

Pervaporation of Benzene–Cyclohexane Mixture by Poly(γ -methyl L-Glutamate) Membrane and Synergetic Effect of Their Mixture on Diffusion Rate

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Synopsis

The pervaporation of binary liquids mixture of benzene and cyclohexane was examined by use of poly(γ -methyl L-glutamate) (PMLG) membrane. The permeation rate–time curve for each of benzene and cyclohexane from their mixtures changed to the longer times side by increasing the cyclohexane in the mixtures. $t_{1/2}$ (the time required to reach a half-value of the steady state permeation rate) for the each component increased exponentially with increasing of cyclohexane, which has a smaller plasticizing effect on PMLG membrane than benzene, in the mixtures. The apparent diffusion coefficients, obtained from the steady state permeation and the sorption experiments, for benzene–PMLG and cyclohexane–PMLG are dependent exponentially on the sorbed amounts of benzene. This result was explained on the bases that the diffusion of cyclohexane was enhanced synergetically with benzene coexisting in the system. This effect influenced negatively the separation of the liquids mixture by pervaporation.

INTRODUCTION

Both benzene and cyclohexane are composed of the six-member rings of aromatic and aliphatic compounds, respectively, and are nonpolar ones. Since the difference of the temperature of boiling points between them is only 0.6°C and the interaction parameter between them is small, the liquid–vapor equilibrium curve of the binary liquids mixture is nearly a close-boiling system, and shows an azeotropic point at 61 mol % of benzene. However, different affinities between these solvents to polymers have been observed. Thus the separation of their mixture by distillation may be difficult, and the separation by use of permselectivity of polymer membrane was examined by some workers.^{1–3}

Huang and Lin¹ showed an existence of maximum permeation rate of their mixture through poly ethylene membrane at a composition of 50% in feed. McCandless et al.² examined the separation of them by poly(vinylidene fluoride) membrane, and obtained a value of separation factor as 20. They added the solvent, such as dimethyl sulfoxide or dimethyl form amide, in the feed mixture to make the permeation rate increase. But the value of separation factor decreased to 6 by adding the solvent. Cabasso et al.³ examined the separation and diffusion mechanism of them through polymeric alloy membranes of various composition of polyphosphonates and acetyl cellulose by using the techniques of sorption, desorption, permeation, and self-diffusion of benzene labelled C¹⁴. They obtained the value of separation factor of about 13, and showed that the diffusion coefficients for benzene depended strongly on its concentration in the polymer and that the diffusion coefficients for mixtures depended on the diffusion time in the sorption experiments.

Fels and Huang⁴ examined theoretically the diffusion rate of liquid in the pervaporation by use of free volume theory.⁵ Then they expanded the theory to the permeation of binary liquids mixture, and examined experimentally with a system of benzene-*n*-hexane-polyethylene by use of techniques of permeation and desorption.⁶

On the other hand, the authors suggested^{7,8} that the diffusion rate of one component may be affected synergetically by the other coexisting in the pervaporation system of binary athermal on the polymer membranes also observed by Krewinghaus.⁹ Uchikura et al.¹⁰ recently reported a similar phenomenon on the permeation of gases mixture of methane-isobutane through the styrene-butadiene-styrene block copolymer membrane.

It is the purpose of this study to examine the diffusion mechanism at non-steady-state and steady-state permeation of binary liquids mixture of benzene and cyclohexane through poly(γ -methyl L-glutamate) (PMLG) membrane, which is plasticized strongly and weakly by benzene and cyclohexane, respectively.

EXPERIMENTAL

Materials

Benzene and cyclohexane were used, the commercial ones (Wako Junyaku Co., Ltd.; spectrum grade), without further purification to the experiments of sorption and pervaporation.

PMLG obtained from Ajicoat A-2000 (Ajinomoto Co., Ltd.) by casting was purified by Soxhlet extraction using 68°C methanol for 5 days. The methanol in the extractor was exchanged for fresh each day. After purifying and drying the PMLG *in vacuo* at 40°C for 2 days, it was dissolved in a benzene-methanol (85:15) mixture,¹¹ and the solution was cast on a glass plate. A transparent and uniform-thickness membrane was formed by slow evaporation of solvents at 20°C. The PMLG membrane was dried at 80°C for 5 days. The thickness of the membrane used for this study was 43 μm . The structure of this membrane was confirmed as an α -helical type one by the ATR method of IR spectroscopy.¹²

Sorption Measurement

The amounts of benzene and cyclohexane sorbed in PMLG membrane were measured, respectively, by gas chromatography of sorbate which was collected by vacuum distillation with a liquid nitrogen trap from swollen PMLG membrane.

