Pervaporation of Methanol–Water Mixture by Poly(γ-methyl L-glutamate) Membrane and Synergetic Effect of Their Mixture on Diffusion Rate

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Synopsis

The pervaporation behaviors of methanol–water by poly(γ-methyl L-glutamate) (PMLG) membrane at non-steady- and steady-state permeation were investigated. The values of $t_{1/2}$ (time required to reach a half value of steady-state permeation flux) for methanol and water changed and did not change with the component in feed, respectively. Both of the average diffusion coefficients for methanol– and water–PMLG from the mixture changed exponentially with the sorption amount of methanol by the synergetic effect on diffusion. The difference in behavior of non-steady and steady state diffusion was explained by whether D_0 (diffusion coefficient at zero penetrant concentration) was influenced by the concentration distribution of penetrant in PMLG membrane.

INTRODUCTION

Separation of water–alcohol mixtures by polymer membranes, the pervaporation, has been investigated by many workers. Heisler et al.[1] have investigated the effect of additive solutes on the separation of water–ethanol mixture using cellophane. In the case of use of a water-soluble and ethanol-insoluble additive, such as sodium formate, the separation factors were greatly increased. Misra et al.[2] explained the effect of solutes as the difference of interaction of solute–water and solute–ethanol within the membrane. Carter and Jagannadhaswamy[3] investigated the separation of a number of pairs of liquids mixtures and polymer membrane including the pair of water–isopropanol mixture and cellophane. They suggested that when only one component of a mixture swells the membrane well, this component diffuses and is selectively separated. But they did not refer to the effects of liquids mixture on the sorption and diffusion. Huang and Jarvis[4] investigated the separation of aqueous alcohol solutions through cellophane and poly(vinyl alcohol) membranes. They suggested that the separation of the water–alcohol solution at given water contents increased as the molecular length of the alcohols increased, and that the water concentration in the binary solution affected the separation of them.

A change of structure of water in liquid phase by adding alcohol was related to their sorption behavior in polymer membrane by Nakajima and Shibukawa[5,6] using poly(vinyl acetate) and poly(vinyl alcohol) membrane. Such an effect of liquids mixture must be considered for the separation of binary liquids mixture by the pervaporation.

Fels and Huang[7] examined the pervaporation by the free volume theory and

they[8] extended the theory to the diffusion of binary liquids mixture. Uchikura et al.[9] investigated the diffusion of gases mixture of methane–isobutane through styrene–butadiene–styrene block copolymer membrane. They found that the diffusion coefficients obtained from time lags of permeation of methane decreased with the increasing of contents of methane in the mixture. Suzuki et al. investigated the effect of liquids mixture on the diffusion from the behaviors of non-steady[10]- and steady[11]-state permeation of athermal liquids mixture and benzene–cyclohexane mixture.[12] If the liquid component has a plasticizing effect on the polymer membrane, a synergetic effect of liquids mixture on the diffusion was observed.

In this paper, the diffusion behavior of the liquids mixture of methanol–water which has strong interaction between them is investigated using the poly(γ-methyl L-glutamate) (PMLG) membrane.

EXPERIMENTAL

PMLG was obtained from Ajicoat A-2000 which was accepted from Ajinomoto Co., Ltd. Its membrane was prepared by casting from its benzene–methanol (85/15) solution.[13]

The apparatuses used to measure the sorption and the pervaporation were described in previous papers.[10,12]

RESULTS AND DISCUSSION

Sorption of Binary Liquids Mixture

The amounts of methanol and water sorbed into PMLG from their mixtures of various compositions are plotted against the weight fractions of water in them. The results are shown in Figure 1. In the sorptions from pure methanol and
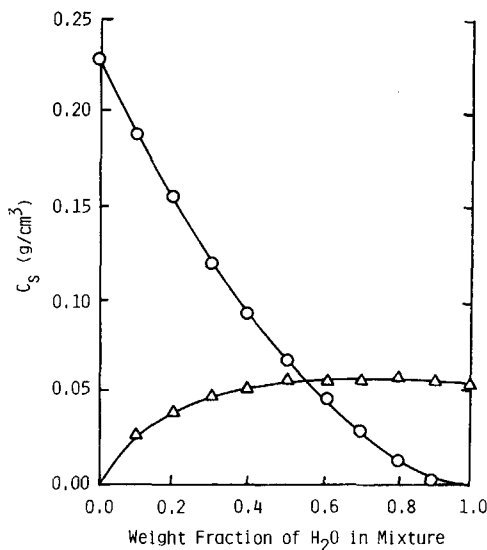

