

# Application of Ionically Crosslinked Latex Membranes to the Separation of Ethanol–Water Mixtures by Pervaporation

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## SYNOPSIS

Ionically crosslinked latex membrane is prepared by treating the latex membrane containing carboxyl groups with salt solutions. Pervaporation separation with these membranes shows that the ionic crosslinking raises the permeability, with the selectivity being maintained or increased. Ionically crosslinked membranes also have a higher pervaporation separation efficiency than the nontreated membranes. Permeability and selectivity increase with increasing ethanol content in feed. The temperature dependence of permeability can be correlated by the Arrhenius relationship. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

With growing interest in pervaporation as an energy saving separation process, intensive study has been conducted aiming at developing satisfactory membrane materials.<sup>1</sup> Latex membranes, made from direct casting of polymer emulsions, have been recently tested for dehydration of ethanol–water mixtures in this laboratory.<sup>2,3</sup> It is shown by our earlier study that the degree of crosslinking and hydrophilic–hydrophobic balance of the membrane are of great importance in determining its pervaporation performances. For example, increasing the degree of crosslinking raises its separation factor, but at the mean time reduces the permeability. It was also shown that incorporating some strong hydrophilic groups in the latex membrane increased the permeability, but was accompanied by a loss in the separation factor.<sup>4</sup> Thus it appears to be an attractive approach if the incorporation of hydrophilic groups is combined with further crosslinking of these groups, especially in the boundary region, to raise both selectivity and permeability.

Multivalent metal salts have been successfully employed to form crosslinks in membranes contain-

ing carboxyl groups.<sup>5–9</sup> Although the mechanism of ionic crosslinking in such systems is still unclear, factors such as the density of ionized sites, cation species, and salt concentration are believed to have an effect on the crosslinking reaction.<sup>7</sup> The ionic crosslinking of the carboxyl groups in a latex membrane can be achieved in two ways. One is to add a salt solution to the latex before the membrane is cast, the other is to treat the dry latex membrane in a salt solution. Since the salt solution causes coagulation of the latex, the other method is used for the treatment.

Pervaporation separation process is characterized by total permeability ( $P_t$ ), permeability for individual component ( $P_i$ ), and separation factor ( $\alpha$ ), which are defined previously.<sup>2</sup> To measure the overall separation ability of a membrane system, Huang and Yeom<sup>10,11</sup> defined a *pervaporation separation index* (PSI), which is a product of separation factor and permeability. A larger PSI value indicates a better performance of the membrane system:

$$PSI = P_i \alpha_{i/j} \quad (1)$$

Dependence of permeability on membrane temperature is correlated by an Arrhenius-type relationship:

$$P_i = A_i \exp\left(\frac{-E_i}{RT}\right) \quad (2)$$

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where  $A$  is the preexponential factor,  $E_i$  is the permeation activation energy of component  $i$ .

The permeation nonideality is indicated by the permeation ratio  $\theta$ , as explained earlier.<sup>2</sup>

## EXPERIMENTAL

### Membrane Preparation

Latex: acrylonitrile-butyl acrylate-acrylic acid copolymer latex was synthesized by emulsion polymerization, as previously described.<sup>3</sup> The polymerization recipe is:

Reactor charge: distilled water, 378 g; sodium dodecyl sulphate, 1.5 g.

Monomer mixture: acrylonitrile, 33.4 g; butyl acrylate, 64.8 g; acrylic acid, 8 g; EGDM, 1.8 g.

Initiator: potassium persulfate (in 1.5 wt % aqueous solution), 0.2 g.

Latex membrane: latex membranes were prepared by direct casting of the latex onto a glass plate, as described earlier.<sup>3</sup> The drying time of the membranes was 10 days. The thicknesses of the films were approximately 100  $\mu\text{m}$ .