Pervaporation Apparatus

The apparatus used for the pervaporation experiment was the same one described in previous papers.^{7,8}

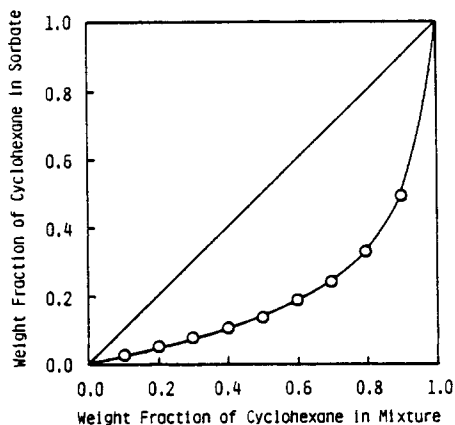


Fig. 1. Relation between weight fraction of cyclohexane in liquids mixture and sorbate in PMLG membrane.

RESULTS AND DISCUSSION

Sorption of Binary Liquids Mixture

The relation between weight fraction of cyclohexane in binary liquids mixture and sorbate in PMLG membrane is shown in Figure 1. The curve lies under the azeotrope line in the whole range of composition of the mixture. This result shows that benzene is sorbed by PMLG membrane in the whole range.

By using the total amounts of mixture sorbed in the membrane and the composition of sorbate as shown in Figure 1, the respective amounts of benzene and cyclohexane in the membrane were obtained. In Figure 2, these amounts were plotted against the composition of cyclohexane in the mixtures. The differences of amount between benzene and cyclohexane in the membrane are large in the lower composition of cyclohexane. PMLG is dissolved into benzene, gellike, at about 80°C, while cyclohexane is scarcely sorbed into the membrane. These results shows a large difference between affinities of both the liquids for PMLG. A good separation for this mixture by the pervaporation through the PMLG membrane may be expected from this result. As shown in Figure 2, the curve

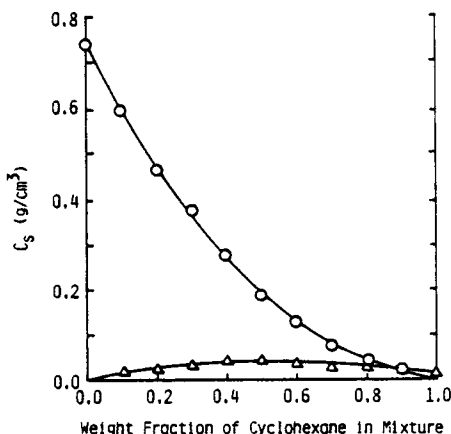


Fig. 2. Plots of amount of sorbed benzene (C_{s1}) and cyclohexane (C_{s2}) in PMLG against weight fraction of cyclohexane in liquids mixture: (O) benzene; (Δ) cyclohexane.

for benzene shows a convex to the axis of abscissa. Little change in the cyclohexane curve was observed in the whole range, but a slight maximum value was observed in the curve at about 50 wt % in the mixture.

The selective sorption factor ($\sigma_{1/2}$) is defined as

$$\sigma_{1/2} = \frac{S_1/S_2}{X_1/X_2} \quad (1)$$

where the S_i 's and X_i 's are the weight fractions (g/g) of the liquid component (i) in the polymer and liquids mixture, respectively. When the subscript $i = 1$ and 2 show benzene and cyclohexane, respectively, the relation between ($\sigma_{1/2}$), and the composition of cyclohexane in the liquids is shown in Figure 3.

