# Preferential Separation of Ethanol from Aqueous Solution Through Hydrophilic Polymer Membranes

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**ABSTRACT:** The pervaporation behaviors of aqueous ethanol mixtures through the poly(ethylene oxide) (PEO)/chitosan (CS) blend membrane were investigated. The results show that both CS and PEO/CS membrane preferentially permeate ethanol at a lower alcohol concentration in feed, and the selectivity of CS membrane toward alcohol can be greatly improved by introducing hydrophilic polymer PEO into CS. The PEO/CS blend membrane gave a separation factor of 4.4 and a flux of 0.9 kg m$^{-2}$ h for 8 wt % of ethanol in the feed at 20°C. At the same time, the reason introducing PEO can improve alcohol-permselectivity of CS membrane is explained on the basis of experimental data. Blending with PEO made the structure of CS chain looser, which resulted in ethanol molecules passing through easily, on the other hand, strengthened the ability of forming water clusters that inhibit the permeation of water molecules. From the experimental results, although the PEO/CS blend membrane was not a usable membrane with high selectivity to alcohol, a new method to prepare alcohol-permselective membranes appears to be developed by modifying hydrophilic polymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1145–1151, 1999

**Key words:** pervaporation; membrane separation; ethanol–water mixture; alcohol–permselective membrane; permselectivity

## INTRODUCTION

The pervaporation technique is considered to be a feasible process for the separation organic liquid mixtures, especially the alcohol/water systems, since the formation of ethanol via fermentation of biomasses will in the near future be an important industrial process, which relates to the energy problem. There are two ways to separate alcohol/water solutions by pervaporation technique. One way is for alcohol to separate through the membrane,[1,2] whereas, the other way is for water to selectively permeate through the membrane.[3–5] Most research of membrane separation of aqueous alcohol solution by pervaporation deals with separation by selective permeation of water. Only a few polymers are known as an alcohol-permselective membrane such as silicone rubber membrane, having low flux and selectivity toward alcohol. However, it is more practical to permeate alcohol through the membrane when it is a minor component in the mixture, so the development of novel polymer membranes for separating ethanol is very important.

It was generally recognized that glassy polymer membranes preferentially permeate water and elastomer membranes preferentially perme-

ate ethanol.[6] In rubber polymers, the polymer segments are in continuous random motion. The penetrating molecules will diffuse into the resulting transient gaps, thereby loosening the polymer network. The consequence is a macroscopic swelling of the membrane. In this state, relatively large molecules can diffuse in the loosened polymer matrix. A higher concentration of molecules inside the membrane (i.e., a membrane with a higher solubility coefficient) results in a higher permeability. In glassy polymers, there is very little free segmental movement of the polymer chain. The diffusion takes place primarily in the amorphous regions between rigid polymer segments, so the permeability is determined mainly by the diffusion contribution.[7] However, some hydrophilic polymer membrane or membrane with the hydrophilic group of preferentially permeated alcohol in the low alcohol concentration region was reported.[8–13] These results indicate that the mechanism that alcohol preferentially permeates through the hydrophilic membrane with is different from that of the rubber polymer membrane, and it is possible to prepare a high performance alcohol-permselective membrane using hydrophilic polymer.

The major purpose of this study is to develop a novel alcohol-permselective membrane that has high selectivity and acceptable flux for separating the alcohol–water system. In this article, we prepared poly(ethylene oxide) (PEO)/chitosan (CS) blend membranes. The pervaporation behaviors of aqueous ethanol mixtures through the blend membrane were investigated. The results show that the selectivity toward alcohol can be greatly improved by introducing hydrophilic polymer PEO into CS. The reason for the marked increase of separation performance is discussed.

## EXPERIMENTAL

### Membrane Materials

CS has a degree of deacetylation of 83.5% and a viscosity-average molecular weight of $5.2 \times 10^5$. PEO has viscosity-average molecular weight of $1 \times 10^6$.

### Membrane Preparation

PEO/CS blend membranes were prepared by casting the aqueous solution with CS and PEO onto a glass plate and evaporating the solvent at 40°C for 8 h, treated with 3 wt % NaOH aqueous solution and washed thoroughly with deionized water. The thickness of the obtained membranes was ~ 20 $\mu$m.

### Pervaporation

Apparatus and procedure of the pervaporation was principally the same as described in our previous article.[3] A constant downstream pressure (530 Pa) was maintained by a vacuum pump. The pervaporate was condensed in either of the two traps cooled in dry ice/acetone mixture (−77°C). The composition of the permeate was determined by a Shimadzu GC-7A gas chromatograph equipped with 1-m long columns packed with Porapak Q.

