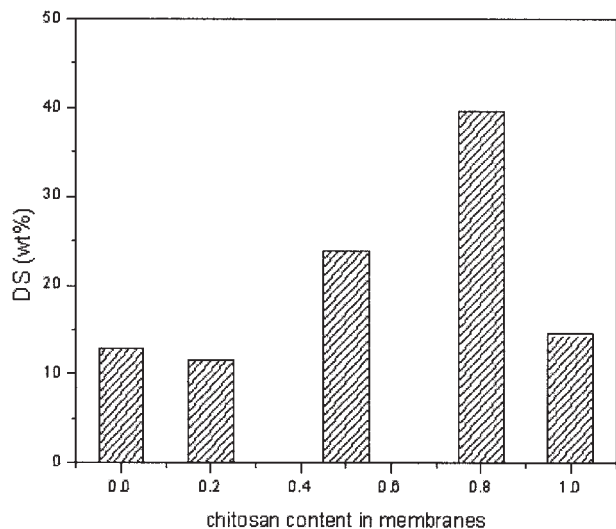


Figure 5 XRD spectra of PVA/CS blend membranes.





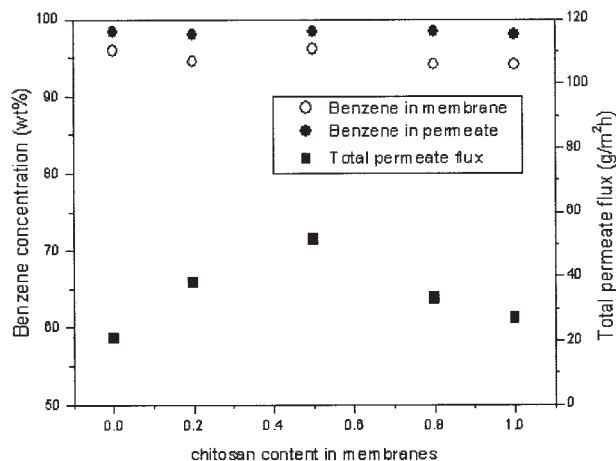
**Figure 6** Effect of chitosan content on the degree of swell of the membranes.

PVA/CS blend membranes, and vice versa of chitosan membrane. This phenomenon agreed well with Wu's work.<sup>22,23</sup> For pure PVA membrane, the high crystallinity was mainly caused by the intramolecular hydrogen bonding. For PVA/CS blend membranes, the decrease in crystallinity of the membranes was probably because of the decrease of intramolecular hydrogen bonding in PVA moiety and increase of intermolecular hydrogen bonding between PVA and chitosan.

### Swelling and sorption behavior of PVA/CS blend membranes

Figure 6 shows the effect of chitosan content on the degree of swelling for the membranes in Bz/Chx mixtures with 50 wt % benzene. The degree of swelling for the blend membranes, which was higher than that of pure PVA membrane and pure chitosan membrane, increased with increasing chitosan content in membranes. This result suggested that the arrangement of the two polymer chains became looser in blend membranes than in pure PVA membrane and chitosan membrane because of the hydrogen bonding between the two polymers. On the other hand, the higher degree of swelling illustrated that the structure of the blend membranes with lower crystallization and incompatibility region was much less compact than pure PVA membrane and pure chitosan membrane. The composition of Bz/Chx sorbed into the membranes for 50 wt % Bz/Chx mixtures was shown in Figure 7. The higher concentration of benzene over cyclohexane in membranes indicated that the swelling of membranes was mainly due to the sorption of benzene rather than cyclohexane.

