Pervaporation of Athermal Mixture of Benzene–Toluene by Poly(ethylene Terepthalate) Membrane and Synergetic Effect on Concentration Dependence of Diffusion Rate

FUMIO SUZUKI, KENJI ONOZATO, and NAOMICHI TAKAHASHI,
Department of Polymer Chemistry, Faculty of Engineering, Yamagata University, 4-Johnan, Yonezawa, 992 Japan

Synopsis

The pervaporation of the athermal liquid mixture of benzene–toluene by a PET membrane was examined. Sorbed amounts of benzene and toluene in the PET membrane were almost similar to each other, and each amount of them sorbed from the mixture showed linear relationships to their weight fraction in the mixture. The permeation rate of benzene from its single liquid was 2.5 times of that of toluene, and the permeation rates of benzene and toluene from mixtures of various composition showed concave and convex curves to the feed axis, respectively. Semilogarithmic relations between the apparent diffusion coefficient for toluene–PET, obained from steady-state permeation rates and sorbed amounts, and its concentration in the membrane showed a negative slope. This result could be explained by the fact that the diffusion rate of one component in pervaporation of the binary liquid mixture was affected by the other coexisting in the system.

INTRODUCTION

Pervaporation, named by Kobers,[1] is a technique of separation of a liquid mixture by permeation through polymer membranes. In this technique, the differences of affinities of the components of the mixture for the polymer membrane and of the diffusion coefficients of the components are used principally to separate them. The affinities relate to thermodynamical interaction parameters not only between each component and the polymer but also between the components[2] in their mixture. On the other hand, the diffusion coefficient depends on the molecular size of the liquids, and in some cases they are influenced by the plasticizing effect of sorbed molecules to polymer chains. The pervaporation technique is complicated by these phenomena; but it can be rid of thermodynamical restrictions shown by Gibbs's phase equilibrium in distillation, and the consequences bear unlimited possibility for the separation of liquid mixtures by this technique.

The separations of binary liquid mixtures by this technique have been examined with many workers. Carter and Jagannadhaswamy[3] reported the separations of benzene/alcohol and ethyl acetate/carbon tetrachloride by polyethylene or water/alcohol by cellophane and related the separation factor to swelling. Huang and Lin[4] studied the separation of binary liquid mixtures of some kinds of hydrocarbon or aqueous alcohol solutions[5] and attempted to establish some of the qualitative characteristics of permeation. They explained the mechanism of liquid transport of mixtures in terms of a combined internal plasticizing and

solubility effect. Michaels et al.[6] indicated that solvent conditioning of poly-ethylene increases membrane permeability to xylene isomers. Sweeny and Rose[7] studied the effect of molecular size and chemical nature of the permeant and the effect of chemical structure of polymer on the permeation rate of liquids. They clarified the relation of selective permeation to the polarities of liquid and polymer. Kim and Kammermeyer[8] investigated the direct measuring of the concentration profile at a steady-state permeation of liquid by use of a stacked membrane. They confirmed that the exponential model represented the directly measured concentration profiles to a satisfactory degree in some case such as the system of nylon 6-water, nylon 6-dioxane, cellulose acetate–water and polyethylene–n-hexane. Fels and Huang[9] attempted to establish the diffusion theory for the liquid transport by the concentration dependence of the diffusion rate and the free volume theory. They examined[10] the appropriateness of this theory for experimental results.

However, these theories or mechanisms were examined almost for transport phenomena based on a single liquid as permeant. These analyses had no regard for effects on solubility and diffusivity by mixing of liquids. In this paper we study the pervaporation for an athermal mixture of benzene and toluene by a poly(ethylene terephthalate) (PET) membrane. Investigation has been carried out on the thermodynamic phase equilibrium between the liquid mixtures and the polymer, and on the synergetic effect of the liquid mixture to the concentration dependence of the diffusion rate.

EXPERIMENTAL

Samples

Benzene and toluene used for this study were commerical ones (spectrum grade) without further purification.

