

Studies on the State of Permeant in the Membrane and Its Effect on Pervaporation Phenomena

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SYNOPSIS

Pervaporation experiments of pure water and 2-propanol through poly-dimethylsiloxane membranes were carried out in order to study the effect of the interaction between permeant and membrane material on pervaporation phenomena. From the effect of downstream pressure on the pervaporation rate, the saturation vapor pressure of water in the membrane was determined to be 2.799×10^3 Pa (21.0 mmHg), which is the same as the literature value, whereas that of 2-propanol in the membrane was estimated to be 5.865×10^3 Pa (44.0 mmHg), which is 8.53×10^2 Pa (6.4 mmHg) higher than that of pure 2-propanol. In the differential scanning calorimetry analyses of permeants in the membrane, it was evident that the state of 2-propanol in the polydimethylsiloxane membrane was different from that of bulk 2-propanol. On the other hand, the state of water in the membrane was assigned to that of bulk water. Throughout the present study, it was observed that the interaction between permeant and membrane material plays an important role in determining pervaporation phenomena.

INTRODUCTION

Membrane separation techniques have been gathering much attention during the last two decades. This may be because the membrane separation technology has been regarded as one of the most promising energy-saving processes and is expected to give a selectivity higher than the conventional industrial separation technologies such as distillation.

When we think about the separation of organic liquid mixtures, pervaporation, where a membrane acts as a barrier material between an upstream solution in the liquid state and a downstream permeate in the gaseous state, is considered as one of the most suitable separation methods among the membrane separation technologies. It is customary for the downstream side to be maintained at reduced pressure to ensure the gaseous state. Since it was first reported by Kober,¹ pervaporation has been especially thought to be applicable to the separation

of a number of organic liquid mixtures, i.e., azeotropic mixtures, mixtures having close boiling points, structural isomers, or heat-sensitive organics, which are difficult to separate. Such a perspective has already been pointed out by Binning and Kelly in the late 1950s.² The energy crisis in the early 1970s especially directed our attention to the pervaporation technique.

In pervaporation study, the investigation of the state of permeant in the membrane not only stimulates our intellectual interest, but also will offer a guideline for development of novel membrane materials for pervaporation. In the study of reverse osmosis, several papers can be found³⁻⁹ in which the state of water in the membrane was examined. In a pervaporation study by one of the authors,¹⁰ the correlation between membrane performance and the state of water in the membrane has been investigated. In the light of these studies, it is expected that organic permeants will also show multiple states in the membrane that may affect the membrane permeation phenomena of such organic molecules. On the basis of the above concept, polydimethylsiloxane membrane was adopted as a typical membrane that shows permselectivity toward organic molecules.¹¹ The objective of this work was, therefore, to investigate the state of some permeants in

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polydimethylsiloxane membranes by thermal analysis and also to investigate the effect of the state of the permeant molecules on the pervaporation phenomena.

EXPERIMENTAL

The water employed here was purified by reverse osmosis (RO). 2-Propanol was purified in the usual manner.¹²

Polydimethylsiloxane membranes, generously supplied by General Electric Co., were adopted as hydrophobic membranes. The cells for the pervaporation experiments were the same as the static cells used in previous reverse osmosis and ultrafiltration experiments.¹³ The effective area of the membrane was $1.39 \times 10^{-3} \text{ m}^2$. About 100 cm^3 of feed liquid was loaded in the cell. The prescribed reduced pressure was applied at the downstream side of the membrane. The permeate sample was condensed and collected in a cold trap with liquid nitrogen. The flux was determined by measuring the weight of the sample collected during a predetermined period. The operating temperature was kept at $23 \pm 0.1^\circ\text{C}$ throughout the pervaporation experiment. The downstream pressure was controlled within $\pm 1 \text{ mmHg}$.

The state of the permeant in the membrane was studied by a DuPont 2100 thermal analyzer coupled to a 910 differential scanning calorimeter (DSC). The instrument was calibrated with indium and zinc, and the heat of fusion of indium was used to establish the cell constant for accurate enthalpy calculations. After the membrane was dried *in vacuo* at ambient temperature for 2 days, the dried membrane sample was immersed in the liquid under study at 23°C for 3 days. After equilibrium was attained, the membranes to be studied by DSC were blotted with a filter paper to remove extra external liquid and then sealed in crimped aluminum sample pans. The samples were cooled to -160°C and then heated at $10^\circ\text{C min}^{-1}$ to 20 and 60°C for 2-propanol and water-treated membranes, respectively. Nitrogen at flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ was used throughout all DSC measurements.

