

# Preparation of PVA Membranes Containing $\beta$ -Cyclodextrin Oligomer (PVA/CD membrane) and Their Pervaporation Characteristics for Ethanol/Water Mixtures

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## SYNOPSIS

Poly(vinyl alcohol) (PVA) membranes were modified by introducing  $\beta$ -cyclodextrin ( $\beta$ -CD) oligomer, which has an inclusion ability sensitive to size, structure, and hydrophilicity of the guest molecule. The modified membranes (PVA/CD membrane) were prepared by casting of the aqueous solutions of PVA and  $\beta$ -CD oligomer. The CD oligomer was immobilized in the membranes by cross-linking with glutaraldehyde. The cross-linking times were 1 and 8 h. The content of CD in the membranes was 33 wt %. The effects of CD on the pervaporation characteristics for water/ethanol were investigated by comparisons with those of the cross-linked PVA membranes. For the 1 h cross-linked membranes, CD increased both the water permeation rate and selectivity at lower ethanol concentrations in the feed. At higher ethanol concentrations, CD increased the water selectivity, but it decreased the water permeation rate. For the 8 h cross-linked membranes, at lower ethanol concentrations, CD increased the water permeation rate, but the water selectivity through the PVA/CD membrane was almost equal to that of the PVA membrane. At higher ethanol concentrations, CD increased the water selectivity and decreased the water permeation rate. These effects of CD can be interpreted in terms of the inclusion strength in the cavity and the reduction of the cross-linking density of the PVA phase in the membranes. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Cyclodextrins (CD) are cage-shaped oligosaccharides that have a hydrophobic cavity of several angstroms diameter. The cavity includes many kinds of compounds and forms inclusion complexes.<sup>1</sup> The inclusion equilibria are sensitive to the size, structure, and hydrophilicity of the guest molecule. CD appear to be good candidate materials for the "molecular recognizing" separation processes.

There have been a few reports on the use of CD for separation membranes. Lee<sup>2</sup> prepared cellulose membranes containing CD and investigated their pervaporation characteristics for mixtures of benzene derivatives. He reported that the selectivity was improved by the existence of CD in the membranes.

As pointed out by Hirai et al.,<sup>3</sup> however, there was a possibility that CD would be dissolved into the feed liquid during the experiments. They prepared cross-linked CD membranes and utilized them in dialysis. They also found that CD were effective for the separation of various kinds of liquid mixtures.<sup>3,4</sup> Ishihara et al.<sup>5</sup> introduced the CD groups into polymeric membranes by chemical methods and utilized them for the optical separation of amino acids.

This study demonstrates the modification of PVA membrane by the addition of the CD oligomer. Recently, many authors have studied pervaporation of ethanol/water through hydrophilic membranes such as cross-linked poly(vinyl alcohol) (PVA) membranes.<sup>6</sup> It is known that ethanol as well as water forms an inclusion complex with CD and the inclusion of ethanol is much stronger than that of water because the cavity of CD is hydrophobic.<sup>1,7</sup> Therefore, the selectivity of PVA membranes can be improved by the modification of CD by using the dif-

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ference in the inclusion strength between water and ethanol. A CD oligomer of relatively low molecular weight ( $< 10,000$ ) has become of interest recently because of its much greater solubility in water and better inclusion ability compared to the parent CD monomer.<sup>8</sup>

In this study, a convenient and simple method of preparation of PVA membranes containing cyclodextrin (PVA/CD membranes) is proposed; based on their pervaporation characteristics for the water/ethanol mixture. To investigate the effects of the use of the CD oligomer on the pervaporation membranes, the performances of the PVA/CD membranes were compared with those of the cross-linked PVA membranes.

## EXPERIMENTAL

### Material

Poly(vinyl alcohol) was supplied by Kuraray Co. (Kuraray Poval 117H; the degree of saponification is more than 99% and the average degree of polymerization is 1700).  $\beta$ -Cyclodextrin oligomer cross-linked by epichlorohydrin was purchased from Katayama Chemical Co. (average degree of polymerization is around 3). Glutaraldehyde was used as a cross-linking reagent for PVA and sulfuric acid as a catalyst. Commercially supplied ethanol was used for the pervaporation experiments without further purification.