The PET membrane used in the pervaporation experiment was supplied by Mitsubishi Resins Co., Ltd., Japan. The membrane thickness was 3.5 μm. The IR spectrum on the membrane is shown in Figure 1, and the degree of crystallinity of one was decided as 2.0% from the spectrum by Ueda's method.[11]
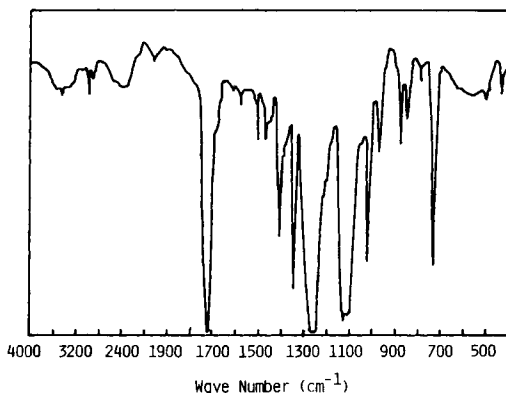

Fig. 1. IR spectrum of poly(ethylene terephthalate) membrane used for pervaporation experiment.

Sorption Measurement

Amounts of benzene and toluene sorbed in PET membrane were obtained, respectively, by gas chromatography of sorbate which was collected by vacuum distillation with a liquid nitrogen trap from the swollen PET membrane.

Pervaporation Apparatus

The apparatus for the pervaporation experiment is shown schematically in Figure 2. The permeation cell was installed in the gas chromatographic carrier gas stream line, and consisted of a glass bell (B) fitted with flanged base (A) which served as the membrane holder. A disk of the membrane supported on its lower surface by a smaller disk of 60-mesh stainless steel screen. The pervaporation cell was constructed with the above parts, and the liquid mixture was filled by syringe through a rubber cap of feed inlet portion. Helium gas was passed through the oulet side of the membrane to pick up the vapor permeated through the membrane. This helium gas passed through the sampler with sampling valves and a separation column of the gas chromatograph. The permeation rate of each component of permeate through the membrane was calculated with the value of the carrier gas rate and the gas chromatographic peak area[12] (count numbers of integrator) of permeate by use of a correction factor, previously obtained for each one.

RESULTS AND DISCUSSION

Sorption

PET membrane of 250 μm thick, the degree of crystallinity of 56%, was used for the sorption experiments.

The temperature dependence sorption data of benzene and toluene are shown in Table I. In this table, C_w is the weight fraction of benzene and toluene sorbed in the PET membrane, C_w^a and v^a are the weight and volume fractions of benzene and toluene sorbed in amorphous regions of the membrane, respectively, and the C_v^a's are the weights of them in unit volume of the region.
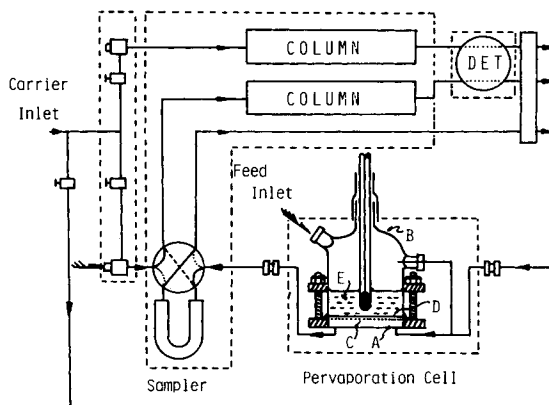

Fig. 2. Schematic diagram of apparatus for pervaporation experiment. (A) metal disk, (B) glass bell, (C) screen, (D) membrane, (E) liquid mixture of feed.

TABLE I
Temperature Dependence of Amounts of Benzene and Toluene Sorbed into PET Membrane

Temp (°C)	C_w (g/g)	C_w^a (g/g)	C_v^a (g/cm^3)	v^a (cm^3/cm^3)	χ^a
Benzene					
30	0.0034	0.0079	0.0058	0.0123	5.52
35	0.0048	0.0113	0.0083	0.0176	5.50
40	0.0053	0.0123	0.0091	0.0191	5.13
45	0.0077	0.0179	0.0132	0.0278	4.82
Toluene					
30	0.0032	0.0075	0.0055	0.0117	5.57
35	0.0043	0.0100	0.0074	0.0156	5.31
40	0.0045	0.0104	0.0077	0.0163	5.27
45	0.0054	0.0153	0.0113	0.0238	4.91

Remark: The superscripts a denote the sorbed amounts corrected by the degree of crystallinity.