RESULTS AND DISCUSSION

Pervaporation of water-ethanol mixtures has been intensively studied with respect to the separation of liquid mixtures by polydimethylsiloxane membranes.¹¹ The melting point of bulk ethanol is re-

ported to be -114.49°C ,¹² but the glass transition temperature, T_g , of polydimethylsiloxane was also observed in the vicinity of the melting point of bulk ethanol.¹⁴⁻¹⁶ For example, the T_g of the polydimethylsiloxane membrane studied in this work was observed at a temperature of around -130°C , as shown later in Figures 3 and 5. Closeness of the melting point and the T_g made it difficult to observe the melting endotherm of bulk ethanol in the polydimethylsiloxane membrane. For this reason, we have adopted 2-propanol, of which the melting point is reported to be -88.0°C .¹² Furthermore, the saturation vapor pressure of 2-propanol at ambient temperature is in the range where pervaporation experiments can be conducted with convenience.¹² Water was used as a hydrophilic permeant.

In Figures 1 and 2, the permeation rates for pure water and pure 2-propanol are plotted against downstream pressure, respectively. In both experiments, the permeation rate decreased abruptly in a nonlinear fashion as the downstream pressure increased to the respective saturation vapor pressure. When the downstream pressure was above the saturation vapor pressure, i.e., when the downstream membrane side is in contact with permeate in the liquid phase, the permeation rate was little affected by the downstream pressure; namely, the permeation rate decreased linearly when the downstream pressure was above the saturation vapor pressure. On the other hand, the permeation rate changed more sharply with a change in the downstream pressure

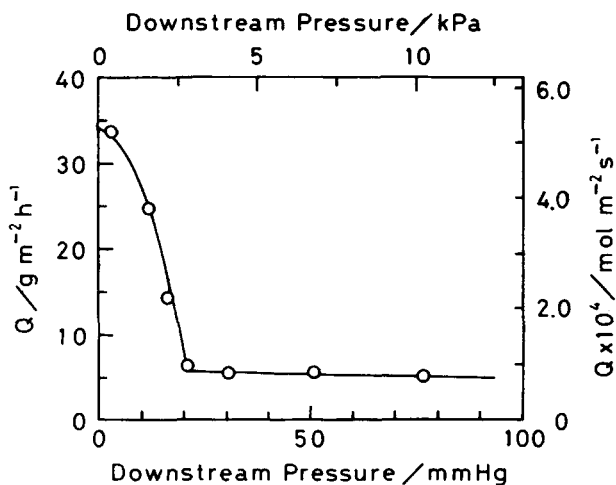


Figure 1 Effect of downstream pressure on pervaporation of pure water through polydimethylsiloxane membrane at 23°C . (The solid line is the calculated line, taking the values $P_2 = 1.013 \times 10^5 \text{ Pa}$, $P_* = 2.799 \times 10^3 \text{ Pa}$, $\delta = 5.08 \times 10^{-5} \text{ m}$, $A = 4.39 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$, and $B = 2.78 \times 10^{-15} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-2}$.)