The sorption selectivity and diffusion selectivity of membranes were calculated according to eqs. (2) and

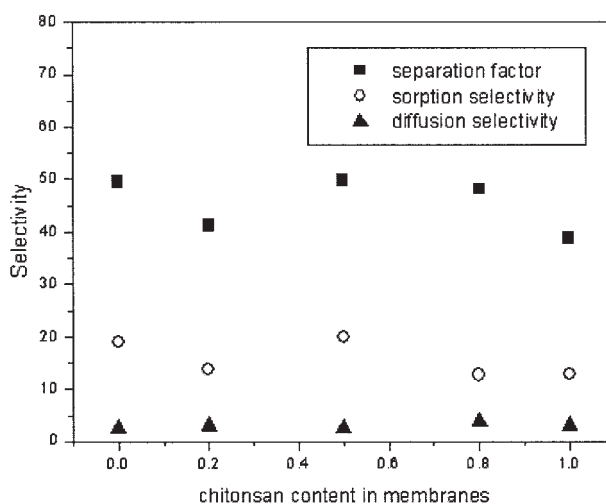


**Figure 7** Effect of chitosan content in membranes on the benzene concentration in membranes and pervaporation performance through the membranes for Bz/Chx mixtures with 50 wt % benzene at 323 K.

(3) and are shown in Figure 8 together with separation factor. It can be seen that the sorption selectivity is higher than the diffusion selectivity in all membranes, which suggested that the separation of Bz/Chx was mainly governed by sorption selectivity.

### Pervaporation performance of PVA/CS blend membranes

Figure 7 shows the effects of chitosan content on total permeation flux and benzene concentrations in permeate for Bz/Chx mixtures with 50 wt % benzene by pervaporation. The total permeation fluxes increased significantly after blending and could be to 51.41 g/(m<sup>2</sup> h) at 50 wt % chitosan content in blend mem-



**Figure 8** Effect of chitosan content in membranes on the separation factor, sorption selectivity, and diffusion selectivity for Bz/Chx mixtures with 50 wt % benzene through the membranes at 323 K.

**TABLE I**  
The Pervaporation Performance of Bz/Chx Mixtures Through PVA/CS Blend Membranes

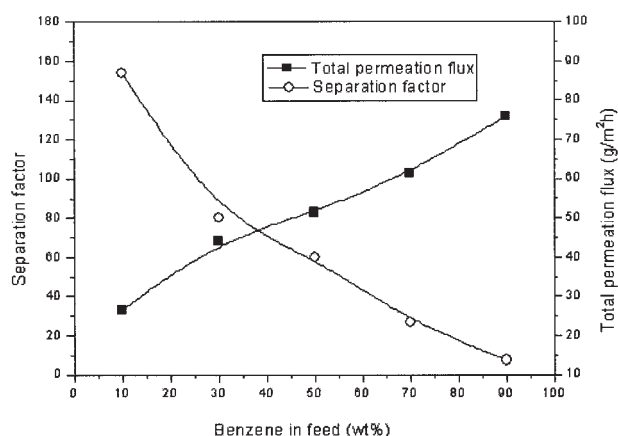
Sample	Weight fraction of chitosan in membranes	$J_{total}$ (g/m <sup>2</sup> h)	$J_{benzene}$ (g/m <sup>2</sup> h)	$J_{cyclohexane}$ (g/m <sup>2</sup> h)
a	0	20.59	20.25	0.34
b	0.2	38.13	37.38	0.75
c	0.5	51.41	50.57	0.84
d	0.8	33.14	32.58	0.56
e	1.0	27.03	26.46	0.57

Benzene in the feed, 50wt%; operation temperature, 323K.

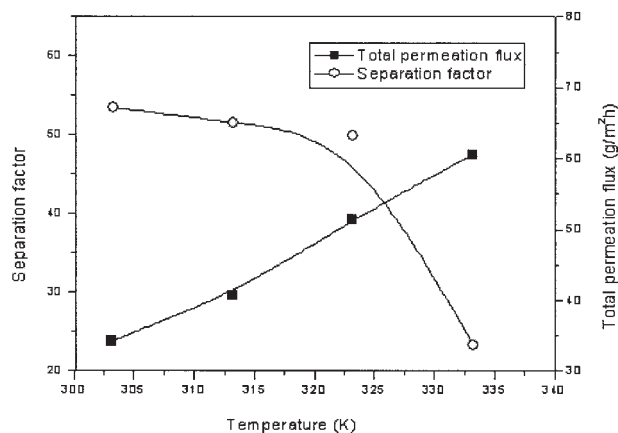
brane. The changing tendency of benzene flux and cyclohexane flux was the same as total permeation flux (Table I). For the blend membranes, the increasing flux was dependent on an increasing degree of swelling, which could be accounted for that intermolecular hydrogen bonding between PVA molecule and chitosan molecule resulted in a looser arrangement of the two polymer chains in blend membranes, consequently an enhancement of the diffusivity of components in the blend membranes. As shown in Figures 2 and 4, there was incompatibility of PVA and chitosan when chitosan content was around 50 wt %.