Fig. 1. Amounts of sorbed (C_v) CH_3OH and H_2O. System: CH_3OH–H_2O–PMLG. (○) CH_3OH; (△) H_2O.
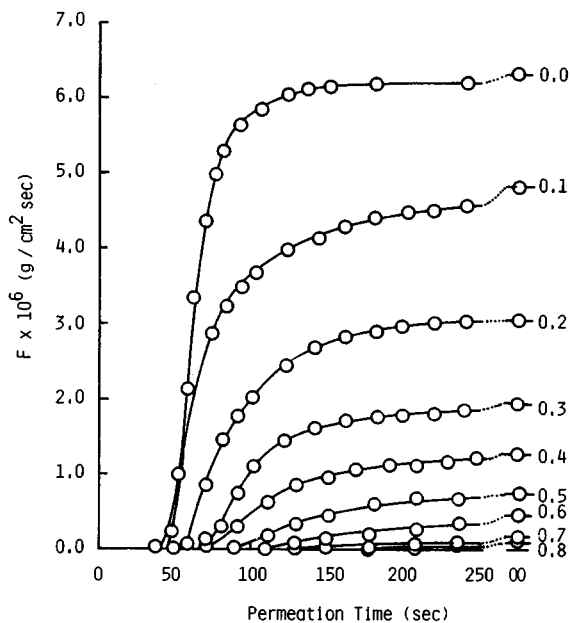
Fig. 2. Permeation fluxes (F) vs. time of CH_3OH. System: CH_3OH–H_2O–PMLG. Numbers: weight fractions of H_2O in feeds.

water, the amount of sorbed methanol was five times that of water. The amounts of sorbed methanol changed monotonically with a change in weight fraction of water (methanol) in the liquids phase. The curve of water in this figure showed a maximum at a range of weight fraction of 0.7–0.8 of water in the liquid phase. This range has been known as the region which is different from the ideal state of thermodynamic interaction by the mixing of binary liquids. The difference based on the strong interaction between binary liquids will contribute to the anomalous sorption behavior. The curve descends suddenly at the weight fraction of 0.4, corresponding to the break in water structure and the formation of idealized mixing.

Non-Steady-State Permeation Behavior of Binary Liquids Mixture

The relation curves of permeation fluxes vs. time of methanol and water using their mixtures as penetrants are shown in Figures 2 and 3, respectively. Numbers in these figures show the weight fractions of water in binary liquids mixtures. As shown in Figure 2, the relation curves of permeation fluxes vs. time for methanol transferred to a side of long time with the increasing of water in feed. The time required to reach a half permeation flux of that at the steady state, $t_{1/2}$, of pure methanol was 52 s, but the one obtained from the mixture of 0.8 weight fraction of water increased to 205 s. The steady-state permeation fluxes decreased with the increasing of water in feed.

The relation curves of permeation fluxes vs. time of water scarcely transferred with mixing of methanol in feeds, differing from the systems of methanol–ethanol–PMLG[10] and benzene–cyclohexane–PMLG[12] reported recently. The steady-state permeation flux showed the maximum value at a weight fraction of 0.3 of water in feed.
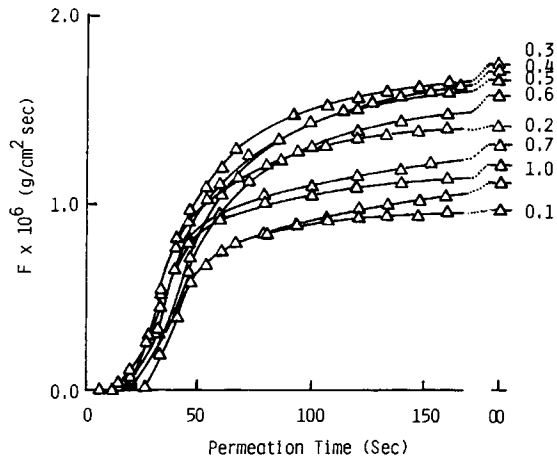
Fig. 3. Permeation fluxes (F) vs. time of H_2O. System: $CH_3OH–H_2O–PMLG$. Numbers: weight fractions of H_2O in feeds.