Membrane treatment: ionic crosslinking of the latex membrane was obtained by submerging the film in 0.25M salt solution. The crosslinking temperature was kept at 25°C. After the treatment, the membrane was taken out of the liquid bath, rinsed with water, and used for the separation without further drying.

### Pervaporation

Pervaporation separation was conducted with ethanol-water mixtures, in the same way as described in the previous study.<sup>2</sup> The feed mixture was circulated by a circulation pump. The pressure at the permeate side was maintained below 3 mmHg. The permeate was collected in glass traps that were immersed in liquid nitrogen. The permeate composition was analyzed using a Perkin-Elmer 8310 Gas Chromatography.

## RESULTS AND DISCUSSION

### Latex Membranes Crosslinked with Different Metal Salts

When the cations diffuse into the latex membrane, interaction between —COOH groups and the ions retains the metal ions inside the membrane, causing

partial or complete neutralization of the pendant carboxyl groups. Unlike typical ionic covalences, the ionic force thus generated is nondirectional and acts at a greater distance.<sup>12</sup> It is also believed that cations having lower charges are relatively mobile in the film, while higher charged cations are located at the carboxyl sites.<sup>7</sup> Some study has shown that the glass transition temperature of a membrane could be raised by 40°C, due to ionic crosslinking.<sup>5</sup>

Although the nature of ionic crosslinking in such systems is not clear, there is no doubt that different cations would have different effects on pervaporation properties of the crosslinked membrane. Table I presents the permeability and selectivity of membranes treated by various salt solutions.

From Table I it is observed that the permeability through all treated membranes is larger than that of the untreated membrane. Also, a comparison in permeability of membranes treated in salt solutions with that treated in pure water showed that the former is much higher. Since treating the membrane in a salt solution is equivalent to aging the membrane in water for a certain time, plus the ionic crosslinking of the membrane, the above effect can be counted as the joint contribution of these two aspects. Earlier experiments show that aging a latex membrane in water decreases the rate of film fusion and maintains a distinct boundary region, which leads to an increase in permeability and a decrease in separation factor; while the chemical crosslinking usually leads to a decrease in permeability and an increase in selectivity.<sup>4</sup> If the crosslinking effect cannot compensate the aging effect, a rise in per-

**Table I. Pervaporation Properties of Latex Membranes Treated by Different Salt Solutions<sup>a</sup>**

Treatment	25°C <sup>b</sup>		35°C	
	$P_t^c$	$\alpha$	$P_t$	$\alpha$
Untreated	2.60	22.9	3.66	11.6
H <sub>2</sub> O	2.72	12.9	4.26	9.9
N <sub>2</sub> SO <sub>4</sub>	3.56	20.7	5.48	12.1
NaOH	4.03	20.6	7.17	12.3
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	4.97	10.5	8.42	7.7
BaCl <sub>2</sub>	5.01	28.7	7.10	14.8
ZnSO <sub>4</sub>	5.34	33.8	7.46	17.4
ZrO(NO <sub>3</sub> ) <sub>2</sub>	6.58	17.8	10.11	10.6
CuSO <sub>4</sub>	7.56	22.2	11.55	11.7
CuCl <sub>2</sub>	5.60	15.0	9.88	9.2

<sup>a</sup> Membrane treatment time: 7 days. Feed composition: 95 wt % ethanol.

<sup>b</sup> Feed temperature.

<sup>c</sup> Permeability,  $\times 10^{-3}$  g/m h.

meability is expected, and vice versa. Since the membrane aged in salt solutions has a higher permeability than that aged in pure water, as shown in Table I, its boundary region may also become more distinctive.

Because the latex membranes were subjected to the same drying and treatment condition, if one considers the aging effects only, all the membranes would have shown the same increment in permeability. From Table I, however, the permeability increments for membranes treated by different salts are not the same, apparently due to the different ionic crosslinking contributions made by ions via interaction or swelling.