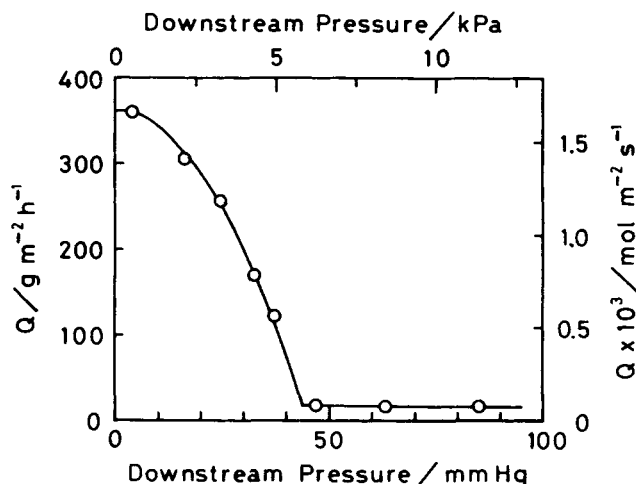


Figure 2 Effect of downstream pressure on pervaporation of pure 2-propanol through polydimethylsiloxane membrane at 23°C. (The solid line is the calculated line, taking the values $P_2 = 1.013 \times 10^5$ Pa, $P_* = 5.865 \times 10^3$ Pa, $\delta = 7.62 \times 10^{-5}$ m, $A = 6.24 \times 10^{-14}$ mol m⁻¹ s⁻¹ Pa⁻¹, and $B = 3.51 \times 10^{-15}$ mol m⁻¹ s⁻¹ Pa⁻².)

when the pressure was below the saturation vapor pressure of the permeant.

To evaluate the saturation vapor pressures for water and 2-propanol in the polydimethylsiloxane membrane, the following set of equations¹⁷ was employed:

$$Q = (A/\delta)(P_2 - P_*) + (B/\delta)(P_*^2 - P_3^2) \quad (1)$$

$$\text{when } P_3 \leq P_*$$

$$Q = (A/\delta)(P_2 - P_3) \quad \text{when } P_3 > P_* \quad (2)$$

where Q (mol m⁻² s⁻¹) is molar flux; A (mol m⁻¹ s⁻¹ Pa⁻¹) and B (mol m⁻¹ s⁻¹ Pa⁻²) denote constants for pervaporation; δ (m) denotes the membrane thickness; and P_2 (Pa), P_* (Pa), and P_3 (Pa) denote upstream pressure, saturation vapor pressure, and downstream pressure, respectively.

Figures 1 and 2 also show the permeation rate data calculated on the basis of Eqs. (1) and (2) with numerical parameters given in the figure captions.

As for the pervaporation of water through a polydimethylsiloxane membrane, the experimental data in Figure 1 closely follow the theoretical line generated using Eqs. (1) and (2) and the literature value for the saturation vapor pressure of water [2.799×10^3 Pa (21.0 mmHg)].¹² These results indicate that there is no observable interaction between the membrane and water. As for the saturation vapor pressure of 2-propanol, 5.865×10^3 Pa (44.0 mmHg) was determined to give the best-fit calculated curve

through the pervaporation data shown in Figure 2. This value is 8.53×10^2 Pa (6.4 mmHg) higher than the expected 5.012×10^3 Pa (37.6 mmHg), which was calculated for bulk 2-propanol at 23°C from data provided in Ref. 12. The discrepancy between the saturation vapor pressure value obtained from the pervaporation experiments and that for bulk 2-propanol leads to the conclusion that there might be a specific interaction between permeant, 2-propanol, and membrane material. Hydrogen bonding between 2-propanol and the polydimethylsiloxane backbone oxygen is regarded as a dominant interaction. However, because of the high volatility of 2-propanol from the membrane, infrared spectroscopy failed as a method of interaction detection. The validity of pervaporation Eqs. (1) and (2) was also verified in the present work as shown by the good agreement of experimental data and the calculated lines. If the above conclusion is correct, a melting point suppression should be observed particularly for the 2-propanol/polydimethylsiloxane membrane system.

An example of the melting endotherm of water in a polydimethylsiloxane membrane is shown in Figure 3(a). The endotherm of melting for the water in the membrane was identical to that of pure water. The membrane contained ca. 1.3×10^{-3} g of water, which quantity corresponds to an endotherm of 0.434 J. The observed endotherm was 0.410 J. The observed value is in fair agreement with the calculated value. From Figure 3(a), therefore, it was concluded that all water in the polydimethylsiloxane membrane can be assigned to free (bulk) water. To confirm this, enthalpic heats of melting for water