The values of the reciprocal of $t_{1/2}$ of methanol and water obtained from the curves of Figures 2 and 3 were plotted against the weight fraction of water in feeds, and the results are shown in Figure 4 with semilogarithmic relations. The results showed, as anticipated from Figures 2 and 3, that the values of the reciprocal of $t_{1/2}$ of methanol decreased with the increasing of water in feeds and that those of water scarcely changed with the mixing of methanol in feeds.

The diffusion data which have been obtained for the other systems of methanol–ethanol–PMLG[10] and benzene–cyclohexane–PMLG[12] in comparison with the system of methanol–water–PMLG, are shown in Table I. The diffusion coefficient for water–PMLG was obtained from the intercept of the plot of $\ln(t^{1/2}F)$ vs. $1/t$[14] for pure water permeation (in Fig. 2). The system of metha-
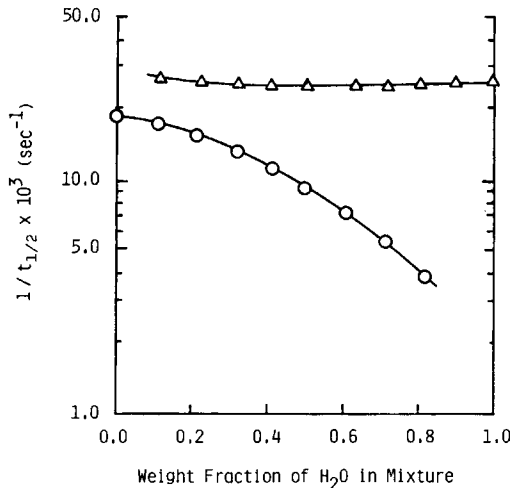

Fig. 4. $\ln 1/t_{1/2}$ vs. weight fraction of H_2O in feeds. System: $CH_3OH–H_2O–PMLG$. (O) CH_3OH; (△) H_2O.

TABLE I
Diffusion Data from Some Pairs of Liquids Mixture through PMLG Membrane

	Penetrant					
	CH_3OH	$C_2H_5OH^a$	C_6H_6	$C_6H_{12}^b$	CH_3OH	H_2O
$D_0 \times 10^8$ (cm²/s)	2.3	1.2	1.4	1.2	2.3	9.6
γ (cm³/g)	6.5	5.5	3.7	$\doteq 0$	6.5 (6.8)^c	0

[a] From Ref. 11.
[b] From Ref. 12.
[c] From this pair.

nol–water–PMLG is different from the two others because the zero concentration diffusion coefficient (D_0) for water–PMLG, which does not show the plasticizing effect (γ),[15] is greater than that for methanol–PMLG with larger γ.

The separation column of gas chromatograph was removed from the permeation apparatus, and the permeates were introduced directly without separating each component into the detector; the relation curves of permeation fluxes vs. time of mixtures are shown in Figure 5. The numbers in this figure show the weight fraction of water in feeds. Each curve shows a two-stage permeation type corresponding to the permeation of water and methanol. This phenomenon did not disappear in the cases of methanol–ethanol–PMLG and benzene–cyclohexane–PMLG systems.[10,12]

