

Characteristics of Permeation and Separation for Propanol Isomers through Poly(vinyl alcohol) Membranes Containing Cyclodextrin

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SYNOPSIS

Poly(vinyl alcohol) membranes containing cyclodextrin (CD-PVA membrane) were prepared and characteristics of permeation and separation for propanol (PrOH) isomers through the CD-PVA membranes were investigated by pervaporation and evapomeation. Evapomeation was more effective for the separation of PrOH isomers through the CD-PVA membrane than was pervaporation. The CD-PVA membrane more preferentially permeated *n*-PrOH than *i*-PrOH from their mixtures. In particular, the mixture of 10 wt % *n*-PrOH concentration was concentrated to about 45 wt % through the CD-PVA membrane. Both permeability and selectivity for *n*-PrOH were improved with an increase of CD content in the membrane. The results were supported by the fact that the affinity of CD for *n*-PrOH was stronger than that for *i*-PrOH. The permeation mechanism of PrOH isomers through the CD-PVA membrane is discussed based on the solution-diffusion theory.

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INTRODUCTION

Aqueous organic solutions can be separated through various polymer membranes by reverse osmosis and pervaporation. Such membrane-separation techniques have more advantages than have conventional methods like distillation. For example, azeotropic mixtures or close-boiling-point mixtures can be separated through polymer membranes, although they cannot be by distillation. Furthermore, the membrane-separation techniques are better than is distillation from the viewpoint of energy saving. In particular, since pervaporation has a high potential to separate aqueous alcoholic solutions and so on, it has attracted much attention. Many workers, therefore, have studied the characteristics of permeation and separation for various organic liquid solutions through various polymer membranes by pervaporation.¹

We previously studied the characteristics of permeation and separation for organic liquid solutions

through hydrophilic or hydrophobic membranes by pervaporation and evapomeation.²⁻¹¹ In pervaporation, the swelling of the membrane by the feed solution often causes a decrease of permselectivity, because the membrane is in direct contact with the feed solution. Therefore, we proposed "evapomeation" as a new membrane-separation technique for the improvement of such disadvantages in pervaporation. The swelling of the membrane can be suppressed in evapomeation, because the membrane is not in direct contact with the feed solution. Consequently, permeation rates in evapomeation were smaller than those in pervaporation, but separation factors in the former were greater than those in the latter.

The separation of organic liquid isomers is interesting owing to its importance in not only scientific but also in industrial fields. Michaels et al.¹² tried to separate xylene isomers through conditioned polyethylene membranes by pervaporation. Smolders et al.¹³ reported that the separation factors for xylene isomers through a cellulose ester membrane could be achieved from 1.16 to 1.43. Moreover, the separation of aromatic C₈-isomers through various commercial polymer membranes was carried out by

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McCandless and Downs.¹⁴ Wessling et al.¹⁵ investigated the influence of process parameters on the permeation and separation for C₈-isomers through a dense homogeneous polyethylene membrane from experimental and theoretical viewpoints. In these studies, the separation factor was very low. This suggests that the separation of organic liquid isomers through ordinary polymer membranes by pervaporation is very difficult because of similar physical and chemical properties of the isomers.

In general, the characteristics of permeation and separation for organic liquid isomers through the polymer membranes are influenced by solubility of permeants into the membrane and diffusivity of permeants in the membrane.¹ In the case of the separation of the components of a mixture whose molecular sizes are similar, it is difficult to separate the mixture based on diffusivity because of similar diffusivity of molecules. Therefore, positive applications of the solubility difference of the molecules into the membrane are desirable for the separation of such mixtures. Sikonia and McCandless¹⁶ prepared poly(vinylidene fluoride) membranes containing Werner complexes, which can recognize the difference between xylene isomers, and investigated the permeation of xylene isomers through the membrane by pervaporation. Like this study, the addition of materials, which can recognize slight differences in the physical and chemical properties between organic liquid isomers, is effective for the separation of isomers through the membrane.

