Concentration of bioethanol and dehydration of organic solvents by porous membranes

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ABSTRACT
In order to obtain higher membrane performance in the concentration of bioethanol and dehydration of organic solvents, porous poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and porous chitosan membranes, respectively, are applied to a temperature-difference controlled evapomeation (TDEV) method in which a temperature difference between the feed solution and the membrane surroundings is established. Pressure treated porous PTMSP membranes showed a high ethanol concentration performance with a high permeation rate and porous chitosan membranes also showed a high dehydration performance in TDEV. Membrane performances through these porous membranes in TDEV are discussed from the viewpoints of physical structure of membranes and permeants.

1. INTRODUCTION
Ethanol that is produced from biomass fermentation is a clean energy source, but its concentration is only about 10 wt% aqueous solution. To effectively apply ethanol in such a dilute aqueous ethanol solution as energy source, it must be concentrated an aqueous solution of dilute ethanol by distillation. In distillation, high energy is required. If an aqueous solution of dilute ethanol can be concentrated by ethanol permeative membranes with high permeation rate and high ethanol selectivity, it is a significant energy saving.

We have developed evapomeation (EV) [1] as a new membrane separation technique which is keeping the advantages of pervaporation (PV) while removing their disadvantages and furthermore developed temperature-difference controlled evapomeation (TDEV) [2,3]. When dense hydrophobic poly(dimethyl siloxane) (PDMS) membranes were applied to TDEV for the concentration of aqueous ethanol solutions, the ethanol/water selectivity was high but the permeation rate was very low. On the other hand, it is well known that poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes have low density in spite of the fact that they are glassy membranes. Hence, we tried to apply to TDEV hydrophobic PTMSP membranes for the concentration of aqueous solutions of dilute ethanol. And also to confirm the mechanism of the permeation and separation characteristics through porous PTMSP membranes in TDEV, dehydration characteristics of dimethyl sulfoxide (DMSO) through porous hydrophilic chitosan membranes in TDEV were investigated. The mechanisms for the permeation and separation characteristics of the ethanol concentration through hydrophobic PTMSP membranes and dehydration of organic solvent through hydrophilic porous chitosan membranes are discussed in detail.

2. EXPERIMENTAL
2.1 Materials
PTMSP (Mw: 1070000, Mn: 374000) was supplied by Nichiyu Co. Ltd. Japan. Chitosan (produced by the bioscience laboratory of Katoki Co. Ltd., Kagawa, Japan) with a degree of deacetylation of 99.4 and an average molecular weight of 5x10^4 – 1x10^5 was used as a membrane material. Acetic acid and sodium hydroxide used for the preparation of chitosan membranes, ethanol or dimethyl sulfoxide (DMSO) employed as one component in the feed mixture and other reagents used in this study were supplied by commercial sources.

2.2 Preparation of membranes
2.2.1 PTMSP membranes
Dense PTMSP membranes were prepared by casting onto Teflon dish 3 wt% PTMSP solution of benzene, cyclohexane or toluene and drying for 24 h at 25 °C. Porous PTMSP membranes were prepared by wet and freeze-drying method. Porous PTMSP membranes in the former method were prepared by pouring 3wt% PTMSP benzene solution onto a glass plate, allowing the solvent to evaporate at 35 °C for a desired period, and immersing the glass plate together with the membrane into acetone bath. After resting in acetone for 24 h, membranes were dried completely under reduced pressure at room temperature. Porous PTMSP membranes in the latter method were prepared by casting 3wt% PTMSP benzene solution onto a Teflon dish, precooling at −5°C in the refrigerator and freezing at −20°C in freezer for 72 h and then freezing dry for 12 h. Porous PTMSP membranes were press treated with at 150-190 °C, for 10 min under 2MPa of pressure.

2.2.2 Porous chitosan membranes
The casting solution was prepared by dissolving chitosan (3.1g) in 1 M CH₃COOH (100 ml) at 25 °C. Porous chitosan membranes were made by pouring the casting solution onto a glass plate treated with silicon oil, precooling at −6 °C for 24 h, freezing at −25 °C for 24 h, freeze drying, and then treating in 1 M NaOH, washing repeatedly by pure water to remove completely NaOH.
and drying at 25 °C.

