Sorption Equilibria and Diffusion Coefficients of Ethanol and Water in the PVA Membranes Containing Cyclodextrin

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SYNOPSIS

Effects of cyclodextrin (CD) on the pervaporation characteristics for water/ethanol through the PVA/CD membranes (PVA membranes containing β-CD oligomer) have been investigated in terms of sorption equilibria and diffusion coefficients based on the sorption–diffusion theory. The increase in water selectivity through the pervaporation by CD was due mainly to the changes in the diffusion coefficients by CD, which depended on the feed composition and the cross-linking time. The water selectivity through the sorption equilibria was not increased by the addition of CD, and the ethanol-sorption amount was increased by CD. These effects of CD were interpreted by the inclusion strength in the CD cavity and the cross-linking density of the PVA phase. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cyclodextrins (CD) are oligosaccharides with a cavity of several angstroms diameter, which can include many kinds of compounds and thus form inclusion complexes.[1] Since inclusion equilibria are sensitive to the physical properties of guest molecules such as size, structure, and hydrophilicity, CD is considered to be a hopeful candidate material for high-performance separation processes.[2]

In a previous paper,[3] we proposed a new method for preparation of cross-linked poly(vinyl alcohol) membranes containing β-CD oligomer (PVA/CD membranes) and reported the effects of the CD oligomer on the pervaporation characteristics for ethanol/water mixtures. The water selectivity was increased by CD in the full range of the feed composition. The permeation fluxes were also changed by CD depending on the feed composition and the cross-linking time. These results could be interpreted by the relative strength of inclusion of the permeants in the CD cavity and the cross-linking density of the PVA phase in the membranes.

In this article, we report a further investigation on the effects of CD on the pervaporation charac-

teristics in terms of sorption equilibria and diffusion coefficients based on the sorption–diffusion theory. According to the theory, pervaporation flux is considered to be a function of solubility and diffusion coefficient.[4-8] Therefore, the effects of CD should also be divided into two parts: effects on the sorption and those on the diffusion. Effects of CD on sorption equilibria should imply the changes of the affinity of the membrane to permeants. On the other hand, effects on the diffusion coefficients should indicate the changes of the mobilities of the permeants in the membrane. The objective of this study was to elucidate which effect of CD is more significant on the pervaporation selectivity. The sorption equilibria were measured by a methanol extraction method. With the results of the sorption equilibria and the pervaporation fluxes, the diffusion coefficients of permeants in the membranes were calculated.

EXPERIMENTAL

Material and Membrane Preparation

Details on the materials and the membrane preparation method were described in the previous article.[3] In brief, the aqueous mixture of PVA and CD oligomer (2 : 1 in weight) was cast onto a glass plate and air-dried at room temperature. The membranes were cross-linked with glutaraldehyde for 1 or 8 h.

Each membrane was perfectly transparent with 100 μm thickness.

Measurements of the Sorption Equilibrium

Sorption equilibria in the membranes were measured by a methanol-extraction method. The procedure was as follows: About 0.1 g of membrane was dried in an oven at 333 K for at least 48 h until it showed no weight change. After the dry weight was measured, the membrane was immersed in an ethanol/water mixture of a known composition at 303 K with stirring. After 12 and 24 h, the membrane was picked out and weighed. For each measurement, no weight change was observed between 12 and 24 h immersion, which indicated that the sorption equilibrium was established within 12 h. Total amount of sorption was calculated by subtracting the dry weight from the wet weight. Then, the membrane was immersed in an excess amount of methanol to extract the sorbed water/ethanol mixture from the membrane for 12 h with stirring. In each case, a perfect extraction was confirmed by comparing the weight after extraction with the initial dry weight. The methanol phase including the extracted water/ethanol was analyzed by gas chromatography to obtain the composition of the sorbed phase in the membrane.

