Pervaporation of Water/Alcohol Mixtures Through the PVA Membranes Containing Cyclodextrin Oligomer

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SYNOPSIS

Pervaporation through the PVA membrane containing β-cyclodextrin oligomer (PVA/CD membrane) was performed for the mixtures of water/ethanol, water/1-propanol, and water/2-propanol. At higher alcohol concentrations, the water selectivities were greatly increased by CD for all the mixtures, in the order of 2-propanol/water > 1-propanol/water > ethanol/water. The water permeation rate was decreased by CD, and the alcohol permeation rate was decreased much more for each mixture. At lower alcohol concentrations, the water selectivity for 1-propanol/water was slightly increased by CD, and that for 2-propanol/water was scarcely affected, whereas that for ethanol/water was greatly increased. The water permeation rate was increased by CD for each mixture, and the relative increases in the water rates for propanols/water were smaller than that for ethanol/water. The permeation rate of 1-propanol as well as that of ethanol was decreased by CD, but the rate of 2-propanol was increased. These effects of CD can be explained in terms of the inclusion strength. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cyclodextrins (CDs) are oligosaccharides with a hydrophobic cavity of several angstroms diameter. The cavity can form inclusion complexes with many kinds of substrate compounds.[1,2] The inclusion equilibria are sensitive to the size, structure, and hydrophilicity of the substrate molecules. Thus CDs have a potential for high performance separation processes.[3] In a previous article, a convenient and simple method of preparation of a poly(vinyl alcohol) (PVA) membrane containing β-cyclodextrin oligomer (the PVA/CD membrane) was reported and its pervaporation characteristics for ethanol/water mixture demonstrated.[4] The results showed that CD increased the water selectivity over the full range of the feed composition. CD also increased the water permeation rate and decreased the ethanol rate at lower ethanol concentrations. At higher ethanol concentrations, CD decreased both permeation rates, but the increase in the ethanol rate was much larger. These effects of CD can be explained mainly by the difference in the inclusion strength between water and ethanol. The mobility of ethanol in the cavity was decreased due to the stronger inclusion, whereas that of water was increased by the weaker inclusion. By using the difference in the inclusion strength, therefore, higher performances of pervaporation, both in selectivity and permeation rates of the weaker included component, can be realized through the PVA/CD membrane.

In the present work, the effect of the inclusion strength on the pervaporation characteristics was investigated by comparing the results for 1-propanol/water and 2-propanol/water with that of ethanol/water through the PVA/CD membrane. It is known that the inclusion equilibrium constants of propanols are much larger than that of ethanol as shown in Table I.[5] Because of the larger difference in the inclusion strength between water and propanols, a larger increase in the water selectivity as well as a larger increase in the water permeation

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Table I Relative Inclusion Strength of Short Chain Alcohols

Alcohol	Relative Inclusion Strength
Ethanol	1.2
1-Propanol	5.0
2-Propanol	7.9

Adapted from Buvari et al.[5]

rate would be expected by the addition of CD to the PVA membrane.

EXPERIMENTAL

Material and Membrane Preparation

Because details were reported in the previous article,[4] the procedure of the membrane preparation is only briefly mentioned here. PVA was kindly supplied by Kuraray Co. (Kuraray Poval 117H, degree of saponification > 99%, average degree of polymerization, 1700). The β-cyclodextrin oligomer cross-linked by epichlorohydrin (Fig. 1, purchased from Katayama Chemical Co.) had an average degree of polymerization of around 3. A definite amount of the mixture of PVA and CD oligomer, in which the CD content was 33 wt %, was dissolved in water at 373 K. The solution was cast onto a glass

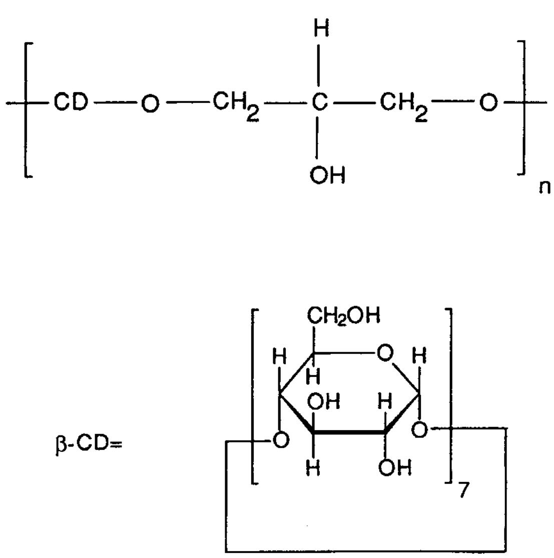

Figure 1 Structure of CD oligomer.