The membranes exhibited high benzene-permselectivity due to the increased hydrophilic group. The benzene concentrations in permeate were around 98 wt %, which were higher than those in membranes. This result indicated that the benzene-permselectivity was not dependent only on the difference solubility of benzene and cyclohexane into the membranes.

Figure 9 shows the effect of weight fraction of benzene in feed on pervaporation of Bz/Chx mixtures. For the membrane (PVA/CS (5/5)), separation factor decreased as the weight fraction of benzene in feed increased; but the total permeation flux increased.



**Figure 9** Effect of weight fraction of benzene in feed on pervaporation of Bz/Chx mixtures through PVA/CS (5/5) membrane at 323 K.



**Figure 10** Effect of operating temperature on pervaporation of Bz/Chx mixtures with 50 wt % benzene through PVA/CS (5/5) membrane.

Separation factor decreased from 154.0 to 7.7 when weight fraction of benzene in feed increased from 10 to 90 wt %, and total permeation flux increased from 26.68 g/(m<sup>2</sup> h) to 75.90 g/(m<sup>2</sup> h). This result might be due to benzene plasticization effect toward the membrane. Generally, hydrophilic membranes have a stronger interaction with benzene than with cyclohexane. When the benzene concentration in the feed was higher, the amorphous region in the membrane became more swollen. Consequently, the polymer chain became more flexible and the energy required for diffusive transport decreased, resulting in an increased total permeation flux. The decrease of separation factor with increasing benzene concentration in the feed can be explained that the less compact structure of blend membrane allows more cyclohexane molecules to pass through.

The effect of operating temperature on pervaporation properties for benzene/cyclohexane mixtures is shown in Figure 10. It could be observed that permeation flux increased and separation factor decreased from 303 K to 333 K, respectively. Total permeation flux could be to 51.41 g/(m<sup>2</sup> h), and separation factor was 49.9 when temperature was 323 K. At higher temperature, the interaction among benzene, cyclohexane, and membrane became weaker and the plasticizing effect of the membrane became more pronounced, which facilitated the transport of both benzene and cyclohexane molecules, but with the different enhancement degree.

## CONCLUSIONS

PVA/CS blend membranes, which exhibited excellent pervaporation performance of Bz/Chx mixtures, were prepared by blending of PVA and chitosan in varying proportions. The total permeation fluxes of blend membranes ranged from 33.14–51.41 g/(m<sup>2</sup> h) for Bz/

Chx mixtures with 50 wt % benzene, which were only 20.59 g/(m<sup>2</sup> h) of pure PVA membrane and 27.03 g/(m<sup>2</sup> h) of pure chitosan membrane. The higher permeability was due to the intermolecular hydrogen bonding between PVA molecules and chitosan molecules, which resulted in looser arrangement of the two polymer chains in blend membranes, consequently an enhancement of the diffusivity of components in blend membranes. Furthermore, because of the existence of sufficient amount of hydrophilic groups in blend membranes, the separation factors were all between 40 and 50 for the blend membranes, which is a bit higher than that of pure PVA membrane. The total permeation flux increased, but separation factor decreased with the increase of weight fraction of benzene in feed and operating temperature, respectively. The total permeation flux of the membrane with 50 wt % chitosan was 51.41 g/(m<sup>2</sup> h) and separation factor was 49.9 when 50 wt % benzene in feed at 323 K.

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