A phase equilibrium theory for ternary components of liquid (1)–liquid (2)–polymer (3) was proposed by Nakajima and Shibukawa¹³ as

$$\ln \frac{v_1/v_2}{v'_1/v'_2} = \chi_{12}(v'_2 - v'_1) - (v_2 - v_1) + (\chi_{13} - \chi_{23}) v'_3 \quad (2)$$

where the χ_{ij} 's are interaction parameters between component (i) and component (j) and the v_i 's and v'_i 's are volume fractions of component (i) in the liquids mixture and polymer, respectively. The interaction parameter (χ_{12}) between binary components of liquid is described by use of the values of activity coefficient (a_1) and volume fraction (v_1) of component (1) (benzene) as¹⁴

$$\ln a_1 = \chi_{12}(1 - v_1)^2 \quad (3)$$

By use of the data of the gas–liquid equilibrium of the benzene–cyclohexane system,¹⁵ the relation between $\ln a_1$ and $(1 - v_1)^2$ were plotted. χ_{12} was decided as 0.38 from the slope of the plot. Since the degree of crystallization of PMLG is not obtained the values of χ_{13} and χ_{23} were not decided. But $(\chi_{13} - \chi_{23}) < 0$ was estimated relatively by the results of $C_{s1} > C_{s2}$ in Figure 2. The values of $v_1/v_2/v'_1/v'_2$ correspond to $1/\sigma_{1/2}$. If the values of $(v'_2 - v'_1)$ and $(v_2 - v_1)$ are comparable, the values of $\chi_{12}[(v'_2 - v'_1) - (v_2 - v_1)]$ are small. The second term on the right side of eq. (2) contributes to the system more strongly than the first term. It is understood that the values of $(v'_2 - v'_1)$ and $(v_2 - v_1)$ are comparable, as shown in Figure 2, and v'_3 decreases with increasing of v_1 and corresponds to

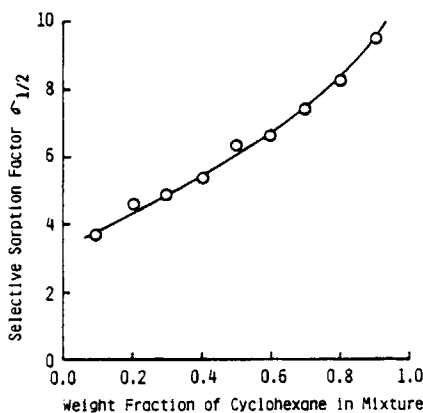


Fig. 3. Relation between selective sorption factor ($\sigma_{1/2}$) and weight fraction of cyclohexane in liquids mixture.

the composition of benzene in the mixtures, and then the values of $\sigma_{1/2}$ decreases with v_1 , increasing of benzene, in this sorption system.

Nonsteady-State Permeation of Liquids Mixture

The permeation cell equipped with PMLG membrane was constructed in a line of carrier gas flow of gas chromatograph.⁸ After the feed of the liquids mixture was charged in the cell, the permeates were carried immediately to the gas chromatographic column (PEG 6000, 60/80 mesh, $0.3\phi \times 75$ cm, 120°C) by carrier gas flow and analyzed in a finite interval. The permeation rate-time curves are shown in Figures 4 and 5 for benzene and cyclohexane, respectively. Numbers in the figures are the weight fraction of cyclohexane in the feed mixtures. As shown in Figure 4, the permeation rates of benzene at steady state increased, and the permeation rate-time curves change to a longer time with increasing content of cyclohexane in the feed mixtures. On the contrary, the

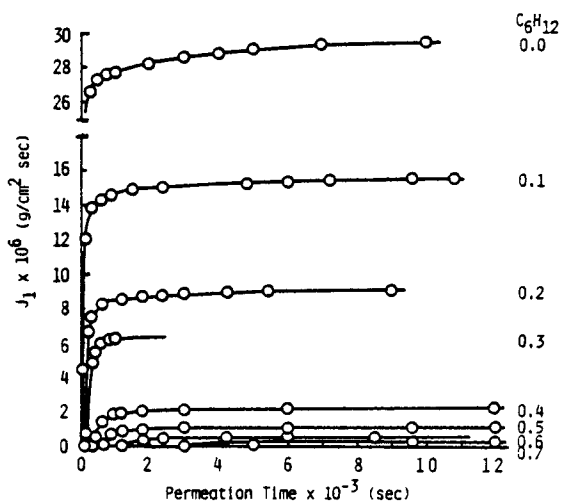


Fig. 4. Relation between permeation rates of benzene (J_1) and time from various composition of mixtures. Numbers: weight fraction of cyclohexane in mixture.