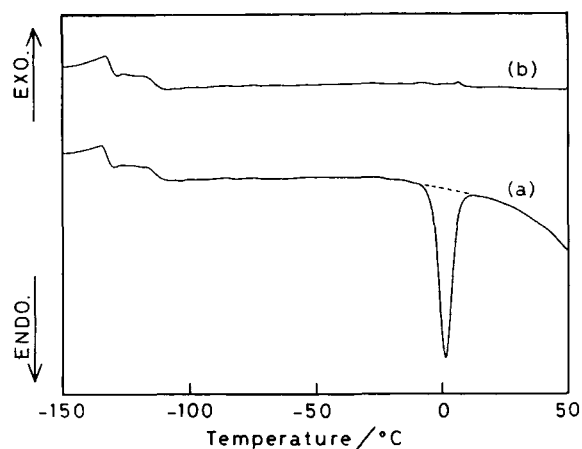


Figure 3 DSC heating curve of polydimethylsiloxane membrane/H₂O (a) and dry membrane (b). (Amount of water in the membrane, ca. 1.3×10^{-3} g. Weight of dry membrane, 1.69×10^{-2} g.)

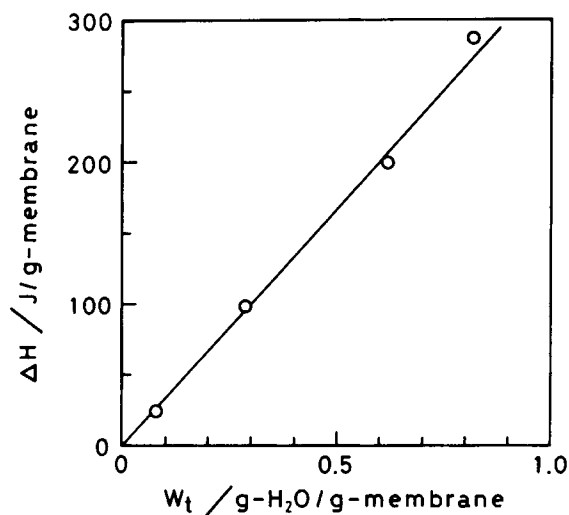


Figure 4 Relationship between enthalpic heat for water in polydimethylsiloxane membrane and total water content.

are plotted as a function of total water content (Fig. 4). As shown in Figure 4, the data plots are indeed linear with a slope that is approximately equal to the literature value of 333.4 J g^{-1} .¹² The results in Figure 4 can support the conclusion that all water in the polydimethylsiloxane membrane is assigned to free (bulk) water. In addition, the glass transition temperature of the polydimethylsiloxane was observed around -130°C .

Melting endotherms of 2-propanol in the membrane, of dry membrane, and of bulk 2-propanol are shown in Figure 5. The areas of the endothermic curve at -88°C decrease with a decrease in 2-propanol content in the membrane [Figs. 5(a)–(d)]. In Figures 5(e)–(g), endotherms of 2-propanol were scarcely observed around its melting point of -88.0°C , even though 2-propanol was still present in the polydimethylsiloxane membrane. No other new endotherm was observed in the temperature range -160°C to 20°C . The membrane in Figure 5(g) contained $3.7 \times 10^{-3} \text{ g}$ of 2-propanol. The endotherm of $4.4 \times 10^{-3} \text{ g}$ of bulk 2-propanol is shown in Figure 5(i). If most of the 2-propanol in the membrane could be assigned as bulk 2-propanol, we should be able to observe an endotherm in Figures 5(e)–(g).

Figure 6 shows the relationship between enthalpic heat and 2-propanol content. If the data are accurate, the points should fall on a straight line with a slope equal to the heat of melting of bulk 2-propanol ($\Delta H_M = 89.9 \text{ J g}^{-1}$ [Ref. 12]). Extrapolation to $\Delta H = 0$ should intercept the 2-propanol content axis at

a point that is equal to the total bound 2-propanol in the membrane. The experimental data indeed showed a straight-line relationship with an slope that was approximately equal to 89.9 J g^{-1} . The total bound 2-propanol content in the polydimethylsiloxane membrane was determined to be $0.47 \text{ g-2-propanol/g-membrane}$ by extrapolating the data to $\Delta H = 0$. Figures 5 and 6 lead to the conclusion that there is the bound 2-propanol in the polydimethylsiloxane membrane. The bound 2-propanol was presumably formed by the specific interaction between 2-propanol and the membrane matrix. As a result, 2-propanol forms a structure that is different from that of bulk 2-propanol.