Calculation of the Diffusion Coefficients

According to the sorption–diffusion theory,[4-8] both interfaces of the membrane are assumed to be in sorption equilibrium with the fluid phase, i.e., the feed liquid and permeate vapor. Permeation inside the membrane is caused by the concentration gradient across the membrane. A steady-state pervaporation flux of component "i", N_i (mol/m^2/s), can be expressed by Eq. (1) (neglecting cross terms):

$$N_i = -D_i(dc_i/dx) \qquad (1)$$

where D_i is the diffusion coefficient (m^2/s), which is, in general, a function of the concentration of the permeant[9]; c_i, the concentration of the permeant "i" in the membrane (mol/m^3); and x, the diffusion length along the membrane thickness (m). To calculate the diffusion coefficient by Eq. (1), it is necessary to know either the concentration profiles of the permeates across the membrane or the accurate concentration dependence of the diffusion coefficient. Instead, in this study, a concentration average diffusion coefficient, D_{im}, was calculated, which can be defined as[10]

$$D_{im}(c_{if}, c_{ip}) = \int_{c_{ip}}^{c_{if}} D(c_i) \, dc_i / (c_{if} - c_{ip}) \qquad (2)$$

where c_{if} and c_{ip} are the concentrations of the feed side and the permeate side of the membrane, respectively. Integration of Eq. (1) yields

$$N_i = (1/L) \int_{c_{ip}}^{c_{if}} D_i(c_i) \, dc_i \qquad (3)$$

where L is the membrane thickness. From Eqs. (2) and (3), we obtain

$$D_{im}(c_{if}, c_{ip}) = N_i L / (c_{if} - c_{ip}) \qquad (4)$$

Note that D_{im} will be equal to a constant diffusion coefficient under the assumption of a linear concentration profile, which does not usually hold.[8,11,12] To calculate the diffusion coefficient by Eq. (4), we assumed that the sorption equilibrium is established between the membrane and feed liquid on the upstream side. On the downstream side, the concentration of the permeants in the membrane is assumed to be 0 because of relatively low downstream pressure (less than 0.5 Torr). Thus, the concentration average diffusion coefficient is expressed as a function of feed liquid composition. Although $D_{im}(c_{if})$ does not express the accurate concentration dependence, we can use it to elucidate the effect of CD on the diffusion coefficient, because, as shown below, the effect of CD on the sorption equilibria, and, hence, on the concentration profiles, is relatively small.
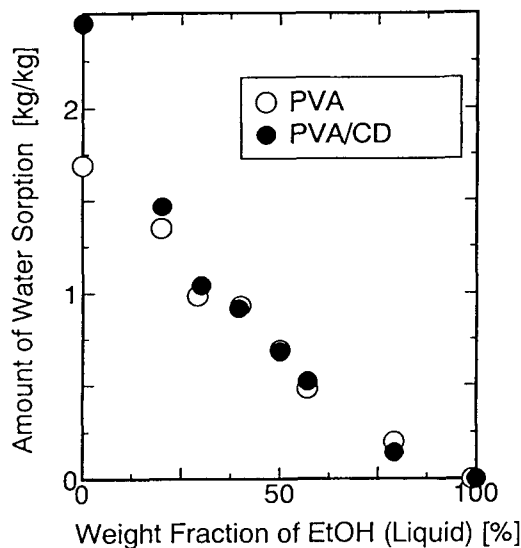
RESULTS AND DISCUSSION

