Pervaporation for the Mixture of Benzene and Cyclohexane through PPOP Membranes

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Pervaporation and sorption for the liquid mixture of benzene and cyclohexane by using poly[bis(phenoxy)phosphazene] (PPOP) membranes were characterized. Diffusivities, solubilities, interaction parameters, plasticization coefficients, and heats of sorption for benzene and cyclohexane in the membrane were determined from the vapor sorption kinetics and isotherms, which were measured gravimetrically by a continuous microbalance. Pervaporation operations offered a maximum selectivity of 3 at 35°C and the 35−50% feed concentration level of benzene. Normalized fluxes increased but the pervaporation selectivity decreased slightly with temperature. The binary transport in the membrane was modeled by the solution−diffusion model with an exponential form diffusivity to the concentration of each permeant. Coupling coefficients imbedded in the model were numerically determined by a proposed computation method. The model can illustrate not only concentration and diffusivity profiles for the permeants within the membrane, but their transport mechanism, which is consistent with the hypothesis of ''two layers'' in the membrane. The analysis of activation energy for transport indicates that the permeation barrier for pervaporation is reduced much more than that of the single-vapor permeation through an unswollen membrane.

Introduction

Membrane pervaporation is a promising process for the separation of azeotropic mixtures, close-boiling components, isomeric mixtures, and heat-sensitive components. The applications of pervaporation processes for dehydration from alcoholic solution have been carried out commercially for several years (Neel, 1991). However, there has been no large-scale application of pervaporation for the separation of organic mixtures in the chemical industry (Park et al., 1994), and the development to replace or improve the conventional distillation for the separation of organics by pervaporation is still at the exploratory stage. The separation of benzene and cyclohexane presents a model system that can benefit from the development of such a process (Cabasso et al., 1974; Lee, 1981; Suzuki and Ozozato, 1982; Sun and Ruckenstein, 1995; Inui et al., 1997a,b). The difference between the boiling points of these two components is only 0.6°C, and there is an azeotropic point at the concentration of about 60% benzene in the mixture.

In comparison with distillation, pervaporation is usually a more energy-saving process because the selectivity toward one of the mixtures is largely improved due to the permselectivity of the membrane. The performance of the membrane plays a key role in determining the technical and economical feasibility in such a process. The selection of a good membrane becomes a prior consideration in the process development. Inorganic phosphazene polymers have recently been used to prepare membranes for a number of gas and organic/water separations because they can be easily processed to make thin films with moderate permeabilities, high-temperature durability, and chemical stability (Kraus and Murphy, 1985; Suzuki et al., 1987; McCaffrey and Cummings, 1993; Peterson et al., 1993, 1995; Roizard et al., 1996). In this study, we report the results of using poly[bis(phenoxy)phosphazene] (PPOP) membranes in a pervaporation process for the separation of benzene and cyclohexane.

PPOP is an inorganic polymer containing alternate phosphorus−nitrogen single and double bonds with two phenoxy side groups being attached to each phosphorus atom:

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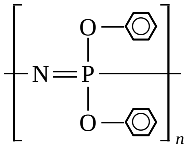

(PPOP)

Due to the structural similarity between the phenoxy side groups and benzene, it is expected that the membrane would be more selective toward benzene than cyclohexane. However, membrane swelling due to sorption of the permeants generally alters the sorption as well as the diffusion selectivity for the membrane, and the coupling phenomena in the multicomponent transport may further complicate the overall permselectivity. The performance of a pervaporation process is hardly predictable from individual single-component sorption, diffusion, or permeation data.

This study presents a way of combining the information obtained from experiments of pervaporation, equilibrium liquid sorption, and kinetic and equilibrium vapor sorption and applying the theory of the solution−diffusion model with a “six-coefficients exponential model” for the diffusivity (Brun et al., 1985) to simulate the transport of penetrants through the membrane. The coupling coefficients imbedded in the six-coefficient exponential model are found by a newly proposed computation scheme. The transport mechanism is well explained with the modeling. The study also presents an analysis to account for the effect of swelling as well as the coupling effect or interaction among penetrants and polymer membrane by comparing the difference of the activation energy of permeation for single-component vapor permeation and pervaporation.

Theory

Pervaporation through a nonporous membrane can be described by the widely accepted solution−diffusion model (Rogers, 1965; Wijmans and Baker, 1995; Feng and Huang, 1997). The permeation of a mixture through the membrane is believed to involve three independent processes: (1) sorption of liquid mixture on the feed (upstream) -side surface of the membrane; (2) diffusion through the membrane; and (3) desorption from the permeate (downstream) -side surface of the membrane into the vapor phase. The first and the third steps are considered as a thermodynamic property, and equilibrium is established on the surface presumably during the operation. In certain cases, the boundary-layer effect can be a problem on the upstream surface (Raghunath and Hwang, 1992), but it is generally neglected because the permeation fluxes are low. The second step is a kinetic factor and it accounts for most of the mass-transfer resistance.

The transport of a single permeant (penetrant) i through the membrane can be satisfactorily described by a Fick’s law relationship:

$$J_i = D_i \frac{dC_i}{dx}, \tag{1}$$

where J_i is the flux, D_i is the diffusivity, C_i is the concentration in the membrane, and x is the distance in the membrane in the direction of transport. For a single-component transport, the diffusivity is generally dependent on the local concentration, C_i, in the membrane and can be expressed by an empirical model (Long, 1965; Fujita, 1968):

$$D_i = D_{i0} \exp(A_i C_i), \tag{2}$$

where D_{i0} is the diffusion coefficient at infinite dilution, and A_i is a plasticization coefficient to account for interaction of the particular permeant and polymer and can be obtained experimentally.