### Membrane Preparation

A definite amount of the mixture of PVA and CD oligomer (10 wt % in total) was dissolved in hot

water at 100°C. After several hours stirring, the crystalline region was dissolved and a transparent solution was obtained. The solution was cast onto a glass plate and the solvent was evaporated in a desiccator at room temperature for 1 week. The membrane was cross-linked by 0.01% glutaraldehyde aqueous solution with 10% Na<sub>2</sub>SO<sub>4</sub> and 0.1 N H<sub>2</sub>SO<sub>4</sub> at room temperature. The cross-linking time was changed from 1 to 8 h. A homogeneous and dense membrane with a thickness of  $100 \pm 5 \mu\text{m}$  was obtained.

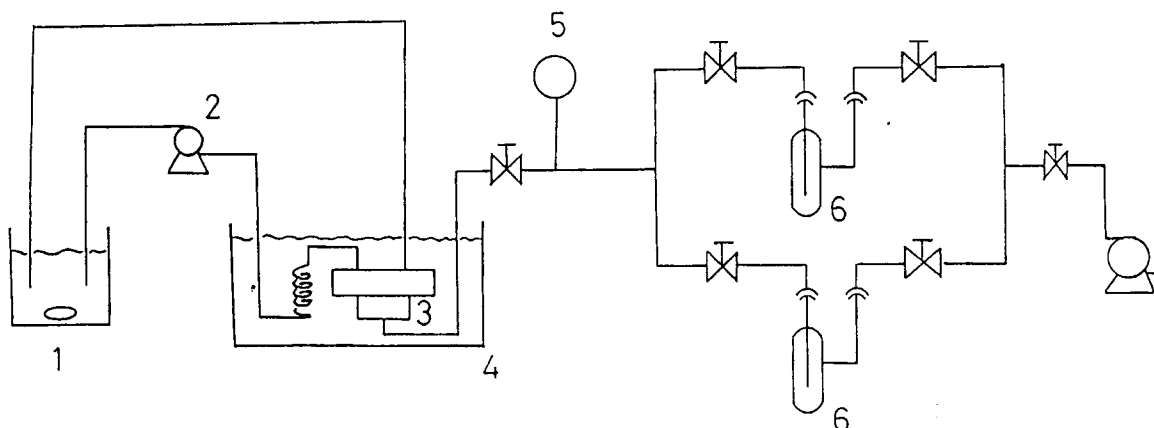
The PVA/CD ratio was 2/1 (CD content was 33%). The membrane in which the CD content was more than 50% was easily broken and could not be used for the pervaporation experiment. The PVA membrane was prepared by a similar method.

### Pervaporation

The schematic diagram of the pervaporation apparatus is shown in Figure 1. The membrane was positioned in the stainless-steel permeation cell. The temperature of the cell was kept at 30.0°C by a thermostat. The liquid mixture of ethanol and water was fed from the reservoir to the cell and recycled to the reservoir. The permeation side of the membrane was evacuated by a rotary vacuum pump to the pressure of 0.1 Torr. The permeate was collected in the glass trap cooled in a liquid nitrogen bath. The permeation rate was calculated from the weight change of the trap. The composition of the permeant was analyzed by gas chromatography (Shimadzu GC-14A).

### Dissolution of CD from Membranes

To evaluate the dissolution of CD from the PVA/CD membranes, the weight changes of the mem-



**Figure 1** Schematic diagram for the experimental apparatus: (1) feed tank; (2) liquid pump; (3) permeation cell; (4) constant temperature bath; (5) pressure gauge; (6) cold trap; (7) vacuum pump.

branes before and after immersion in water were measured. Table I shows the relative membrane weight to the dry weight after casting (= 100). All the weights were measured after drying in an oven at 60°C for 24 h.