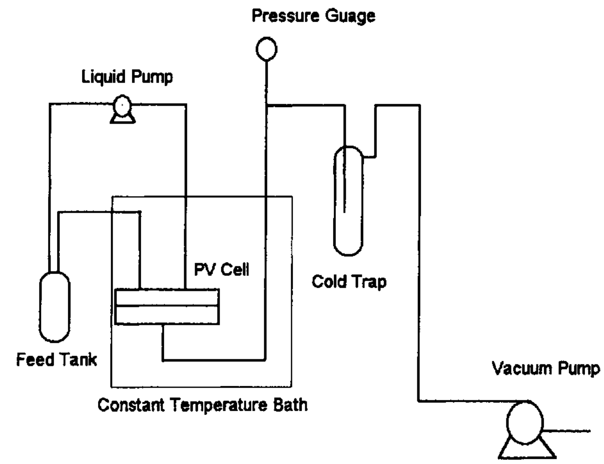

Figure 2 Schematic diagram of the pervaporation setup.

plate, and the solvent was evaporated in a desiccator at room temperature for a week. The membrane was cross-linked by 0.01% glutaraldehyde with 10% Na_2SO_4 and 0.1 N H_2SO_4 at room temperature. The cross-linking time was 1 h. The membrane thickness was 100 μm. The cross-linked PVA membrane was prepared by a similar method using a pure PVA solution.

Pervaporation

A schematic diagram for the pervaporation apparatus is shown in Figure 2. The membrane was positioned in the permeation cell, which was immersed in a constant temperature bath of 308 K. The permeation side of the membrane was evacuated by a rotary vacuum pump to the pressure of 0.1 Torr. At such a low downstream pressure, neither the selectivity nor permeation rate depends on the downstream pressure. The permeate was collected in the glass trap cooled in a liquid nitrogen bath for at least 4 h. 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).

RESULTS AND DISCUSSION

Separation Diagram

The separation diagrams for ethanol/water, 1-propanol/water, and 2-propanol/water are shown in Figures 3–5, respectively. Water selectivities for 1-propanol/water and 2-propanol/water through the

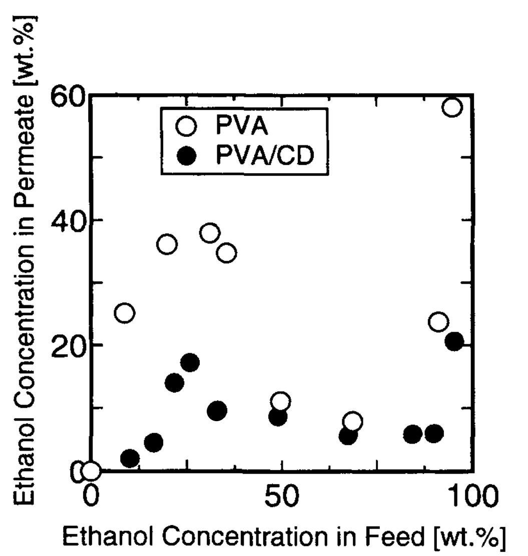

Figure 3 Separation diagram (ethanol/water).

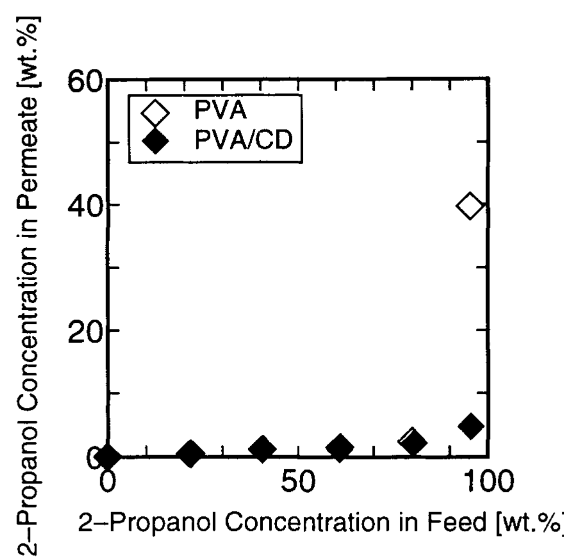

Figure 5 Separation diagram (2-propanol/water).