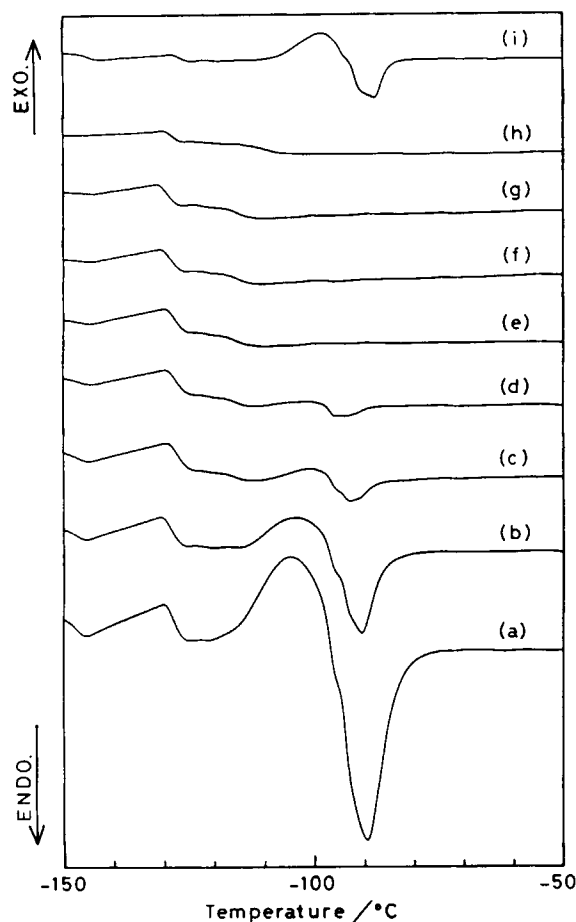


Figure 5 DSC heating curves of polydimethylsiloxane membrane/2-propanol (a–g), dry membrane (h), and pure 2-propanol (i). [Amount of 2-propanol in the membrane: (a) $1.64 \times 10^{-2} \text{ g}$; (b) $1.02 \times 10^{-2} \text{ g}$; (c) $9.1 \times 10^{-3} \text{ g}$; (d) $7.1 \times 10^{-3} \text{ g}$; (e) $5.8 \times 10^{-3} \text{ g}$; (f) $4.7 \times 10^{-3} \text{ g}$; (g) $3.7 \times 10^{-3} \text{ g}$. Amount of pure 2-propanol (i), $4.4 \times 10^{-3} \text{ g}$. Weight of dry membrane, $1.74 \times 10^{-2} \text{ g}$.]

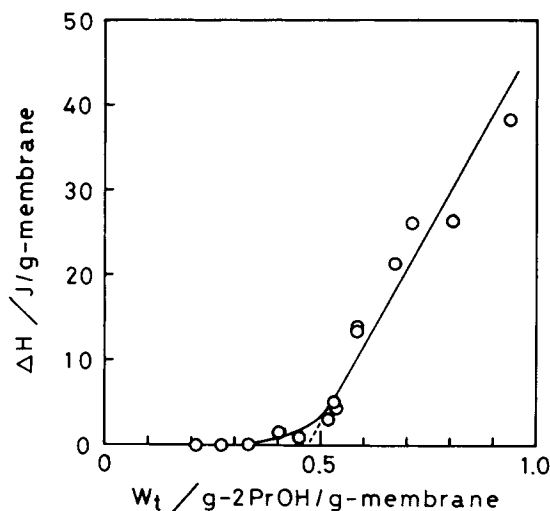


Figure 6 Relationship between enthalpic heat for 2-propanol in polydimethylsiloxane membrane and total 2-propanol content.

CONCLUSIONS

From the present study, the following conclusions can be drawn:

1. The saturation vapor pressure of water in a polydimethylsiloxane membrane is that of bulk water.
2. The saturation vapor pressure of 2-propanol in a polydimethylsiloxane membrane is higher than that of bulk 2-propanol.
3. The state of water in the membrane is that of bulk water.
4. The state of 2-propanol in the membrane is different from that of bulk 2-propanol.
5. There is a melting point suppression for 2-propanol in the membrane.
6. The specific interaction between permeant and membrane material plays an important

role in determining pervaporation phenomena.

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