It is well known that cyclodextrin (CD) selectively forms inclusion complexes with a large number of organic and inorganic molecules.¹⁷ Incorporation of guest molecules into CD has been reported by many workers. Such incorporation factors are hydrophobic interaction,^{18–20} hydrogen bonding,^{21,22} van der Waals forces,^{23–26} relaxation of the conformational strain in the ring of CD,²⁷ and release of partially hydrogen-bonded water molecules from the cavity of CD.²⁸ Furthermore, the steric fit between the cavity of CD molecules and the guest molecules plays an important role in selective inclusion. For example, CD more easily forms inclusion complexes with the *p*-derivative of aromatic compounds compared with the *o*-derivative due to good steric fit¹⁷; CD can recognize the slight difference between the chemical structures of isomers. The separation of isomers by polymer membranes containing CD, therefore, attracts our attention because high selectivities of such membranes are expected. Some workers have already reported the usefulness of CD in chromatography and liquid–liquid extraction to separate and purify several aromatic compounds.

^{29–37} Furthermore, the addition of CD to the membrane may be effective for separation based on the affinity of permeants for the membrane. Lee³⁸ carried out pervaporation of xylene isomers through a hydroxypropylmethyl cellulose membrane containing CD and reported that the selectivity was in the order of *p* → *m* → *o*-derivative, but the separation factor was very low.

In this study, membranes containing CD were prepared in order to construct a membrane-separation system for organic liquid isomers. We selected the poly(vinyl alcohol) (PVA) membrane as a matrix polymer, since it has been reported that PVA has good compatibility with CD.³⁹ The PVA membrane also has an advantage in that the swelling of the membrane, which causes permselectivity to decrease, occurs with difficulty in propanol (PrOH) isomers. The effects of CD on the characteristics of permeation and separation for PrOH isomers through the PVA membranes containing CD (CD–PVA membrane) were investigated by pervaporation and evapomeation. Furthermore, the usefulness of evapomeation in the separation of organic liquid isomers through the CD–PVA membrane was examined and compared with pervaporation. The characteristics of permeation and separation were also discussed based on the solution–diffusion theory.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) (produced by Nihon Gosei Co., NH-17Q) with a degree of polymerization of 1650 and a degree of saponification of 99.7% was used as a membrane material. β -CD was purchased from Wako Pure Chemical Industries. All analytical-grade reagents from commercial sources were used without further purification.

Preparation of Membrane

Prescribed amounts of PVA and CD were dissolved in dimethyl sulfoxide (DMSO) at 25°C and total solid content of the solutions was 4 wt %. CD–PVA membranes were prepared by pouring the casting solutions onto a rimmed glass plate and allowing the solvent to evaporate completely at 80°C. The thickness of the resulting membrane was about 40 μ m. The membrane was transparent. This demonstrates that CD molecules are individually dispersed in the PVA membrane and that PVA has good compatibility with CD, as reported by Kuranuki et al.³⁹

Permeation Measurements

Pervaporation and evapomeation were carried out using the apparatus reported in earlier papers²⁻¹¹ under the following conditions: permeation temperature, 40°C; and pressure of permeation side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm². The mixture of *n*-propanol (*n*-PrOH) and *i*-propanol (*i*-PrOH) was used as a feed solution. The compositions of the feed solution and permeate were determined by gas chromatography (Shimadzu GC-9A) equipped with flame ionization detector (FID) and Gaskuropack 54 column (Gasukuro Kogyo, Japan) heated at 200°C.

The separation factor ($\alpha_{n\text{-PrOH}/i\text{-PrOH}}$) of the pervaporation and evapomeation was computed by eq. (1):

$$\alpha_{n\text{-PrOH}/i\text{-PrOH}} = (P_{n\text{-PrOH}}/P_{i\text{-PrOH}})/(F_{n\text{-PrOH}}/F_{i\text{-PrOH}}) \quad (1)$$

where $F_{n\text{-PrOH}}$, $F_{i\text{-PrOH}}$ and $P_{n\text{-PrOH}}$, $P_{i\text{-PrOH}}$ are the compositions of components *n*-PrOH and *i*-PrOH in the feed and permeate, respectively. In evapomeation, the separation factor was calculated using the vapor compositions vaporized from the feed solutions instead of the liquid compositions, because the membrane contacts vapor on the feed side of the membrane.