PVA membrane were much larger than that for ethanol/water over the whole range of feed composition. By the addition of CD, the water selectivity of ethanol/water was increased, especially at low (< 35%) and high (> 90%) ethanol concentrations in the feed. At higher alcohol concentrations, a larger increase in the water selectivity was observed for 1-propanol/water, and the increase for 2-propanol/water was still larger. At lower alcohol concentrations, the increase in the water selectivity by CD for 1-propanol/water was smaller than that for ethanol/water. The water selectivity for 2-propanol/water through the PVA/CD membrane was almost equal to that through the PVA membrane.

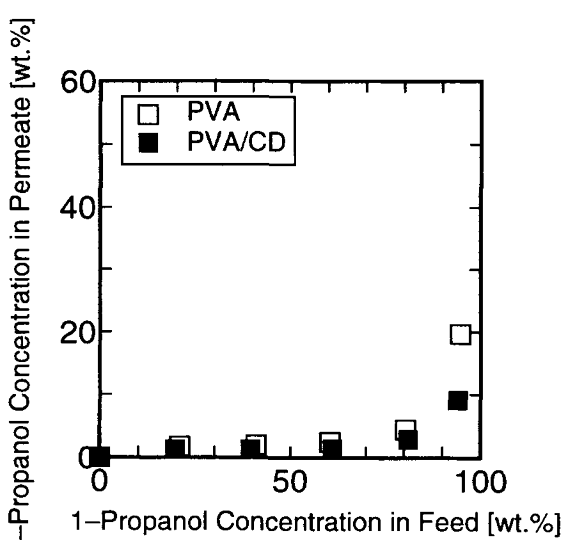

Figure 4 Separation diagram (1-propanol/water).

Permeation Rates

The permeation rates of water are shown in Figures 6–8 as a function of feed composition. For each mixture, the water permeation rate was decreased with an increase in the alcohol concentration in the feed. For an equal alcohol concentration, the water permeation rates through the PVA membrane for propanols/water were larger than that for ethanol/water, presumably because the amounts of sorption of

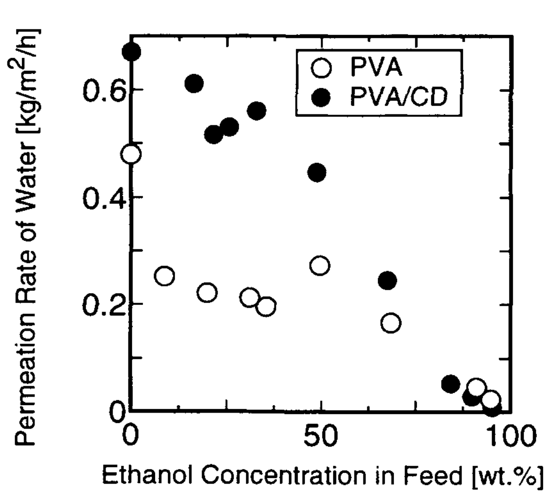

Figure 6 Permeation rate of water (water/ethanol).

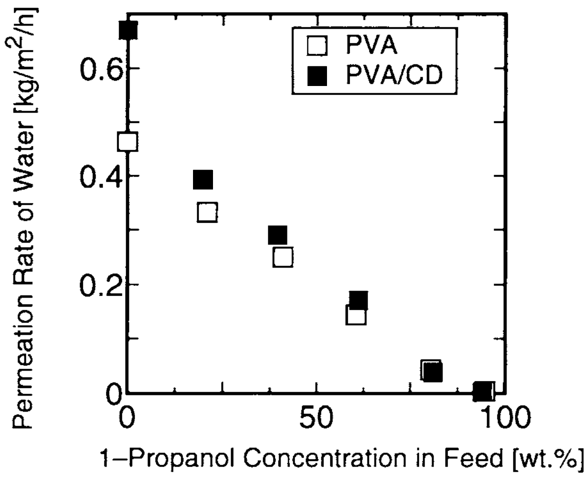

Figure 7 Permeation rate of water (water/1-propanol).

water in PVA should be larger for propanols/water than that for ethanol/water.