Sorption Equilibria

The sorption equilibrium diagrams for 1 h cross-linked membranes are shown in Figure 1. The sorption equilibrium for each membrane was water-selective in the full range of liquid composition. The shapes of the sorption diagrams were much different from those of the pervaporation separation diagrams (Fig. 2). The water selectivity of the PVA/CD membrane through the sorption equilibria was slightly decreased by the addition of CD, whereas the water selectivity through pervaporation was increased by CD. The sorption amounts of water and ethanol are shown in Figures 3 and 4, respectively, as a function of liquid composition. The water-sorption amounts decreased with a decrease in the water concentration in the liquid phase. The ethanol sorp-
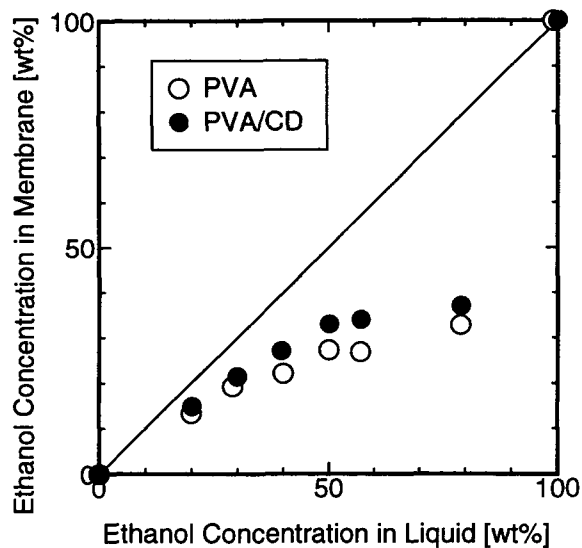
Figure 1 Sorption equilibrium diagram: 1 h cross-linked membranes.
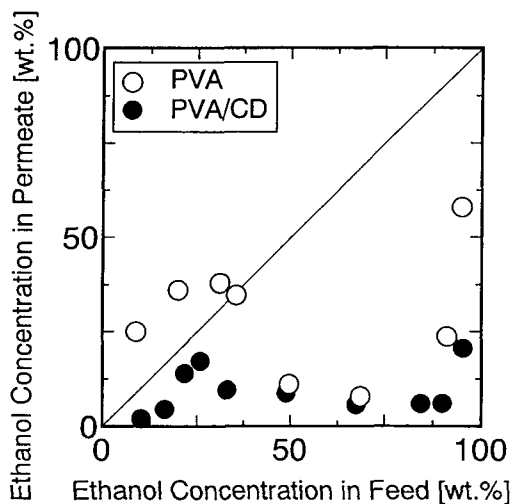

Figure 3 Equilibrium sorption amount of water: 1 h cross-linked membranes.

tion amounts showed a maximum value at about 50% ethanol concentration. A similar dependence on the liquid concentrations was reported for PVA by Hauser et al.[13] By the addition of CD, the sorption amounts of ethanol were increased, whereas those of water were scarcely changed.
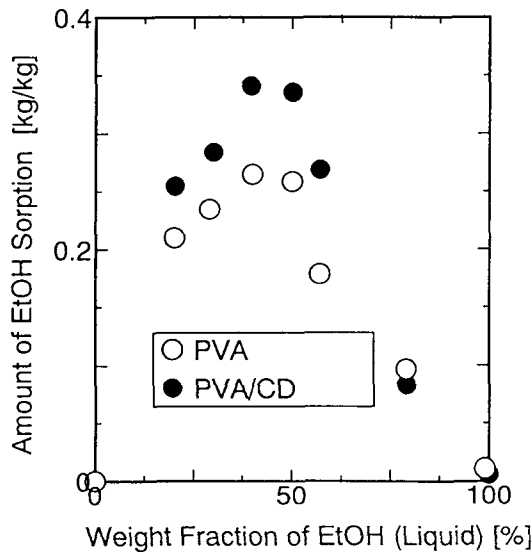
Figure 5 shows the sorption equilibrium diagrams for 8 h cross-linked membranes. Pervaporation separation diagrams for these membranes are shown in Figure 6. For each membrane, the sorption equilibrium as well as the pervaporation separation were water-selective in the full range of compositions. By the addition of CD, the water selectivity through

the sorption equilibria was scarcely affected, whereas the water selectivity through pervaporation was increased. The sorption amounts of water as well as those of ethanol were increased by the addition of CD, as shown in Figures 7 and 8.
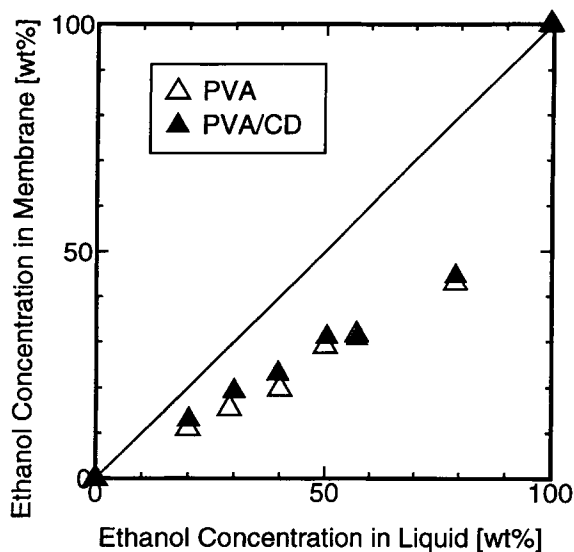
The increase in the sorption amount of ethanol can be explained by the stronger inclusion of ethanol; since the CD cavity is hydrophobic, the interaction between ethanol with CD through inclusion should be stronger than with PVA. The stronger interaction should result in the increase in the sorp-