The permeation rates in both pervaporation and evapomeation were determined from the weight of permeate collected in a cold trap, permeation time, and effective membrane area.

Degree of Swelling of the Membrane

The membrane was completely dried under reduced pressure at room temperature and weighed. The dried membrane was exposed to the vapor of the mixture of *n*-PrOH and *i*-PrOH in a sealed vessel at 40°C until equilibrium was reached. Then, the membrane was taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (*DS*) of the membrane was determined from eq. (2):

$$DS = W_S/W_D \quad (2)$$

where W_S is the weight of the membrane swollen in the vapor of PrOH isomers, and W_D , the weight of the dried membrane.

Composition of Solution Sorbed in Membrane

The dried membrane was exposed to the vapor of the mixture of *n*-PrOH and *i*-PrOH in a sealed vessel

at 40°C until equilibrium was reached. Then, the membrane was taken out of the vessel and wiped quickly with filter paper. The composition of PrOH isomers sorbed in the membrane was directly measured by pyrolysis gas chromatography (Shimadzu GC-14A) equipped with an FID and Gaskuropack 54 column (Gasukuro Kogyo) heated at 200°C.

Measurement of Adsorption of PrOH Isomers in CD

Fifty milligrams of each PrOH isomer was mixed with 1 g of water, in which 0.2 g of CD was dispersed. The mixture was kept at 40°C, stirring sufficiently until equilibrium was reached. Then, CD was removed by centrifugation and the concentration of the supernatant was measured by the above gas chromatography. The amount of PrOH isomer adsorbed in CD was determined from the difference in PrOH concentration of the supernatant before and after the adsorption.

RESULTS AND DISCUSSION

Difference of Pervaporation and Evapomeation

The relationship between *n*-PrOH concentrations in the feed (*n*-PrOH/*i*-PrOH mixture) and in the permeate through the CD-PVA membrane by pervaporation and evapomeation at 40°C is shown in Figure 1, in which the CD content was 40 wt %. The

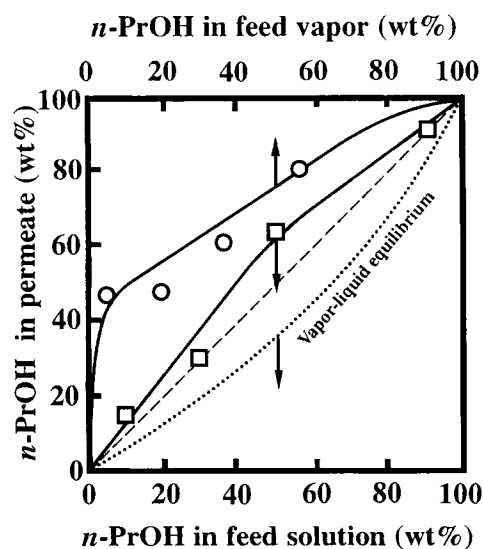


Figure 1 Effect of feed composition on the *n*-PrOH concentration in the permeate through the CD-PVA membrane (the amount of CD in the membrane; 40 wt %) by (□) pervaporation and (○) evapomeation.

n-PrOH concentration in the permeate through the CD-PVA membrane by pervaporation was approximately same as that in the feed solution, namely, the PrOH isomers could hardly be separated through the CD-PVA membrane by pervaporation. On the other hand, the *n*-PrOH concentration in the permeate by evapomeation was higher than that in the feed solution. This result implies that the CD-PVA membrane in evapomeation permeates *n*-PrOH in preference to *i*-PrOH. This result can be explained by the tentative illustration shown in Figure 2. In pervaporation, it is difficult for each PrOH to interact specifically with the CD-PVA membrane, because the PrOH isomers associate in the feed solution. In evapomeation, however, *n*-PrOH can be preferentially sorbed into the CD-PVA membrane, because each PrOH is isolated in the feed vapor. These results support the thesis that evapomeation is more effective for the separation of the PrOH isomers through the CD-PVA membrane than is pervaporation. Therefore, mainly, permeation of the PrOH isomers by evapomeation was investigated for the later work.