By the addition of CD, at lower alcohol concentrations (< 50%), the water permeation rates for propanols/water were slightly increased, whereas that for ethanol/water was greatly increased. The relative increase in the water permeation rate for 1-propanol/water was slightly larger than that for 2-propanol/water. The large increase in the water permeation rate by CD at lower ethanol concentrations for ethanol/water can be interpreted by the weaker inclusion of water[4]; the permeation of water through the cavity of CD is much larger than that in the PVA phase because the cavity is more hydrophobic and larger than the PVA network. However, for the mixtures of propanols/water, because the inclusion of propanols is much stronger than that of ethanol, the permeation of water through the cavity should be hindered largely by the included propanol molecules, which should spend longer time in the cavity.[6,7] Such a hindrance effect by ethanol should be much smaller than those by propanols because of the relatively weaker inclusion of ethanol. Therefore, the increases in the water rates for propanols/water were much smaller than that for ethanol/water. The hindrance effect should be larger by 2-propanol than by 1-propanol because the inclusion of 2-propanol is stronger, which should result in the smaller increase in the water rate for 2-propanol/water than for 1-propanol/water.

At higher alcohol concentrations, the increases in the water permeation rate became smaller in all cases. Where the alcohol concentration is more than 90%, the water rate was decreased by the addition of CD. These results also can be explained by the hindrance effect by the included alcohol molecules: at higher alcohol concentrations, this effect should be larger than at lower concentrations because more cavities of CD should be included by alcohol molecules. Even for ethanol/water, at higher ethanol concentrations, most of the cavities should be occupied by ethanol, which should reduce the water permeation rate. The order of the relative decrease in the water rate by CD was 2-propanol/water > 1-propanol/water > ethanol/water. This result indicates that the stronger inclusion of alcohol causes the larger decrease in the water rate.

The permeation rates of alcohols are shown in Figures 9–11. Each alcohol rate showed a maximum value (at 20% for ethanol and for 1-propanol, at 40% for 2-propanol). For the PVA membrane, the rate of ethanol was largest, which is more than 10 times larger than that of 1-propanol. The rate of 2-propanol was smallest. By the addition of CD, the permeation rate of 1-propanol as well as that of ethanol was decreased at lower alcohol concentrations. The relative decrease in the rate of 1-propanol was smaller than that of ethanol. The permeation rate of 2-propanol was increased by CD. At higher alcohol concentrations, the permeation rates of all the alcohols were greatly decreased by CD. The relative decreases in the alcohol rates at higher concentrations were much larger than that of water. The order of decrease was 2-propanol > 1-propanol > ethanol.

The decrease in the alcohol permeation rate can be interpreted by the strong inclusion of alcohols that should reduce the mobility in the cavity of CD.[4] However, the stronger inclusion, on the other hand, should increase the amount of sorption in the mem-

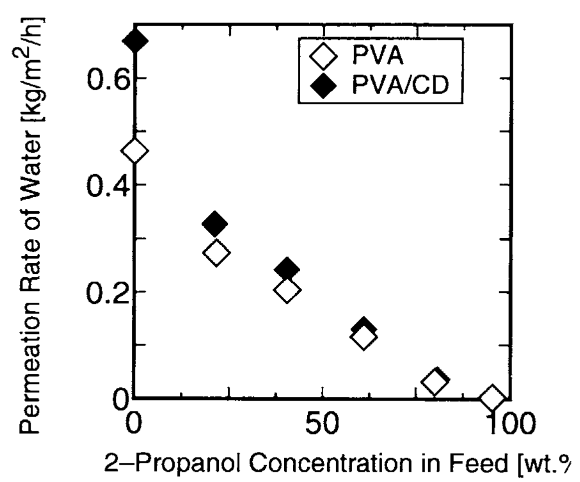

Figure 8 Permeation rate of water (water/2-propanol).

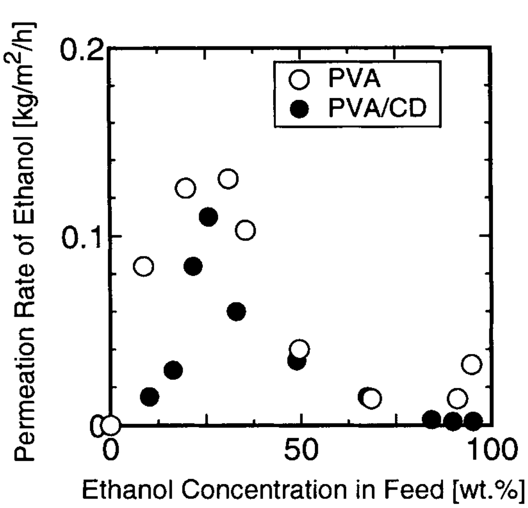

Figure 9 Permeation rate of ethanol.