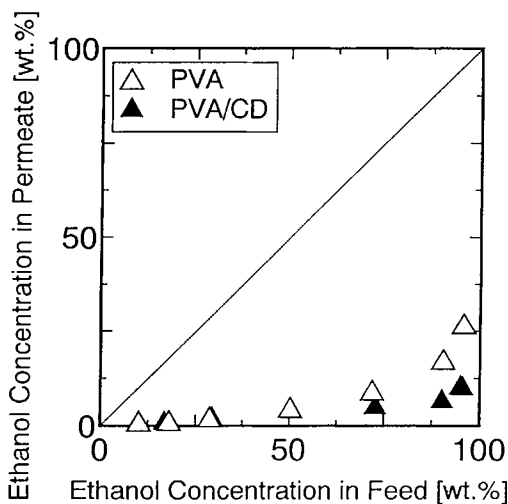**Figure 2** Separation diagram through pervaporation: 1 h cross-linked membranes.

Figure 4 Equilibrium sorption amount of ethanol: 1 h cross-linked membranes.
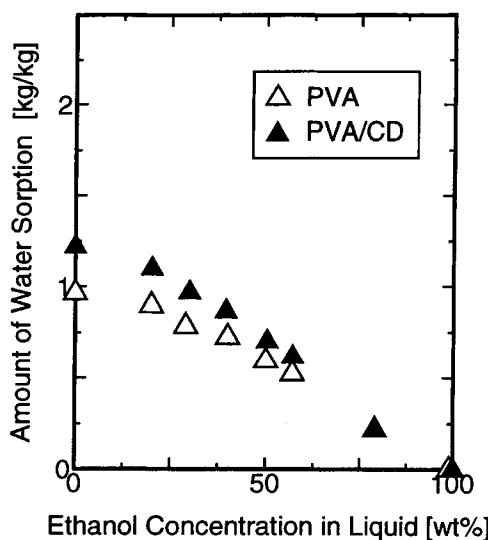
Figure 5   Sorption equilibrium diagram: 8 h cross-linked membranes.

Figure 7   Equilibrium sorption amount of water: 8 h cross-linked membranes.

tion amount of ethanol. For water, the weaker inclusion would result in a decrease in the sorption amount by the addition of CD. However, the cross-linking density of the PVA phase in the PVA/CD membrane should be lower than that in the PVA membrane of same cross-linking time because the CD oligomer in the PVA/CD membranes should retard the cross-linking reaction of PVA with glutaraldehyde. The lower cross-linking density of the PVA phase in the PVA/CD membrane should increase the sorption amount. For 1 h cross-linked membranes, the water-sorption amount appeared not to be affected by CD because the decrease due

to the weaker inclusion should be compensated by the increase due to the lower cross-linking density. With an increase in the cross-linking time, the difference in the cross-linking density between the PVA membrane and the PVA/CD membrane should be more significant. Thus, the water-sorption amount was increased by CD for 8 h cross-linked membranes.

These results indicate that the effect of CD on the sorption equilibrium was less significant for the effects of CD on the pervaporation separation. The increase in the water selectivity, therefore, should