Effect of CD Content on Characteristics of Permeation and Separation

Figure 3 shows the effect of CD content on the *n*-PrOH concentration in the permeate and normalized permeation rate through the CD-PVA membrane by evapomeation. The normalized permeation rate is the product of the permeation rate and the mem-

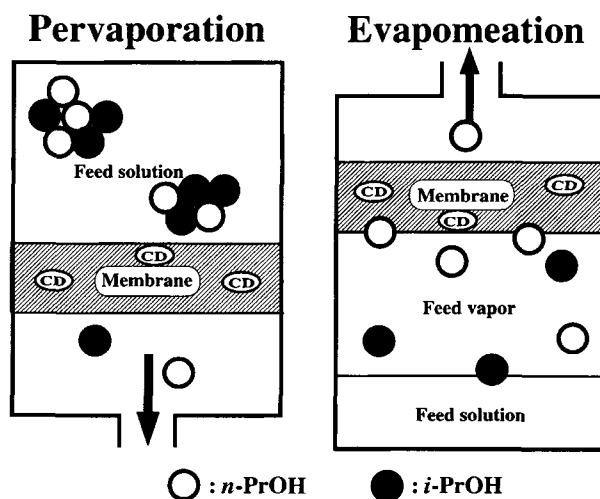


Figure 2 Tentative illustration of an interaction between the permeant and CD in pervaporation and evapomeation.

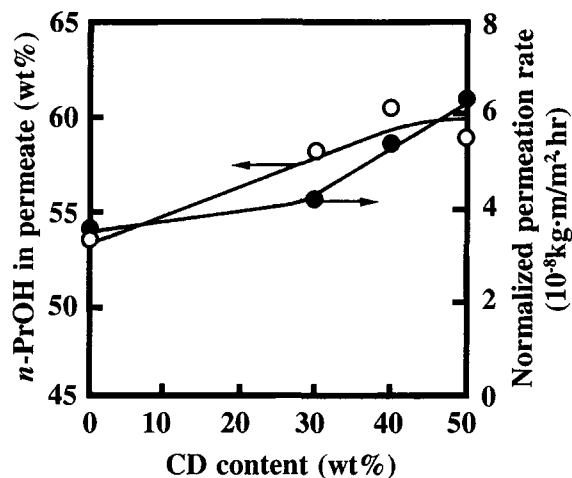


Figure 3 Effect of CD content on the *n*-PrOH concentration in the permeate and the normalized permeation rate through the CD-PVA membrane by evapomeation. Feed solution: *n*-PrOH/*i*-PrOH = 50/50 (w/w). Feed vapor: *n*-PrOH/*i*-PrOH = 37/63 (w/w).

brane thickness. The composition of the *n*-PrOH/*i*-PrOH mixture as a feed solution was 50/50 (w/w), i.e., 37/63 (w/w) in the feed vapor. The PrOH isomers could be separated a little by the PVA membrane by evapomeation. With increasing CD content in the CD-PVA membrane, both the *n*-PrOH concentration in the permeate and normalized permeation rate increased. This result means that the addition of CD in the PVA membrane leads to both improvements of the permeability and selectivity.