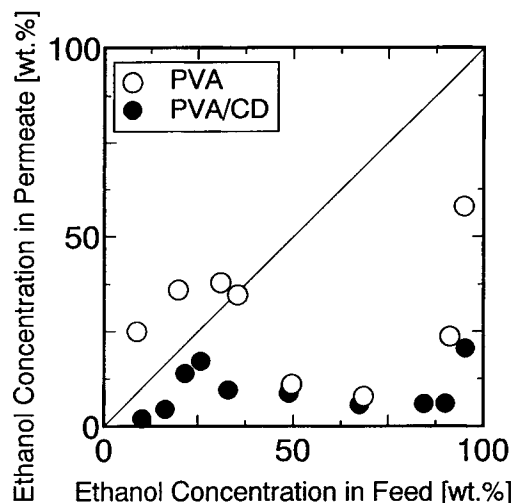
During cross-linking, the weights of the PVA/CD membranes decreased by 1–2%; a small portion of CD oligomer in the membrane had dissolved into water. However, the weights of the PVA/CD membranes remained almost constant after 1 and 3 days immersion trials; more than 90% of the CD oligomer remained in the PVA/CD membranes. Without cross-linking, the weight of the PVA/CD membrane decreased by more than 20% even after 1 day immersion; almost 70% of the CD oligomer in the non-cross-linked PVA/CD membrane had dissolved into water. The weight loss of the PVA/CD–monomer membrane was significant in spite of the cross-linking. These results demonstrated that both the cross-linking of PVA and the use of the CD oligomer were essential to immobilize CD in the PVA/CD membranes.

## RESULTS AND DISCUSSION

### One Hour Cross-linked Membranes

Figure 2 shows the separation diagram of the pervaporation. The water selectivity was increased by the addition of CD, especially at lower (< 35%) and higher (> 85%) ethanol concentrations in the feed.

The effects of CD on the permeation rates are shown in Figures 3 and 4. At lower ethanol concentrations (< 35%), the water permeation rate was greatly increased by CD, whereas the ethanol permeation rate was decreased by CD. At mid-ethanol



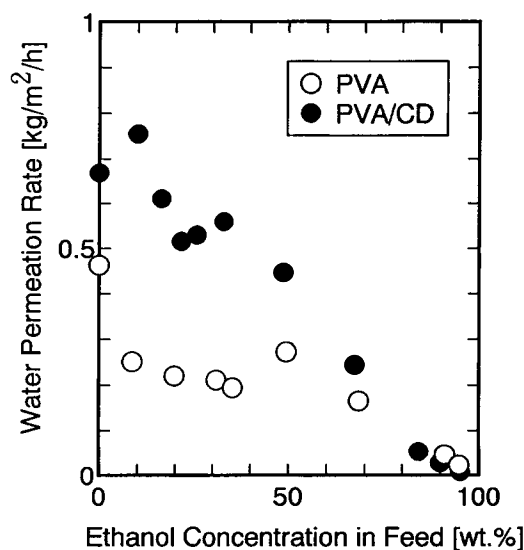
**Figure 2** Separation diagram for 1 h cross-linked membranes.

concentrations (50–70%), the water permeation rate was slightly increased, whereas the ethanol rate was slightly decreased by CD. At higher ethanol concentrations (> 85%), the ethanol permeation rate was greatly decreased, and the water rate was slightly decreased by CD.

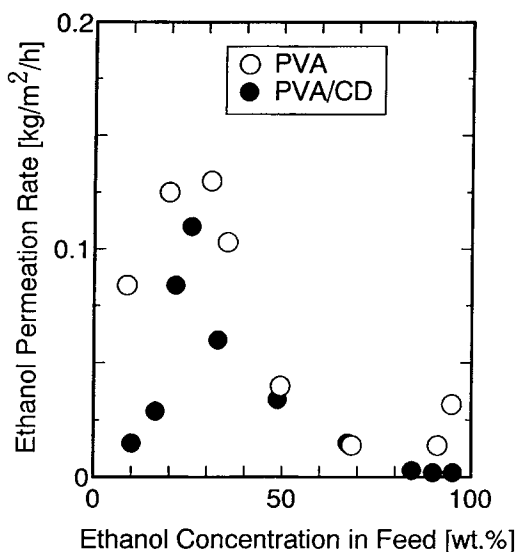
The increase in the water selectivity by CD can be explained in terms of the inclusion in the cavity of CD. It is known that both water and ethanol can form an inclusion complex with CD, and the inclusion of ethanol is stronger than that of water because of the stronger interaction between ethanol and the hydrophobic cavity of CD.<sup>1,7</sup> The stronger inclusion

**Table I** Weight Changes of the Membranes

Cross-linking Time (h)	Cross-linking		Immersion	
	Before	After	1 Day	3 Days
<b>PVA</b>				
0	100	—	99.4	99.7
1	100	101	100	100
8	100	103	103	103
<b>PVA/CD-oligomer</b>				
0	100	—	78.1	76.2
1	100	97.3	95.8	95.8
8	100	99.0	97.9	97.8
<b>PVA/CD-monomer</b>				
1	100	85.8	77.9	