2.3 Apparatus and measurements

The apparatus and permeation cell for the TDEV experiments are shown in Figures 1 and 2. The TDEV experiments were performed by controlling the temperature of feed mixture and of the membrane surroundings, and maintaining a desired reduced pressure on the permeation side. Ethanol and DMSO concentrations in the feed and permeate were determined by gas chromatography (Shimadzu GC-9A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd.; Shimalite F) heated to 200°C. The results from the permeation of aqueous ethanol or DMSO solutions during TDEV were reproducible, and the errors inherent in the permeation measurements were on the order of a few percent.

The separation factors, \( \alpha_{\text{DMSO/H}_2\text{O}} \), was calculated from Equation (1).

\[
\alpha_{\text{DMSO/H}_2\text{O}} = \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{DMSO}}} \right) \left( \frac{F_{\text{H}_2\text{O}}}{F_{\text{DMSO}}} \right)
\]

where \( F_{\text{H}_2\text{O}} \) and \( F_{\text{DMSO}} \), \( P_{\text{H}_2\text{O}} \) and \( P_{\text{DMSO}} \) are the weight fractions of water and DMSO in the feed mixture and the permeate, respectively.

2.4 Scanning electron microscope measurement

The lyophilized porous PTMSP, chitosan membranes were coated with a layer of evaporated gold and then observed in the scanning electron microscope (JSM-6100).

2.5 Measurement of membrane density

Densities of dense PTMSP membranes were determined from the weight and volume of membrane.

2.6 Measurement of contact angle

Contact angles for water on the surface of PTMSP membranes were measured by a contact angle meter (Erma Model G-1).

2.7 Pressure treatment

Porous PTMSP membranes prepared by freeze-drying method were press treated using Mini Test Press-10 Toyoseiki Co. Ltd.

3. RESULTS AND DISCUSSION

3.1 Effects of casting solvents on the permeation and separation characteristics through dense hydrophobic PTMSP membranes

Figure 3 shows the effects of the temperature of feed solution on the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through dense PTMSP membranes prepared from various casting solvents. As can be seen from Figure 3, with increasing temperature of feed solution, in every membranes, both the permeation rate and ethanol concentration in the permeate increased. The increase in the permeation rate is due to an increase of the mobility of vapors with an increase of feed temperature. On the other hand, the increase in the ethanol concentration in the permeate depends upon an increase in the ethanol concentration in the vapor with increasing feed temperature. From these three figures, we can find both permeation rate and ethanol perm selectivity are benzene > cyclohexane > toluene.

In Table 1, effects of casting solvent on the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through dense PTMSP membranes in TDEV, and chemical and physical structure of dense PTMSP membranes are shown. You can see from Table 1, the permeation rate is strongly influenced by the membrane density and the ethanol permeability is significantly dependent upon the contact angle. These results suggest that the chemical and physical structure of the membrane could be remarkably attributed to the permeation and separation characteristics. However, both the permeation rate and ethanol permeability of dense PTMSP membranes are not high.

Then, porous PTMSP membranes were applied to TDEV to concentrate effectively ethanol in an aqueous solution of dilute ethanol. In Figure 4, in which the feed temperature is kept constant at 40°C and the temperature of membrane surroundings is changed, three types porous PTMSP membranes prepared by wet method, freeze-drying, and freeze dry and press treatment were used. As can be seen in Figure 4, with decreasing the
temperature of membrane surroundings, although a little
decrease in the permeation rate was observed but the
ethanol concentration in the permeate remarkably
increased in every porous PTMSP membranes. Specially,
when a porous PTMSP membrane prepared by freeze-
drying method was press treated, the highest ethanol
permselectivity was given and also a considerably high
permeation rate was shown.

Table 1. Effects of the casting solvent on the permeation
and separation characteristics, physical and chemical
structure of dense PTMSP membranes.

<table>
<thead>
<tr>
<th>Casting solvent</th>
<th>Permeation rate (kg/m² hr)</th>
<th>EtOH in permeate (wt%)</th>
<th>Membrane density (g/cm²)</th>
<th>Contact angle (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.31</td>
<td>27.5</td>
<td>0.32</td>
<td>98.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.25</td>
<td>23.8</td>
<td>0.41</td>
<td>97.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.18</td>
<td>22.2</td>
<td>0.59</td>
<td>96.8</td>
</tr>
</tbody>
</table>

Figure 3. Effects of the feed solution temperature on the
ethanol concentration in permeate (●) and permeation rate
(○) for an aqueous solution of 10wt% ethanol through
the dense PTMSP membrane during TDEV. Pressure: 5.0×10²Pa; the temperature of membrane surroundings:
40 ºC; Solvent: (a) Benzene, (b) Cyclohexane, (c) Toluene.