To reveal the reason for the improvement, the effect of CD content on the degree of swelling of the CD-PVA membrane in the *n*-PrOH/*i*-PrOH feed vapor and *n*-PrOH concentration sorbed in the membrane was investigated. These results are shown in Figure 4. The degree of swelling of the CD-PVA membrane increased with increasing CD content. This implies that the addition of CD strengthens the affinity of permeants for the CD-PVA membrane. The increase of the permeation rate in Figure 3 is due to the swelling of the CD-PVA membrane with an increase of the CD content. On the other hand, with increasing CD content, the *n*-PrOH concentration in the membrane increased and the CD-PVA membrane sorbed *n*-PrOH in preference to *i*-PrOH. These results suggest that CD plays an important role in the preferential sorption of *n*-PrOH in the membrane. Furthermore, this preferential sorption significantly affects a preferential permeation of *n*-PrOH through the CD-PVA membrane.

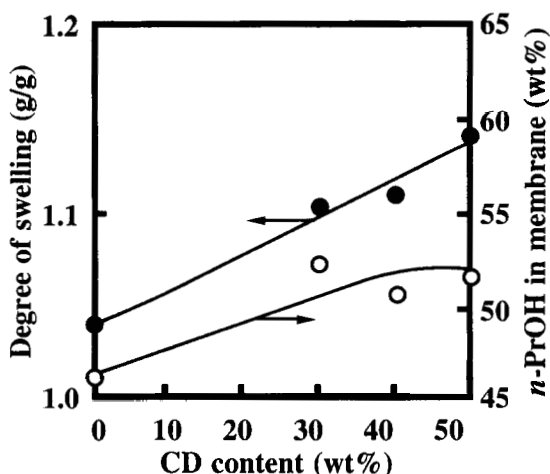


Figure 4 Effect of CD content on the degree of swelling of the CD-PVA membrane by the vapor of PrOH isomers and the *n*-PrOH concentration sorbed in the membrane. Feed solution: *n*-PrOH/*i*-PrOH = 50/50 (w/w). Feed vapor: *n*-PrOH/*i*-PrOH = 37/63 (w/w).

The amount of adsorption of each PrOH isomer into CD was measured for the investigation of the affinity of PrOH isomers for CD. Since it is difficult to measure the amount of each PrOH isomer adsorbed into CD in the membrane, the amount of the adsorption into CD in water was measured by replacing the PVA membrane with water as a model as shown in Figure 5. The adsorption amounts of *n*-PrOH and *i*-PrOH for 1 mol of CD in water were 0.8 and 0.6 mol, respectively. This indicates that the affinity of CD for *n*-PrOH is stronger than that for *i*-PrOH. Generally, CD forms inclusion compounds by incorporating various small molecules in its hydrophobic cavity.¹⁷ As mentioned in the Introduction, the driving force of the inclusion is thought to be hydrophobic interactions,¹⁸⁻²⁰ hydrogen bonding,^{21,22} van der Waals forces,²³⁻²⁶ relaxation of the

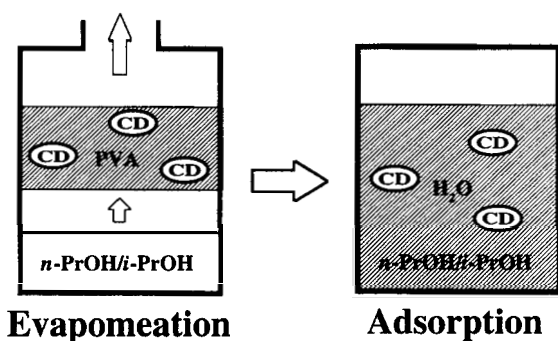


Figure 5 Concept of adsorption of the PrOH isomers for CD to investigate the interaction of CD with each PrOH.

conformational strain in the macrocyclic ring of CD,²⁷ and release of partially hydrogen-bonded water molecules from the cavity.²⁸ The main factor that determines the selectivity of CD is the steric fit of the guest molecules for the cavity of CD. For example, *p*-derivatives of aromatics are well known to be preferentially included in CD than are *o*- or *m*-derivatives, owing to the steric fit for the cavity.¹⁷ In our case, since *i*-PrOH is more bulky than is *n*-PrOH, *n*-PrOH may be more easily included in the cavity and preferentially interact with CD. This may be the reason why the affinity of CD for *n*-PrOH is stronger than that for *i*-PrOH. Furthermore, the stronger affinity of CD for *n*-PrOH results in the preferential sorption of *n*-PrOH into the CD-PVA membrane as shown in Figure 4. As the result of preferential sorption of *n*-PrOH, *n*-PrOH permeates through the CD-PVA membrane more readily than does *i*-PrOH.