The interaction parameters (χ^a) of them were calculated by the Flory–Rehner theory[13] for swollen polymers. χ^a values showed a depression of only about 5% when corrected for the density of the elastic effective chain of the PET which was 0.39 mol/cm^3 from the Mooney–Riblin plot, by use of the data of stress–strain curve of PET.

These values indicated that this polymer had very small affinity to these solvents in spite of aromatic rings in its main chain. At lower temperatures the data are hardly different between these solvents. The heats of sorption obtained from the temperature dependence of sorption were 43.5 and 30.5 kJ/mol for benzene and toluene, respectively. Therefore, the sorbed amount of benzene was a little more than that of toluene at higher temperature.

The sorbed amounts of benzene (C_v^{aB}) and toluene (C_v^{aT}) into the PET membrane from the mixtures of various compositions are plotted together in Figure 3 against the weight fraction of toluene in the liquid mixture. Both plots showed linear relations for the change of the composition of the mixture.
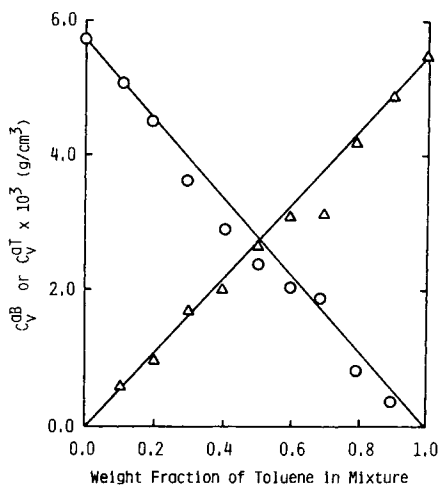

Fig. 3. Effect of composition of liquid mixture on sorbed amounts of benzene (C_v^{aB}) and toluene (C_v^{aT}) at 30°C. (O) benzene, (△) toluene.

These results will be explained as follows. Flory[13] showed the phase equilibrium theory for the ternary component system of single polymer and binary solvents applying the single-solvent approximation to the interaction parameter of the mixed solvents. This theory was developed by Nakajima and Shibukawa[2] to calculate selective sorption into the polymer as

$$\ln \frac{v^B/v^T}{v^{aB}/v^{aT}} = \chi^{BT}(v^{aT} - v^{aB} - v^T + v^B) + (\chi^{Bp} - \chi^{Tp})v^{ap} \qquad (1)$$

where v^B and v^T are the volume fractions of benzene and toluene in the liquid mixture, v^{aB}, v^{aT}, and v^{ap} are those of benzene, toluene, and the polymer in the swollen polymer, respectively. χ^{Bp}, χ^{Tp}, and χ^{BT} are the interaction parameters of benzene—PET, toluene—PET, and the benzene–toluene system, respectively. In the athermal mixing system of benzene and toluene, χ^{BT} can be assumed to be zero. Therefore, eq. (1) can be simplified to

$$\ln \frac{v^B/v^T}{v^{aB}/v^{aT}} = (\chi^{Bp} - \chi^{Tp})v^{ap} \qquad (2)$$

It is obvious from Table I that the interaction parameters of benzene and toluene for PET are almost equal and so the eq. (2) can be simplified still more to

$$\ln \frac{v^B/v^T}{v^{aB}/v^{aT}} = 0 \qquad (3)$$

Equation (3) shows that the ratio of volume fractions of benzene and toluene in the liquid mixture to those in the swollen PET are almost equal in the whole composition range of the mixture; in other words, the selective sorption of benzene to toluene does not occur in the PET membrane. The experimental results of Figure 3 can be explained reasonably by this equation.

It is supposed from this fact that benzene and toluene do not have any specific interaction between them in the PET membrane as in the case of the liquid mixture.