Steady-State Permeation Behavior of Binary Liquids Mixture

The steady-state permeation fluxes of methanol and water through PMLG membrane are plotted against the weight fractions of water in feeds mixture and shown in Figure 6. The permeation fluxes of methanol decreased monotonically with the increasing of water in the feeds mixture. In contrast, the permeation fluxes of water showed a maximum value at the weight fraction of 0.3–0.4 and decreased quickly below this fraction. These curves were similar to the shapes of the sorption curves shown in Figure 1. This result shows that the sorption behavior strongly influences permeation.
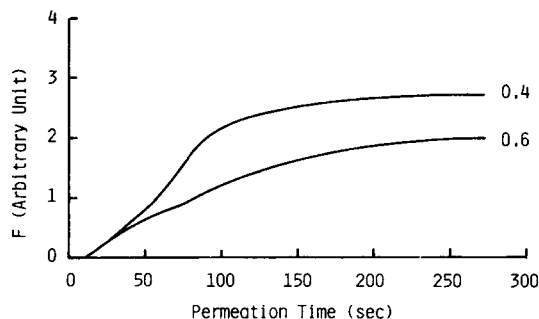

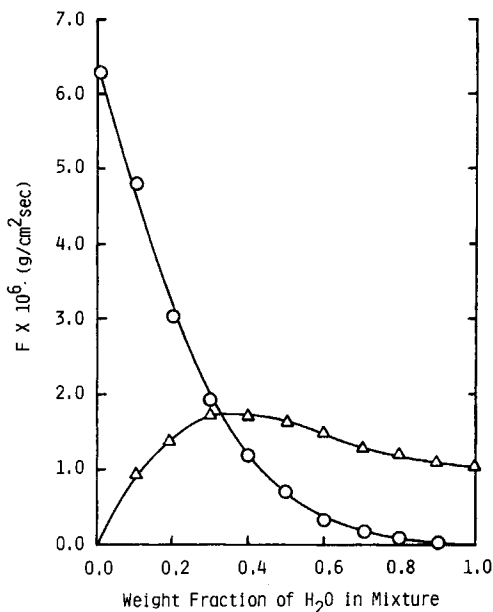Fig. 5. Permeation fluxes (F) vs. time of CH_3OH–H_2O mixtures. System: CH_3OH–H_2O–PMLG. Numbers: weight fractions of H_2O in feeds.

Fig. 6. Steady-state permeation fluxes (F) vs. weight fractions of H_2O in mixture. System: $CH_3OH-H_2O-PMLG$. (O) CH_3OH; ($\triangle$) H_2O.

Diffusion Behavior of Binary Liquids Mixture

By use of the values of sorption and permeation fluxes shown respectively in Figures 1 and 4, the average diffusion coefficients $\overline{D}$ are obtained by,

$$\overline{D} = \frac{F \times l}{C_s} \tag{1}$$

where l is the membrane thickness.

The semilogarithmic relation between the average diffusion coefficients and the sorption amounts are shown in Figure 7. The diffusion coefficients for methanol(1)–PMLG change exponentially with the sorption amount of methanol. But the ones for water(2)–PMLG show an anomalous behavior to the sorption amounts of water. When $\overline{D}_2$ for water–PMLG were plotted to the amounts of sorbed water (C_{s2}), there was a relationship convex to the sorption axis, and when these were plotted to the sorption amounts of methanol (C_{s1}), the linear relationship was obtained. This result was similar to that for the diffusion of cyclohexane in the system of benzene–cyclohexane–PMLG shown in the previous paper.[12]

Assuming the synergetic effect on the concentration dependence of the diffusion coefficient,[10-12] the diffusion coefficients are expressed by assuming the exponential relation to be