The separation factor ($\alpha_{e/w}$) for alcohol permselective is defined as follows:

$$\alpha_{e/w} = \frac{Y_{EtOH}/Y_w}{X_{EtOH}/X_w}$$

and the separation factor ($\alpha_{w/e}$) for water permselective is defined:

$$\alpha_{w/e} = \frac{Y_w/Y_{EtOH}}{X_w/X_{EtOH}}$$

where $X_w$ and $X_{EtOH}$ are water and alcohol contents (wt %) in the feed, respectively, and $Y_w$ and $Y_{EtOH}$ are water and alcohol contents (wt %) in the permeate, respectively.
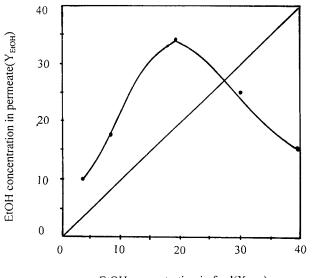
### Swelling Characteristics and Evaluation of Solubility Selectivity

A membrane sample was immersed in a water–alcohol mixture at 15°C for 72 h. After the sorption equilibrium was reached, the membrane was rapidly taken out from the immersing solution, wiped with tissue paper to remove adherent solvent, and weighed immediately. The swelling degree ($S$) was determined as

$$S = (W_s - W_d)W_d$$

where $W_d$ and $W_s$ are the weight of dry and swollen membranes, respectively.

The solvent in the swollen membrane was allowed to evaporate under reduced pressure and

**Figure 1** Permeate concentration versus feed concentration, chitosan membrane, $T = 20°C$.



**Figure 2** Dependence of separation factor ($\alpha_{e/w}$) and permeation flux on PEO/CS blend ratio (wt%). $T = 20°C$, feed concentration: 8 wt % ethanol.

collected in a cold trap. The composition of the solvent was determined by gas chromatograph.

## RESULTS AND DISCUSSION

### Pervaporation Performance of CS Membrane

Figure 1 shows the relation between pervaporation performance and EtOH concentration in feed. The results reveal that ethanol concentration in feed greatly influenced the pervaporation properties of the CS membrane, and the hydrophilic membrane became alcohol permselective, whereas ethanol concentration was under 25 wt %.

The relationship between the composition of the liquid mixture inside the swollen membranes and the feed composition is shown in Table I. The results show that the swelling degree of the CS membrane decreases with increasing ethanol con-

**Table I  Relationship Between the Swelling Degree, the Composition of the Liquid Mixture Inside the Swollen Chitosan Membrane, and the Feed Composition**
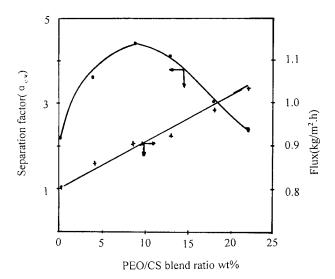
| Ethanol in feed (wt %) | 10 | 30 | 50 |
|---|---|---|---|
| Swelling degree (%) | 70 | 59 | 48 |
| Ethanol in swollen membrane (wt %) | 5.7 | 7 | 28.8 |

centration and the water content in the swollen membrane exceed that in the feed. This indicates that water is sorbed preferentially over the entire range of feed composition even though ethanol permeates preferentially at low ethanol concentration.

### Pervaporation Performance of PEO/CS Blend Membranes

The pervaporation performance of the blend membrane is shown in Figure 2 as a function of blend ratio in PEO/CS. Both CS and PEO/CS blend membrane selectively permeate ethanol. Flux increased with increasing PEO/CS blend ratio, whereas selectivity reached a maximum value at the blend ratio of 8 wt % PEO, where separation factor was about twice as much as that of CS membrane. This membrane gave a separation factor of 4.4 and a flux of 0.9 kg m$^{-2}$ h for 8 wt % of ethanol in the feed at 20°C.

The relation between the pervaporation results and alcohol concentration in the feed is shown in Figure 3. It was found that the selectivity to alcohol in alcohol/water system increases with increasing water content in feed. This result is identical to the poly(dimethyl siloxane) membrane.[1]

Figure 4 shows that the effect of operating temperature on permeation flux and separation factor ($\alpha_{e/w}$) through the blend membrane (PEO/CS = 8 wt %). The permeation flux increased as the temperature increased, whereas
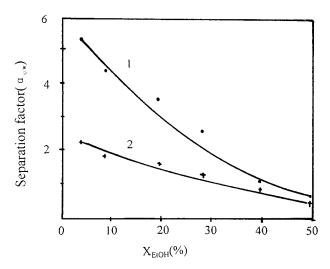
**Figure 3** Dependence of separation factor ($\alpha_{e/w}$) on ethanol concentration in feed through the blend membrane (PEO/CS = 8 wt %), (1) $T = 20°C$, (2) $T = 30°C$.

separation factor decreased. At the same time, from this Arrhenius plot, the apparent activation energies of transport for alcohol–water are different in the range of 20–30°C and over 30°C.