Pervaporation and Permeation

Plots of the weight fractions of toluene in feeds against those in permeates are shown in Figure 4, as compared with distillation curve of benzene–toluene. In this pervaporation system, the separation factor showed unity in the whole composition range of feed no matter whether the distillation curve showed a convex one to feed axis. A phenomenon of this sort is hard to find not only in pervaporation but in distillation of binary liquid mixtures except in some cases such as heptane–methylcyclohexane, benzene-dichloroethane, etc.[14]

The permeation rates of the components are shown in Figure 5 as a function of the weight fraction of toluene in feeds. Both of the curves did not show linear relationships differing from the sorption ones, and showed convex and concave shapes to the feed axis. In their respective single solvent feeds, the rate of benzene showed about 2.5 times as much as that of toluene.

In Figure 6 the permeation ratios of benzene and toluene in the mixture are plotted against the weight fraction of benzene and toluene in liquid mixture, respectively. The permeation ratios of toluene showed higher values than unity in the whole composition range of feed, but for benzene it was lower. These
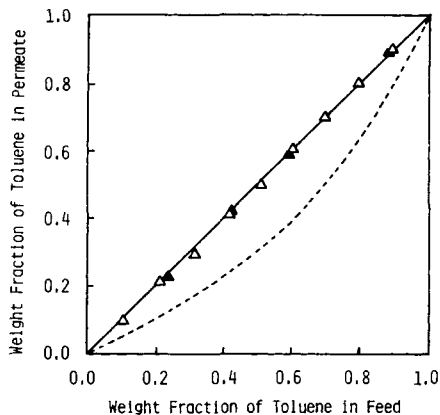
Fig. 4. Plots of weight fraction of toluene in permeate against in feed. ($\triangle$) pervaporation curve at 30°C, ($\blacktriangle$) pervaporation curve at 40°C, (·····) distillation curve at 30°C.

results showed apparently that the permeation of toluene was enhanced by the existence of benzene, but toluene was affected inversely to benzene.

It is supposed from the above result that the difference of permeation rates of toluene and benzene may be due to the difference of diffusion coefficients, based on their molecular volumes or their plasticizing effects on the polymer.

Apparent Diffusion Coefficient

Assuming Henry's law, the apparent diffusion coefficients for benzene–PET (D^B) and toluene–PET (D^T) were obtained from the values of sorption and steady-state permeation rates shown in Figures 3 and 5, respectively. Logarithmic values of the apparent diffusion coefficients were related to the sorbed amounts to benzene (C_v^{aB}) and toluene (C_v^{aT}) from their mixture of various composition, respectively, and are shown in Figure 7.
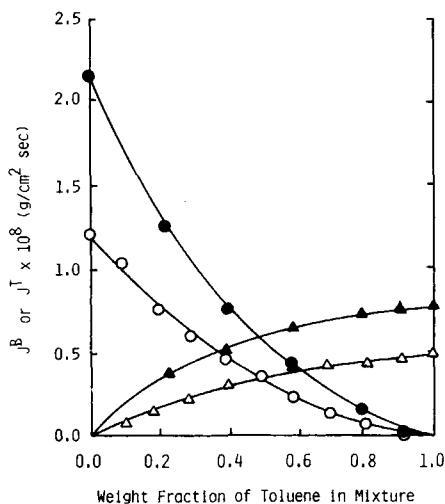

Fig. 5. Effect of composition of mixture on permeation rates of benzene (J^B) and toluene (J^T). ($\bigcirc$) benzene at 30°C, ($\bullet$) benzene at 40°C, ($\triangle$) toluene at 30°C, ($\blacktriangle$) toluene at 40°C.
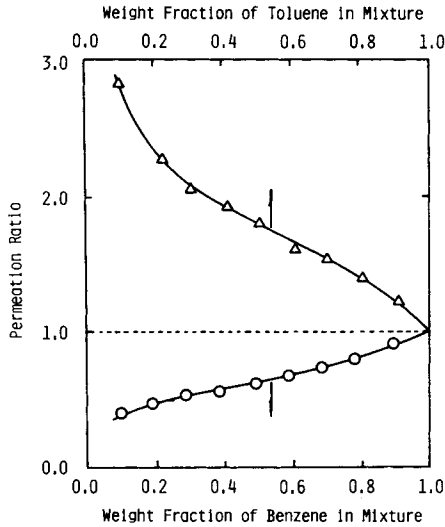
Fig. 6. Effect of composition of benzene and toluene mixture on permeation ratio. (O) benzene, (△) toluene.