$$\overline{D}_1 = D_{01} \exp(\gamma_1 C_{s1} + \gamma_2 C_{s2}) \tag{2}$$

and

$$\overline{D}_2 = D_{02} \exp(\gamma_1 C_{s1} + \gamma_2 C_{s2}) \tag{3}$$

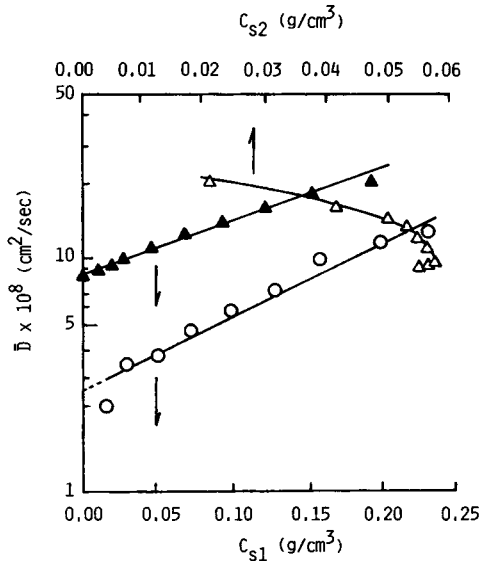Fig. 7. $\ln \overline{D}$ vs. C_s.   System: CH$_3$OH(1)–H$_2$O(2)–PMLG.   (○) $\ln \overline{D}_1 \sim C_{s1}$; (△) $\ln \overline{D}_2 \sim C_{s2}$; (▲) $\ln \overline{D}_2 \sim C_{s1}$.

If the parameter of γ_2 (for water–PMLG) is zero,[15] eqs. (2) and (3) are simplified to[12]

$$\overline{D}_1 \doteqdot D_{01} \exp(\gamma_1 C_{s1}) \tag{4}$$

and

$$\overline{D}_2 \doteqdot D_{02} \exp(\gamma_1 C_{s1}) \tag{5}$$

Therefore, the relation between $\ln \overline{D}_2$ vs. C_{s1} will be shown as the nearly linear relationship with similar slopes.   From the interception of the relation between $\ln \overline{D}_1$ vs. C_{s1}, D_{01} turns out to be 2.3×10^{-8} cm^2/s, which is the same as the value obtained from the methanol–ethanol–PMLG system.[11]   The value of γ_1 (methanol–PMLG) is 6.8 cm^3/g, and it is also similar to the value of 6.5 cm^3/g obtained from the methanol–ethanol–PMLG system.[11]   These results show that there is no large error in this assumption.

It is clear from Figure 7 that the diffusion coefficients for water–PMLG change with the sorption amounts of methanol differing from the case of $t_{1/2}$, which is well known to be proportionate for reciprocals of the diffusion coefficient,[16] shown in Figure 4.   It may be considered that the difference between diffusion behaviors of the non-steady- and steady-state permeations is based on a dependence of D_0 (Ref. 17) on the concentration distribution of penetrants at non-steady- and steady-state permeation.

The concentration distribution of methanol and water at non-steady-state permeation is shown in Figure 8.   These curves were obtained for 0.3 weight fraction of water in feed.   The conditions to obtain[18] the figure are shown as follows: methanol, $C_{eq} = 0.102$ g/cm^3, $D_{01} = 2.3 \times 10^{-8}$ cm^2/s, $\gamma_1 = 6.8$ cm^3/g; water, $C_{eq} = 0.05$ g/cm^3, $D_{02} = 9.6 \times 10^{-8}$ cm^2/s, $\gamma_2 = 0$; permeation time, 10 s; membrane thickness, 43 μm.
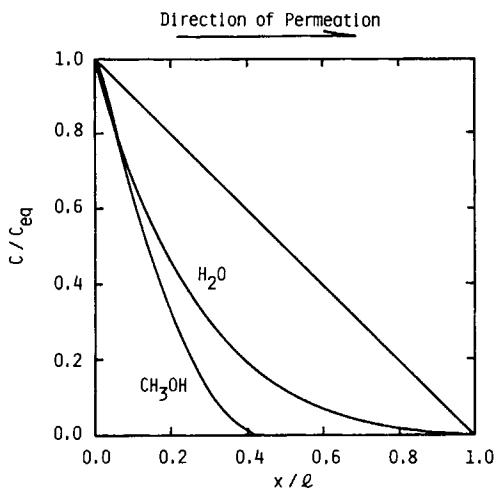
Fig. 8. Concentration profiles of CH_3OH and H_2O at non-steady-state permeation through PMLG membrane. Systems: CH_3OH–PMLG, H_2O–PMLG. Permeation time: 10 s. Membrane thickness: 43 μm.

It is clear from this figure that the diffusion of water at an earlier time precedes that of methanol at even a 0.3 weight fraction of methanol in feed. This figure will support the suggestion because of the difference of diffusion behavior at non-steady- and steady-state permeation.

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