Similarly, the separation factors, as shown in Table I, are not the same for membranes treated by different solutions. Only membranes treated by  $\text{BaCl}_2$  and  $\text{ZnSO}_4$  solutions display an increase in selectivity, while the others show more or less reductions comparing to the untreated membrane. Still, membranes treated by metal solutions (except aluminum sulfate) show higher selectivity than those aged in pure water, clearly due to ionic crosslinking.

In order to compare the overall pervaporation performance, the PSI is calculated from Eq. (1) and given in Table II. As seen from this table, the PSI values of the treated membranes are significantly higher than the untreated one (except aluminum sulfate at  $25^\circ\text{C}$ ), indicating that ionic crosslinking makes the pervaporation separation process more efficient.

From the data in Tables I and II, several observations are also made:

**Table II. Pervaporation Separation Index (PSI) of Ionically Crosslinked Latex Membranes<sup>a</sup>**

Treatment	PSI $\times 10^{-2}$ <sup>b</sup> ( $25^\circ\text{C}$ ) <sup>c</sup>	PSI $\times 10^{-2}$ ( $35^\circ\text{C}$ )
Non	5.95	4.23
$\text{H}_2\text{O}$	3.49	4.20
$\text{NiSO}_4$	7.34	6.61
$\text{NaOH}$	8.29	8.78
$\text{Al}_2(\text{SO}_4)_3$	5.23	6.45
$\text{BaCl}_2$	14.35	10.53
$\text{ZnSO}_4$	18.02	12.97
$\text{SrO}(\text{NO}_3)_2$	11.72	10.75
$\text{CuSO}_4$	16.78	13.51
$\text{CuCl}_2$	8.40	9.09

<sup>a</sup> Membrane treatment time: 7 days. Feed composition: 95 wt % ethanol.

<sup>b</sup> PSI unit: g/m h.

<sup>c</sup> Feed temperature during pervaporation.

1. The latex membrane treated with  $\text{CuSO}_4$  exhibits the highest permeability at both feed temperatures, which also maintains a high selectivity. The membrane had a high pervaporation separation efficiency at both feed temperatures.
2. The latex membrane treated with  $\text{ZnSO}_4$  has the highest selectivity and PSI.
3. Membrane treated by  $\text{NaOH}$  has a slight reduction in selectivity. Its superior performance to some other multivalent ions may be due to the higher concentration of  $\text{Na}^+$  in the membrane, which comes from a higher degree of neutralization of the pendant carboxyl groups by the alkali.
4. Latex membrane treated by  $\text{Al}_2(\text{SO}_4)_3$  has the lowest selectivity, possibly because of its difficulty in diffusing into the membrane, and performing the crosslinking.

By comparing the permeability and separation factor of membranes treated by  $\text{CuCl}_2$  and  $\text{CuSO}_4$ , shown in Table I, it is obvious that the ionic crosslinking is also affected by the type of anion. However, it is unable to correlate the type of cation or anion with its crosslinking behavior or the pervaporation properties. There is also no evidence showing that transition metal ions are better than the nontransitional, and the multivalent ions are more effective than the single-valent ones, in terms of separation efficiency enhancement.