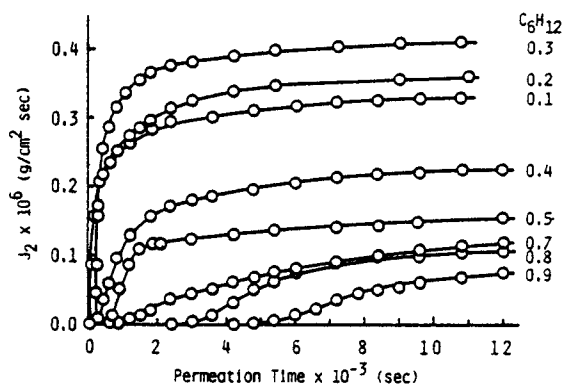


Fig. 5. Relation between permeation rates of cyclohexane (J_2) and time from various composition of mixtures. Numbers: weight fraction of cyclohexane in mixture.

permeation rates of cyclohexane at steady state show a maximum value at the weight fraction of 0.3 of cyclohexane in the feeds. The permeation rate-time curves of cyclohexane transfer also to the long-time side with increasing of one in the feed, i.e., with decreasing of benzene in the feeds.

The plots of logarithmic time required to reach the half-values of permeation rates at steady state for benzene and cyclohexane against the composition of cyclohexane in the feeds are shown in Figure 6. As shown in this figure, the times ($t_{1/2}$) for both of the liquids increase with the composition of cyclohexane in the feed mixtures. It is well known that the value of $t_{1/2}$ corresponds to a reciprocal of the diffusion coefficient. If the diffusion coefficients (D) does not depend on the concentration of diffusant, the relation between $t_{1/2}$ and D suggested by Ziegel¹⁶ is

$$D = \frac{l^2}{7.199 \times t_{1/2}} \quad (4)$$

These results show that the diffusion rates of both liquids increase with increasing of benzene in the system. These curves are linear relationships having almost similar slopes. As shown in previous papers,^{7,8} the diffusion rate of cyclohexane may be enhanced by existence of benzene in the diffusion system and vice versa.

Steady-State Permeation of Liquids Mixture

The permeation rates of benzene and cyclohexane at steady-state were obtained from Figures 4 and 5, respectively. These values are plotted against the composition of cyclohexane in the feeds mixture, and the relations are shown in Figure 7. The permeation rates of pure benzene was about 370 times that of pure cyclohexane. This can be explained on the basis of the fact that benzene has a higher solubility and, consequently, has more plasticizing effect on PMLG than cyclohexane.

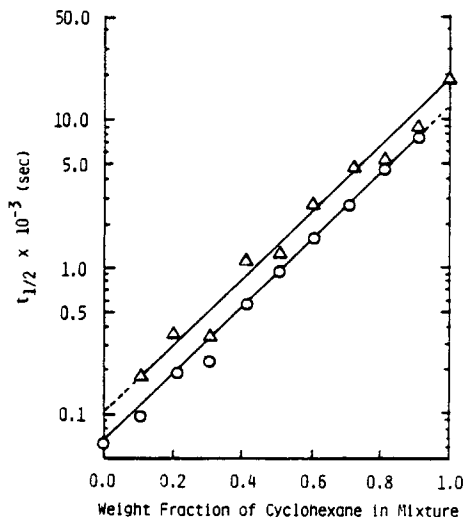


Fig. 6. Semilogarithmic plots of time ($t_{1/2}$) required to reach a half-value of steady-state permeation rates of benzene and cyclohexane against weight fraction of cyclohexane in mixtures: (O) benzene; (Δ) cyclohexane.

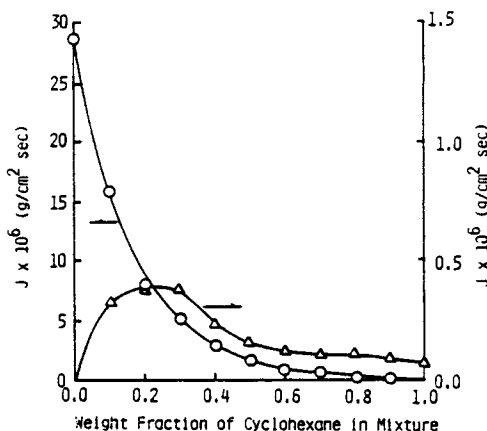


Fig. 7. Plots of permeation rates (J) of benzene and cyclohexane against weight fraction of cyclohexane in liquids mixtures: (O) benzene; (Δ) cyclohexane.