Figure 6   Separation diagram through pervaporation: 8 h cross-linked membranes.
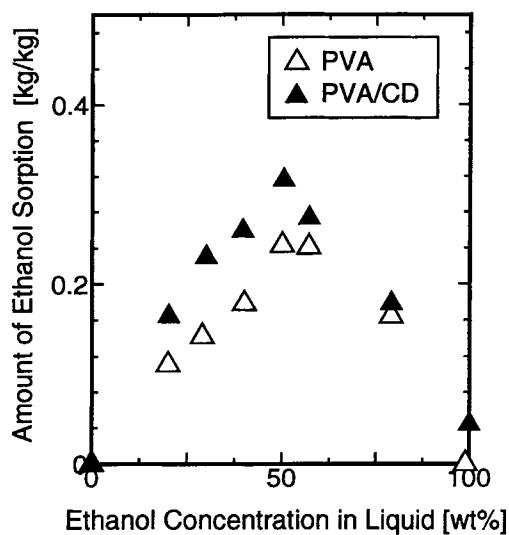
Figure 8   Equilibrium sorption of amount of ethanol: 8 h cross-linked membranes.
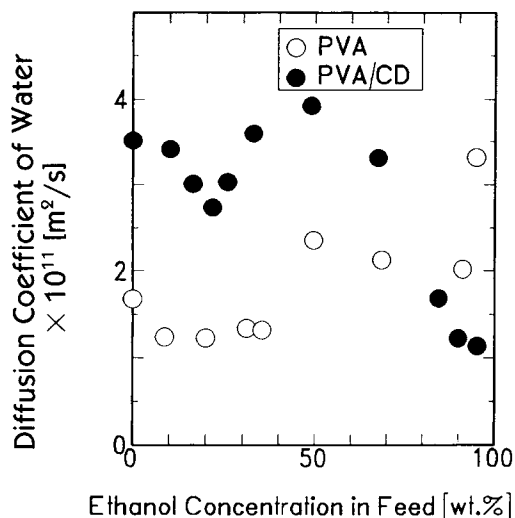
Figure 9   Diffusion coefficient of water: 1 h cross-linked membranes.
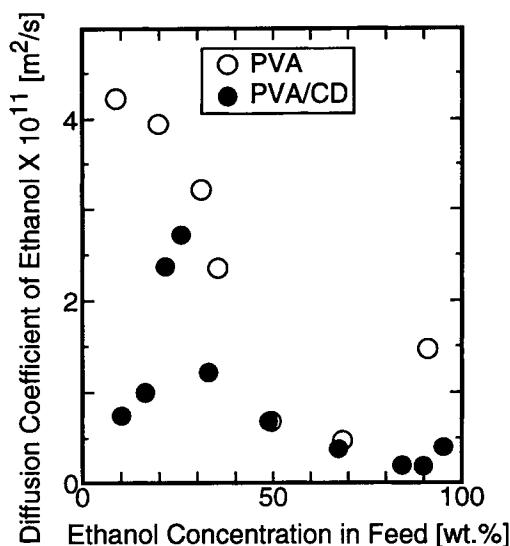

Figure 11   Diffusion coefficient of ethanol: 1 h cross-linked membranes.

be due mainly to the effects on the diffusion coefficients, which should greatly increase the water selectivity.
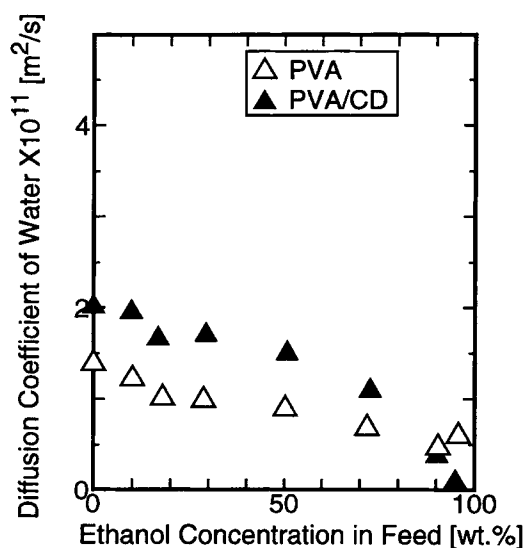
Diffusion Coefficients