For benzene, the exponential concentration dependence of the apparent diffusion coefficient was related positively to its concentration in the PET membrane, as known in other cases, but, for toluene, it showed a negative relation to its concentration in the PET membrane, contrary to the general cases.

If diffusion coefficient is dependent exponentially on the concentration of penetrants in a polymer, the coefficient is expressed as

$$D = D(0) \exp(\gamma \cdot C) \tag{4}$$

where $D(0)$, γ, and C are the diffusion coefficients at zero penetrant concentration, the plasticizing coefficient, and the penetrant concentration, respectively. Since the segmental motion of polymer chain which contributes to the diffusion
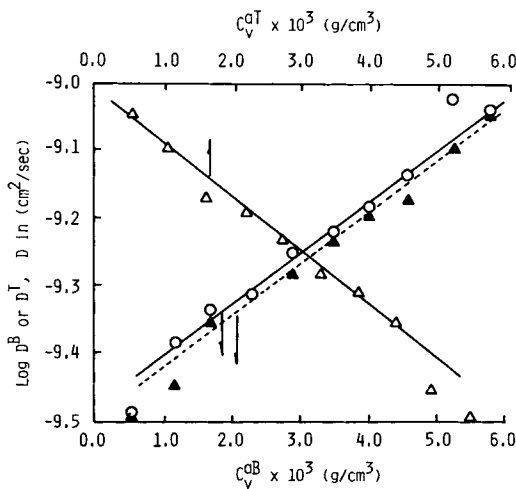

Fig. 7. Concentration (C_v^{aB} or C_v^{aT}) dependence of apparent diffusion coefficients for benzene–PET (D^B) and toluene–PET (D^T) at 30° C. (O) D^B (plotted to C_v^{aB}), (△) D^T (plotted to C_v^{aT}), (▲) D^T (plotted to C_v^{aB}).

of the penetrant is enhanced usually by the sorption of a penetrant such as organic solvent, the plasticizing coefficient hardly shows negative value.

The negative slope of the toluene curve will be explained as follows. In the pervaporation system of binary liquid mixtures, the polymer chain will be plasticized under the coexistence of both liquids, and the amount of one component sorbed in the membrane correlates with the amount of the other. The relation between the sorbed amounts of benzene (C_v^{aB}) and toluene (C_v^{aT}) are obtained from Figure 3 as

$$C_v^{aB} = \left(C_v^p - \frac{k^B}{k^T} C_v^{aT} \right) \tag{5}$$

and

$$C_v^{aT} = \frac{k^T}{k^B} (C_v^p - C_v^{aB}) \tag{6}$$

where C_v^p is the amount of benzene sorbed from its single liquid, the k's are the proportional constants in the relation between the concentration of toluene in the liquid mixture and sorbed amounts (C_v^a's) of benzene and toluene into the PET membrane, and the subscripts B and T express benzene and toluene, respectively.

Assuming the synergetic effect by benzene on the concentration dependence of the diffusion coefficient which will be induced by mixing of toluene, and vice versa, the apparent diffusion coefficients for benzene—PET (D^B) and toluene—PET (D^T) will be presented as

$$D^B = D^B(0) \exp(\gamma_c^B \cdot C_v^{aB} + \gamma_c^T \cdot C_v^{aT}) \qquad \text{(for } C_v^{aB} > 0)$$
$$= D^B(0) \exp\{[\gamma_c^B - (k^T/k^B) \cdot \gamma_c^T] \cdot C_v^{aB} + (k^T/k^B) \cdot \gamma_c^T \cdot C_v^p\} \tag{7}$$

and

$$D^T = D^T(0) \exp(\gamma_c^T \cdot C_v^{aT} + \gamma_c^T \cdot C_v^{aB}) \qquad \text{(for } C_v^{aT} > 0)$$
$$= D^T(0) \exp\{[\gamma_c^T - (k^B/k^T) \cdot \gamma_c^B] \cdot C_v^{aT} + \gamma_c^B \cdot C_v^p\} \tag{8}$$

where γ_c^B and γ_c^T are effective plasticizing coefficients caused by mixing of benzene and toluene, respectively, and they do not always coincide with the γ of the single liquid (penetrant) in eq. (4). Since the proportional constants k^B and k^T will be assumed to be similar as estimated from Figure 3, eqs. (7) and (8) can be simplified to

$$D^B = D^B(0) \exp[(\gamma_c^B - \gamma_c^T) \cdot C_v^{aB} + \gamma_c^T \cdot C_v^p] \tag{9}$$

and

$$D^T = D^T(0) \exp[(\gamma_c^T - \gamma_c^B) \cdot C_v^{aT} + \gamma_c^B \cdot C_v^p] \tag{10}$$