The results of PEO/CS blend membrane solubility selectivity is the same as that of CS membrane (shown in Fig. 5). Water is also sorbed preferentially over the entire range of PEO/CS blend ratio we prepared. In short, the alcohol-permselectivity to CS and PEO/CS blend membrane are not caused by absorbing ethanol preferentially. At the same time, the swelling degree increases with the increase of PEO/CS blend ratio.
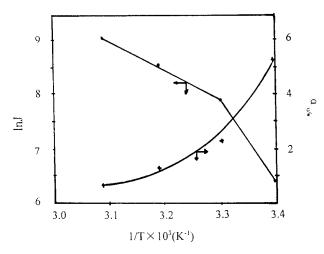


**Figure 4** Dependence of separation factor and flux on the operating temperature through membrane (PEO/CS = 8 wt %). Feed: 4 wt % ethanol.
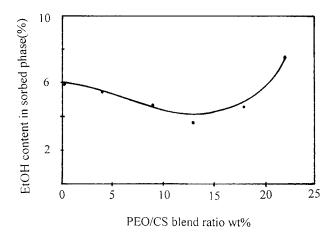


**Figure 5** Dependence of the composition of the liquid mixture inside the swollen membrane on the PEO/CS blend ratio. Feed: 10 wt % ethanol.

## Discussion on Alcohol Permselectivity of Hydrophilic Membrane

Why did ethanol permeate preferentially through CS membrane at low ethanol content in feed and selectivity toward ethanol increase by introducing PEO into CS membrane? To answer this question, the pervaporation performance of hydrophilic membrane at high ethanol content in the feed was examined. The effects of operating temperature on the separation factor of PEO/CS blend membranes are shown in Figure 6. The data indicate that water permeates preferentially through the blend membrane in feed with high ethanol content, and for the membranes with low PEO/CS blend ratio, the separation factor for water permselective ($\alpha_{w/e}$) decreases with the increase of temperature as most membranes do. At the same time, with the increasing PEO/CS blend ratio, the membrane selectivity decreases and the change of separation factor with temperature becomes smaller. Until for the membranes with higher PEO/CS blend ratio such as PEO/CS = 33 wt %, both the separation factor for water permselective and flux increase with the increase in temperature. An increase in flux and decrease in separation factor after blending with PEO is believed to be due to which structure made the modified CS membrane more loose. This also could be proved from DSC curves (shown in Fig. 7). The endothermic peak at about 250°C indicated the crystal structure of the CS membrane shifted to a lower temperature and became weak. This result implies that the increase in PEO/CS blend ratio
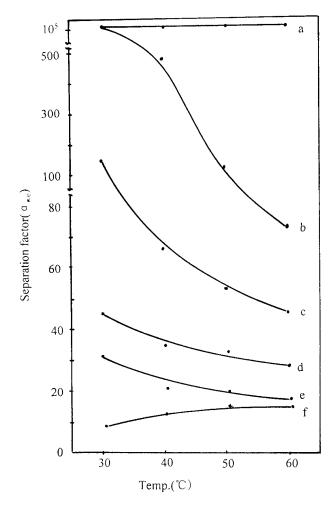
**Figure 6** Dependence of separation factor ($\alpha_{w/e}$) for water permselective of PEO/CS blend membrane on operating temperature (feed: 90 wt % ethanol). (a) 0/100, (b) 4/100, (c) 8/100, (d) 13/100, (e) 18/100, (f) 33/100.

decreases the crystallinity of the membrane. So according to Eyring's hole theory, the holes of the blend membrane increase with increasing the PEO content; when the holes are large enough for ethanol molecular to pass through, the effects of operating temperature on separation factor is very small.

From the Arrhenius plot, the apparent activation energies of each component permeating through the different PEO/CS blend membranes are calculated and the results are shown in Table II. Its energies for ethanol decrease and for water increase with increasing PEO/CS blend ratio; at last, the apparent activation energy for water is more than that for ethanol. Yasuda and Stannett[14] attributed the sorption and diffusion be-
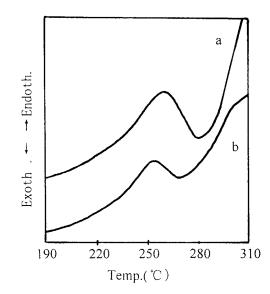


