SHORT COMMUNICATIONS

Studies on the State of Methanol in a Polydimethylsiloxane Membrane by Differential Scanning Calorimetry and Pervaporation Technique

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The study of the state of permeant in the membrane not only stimulates our intellectual interest but also is one of the most important studies to understand membrane transport phenomena. Furthermore, this study provides information on the interaction between low molecular weight compounds and macromolecules.

Several papers have been published on the state of water in the membrane which was examined in connection with reverse osmosis.^{1–7} For pervaporation investigations have been started recently by the authors^{8–11} in connection with the study on the relation between permselectivity and the state of permeants in the membrane. The state of organic compounds in the membrane attracts the authors' attention partly because pervaporation technique is regarded as a suitable and alternative separation technique for separation of organic liquids including azeotropic mixtures, mixtures having close boiling points, structural isomers, or heat-sensitive organics, which are difficult to separate, and partly because this study is important not only for the pervaporation study but also for the study on the state of organic liquids in

macromolecules in general. We have investigated the state of 2-propanol,^{9,10} and ethanol¹¹ in polydimethylsiloxane membranes and found that they are present in the bound as well as the bulk state in the membrane.

In the present short communication, our attention is focused on the pervaporation of methanol through a polydimethylsiloxane membrane and its state in the membrane, since methanol is one of the most important organic intermediates in the chemical industry¹² and one of top fifty chemicals production.¹³

Methanol employed in this study was purified in the usual manner.¹⁴ Polydimethylsiloxane (PDMS) membranes of thickness 7.62×10^{-5} m, generously supplied by General Electric Co., were used for membrane samples.

The saturation vapor pressure of methanol in PDMS membrane was estimated by using the data obtained from pervaporation experiments. The static cells for pervaporation experiments were the same as one used in reverse osmosis and ultrafiltration experiments.¹⁵ The effective area of the membrane was 1.39×10^{-3} m². About 200 cm³ of feed liquid was loaded in the cell. The prescribed reduced pressure was applied to the down-

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stream 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 prescribed period. The operating temperature was kept at $23.0 \pm 0.1^\circ\text{C}$ throughout the period. The downstream pressure was controlled within 1 mmHg.

The state of methanol in the membrane was studied by a SEIKO DSC 200 coupled with SSC 5000. After the membrane was dried *in vacuo* at 56°C for 2 days, the dried membrane sample was immersed in methanol at 25°C for at least 4 days. After equilibrium was attained, the membranes to be studied by DSC were blotted with a filter paper to remove extra liquid and transferred to the aluminum pan which was hermetically sealed. The sample was cooled to -160°C and then heated at the speed of $10^\circ\text{C min}^{-1}$ to 20°C . Nitrogen at the flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$ was used throughout all DSC measurements.

In Figure 1, the flux for pure methanol is plotted against downstream pressure. The flux decreased abruptly in a nonlinear fashion as the downstream pressure increased to the saturation vapor pressure. When the down-

stream pressure was above the saturation vapor pressure, that is, when the downstream membrane side is in contact with permeant (methanol) in the liquid phase, the flux decreased linearly. A similar profile was also observed and analyzed in pervaporation of hexane through a polyethylene membrane,¹⁶ that of 2-propanol,^{9,10} and ethanol¹¹ through a PDMS membrane.

In the previous papers,⁹⁻¹¹ we reported the increase in the saturation vapor pressure of permeants in PDMS membrane. In the present study, it is also expected that the saturation vapor pressure of methanol in a PDMS membrane is higher than that of bulk methanol as observed for 2-propanol and ethanol in PDMS membrane, since the permeant methanol belongs to a family of monohydric lower alcohols such as 2-propanol and ethanol. In order to evaluate the saturation vapor pressure of methanol in the PDMS membrane, the following set of equations were employed.¹⁷

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

when

$$P_3 \leq P_*$$

$$Q = (A/\delta)(P_2 - P_3) \quad (2)$$

when

$$P_3 > P_*$$

where Q ($\text{mol m}^{-2} \text{ s}^{-1}$) is molar flux; A ($\text{mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) and B ($\text{mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-2}$) denote constants characteristic to membranes; δ (m) is the membrane thickness; P_2 (Pa), P_* (Pa), and P_3 (Pa) denote upstream pressure, saturation vapor pressure, and downstream pressure, respectively.

Figure 1 shows the flux data calculated on the basis of eq 1 and 2 with numerical parameters given in the captions.