From the data of the amounts of sorption and the permeation rates in Figures 2 and 7, respectively, the apparent diffusion coefficients (\bar{D}) are obtained by

$$\bar{D} = \frac{J \times l}{C_s} \quad (5)$$

where J is the permeation rate and l the thickness of membrane. The relation between $\ln \bar{D}$ and C_s are shown in Figure 8 for benzene and cyclohexane. \bar{D} for benzene-PMLG depended on the sorbed amounts of benzene exponentially, as is well known. However, \bar{D} for cyclohexane-PMLG showed a complicated dependence on the sorbed amounts of cyclohexane. The curve showed a concave one to the axis of ordinates. Thus the \bar{D} for the latter system shows an anomalous behavior.

As shown in previous papers for the diffusion of methanol and ethanol from

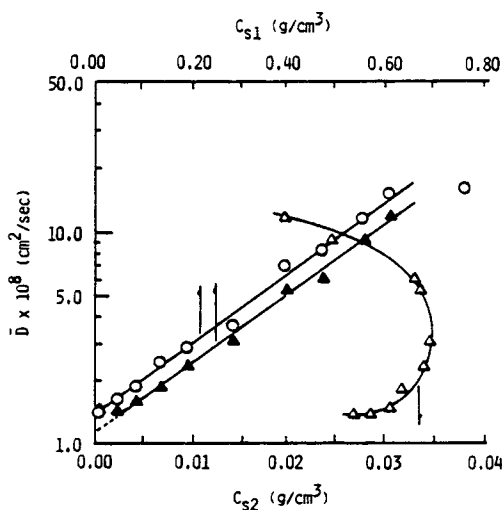


Fig. 8. Plots of logarithmic apparent diffusion coefficients (\bar{D}) for benzene-PMLG and cyclohexane-PMLG against amounts of sorbed benzene (C_{s1}) and cyclohexane (C_{s2}): (O) benzene plotted to C_{s1} ; (Δ) cyclohexane plotted to C_{s2} ; (\blacktriangle) cyclohexane plotted to C_{s1} .

their athermal mixture through the PMLG membrane,^{7,8} \bar{D} in the pervaporation system of binary liquids mixture may be affected synergetically by the liquids as

$$\bar{D}_1 = D_1^0 \exp(\gamma_1 C_{s1} + \gamma_2 C_{s2}) \quad (6)$$

$$\bar{D}_2 = D_2^0 \exp(\gamma_1 C_{s1} + \gamma_2 C_{s2}) \quad (7)$$

where the D_i^0 's are the diffusion coefficients for zero concentration and then γ_i 's are the plasticizing coefficients of liquid (i).

In this case of the pervaporation of benzene and cyclohexane by PMLG membrane, benzene has a higher solubility in and larger plasticizing effect on PMLG than cyclohexane, as mentioned previously. Thus $\gamma_1 C_{s1} \gg \gamma_2 C_{s2}$ can be assumed in the eqs. (6) and (7) in a region of higher concentration of benzene (C_{s1}) at least. By this assumption, eqs. (6) and (7) are simplified, respectively, as

$$\bar{D}_1 \approx D_1^0 \exp(\gamma_1' C_{s1}) \quad (8)$$

$$\bar{D}_2 \approx D_2^0 \exp(\gamma_1' C_{s1}) \quad (9)$$

where γ_1' is the apparent plasticizing coefficient of benzene for PMLG membrane and it is not always equal to γ_1 in eqs. (6) and (7) on account of the interaction between liquids. According to eq. (9), the apparent diffusion coefficients for cyclohexane-PMLG are plotted against the amounts of benzene sorbed in PMLG (C_{s1}). The results are shown by the symbol of \blacktriangle in Figure 6. The linear relationship was obtained. D_1^0 (benzene) and D_2^0 (cyclohexane) can be estimated as 1.4×10^{-8} and 1.1×10^{-8} cm²/s, respectively. They may be reflected by the magnitudes of the molecular volume of them (89.4 for benzene, 108.2 for cyclohexane). However, these values show no more than the relative values, since they are estimated by the assuming that $\gamma_2 C_{s2} = 0$.