Figure 6 shows the effect of feed composition on the *n*-PrOH concentration in the permeate through the CD-PVA containing 40 wt % CD and PVA membrane by evapomeation. The CD-PVA membrane permeated a larger amount of *n*-PrOH than did the PVA membrane. In particular, 10 wt % *n*-PrOH in the feed solution (feed vapor, 7 wt %) was concentrated to about 45 wt % through the CD-PVA membrane. Thus, the separation factor was about 15. This value of the separation factor is high for the separation of organic isomers through polymer membranes. Consequently, the addition of CD in the PVA membrane enables the membrane to

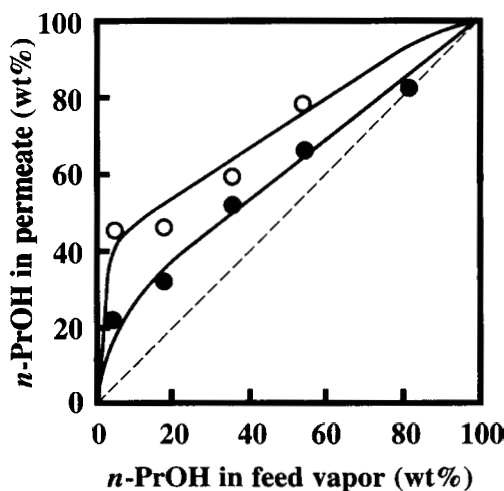


Figure 6 Effect of feed composition on the *n*-PrOH concentration in the permeate through the (○) CD-PVA (CD content: 40 wt %) and (●) PVA membrane by evapomeation.

permeate *n*-PrOH preferentially from *n*-PrOH/*i*-PrOH mixtures.

Discussion Based on Solution–Diffusion Theory

In general, the characteristics of the permeation and separation for organic liquid mixtures through polymer membranes by pervaporation can be discussed based on solution–diffusion theory.⁴⁰ Therefore, the permeation and separation of PrOH isomers through the CD–PVA membrane by evapomeation are thought to be dependent on the solubility of the PrOH isomers in the membrane and diffusivity of them through the membrane. The solubility can be discussed by the sorption selectivity of the CD–PVA membrane, α_{sorp} , which is obtained from the composition of the PrOH isomers sorbed in the membrane using eq. (3):

$$\alpha_{\text{sorp}} = (M_{n\text{-PrOH}}/M_{i\text{-PrOH}})/(F_{n\text{-PrOH}}/F_{i\text{-PrOH}}) \quad (3)$$

where *F* and *M* are the composition of the one component in the feed and membrane, respectively. Furthermore, the diffusion selectivity of the CD–PVA membrane, α_{diff} , can be determined from the separation factor obtained by eq. (1) and the sorption selectivity, using eq. (4):

$$\alpha_{\text{diff}} = \alpha_{\text{sep}}/\alpha_{\text{sorp}} \quad (4)$$

Such a division of the separation factor into its sorption and diffusion selectivities leads to detailed discussions to elucidate the permeation mechanism of the PrOH isomers through the CD–PVA membrane.

Table I lists the separation factors and sorption and diffusion selectivities of the CD–PVA and PVA membranes for the *n*-PrOH/*i*-PrOH mixture [50/50 (w/w)]. The separation factor of the PVA membrane was about two. Its sorption selectivity

Table I Separation Factors and Sorption and Diffusion Selectivities of the CD–PVA and PVA Membrane for the *n*-PrOH/*i*-PrOH Mixture^a by Evapomeation

CD Content (Wt %)	α_{sep}	α_{sorp}	α_{diff}
0	2.01	1.89	1.06
40	2.61	2.07	1.26

^a *n*-PrOH/*i*-PrOH = 50/50 (w/w).