Figure 4. Effects of the temperature of membrane surroundings on the permeation rate and ethanol concentration in the permeate for an aqueous solution of 10wt% ethanol through porous PTMSP membranes during TDEV. Feed: 10wt% EtOH (40 ºC); pressure: 5.0x10²Pa.

3.2 SEM observation of porous PTMSP membranes
It was confirmed by the SEM observation that a press
treated porous PTMSP membrane had smaller pore size
compared to a non press porous PTMSP membrane.

3.3 Mechanism of permeation and separation for an aqueous solution of ethanol through porous PTMSP membranes in TDEV
A mechanism of the ethanol permselectivity for aqueous ethanol solutions through porous PTMSP membranes in TDEV can be understood by a tentative illustration as shown in Figure 5. Namely, when water and ethanol molecules vaporized from the feed solution come close to the membrane surroundings kept at lower temperature in TDEV, the water vapor aggregates much easier than the ethanol vapor, because the freezing point of water molecule (0 °C) is higher than that of ethanol molecule (-114 °C), and this aggregated water molecules tend to be liquefied as the temperature of the membrane surroundings becomes lower. On the other hand, since the PTMSP membrane has a high affinity to the ethanol molecules, the ethanol molecules easily are sorbed inside pore in a porous PTMSP membrane and such a sorbed layer of the ethanol molecules is formed in an initial stage of the permeation. The vaporized ethanol molecule may be able to be permeated by a surface diffusion on the sorbed layer of the ethanol molecules inside pore. Both the aggregation of the water molecules and the surface diffusion of the ethanol molecule in the pore are responsible for the increase in the ethanol/water selectivity through a porous PTMSP membrane in TDEV. The increase of the ethanol/water selectivity in TDEV can be attributed to both the degree of aggregation of the water molecules on the membrane surroundings and the thickness of the sorbed layer of the ethanol molecules inside pore, which are significantly governed by the temperature of the membrane surroundings. When the temperature of the membrane surroundings becomes lower, the degree of aggregation of the water molecules and the thickness of the sorbed layer of the ethanol molecules are increased. Therefore, the increase in the ethanol/water selectivity for aqueous ethanol solutions was observed with decreasing temperature of the membrane surroundings.

3.4 Effect of press treatment conditions

Effects of the press temperature on the permeation rate and ethanol concentration in the permeate are shown in Figure 6 in which press time is 10 min and press pressure is 2 MPa. With increasing press temperature the permeation rate decreased but the ethanol concentration in the permeate increased. These results could be attributed to the fact that the pore size became smaller with an increase of press temperature.

3.5 Effect of ethanol concentration in the feed

Figure 7 shows the effect of the ethanol concentration in the feed on the permeation separation characteristics through a porous PTMSP membrane in TDEV, in which the feed temperature is 40 °C and the temperature of membrane surroundings is 0 °C, and pressure is 5.0x10²Pa.

![Figure 6. Effect of the press temperature on the ethanol concentration in the permeate and the permeation rate for an aqueous solution of 10wt% ethanol through press treated porous PTMSP membranes during TDEV. Feed temperature: 40°C; the temperature of membrane surroundings: 0°C; pressure: 5.0x10²Pa.](image)

![Figure 7. Effects of the ethanol concentration in the feed solution on the ethanol concentration in permeate (●) and permeation rate (○) through a porous PTMSP membrane during TDEV. Feed temperature: 40°C; the temperature of membrane surroundings: 0 °C; pressure: 5.0x10²Pa.](image)
When the feed solution in first TDEV permeation experiment through a porous PTMSP membrane was an aqueous solution of 10 wt% ethanol, the ethanol concentration in the permeate was 52.3 wt%. When this 52.3 wt% ethanol was used as the feed solution in second TDEV permeation experiment, the ethanol concentration in the permeate was 71.1 wt%. When a similar experiment was carried out, 82.1 wt% ethanol solution in the permeate was obtained. These results could be proposed as a new membrane separation technique for practical applications in the concentration of bio-ethanol of porous hydrophobic polymer membranes.