This figure confirms the suggestion^{7,8} that the diffusion rates of one component may be affected by the other coexisting in the pervaporation system of binary liquids mixture, i.e., by the free volume change formed by the other in the system.^{6,9}

In Figure 9, relations between C_{s1} (benzene), C_{s2} (cyclohexane) and $\ln \bar{D}_2$ are

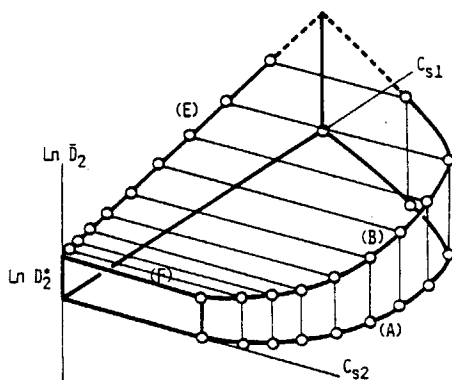


Fig. 9. Schematic illustration curve of concentration dependence of apparent diffusion coefficients (\bar{D}_2) for cyclohexane-PMLG from liquids mixture. (A) $C_{s1} \sim C_{s2}$; (B) $\ln \bar{D}_2 \sim C_{s2}$; (E) $\ln \bar{D}_2 \sim C_{s1}$; (F) $\ln \bar{D}_2 \sim C_{s2}$ from pure vapor.

illustrated schematically by a space coordinates. Curve (A) and curve (B) are the relations between C_{s1} and C_{s2} obtained from Figure 3 and between C_{s2} and $\ln \bar{D}_2$, respectively. Curve (E) is the relation between C_{s1} and $\ln \bar{D}_2$ according to eq. (10), and this curve is projected from curve (B) to the coordinates of $C_{s1} \sim \ln \bar{D}_2$. Curve (F) is meant to show a true concentration dependence of diffusion coefficients, which is obtained from the experiments of the permeation and sorption under the various vapor pressure. This curve is not examined in this work.

Separation of Liquids Mixture

The separation of benzene and cyclohexane mixtures by PMLG membrane is shown in Figure 10 over the whole range of compositions. The relation between the compositions of cyclohexane in feeds and permeates shows a convex curve to the axis of abscissa like the curve of selective sorption factor $\sigma_{1/2}$ shown in Figure 3. The relation differs largely from the one of gas-liquid equilibrium shown in the same figure by the broken line. The separation factor ($\alpha_{1/2}$) is obtained by

$$\alpha_{1/2} = \frac{Y_1/Y_2}{X_1/X_2} \tag{10}$$

where the Y_i 's are the weight fractions of the permeates.

As shown in Figure 10, $\alpha_{1/2}$ changes from about 12 to 5 with decrease of cyclohexane in the feeds. The values are not larger than that expected from the permeation rate of each of the pure liquid described in previous section. These results may be explained that the diffusion rates of both liquids are controlled

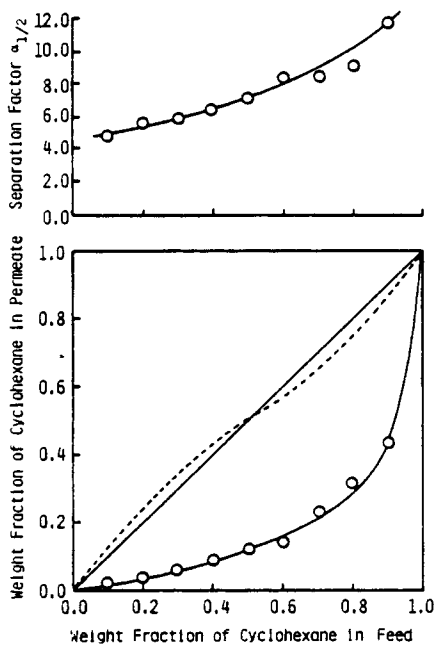


Fig. 10. Separation of benzene-cyclohexane mixture by PMLG membrane: (---) gas-liquid equilibrium curve.

by only a little difference of the zero concentration diffusion coefficients and the almost same plasticizing effects by synergetic effect of mixture. Thus the separation is due to the differences of the amount of both liquids sorbed in PMLG membrane chiefly in this case. It may be necessary to note this effect in the separation of the liquids mixture by pervaporation.

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