As for the saturation vapor pressure of methanol in a PDMS membrane, 1.57×10^4 Pa (118.0 mmHg) was determined to give the best fit calculated curve through the pervaporation data shown in Figure 1. This value is 500 Pa

Figure 1. Effect of downstream pressure on pervaporation of pure methanol through polydimethylsiloxane (PDMS) membrane at 23°C . (The solid line is calculated from the values of $P_2 = 1.013 \times 10^5$ Pa, $P_* = 1.57 \times 10^4$ Pa, $\delta = 7.62 \times 10^{-5}$ m, $A = 7.15 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$, and $B = 4.49 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-2}$.)

(3.6 mmHg) higher than the expected 1.52×10^4 Pa (114.4 mmHg), which was calculated for bulk methanol at 23°C from data provided in ref 14. The increase in saturation vapor pressure indicates that the interactions between the permeant methanol and the PDMS membrane are weaker than the methanol-methanol interaction in the pure liquid. The discrepancy between the saturation vapor pressure obtained from the pervaporation experiments and that for bulk methanol leads to the conclusion that there is a specific interaction between permeant methanol and the membrane material. At present, two different kinds of interactions come into our mind such as specific interactions: hydrogen bonding interaction and hydrophobic interaction. The former is the interaction between hydroxyl moiety in methanol and oxygen atom in a PDMS repeating unit. In this case, methanol plays the role as a hydrogen donor and PDMS as a hydrogen acceptor. The latter interaction is that between the methyl group in methanol and methyl moiety in a PDMS. It is, at present, impossible to specify the nature of interaction which caused the increase in saturation vapor pressure of methanol in a PDMS membrane.

From the results obtained in the 2-propanol/PDMS membrane system^{9,10} and the ethanol/

Figure 2. Relationship between enthalpic heat for methanol in polydimethylsiloxane (PDMS) membrane and total methanol content in the membrane.

PDMS membrane system,¹¹ it is anticipated that a melting point suppression should be observed for the methanol/PDMS membrane system, too. Figure 2 shows the relationship between enthalpic heat and methanol content in the membrane. The plot of the data indeed shows linearity with a slope of 107 J g^{-1} , which is approximately equal to the literature value of 100 J g^{-1} .¹⁴ The straight line, however, does not pass through the origin. The intercept of the straight line with $\Delta H=0$ should coincide with the amount of bound methanol, which according to Figure 2 is 0.10g-methanol/g-membrane. In our earlier works we have reported that 2-propanol^{9,10} and ethanol¹¹ are present in the PDMS membrane both in bound and bulk state. Whereas the total amount of bound 2-propanol in the PDMS membrane was determined to be 0.47g-2-propanol/g-membrane,^{9,10} that of ethanol has never been evaluated because of the closeness of the melting point of ethanol to the glass transition temperature, T_g , of PDMS.¹¹ In order to compare the methanol/PDMS membrane with the 2-propanol/PDMS membrane system, the amount of bound permeant (mol-alcohol/g-membrane) and the ratio of surface area of alkyl moiety to that of hydroxyl group in alcohol¹⁸ are summarized in Table I. According to the table, more 2-propanol is present in the bound state in the membrane than methanol. Since large surface area ratio indicates the stronger hydrophobicity of a molecule, according to Table I 2-propanol is

Table 1. Bound permeant in the PDMS membrane

	Amount of bound alcohol		Surface area ratio ^a
	g-alcohol	mmol-alcohol	A_R/A_{-OH}
	g-membrane	g-membrane	
Methanol	0.10	3.1	1.5
2-Propanol	0.47 ^b	7.8 ^b	3.3

^a Calculated by the data provided in ref 18.

^b Cited from ref 9 and 10.

more hydrophobic than methanol, which is of course well known.¹⁹ Table I indicates that the specific interaction between permeant and membrane material becomes stronger as the carbon number of permeant increases and, as a consequence, hydrophobicity of permeant increases. However, this does not necessarily mean that the hydrophobic interaction is predominant. Moreover, with a further increase in the carbon number of permeant alcohol, the formation of the bound permeant may be hindered due to the fluctuation of the long alkyl chain.

In the present study, it was found that methanol in the polydimethylsiloxane (PDMS) membrane exhibits anomalous physicochemical properties, such as an increase in the saturation vapor pressure and melting point suppression. The observed phenomena are important not only for the pervaporation study but also for the study on the state of organic liquids in macromolecules. Further studies on the state of higher alcohols and other organic liquids in the PDMS membrane is in progress and results will be reported shortly.

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