Therefore, in the case of diffusion of toluene, if ($\gamma_c^T - \gamma_c^B$) is negative, the relation between ln D^T and C_v^{aT} is expected to show a negative slope line according to eq. (8). Since both of the exponential terms in eqs. (7) and (8) are essentially similar to each other, if ln D^T is plotted vs. C_v^{aB}, the slope ought to be positive, and a line of similar slope to that of ln D^B vs. C_v^{aB} is expected. The experimental results support this assumption as shown in Figure 7 by the dotted line (... ▲ ...). The intercepts of these plots ought to have the values of $D^B(0)$ exp($\gamma_c^T \cdot C_v^p$) and $D^T(0)$ exp($\gamma_c^B \cdot C_v^p$) for benzene and toluene, respectively.

The theoretical relative permeation rates of benzene (J^B/J^{pB}) and toluene (J^T/J^{pT}) were calculated by

$$J^B = \frac{C_v^{aB} \cdot D^B(0)}{L} \exp(\gamma_c^B \cdot C_v^{aB} + \gamma_c^T \cdot C_v^{aT}) \tag{11}$$

$$J^{pB} = \frac{C_v^{aB} \cdot D^B(0)}{L} \exp(\gamma^B \cdot C_v^{aB}) \tag{12}$$

and

$$J^T = \frac{C_v^{aT} \cdot D^T(0)}{L} \exp(\gamma_c^T \cdot C_c^{aT} + \gamma_c^B \cdot C_v^{aB}) \tag{13}$$

$$J^{pT} = \frac{C_v^{aT} \cdot D^T(0)}{L} \exp(\gamma^T \cdot C_v^{aT}) \tag{14}$$

In this calculation, it was assumed that $\gamma^B = \gamma_c^B$ and $\gamma^T = \gamma_c^T$, which were calculated as $\gamma_c^B = 290$ and $\gamma_c^T = 140$ cm³/g by a trial and error method. In Figure 8, the theoretical relative permeation rates were compared with the observed ones of benzene and toluene and plotted vs. C_v^{aB}/C_v^p and C_v^{aT}/C_v^p, respectively. Close agreement between them were obtained as seen in the figure.

To satisfy the results of Figure 4, the values of $D^B(0)$ and $D^T(0)$ must be similar to each other, and from the values of permeation rate in Figure 5, both values of $D^B(0)$ and $D^T(0)$ are calculated as 1.4×10^{-10} and 1.2×10^{-10} cm²/s. These results satisfied the above conditions.

From above discussions, it is concluded that the inseparability phenomenon on the pervaporation of the benzene and toluene mixture through a PET membrane is caused by the similarity of the zero penetrant concentration diffusion coefficient for benzene—PET to that for toluene—PET and by the influence of the plasticizing effect of one component coexisting in the system on the diffusion of another.

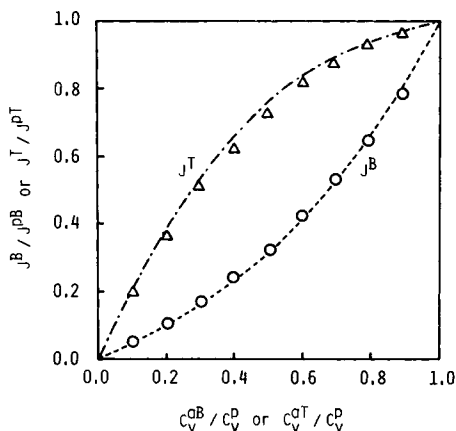This influence is confirmed also in non-steady-state permeation on the other system.[15]

Fig. 8. Comparison of observed and calculated relative permeation rates. (O) benzene (obs.), (△) toluene (obs.), (·····) calculated by eqs. (11) and (12), (—·—·—·—) calculated by eqs. (13) and (14).

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