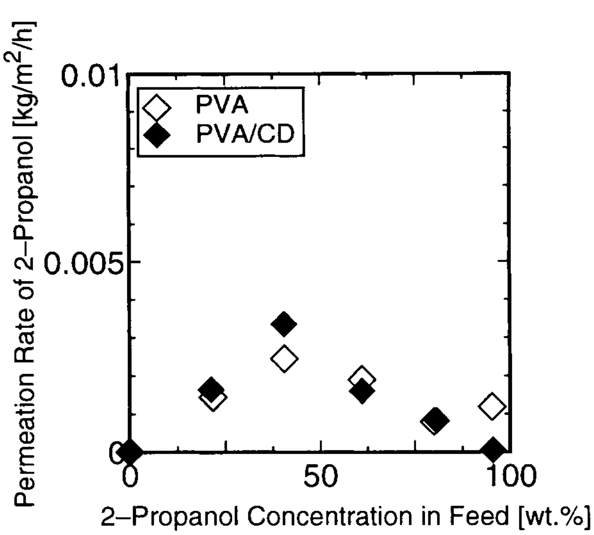

Figure 11 Permeation rate of 2-propanol.

brane. For 2-propanol at lower concentrations, because of the strongest inclusion of the three alcohols studied, the amount of the sorption in the membrane should be greatly increased by CD, and therefore the permeation rate of 2-propanol should be increased, despite the larger decrease in the mobility in the cavity. The decrease in the rate of 1-propanol by CD, which is smaller than that of ethanol, is that the decrease in the mobility of 1-propanol is compensated for by the increase in the amount of sorption. For ethanol, the increase in the amount of sorption should be so small that the decrease in the mobility should result in the larger decrease in the permeation rate. At higher alcohol concentrations,

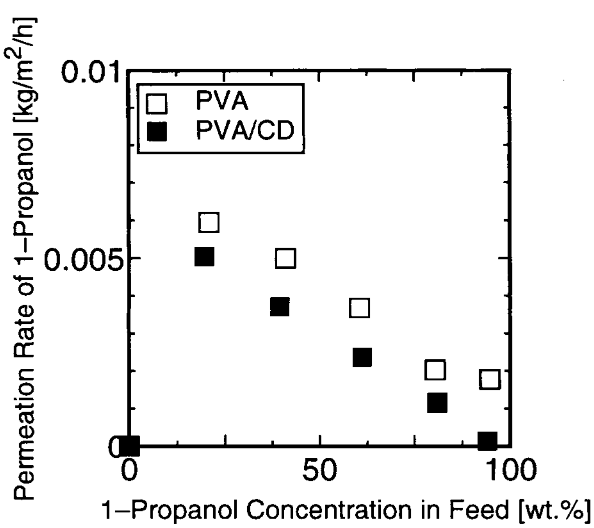

Figure 10 Permeation rate of 1-propanol.

because of more cavities of CD being included by alcohol molecules, the hindrance effect on the alcohol permeation through the CD cavity by the included alcohol molecules should become significant. This effect should be the reason for the decreases in the rates of all the alcohols at higher concentrations. The hindrance effect should be stronger by more strongly included alcohols, and therefore, the relative decreases in the permeation rates are larger for propanols at higher alcohol concentrations.

CONCLUSIONS

The stronger inclusion of propanols in the cavity of CD resulted in a larger increase in the water selectivity only at higher alcohol concentrations.

At lower alcohol concentrations, the water selectivity was slightly increased for 1-propanol/water by CD, and that for 2-propanol/water was scarcely affected, whereas the water selectivity for ethanol/water was greatly increased. The water permeation rates for propanols/water were increased by CD as well as that for ethanol/water. The relative increase was much smaller for propanol/water than for ethanol/water, which should be due to the hindrance on the water permeation by the strongly included propanol molecules in the CD cavities. The permeation rate of 1-propanol as well as that of ethanol was decreased by CD, but the relative decrease in the rate of 1-propanol was smaller than that of ethanol. The rate of 2-propanol was increased by CD at lower concentrations. A smaller decrease or increase in the permeation rates of propanols can be explained by an increase in the amount of sorption caused by the stronger inclusion of propanols.

At higher alcohol concentrations, although the water permeation rate was decreased by CD, the permeation rates of the propanols were decreased much more. These decreases can be explained by the larger hindrance effect of the included alcohol molecules, presumably due to most of the cavities being occupied by included alcohols.

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