**Figure 3** Permeation rate of water through the 1 h cross-linked membranes.



**Figure 4** Permeation rate of water through the 1 h cross-linked membranes.

of ethanol should decrease the mobility of ethanol in the membrane and, on the other hand, the weaker inclusion of water (the interaction of the cavity of CD and water should be weaker than that between PVA and water) should increase the mobility of water. The smaller size of the water molecule should also increase the water permeation rate in the cavity. Thus, the inclusion effect should increase the water permeation rate and decrease the ethanol permeation rate and, consequently, increase the water selectivity.

However, to explain the concentration dependence of the effects of CD on the permeation rates, the cross-linking density of the PVA phase should be considered as well; the addition of CD should decrease the cross-linking density of the PVA phase in the membrane because the existence of CD in the PVA network should retard the cross-linking reaction. The lower cross-linking density increases the permeation rates of both components and decreases the selectivity because of greater swelling. The relative weight of the effects of the inclusion and the lower cross-linking density should depend on the feed composition, i.e., swelling of the PVA phase in the membrane.

At lower ethanol concentrations, where the swelling of the PVA phase in the membrane is large, both ethanol and water permeate considerably and freely in the PVA phase of the membranes; the effect due to the difference in the cross-linking density of the PVA phase was small. The decrease in the ethanol permeation rate by the addition of CD

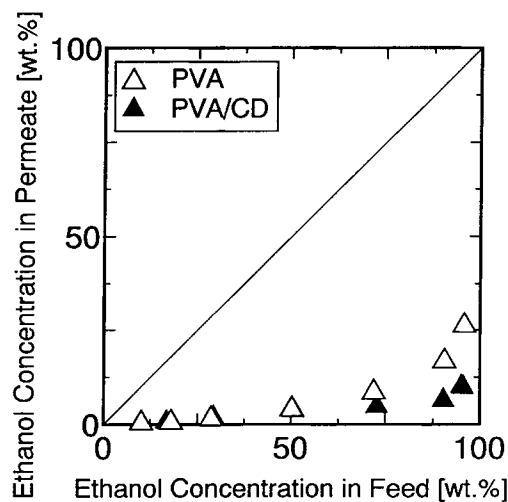
should be due mainly to the strong inclusion of ethanol, and, on the other hand, the increase in the water permeation rate should be due to the weaker inclusion of water.

With an increase in the ethanol concentration, the swelling of the PVA phase in the membrane was decreased. At mid-ethanol concentrations, the permeation rates should depend on the cross-linking density more strongly than at low ethanol concentrations. In this range, the increase in the water permeation rate can be explained by both the weaker inclusion of water and the lower cross-linking density of the PVA/CD membrane. The increase in the ethanol permeation rate due to the lower cross-linking density should be compensated by the decrease due to the stronger inclusion; the ethanol permeation rate appears to be slightly decreased.

At higher ethanol concentrations, where the swelling is considerably smaller, the difference in the cross-linking density would not affect the permeation rates. In this range of ethanol concentrations, it is considered that most of the cavities of CD are occupied by ethanol; this should decrease the accessible cavities for water and, therefore, decrease the permeation rate of water. The ethanol permeation rate should also be decreased because of the stronger inclusion.

#### Eight Hours Cross-linked Membranes

Figure 5 shows the separation diagram for the 8 h cross-linked membranes. Both of the 8 h cross-linked membranes were more water selective than



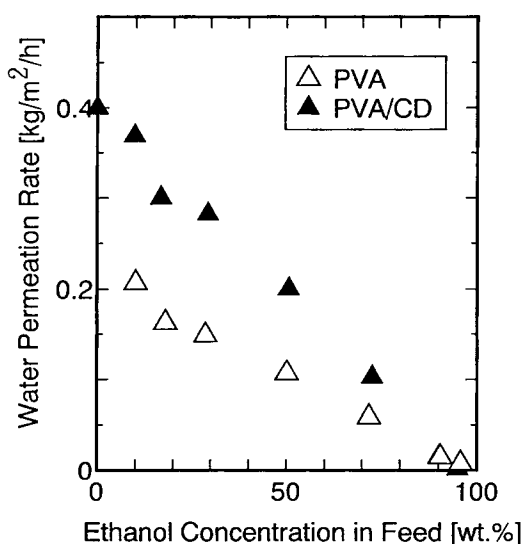
**Figure 5** Separation diagram for the 8 h cross-linked membranes.

were the 1 h cross-linked membranes. For the 8 h cross-linked membranes, the water selectivity at low ethanol concentrations in the feed (< 50%) was not changed by CD. At higher ethanol concentrations (> 70%), the water selectivity was greatly increased by CD.