Figures 9 and 10 show the water-diffusion coefficients in the membranes as a function of the feed liquid composition. For each cross-linking time, the diffusion coefficient was increased greatly by the addition of CD at lower ethanol concentrations in the feed (< 70%). At higher ethanol concentrations, however, the diffusion coefficient of water was de-
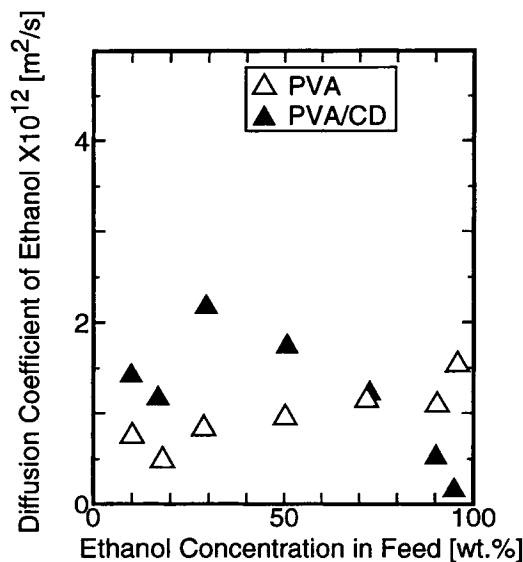
creased by CD. The diffusion coefficients of ethanol are shown in Figures 11 and 12. For 1 h cross-linked membranes, the ethanol diffusion coefficient was decreased by CD, especially at higher ethanol concentrations. For 8 h cross-linked membranes, the ethanol diffusion coefficient was increased by CD at lower ethanol concentrations (< 50%), whereas it was greatly decreased at higher ethanol concentration (> 70%).

These effects of CD on the diffusion coefficients, which depend on the feed composition and the cross-linking time, have a tendency to increase the water

Figure 10   Diffusion coefficient of water: 8 h cross-linked membranes.

Figure 12   Diffusion coefficient of ethanol: 8 h cross-linked membranes.

selectivity. The effects of CD on the diffusion coefficient can be interpreted in terms of the inclusion strength and the cross-linking density. A stronger inclusion of ethanol should decrease the mobility of ethanol in the cavity of CD.[14,15] The lower cross-linking density of the PVA phase in the PVA/CD membrane should increase the mobility of ethanol in the PVA phase. Both of these opposite effects should affect the diffusion coefficient depending on the cross-linking time. For 1 h cross-linked membranes, the decrease in the diffusion coefficient due to the stronger inclusion should be larger than the increase due to the cross-linking density; in this case, the difference in the cross-linking density between the PVA membrane and the PVA/CD membrane should be less significant for the ethanol diffusion because the molecular size of ethanol should be much smaller than the network size of the PVA phase. With an increase in the cross-linking time, the network size should become comparable to the molecular size of ethanol. Thus, for 8 h cross-linked membranes, at lower ethanol concentrations, the increase due to the lower cross-linking density should be larger than the decrease due to the stronger inclusion. In other words, for 8 h cross-linked membranes, the difference in the cross-linking density should be more critical for the diffusion of ethanol. At higher ethanol concentrations, more cavities should be occupied by ethanol molecules, and the included ethanol molecules should prevent the accessing of other molecules to the cavities. This effect should result in the decrease in the diffusion coefficient at higher ethanol concentrations.

The increase in the water-diffusion coefficients at lower ethanol concentrations can also be interpreted by the inclusion strength and the cross-linking density. Because of the weaker interaction of water with the CD cavity than with PVA, the mobility of water should be larger in the cavity than in the PVA phase. The lower cross-linking density of the PVA phase in the PVA/CD membrane compared to the PVA membrane of the equal cross-linking time should increase the mobility of water in the PVA phase. Hence, the addition of CD should increase the water-diffusion coefficient compared to the pure PVA membrane. The decrease in the water-diffusion coefficients as well as in the ethanol-diffusion coefficients at higher ethanol concentrations can be explained by the decrease in the accessible cavities.

From the above discussion, the effects of CD on the diffusion coefficients can be explained in terms of the inclusion strength and the cross-linking density of the PVA phase.

CONCLUSIONS

The effects of CD on the diffusion coefficients, which depended on the feed composition and the cross-linking time, were the main reason for the increase in the water selectivity through pervaporation by the addition of CD to the cross-linked PVA membranes. The water selectivity through sorption equilibrium was not increased by CD; on the contrary, CD increased the ethanol-sorption amounts. These effects of CD can be interpreted in terms of the inclusion strength in the CD cavity and the cross-linking density of the PVA phase.

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