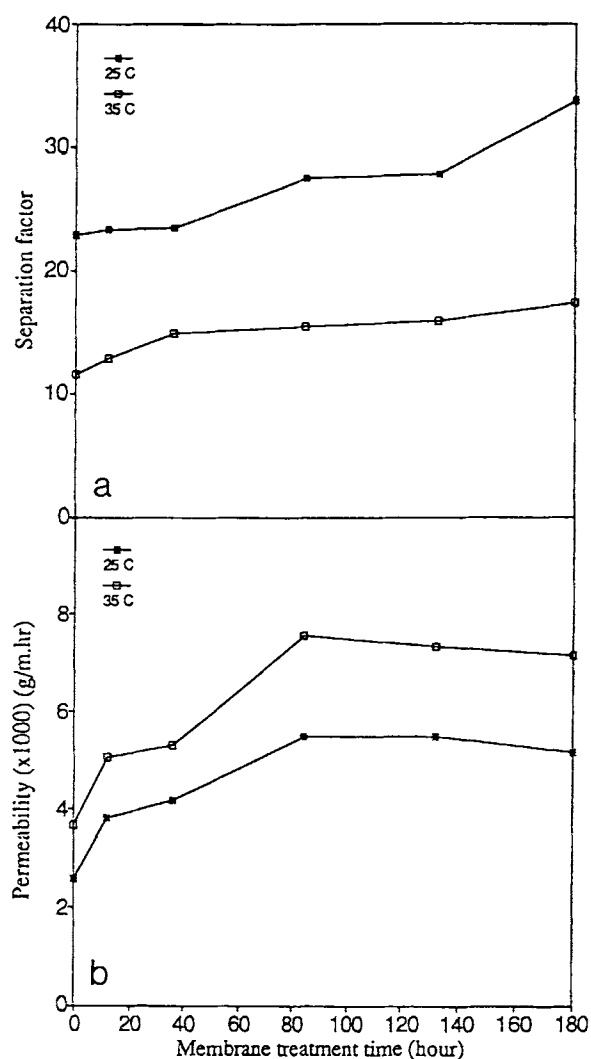
As shown in Table I, increasing feed temperature leads to an increase in permeability and a decrease in selectivity. But from Table II, it is shown that some membrane systems are better operated at higher feed temperature, e.g., the membranes treated by  $\text{CuCl}_2$  or  $\text{Al}_2(\text{SO}_4)_3$ , as suggested by their higher PSI at higher temperature.

### Effect of Membrane Treatment Time

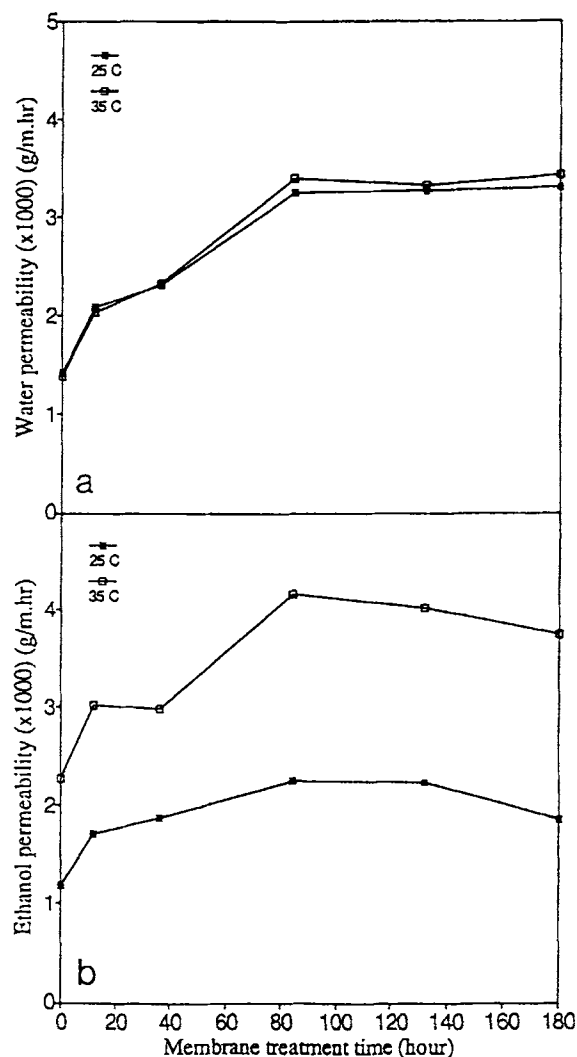
Since the ionic crosslinks in this experiment are obtained by treating the latex membrane in a salt solution, the degree of neutralization of pendant carboxyl groups, thus the degree of crosslinking, is also controlled by the membrane treatment time. It is demonstrated earlier that the degree of ionic crosslinking increases with increasing treatment time, before finally reaching a saturation point.<sup>5</sup> Ionic crosslinks are obtained after the ions diffuse into the film and interact with the carboxyl groups. For latex membranes, the crosslinking may take place first in the boundary region, because  $-\text{COOH}$  groups tend to distribute on the surface of the latex