**Figure 7** DSC curves of (a) CS and (b) PEO/CS = 22/100 blend membranes.

havior to clustering of water molecules in the polymer when the mechanism of water vapor permeation through hydrophilic polymer membranes was studied. DSC verified that water molecules in the ionomer membranes were classified into three types, and one of the three types is clustering.[15] Therefore, we think that the diffusion for ethanol molecules becomes easy because of the increase of the holes and decrease of the action between CS chains when the PEO/CS blend ratios raise. At the same time, the existence of PEO inhibits the formation of hydrogen bonds among the CS chains and PEO itself is a good hydrophilic polymer, and both are in favor of forming clustering of water molecules in the membrane. As water clusters are large, it is very difficult to permeate through the membrane. By raising operating temperature, clustering of water molecules was destroyed. The change of water flux is larger than

**Table II  The Apparent Permeation Activation Energies of Ethanol and Water in PEO/CS Blend Membrane (feed: 90 wt % ethanol)**

| PEO/CS | $E_{app}$ (kJ mol$^{-1}$) | |
| | Ethanol | Water |
| --- | --- | --- |
| 8/100 | 65.2 | 33.6 |
| 13/100 | 52.2 | 39.6 |
| 33/100 | 36.8 | 49.1 |

**Table III   The Effect of Operating Temperature on Component Permeation Flux (PEO/CS = 22/100, feed: 80 wt % ethanol)**

| | Operating Temperature (°C) | | | |
|---|---|---|---|---|
| | 30 | 40 | 50 | 60 |
| Water flux (g m$^{-2}$ h) | 440 | 669 | 955 | 1171 |
| Ethanol flux (g m$^{-2}$ h) | 330 | 433 | 437 | 500 |

that of ethanol with the increase of operating temperature (see Table III), which results in the separation factor ($\alpha_{w/e}$) increasing with the increase of temperature [see Fig. 6(f)]. The increase of water content in feed also strengthens the ability of forming water clusters, similar to the increase of PEO content in the membrane. Ethanol content in feed which separation factor increase with increasing of temperature rise as increasing PEO/CS blend ratio (see Table IV).

By increasing water content in the feed and the PEO/CS blend ratio, the swelling degree of the membrane rises, which results in the ethanol molecule permeating the membrane easily, but permeates water more difficultly as it forms clusters. Therefore, ethanol permeates preferentially through the membrane at lower ethanol concentration, and the alcohol-permselectivity of CS membrane can be greatly improved by blending with PEO. At lower temperatures, increasing temperature water clusters were destroyed, so the relationship between ln $J$ and $1/T$ were not in the same straight line (see Fig. 4). This explanation corresponds well to all results above.

The results above show that a new field for alcohol-permselectivity membrane will be devel-oped. The separation factor may be raised by way of strengthening the ability of forming water clusters that inhibits the diffusion of water molecules and decreases inhibition of ethanol diffusion. So not only elastomic polymer, of which alcohol was absorbed preferentially, was used as alcohol-selective membrane material as most people, but also hydrophilic polymer, of which water was absorbed preferentially. At the same time, on the basis of the experimental results above, hydrophilic membranes permeating alcohol preferentially reported in some references[8–12] can be explained and development of novel alcohol–selective membrane with good performance will be reported in our other article.

## CONCLUSIONS

The PEO/CS membranes with different blend ratios were prepared and its pervaporation behaviors for separating aqueous ethanol mixtures were investigated. The results show that both CS and PEO/CS membranes preferentially permeate ethanol at lower ethanol concentration in feed, and the selectivity of CS membrane toward alcohol can be greatly improved by introducing hydrophilic polymer PEO into CS. The PEO/CS blend membrane gave a separation factor of 4.4 and a flux of 0.9 kg m$^{-2}$ h for 8 wt % of ethanol in the feed at 20°C. At the same time, we thought that improving ethanol selectivity of CS by introducing PEO mainly strengthens the ability of forming clusters of water molecules, which inhibits water permeation through the membrane, and one of ethanol diffusion. This was verified by experimental data. At present, it is difficult to say that PEO/CS blend membrane was a usable mem-

**Table IV   The Effect of Operating Temperature on Separation Factor ($\alpha_{w/e}$)**

| Operating Temperature (°C) | PEO/CS = 0/100 | | | | PEO/CS = 13/100 | | | | PEO/CS = 33/100 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 70% | 60% | 50% | 40% | 90% | 80% | 70% | 60% | 96% | 90% |
| 30 | 10$^5$ | 394 | 7 | 5 | 46 | 20 | 3 | 3 | — | 10 |
| 40 | 10$^5$ | 77 | 10 | 7 | 35 | 13 | 5 | 4 | 19 | 13 |
| 50 | 190 | 28 | 13 | 8 | 34 | 12 | 6 | 5 | 18 | 15 |
| 60 | 84 | 26 | 21 | — | 29 | 12 | 8 | 6 | 18 | 16 |

%, ethanol concentration in feed, PEO/CS, blend ratio.

brane with high selectivity to alcohol. However, this study appears to be useful as a new method to prepare alcohol-permselective membrane.

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