3.6 Structure of porous chitosan membrane

Figure 8 shows SEM images of the surface and cross section of the porous chitosan membrane. As can be seen from these images, the chitosan membrane prepared in this study has a porous structure. In Figure 9, the pore distribution and pore size of the porous chitosan membrane are shown. This membrane has a pore distribution and average pore size estimated about 10 µm. The maximum pore size determined by the bubble point method [5,6] was about 20 µm.

In Figure 10, the temperature of the feed solution was kept constant at 40°C and the temperature of the membrane surroundings was changed; the pressure on the downstream side was kept at 2x10⁴ Pa. As can be seen from Figure 10, with decreasing temperature of the membrane surroundings, the permeation rate decreased and the separation factor for the H₂O/DMSO selectivity increased. This decrease in the permeation rate can be explained by the temperature conditions. When the temperature difference between the temperature of the feed solution, T_L, and that of the feed vapor, T_V, and the pressure difference between the pressure on the feed side, P_f, and that on the permeate side, P_p are defined as ∆T and ∆P, respectively, it was suggested that an increase in ∆T results in a decrease in ∆P and a decrease in the permeation rate. Consequently, the decrease in the permeation rate with decreasing temperature of the membrane surroundings in Figure 10 significantly depends upon a decrease in ∆P.

On the other hand, the increase in the separation factor for H₂O/DMSO selectivity shown in Figure 10 through a porous chitosan membrane with decreasing temperature
of the membrane surroundings, can be attributed to a tentative mechanism shown in Figure 11.

Figure 11. Tentative mechanism of the permeation and separation characteristics for aqueous DMSO solutions through porous chitosan membranes in TDEV.

3.8 Mechanism of permeation and separation characteristics for an aqueous solution of DMSO through porous chitosan membranes in TDEV

When water and DMSO molecules, vaporized from the feed solution, come close to the membrane surroundings kept at lower temperature in TDEV, the DMSO vapor aggregates much easier than the water vapor, because the freezing point of DMSO molecules (18.5 °C) is much higher than that of water molecules (0 °C), and the aggregated DMSO molecules tend to be liquefied as the temperature of the membrane surroundings becomes lower. Both the aggregation of the DMSO molecules and the surface diffusion of the water molecules in the pores of hydrophilic chitosan membrane are responsible for the increase in the H₂O/DMSO selectivity through a porous chitosan membrane in TDEV. The results in the separation for aqueous DMSO solutions through a water selective porous chitosan membrane in TDEV could support the mechanism in the concentration of ethanol for aqueous ethanol solutions through an ethanol selective porous PTMSP membrane in TDEV mentioned before.

We have reported the permeation and separation characteristics for an aqueous solution of 50 wt% of DMSO through a dense chitosan membrane in TDEV. The permeation rate and the separation factor in a dense chitosan membrane were 0.02 – 0.18 kg/m² hr and 105 – 250, respectively [6]. As can be seen in Figure 10, those in a porous chitosan membrane are 0.05 – 0.28 kg/m² hr and 110 – 1000, respectively. Remarkable difference in the permeation rate and the separation factor for H₂O/DMSO selectivity between dense and porous chitosan membranes can be attributed to the fact that the permeation through a dense chitosan membrane is due to the solution-diffusion model and that through a porous chitosan membrane is based on pore flow, as shown in Figure 11.

On the basis of the above results, it is suggested that an application of porous hydrophilic polymer membranes to TDEV for the dehydration of aqueous DMSO solutions is very advantageous.

CONCLUSIONS

In order to improve the membrane performance in the concentration of ethanol in a dilute bioethanol solution and dehydration of DMSO from aqueous DMSO solution, porous hydrophobic PTMSP and porous hydrophilic chitosan membranes, respectively were applied to TDEV. When the temperature of the feed solution was kept constant and the temperature of the membrane surroundings was set lower than the temperature of the feed solution, both the permeation rate and the EtOH/H₂O or H₂O/DMSO selectivity were significantly improved. These high EtOH/H₂O and H₂O/DMSO selectivity could be attributed to the fact that a certain vapor molecule in a mixture could be easily aggregated on the membrane surroundings at a lower temperature compared with the other vapor molecule.

When the combination of both of the freezing point of the permeants and affinity between polymer membrane and permeant are took into consideration, and a porous polymer membrane is applied to TDEV for the separation of organic liquid mixtures, it was found that more effective separation performance for organic liquid mixtures can be given.

REFERENCES