particles and this boundary region is less dense than the polymer bulk, followed by the crosslinking of the carboxyl groups in the polymer bulk. Figure 1 gives the pervaporation properties of  $ZnSO_4$  treated membrane as a function of treatment time. Figure 1 indicates that permeability and separation factor both increase with increasing treatment time. The biggest change appears during the 0–80 h period, after which a saturation point is reached and the membrane exhibits no significant change in its properties.

From Figure 2 in which the individual permeability is plotted as a function of membrane treatment time, it is found that water and ethanol permeability increase with treatment time. But the wa-



**Figure 1** Pervaporation properties of ionically cross-linked membrane as a function of treatment time. Feed composition: 95 wt % ethanol. (a) Separation factor and (b) permeability.

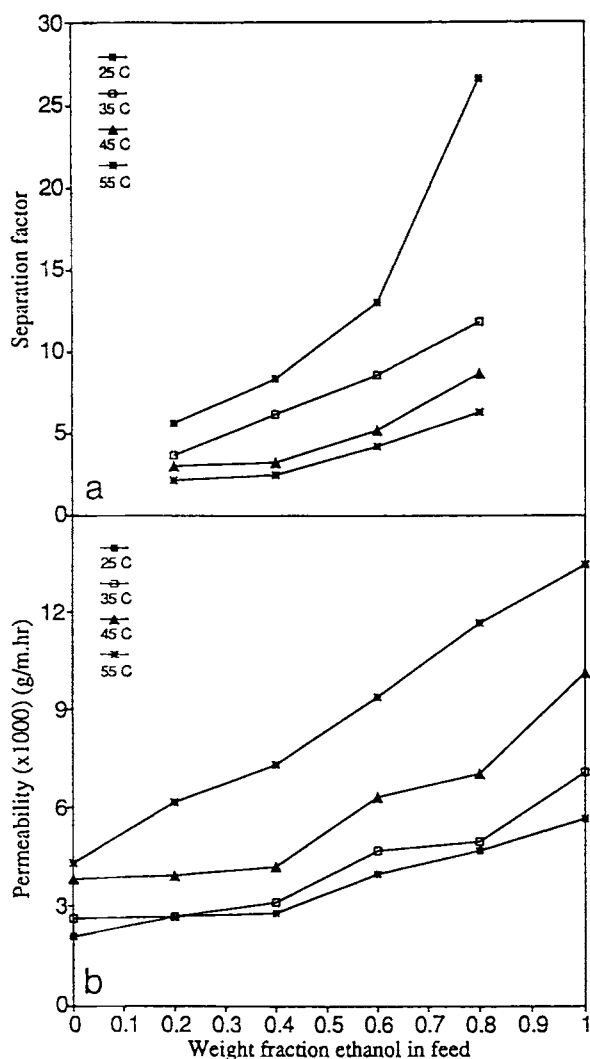


**Figure 2** Individual permeability vs. membrane treatment time. Feed composition: 95 wt % ethanol. (a) Water permeability and (b) ethanol permeability.

ter permeability is raised in a larger extent, which is responsible for the increase in separation factor, due to stronger interactions between the membrane and water after the treatment.