Table II Separation Factors and Sorption and Diffusion Selectivities of the CD–PVA Membrane^a for the *n*-PrOH/*i*-PrOH Mixtures by Evapomeation

<i>n</i> -PrOH Content (Wt %)	α_{sep}	α_{sorp}	α_{diff}
10	15.2	3.68	4.14
50	2.61	2.07	1.26

^a CD content is 40 wt %.

was more than unity, but its diffusion selectivity was about unity. This demonstrates that the diffusivity of *n*-PrOH in the PVA membrane is similar to that of *i*-PrOH because *n*-PrOH has a similar molecular size to that of *i*-PrOH. Therefore, the separation of the PrOH isomers is not due to the difference between diffusivity of *n*-PrOH and *i*-PrOH but to the difference between solubility of them in the PVA membrane. On the other hand, the separation factor of the CD–PVA membrane was larger than that of the PVA membrane. The larger separation factor is attributable to both larger sorption and diffusion selectivities, namely, the addition of CD in the PVA membrane causes the membrane to sorb *n*-PrOH preferentially and enhances the diffusivity of *n*-PrOH in the membrane. It is worth noticing that the diffusion selectivity of the CD–PVA membrane is greater than unity, differing from that of the PVA membrane. This implies that the permeation mechanism of PrOH isomers through the CD–PVA membrane is different from that through the PVA membrane.

The effect of feed composition on the separation factors and sorption and diffusion selectivities of the CD–PVA membrane is summarized in Table II, in which the CD content was 40 wt %. The separation factor in the case of *n*-PrOH/*i*-PrOH at 10/90 was about 15 and much larger than that for *n*-PrOH/*i*-PrOH at 50/50. This separation factor is very high for the separation of organic liquid isomers through polymer membranes. Both the sorption and diffusion selectivities in *n*-PrOH/*i*-PrOH at 10/90 also became larger than those at 50/50. The combined action of the preferential sorption and diffusion of *n*-PrOH results in high permselectivity. The reason why the membrane performance is better for the low concentration of *n*-PrOH can be explained by the relative amount of CD to *n*-PrOH in the PrOH isomers. We calculated the number of moles of CD and *n*-PrOH sorbed in 1 g of the CD–PVA membrane. When the amount of CD in the mem-

brane was 40 wt %, 1 g of the membrane contained 3.52×10^{-4} mol of CD. On the other hand, 0.83×10^{-4} and 1.92×10^{-4} mol of *n*-PrOH were sorbed in 1 g of the membrane in the case of *n*-PrOH/*i*-PrOH at 10/90 and 50/50, respectively. Then, the ratio of CD to *n*-PrOH in the former was four and that in the latter was less than two. This indicates that the membrane contained much more than sufficient CD to interact with *n*-PrOH in the former than with the latter; because the ratio of CD to *n*-PrOH is small in the case of the high concentration of *n*-PrOH, only part of *n*-PrOH can specifically interact with CD. The excess of *n*-PrOH and *i*-PrOH is nonspecifically sorbed and diffuses in the PVA matrix. Therefore, the permselectivity of the CD-PVA membrane becomes low in the high concentration of *n*-PrOH. In the low concentration of *n*-PrOH, however, the amount of CD that can interact with *n*-PrOH is relatively larger. Consequently, a large amount of *n*-PrOH can be preferentially sorbed and diffused in the CD-PVA membrane due to the specific interaction of *n*-PrOH with CD. As these results show, the permselectivity in the low concentration of *n*-PrOH is greater than that in the high concentration. Furthermore, the diffusion selectivity in the case of *n*-PrOH/*i*-PrOH as 10/90 feed was very high. This suggests that the diffusivity of *n*-PrOH is greater than that of *i*-PrOH, even though their molecular sizes are similar.