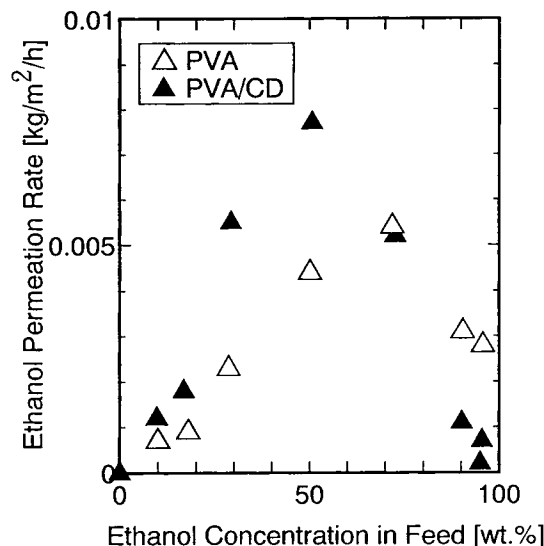
The effects of CD on the permeation rates are shown in Figures 6 and 7. At lower ethanol concentrations, both permeation rates of water and ethanol were increased by CD. At higher ethanol concentrations, the ethanol permeation rate was greatly decreased by CD and the water permeation rate was slightly decreased by CD.

These results for the highly (8 h) cross-linked membranes can also be interpreted in terms of the inclusion and the cross-linking density. Since the swelling of the highly cross-linked membranes should be rather small even at low ethanol concentrations, the effect of the cross-linking density on the permeation rates should be as large as the inclusion effect. The increase in the water permeation rate can be interpreted by the lower cross-linking density of the PVA phase in the PVA/CD membrane and the weaker inclusion of water as well. The increase in the ethanol permeation rate would be caused by the lower cross-linking density, in spite of the stronger inclusion.

At higher ethanol concentrations, the effects of CD were the same as those for 1 h cross-linked membranes; therefore, these effects can be explained by the same mechanism for the 1 h cross-linked membranes at higher ethanol concentrations.



**Figure 6** Permeation rate of water through the 8 h cross-linked membranes.



**Figure 7** Permeation rate of ethanol through the 8 h cross-linked membranes.

## CONCLUSIONS

Poly(vinyl alcohol) membranes containing  $\beta$ -cyclodextrin oligomer of 33 wt % (PVA/CD membrane) were prepared, and the pervaporation characteristics were studied for water/ethanol mixtures. The dissolution of CD from the PVA/CD membrane was prevented by the cross-linking (1 and 8 h) of the PVA phase with glutaraldehyde and the use of the CD oligomer.

For the 1 h cross-linked membranes, at lower ethanol concentrations, CD increased the water permeation rate and the water selectivity. At higher ethanol concentrations, CD slightly decreased the water permeation rate, but greatly increased the water selectivity. The ethanol permeation rate was decreased by CD in the full range of the feed composition. For the 8 h cross-linked membranes, at lower ethanol concentration, CD increased both permeation rates of water and ethanol; the water selectivity through the PVA/CD membrane was almost equal to that of the PVA membrane. At higher ethanol concentrations, CD increased the water selectivity greatly, but slightly decreased the water permeation rate.

The increase in the water selectivity by CD can be interpreted by the difference in the inclusion strength between water and ethanol in the cavity of CD: the stronger inclusion of ethanol in the cavity of CD would decrease the mobility and permeation rate of ethanol, and the weaker interaction between water and CD, weaker than that between water and

PVA, would increase the permeation rate of water. These effects of CD on the permeation rates depend on the feed composition; the dependence can be interpreted by the lower cross-linking density of the PVA phase in the PVA/CD membranes, due to the hindrance of the cross-linking reaction of PVA by CD.

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