#### Effect of Feed Concentration and Temperature

Figure 3 presents pervaporation properties as a function of feed composition and temperature. The permeability and selectivity all increase with increasing ethanol concentration in feed. The increase in permeability with increasing ethanol concentration is due to a greater swelling of the membrane caused by ethanol. Figure 4 presents the individual permeability as a function of feed composition and temperature. In Figure 4, both water and ethanol

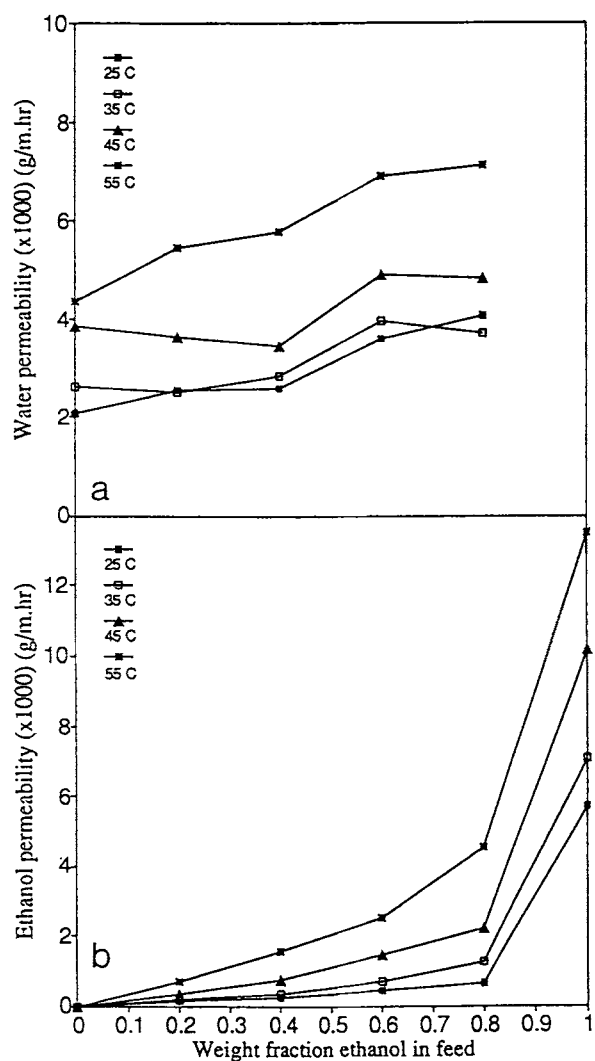


**Figure 3** Pervaporation properties of ionically cross-linked latex membrane vs. feed composition at different temperatures. Membrane treatment:  $\text{ZnSO}_4$  solution for 7 days. (a) Separation factor and (b) permeability.

permeability increase with increasing ethanol content. However, ethanol permeability increases sharply only at very high ethanol concentration. The larger water permeability is due to its smaller molecule size and greater interaction with the ionically crosslinked membrane, compared with ethanol. The permeation ratios given in Figure 5 show nonideal permeation. This figure indicates that water permeation is enhanced by the presence of ethanol, due to the increasing membrane swelling; while the ethanol permeation is retarded by the presence of water, for the interaction between water and the membrane is stronger.

As expected, raising feed temperature leads to a

higher permeability and a lower selectivity, as shown in Figure 3. Feed temperature and the permeability of individual components is processed using the Arrhenius relationship, from which the activation energy ( $E$ ), pre-exponential factor ( $A$ ), and the regression coefficient of determination ( $R^2$ ) are calculated and listed in Table III. From the  $R^2$  values in Table III, it is seen that the Arrhenius equation is more accurate in describing the temperature effect on ethanol permeability than water permeability. Since the pre-exponential factor is related to the plasticizing effect,<sup>10</sup> the larger  $A$  values in Table III suggest that ethanol contributes more to the membrane plasticization, in other words, it causes a