Nishide et al.^{41,42} prepared membranes containing the porphyrin-cobalt complex as a fixed carrier and investigated the permeation of oxygen through their membranes. They reported that the transport mechanism of oxygen in the membrane is based on a dual-mode model.^{43,44} Their dual-mode model consists of the Henry mode, attributed to the matrix, and the Langmuir mode, attributed to the fixed carrier. They proposed that the permselectivity of oxygen through the membrane containing the porphyrin-cobalt complex is mainly due to the Langmuir mode. In our case, also, CD in the PVA membrane can be regarded as a fixed carrier. Therefore, the permeation mechanism of PrOH isomers through the CD-PVA membrane can be explained by a tentative illustration as shown in Figure 7. At first, *n*-PrOH is more preferentially sorbed into the CD-PVA membrane than is *i*-PrOH. After that, CD plays a role in a fixed carrier and *n*-PrOH is transported by hopping between CDs. In the PVA matrix, however, since the diffusivity of *n*-PrOH is similar to that of *i*-PrOH, *n*-PrOH cannot be transported selectively. In total, the CD-PVA membrane permeates *n*-PrOH more readily than does *i*-PrOH by hopping between CDs.

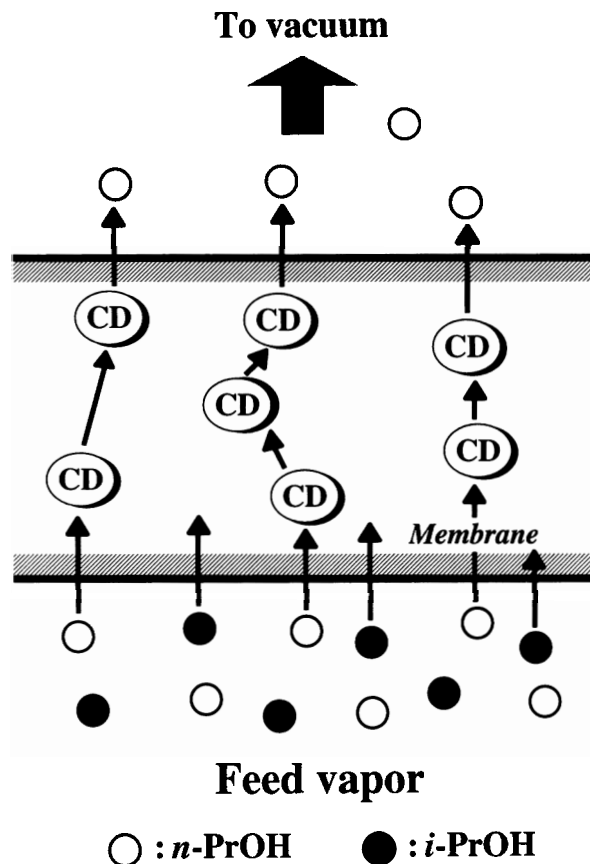


Figure 7 Tentative permeation mechanism of the PrOH isomers through the CD-PVA membrane by evapomeation.

CONCLUSIONS

The characteristics of permeation and separation for the PrOH isomers through the PVA membrane containing CD were investigated by pervaporation and evapomeation. The PrOH isomers could be separated very little through the CD-PVA membrane by pervaporation. However, the CD-PVA membrane permeated *n*-PrOH in preference to *i*-PrOH by evapomeation. In particular, 10 wt % *n*-PrOH in the feed mixture (feed vapor concentration, 7 wt %) was concentrated to about 45 wt % through the CD-PVA membrane. These indicated that evapomeation was more effective for the separation of PrOH isomers through the CD-PVA membrane than was pervaporation. The *n*-PrOH concentration in the permeate and the normalized permeation rate increased with increasing CD content in the CD-PVA membrane. The addition of CD in the PVA membrane resulted in an increase of the degree of swelling and preferential sorption of *n*-PrOH. These results were due to the fact that the affinity of CD for *n*-

PrOH was stronger than that for *i*-PrOH. The characteristics of the permeation and separation through the CD-PVA membrane were discussed from the viewpoint of separation factors and sorption and diffusion selectivities.

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