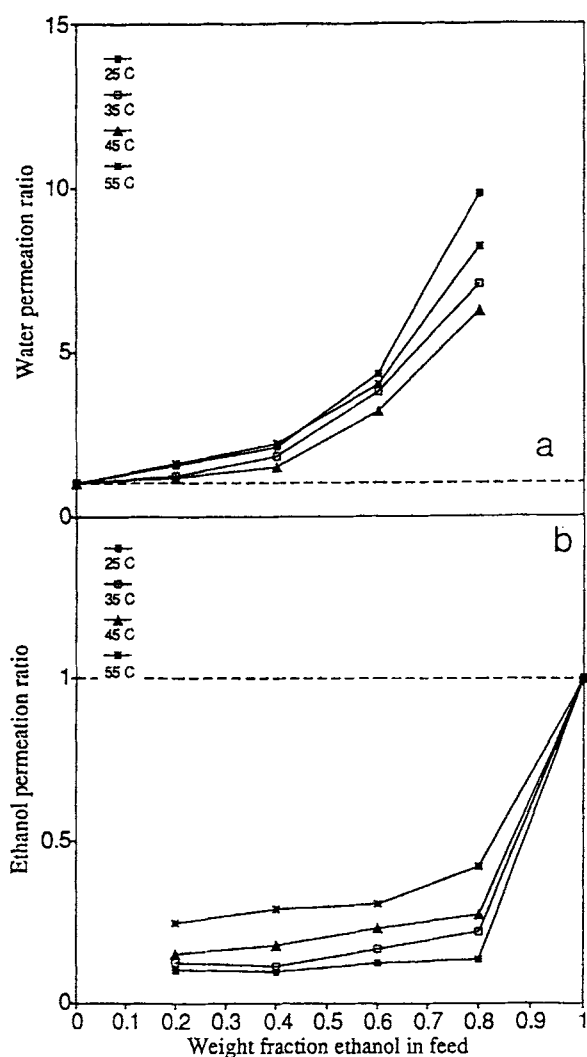
**Figure 4** Individual permeability vs. feed composition at different temperatures. Membrane treatment:  $\text{ZnSO}_4$  solution for 7 days. (a) Water permeability and (b) ethanol permeability.

**Table III. Parameters Calculated from Arrhenius Correlation<sup>a</sup>**

Ethanol Weight Fraction in Feed	Ethanol			Water		
	$E_e$ (kcal/mol)	$\ln A$	$R^{2b}$	$E_w$ (kcal/mol)	$\ln A$	$R^2$
0.0				5.09	2.41	0.971
0.2	11.33	9.94	0.973	5.08	2.48	0.858
0.4	13.35	13.92	0.971	5.01	2.41	0.865
0.6	11.85	12.17	0.995	4.20	1.40	0.928
0.8	12.81	14.21	0.998	3.74	0.67	0.736
1.0	5.72	4.45	0.989			
average	11.01			4.62		

<sup>a</sup> Membrane treatment time: 7 days. Feed composition: 95 wt % ethanol.

<sup>b</sup> Regression coefficient.



**Figure 5** Individual permeation ratio vs. feed composition in feed. Membrane treatment:  $ZnSO_4$  solution for 7 days. (a) Water permeation ratio and (b) ethanol permeation ratio.

greater membrane swelling compared to water. The activation energies in Table III show that the energy barrier for the permeation of water is much lower than for ethanol, thus is preferentially permeated. The higher activation energy for ethanol permeation is due to its larger molecule size and weaker interaction with the membrane.

## CONCLUSIONS

It is demonstrated by this study that, through proper choice of ionic crosslinking for a carboxyl containing latex membrane, the permeability can be raised without losing its selectivity. The ionic crosslinking also increases the pervaporation separation efficiency. The permeability and selectivity of ionically crosslinked latex membranes increase with increasing ethanol content in feed. Both water and ethanol permeation are nonideal. Arrhenius relationship can be used to describe ethanol permeability, but error occurs when used for water permeability.

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## LIST OF SYMBOLS

A	pre-exponential factor in Arrhenius function
$E_p$	activation energy of permeation
P	permeability
T	membrane temperature in Kelvin scale
$\alpha$	selectivity
$\theta$	permeation ratio

**Subscript**

i, j type of feed component

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