For a multicomponent system, the transport is more difficult to analyze due to flux coupling and thermodynamic interaction among the permeants and the polymer. Many models have been proposed to describe the transport in pervaporation operation with a certain degree of success, but no overall theory exists to explain it. Fleming and Slater (1992) and Feng and Huang (1997) have highlighted these models in their review articles. In this work, we adopt the approach presented by Brun et al. (1985), that is, a “six-coefficients exponential model” for the binary transport in the membrane. The diffusivity of each species is dependent on the concentration of each individual component:

$$\begin{aligned} D_1 &= D_{10} \exp(A_{11}C_1 + A_{12}C_2) \\ D_2 &= D_{20} \exp(A_{21}C_1 + A_{22}C_2). \end{aligned} \tag{3}$$

This model takes the coupling effect between permeants into consideration. Here A_{11} and A_{22} are the main coefficients; A_{12} and A_{21} are the coupling coefficients; and D_{10} and D_{20} carry the same meaning as in Eq. 2. The six coefficients can be empirically determined according to the proposed computation scheme (Brun et al., 1985). However, the procedure is complicated, and suitable fits can be obtained to a given set of data using different sets of parameters (Sferrazza et al., 1988). Consequently, the physical significance of the parameters becomes suspect. In this work, an independent vapor sorption experiment was carried out for each permeant to determine the two parameters in Eq. 2. The diffusivities at infinite dilution D_{10} and D_{20} should be the same for Eqs. 2 and 3, and it is reasonable to assume that the main coefficient in Eq. 3 is equal to its individual plasticization coefficient in Eq. 2, that is, $A_{11} = A_1$ and $A_{22} = A_2$. This leaves only two parameters in Eq. 3 to be determined. In a pervaporation operation, the concentration of each component on the upstream surface can be independently determined from the liquid sorption experiment, and zero concentration is assumed for the downstream surface. Once the flux of each component is known, the coupling coefficients as well as local diffusivity and concentration for each component at any position within the membrane can be calculated according to Eq. 1. Two coupled first-order nonlinear differential equations are to be solved:

$$\begin{aligned} \frac{dC_1}{dz} &= -\frac{J_1 l}{D_{10} \exp(A_{11}C_1 + A_{12}C_2)} \\ \frac{dC_2}{dz} &= -\frac{J_2 l}{D_{20} \exp(A_{21}C_1 + A_{22}C_2)}, \end{aligned} \tag{4}$$

where l is the membrane thickness and z is the dimensionless distance within the membrane in the transport direction.

Experimental Methods

Materials

PPOP was prepared through the ring-opening polymerization of hexachlorocyclotriphosphazene (Aldrich, USA), after which the chlorine atoms were substituted in the linear chlorophosphazene polymer with phenoxy groups. The procedures were similar to those reported in the literature (Singler et al., 1975; Potin and De Jaeger, 1991; Allcock et al., 1995; Sun et al., 1997). The average molecular weight of PPOP was determined by GPC, which was calibrated with the polystyrene standard. The $\overline{M_w}$ was 171,000 with a polydispersity index of 1.51. Tetrahydrofuran (THF), benzene, cyclohexane, and ethanal were from Merck (Germany), and all the other chemicals were of reagent or higher grade. No further purification was carried out for the solvents used in pervaporation or sorption experiments, but all the other reagents used in the preparation of the polymer were carefully dried before use.

Membrane preparation

Synthesized PPOP was dried and dissolved in THF (10 wt. %). The solution was thoroughly mixed, filtered, degassed with ultrasonic device, and then poured onto a rimmed glass plate with an inner dimension of 130×130 mm. The cast solution was dried for 24 h at ambient temperature to evaporate the solvent and leave a continuous membrane. The membrane was removed from the plate and washed with ethanol and pure water, and then dried in an oven at 80°C. A digital micrometer (Mitutoyo, IDF-112) was used to measure the thickness of the membranes. The reported thickness was an average of 10 measurements at different points on the membranes. The thickness could be adjusted by the amount of casting solution poured onto the glass plate, and it ranged from 36.8 to 45.3 μm with a standard deviation within 0.4 μm for membranes tested in the pervaporation and sorption experiments.

Pervaporation experiments

The experiments were carried out in a conventional pervaporation apparatus similar to the one used by Huang and Feng (1992). A permeation cell with 12.6 cm^2 effective membrane area was enclosed in an oven at a constant temperature. There was a storage tank (1 L) and a circulating pump in the feed stream. A mixture of benzene and cyclohexane was pumped from the storage tank, circulated through the upper side of the permeation cell, and then sent back to the storage tank. In each run, the amount of permeates was minimal in comparison with that of the feed, so the concentration in the feed stream could be considered constant throughout the experiment. The permeate stream was evacuated by a vacuum pump, and the permeated mixture was collected alternately by two liquid-nitrogen traps. The permeate-side pressure was monitored by a pressure transducer and was maintained below 1 mmHg. The fluxes of the permeates were determined by weighing the sample collected within a predetermined time interval. Since the membranes were dense and uniform in the permeation direction, a normalized flux ($F_i = J_i l$) was used to correlate the experimental results from membranes of different thicknesses, and it was calculated as the product of the measured flux (J_i) and the membrane thickness (l). The composition of the permeate was analyzed by a gas chromatograph (HP-5890) equipped with a 6-ft packed column of 10% Carbowax 20 M on Chromosorb W-HP (Altech) and a TCD detector. The pervaporation selectivity (α_{PV}) for the mixture of benzene and cyclohexane is defined as

$$\alpha_{PV} = \frac{(y_B/y_C)}{(x_B/x_C)}, \tag{5}$$

where x_B and x_C are the weight fraction of benzene and cyclohexane in the feed solution, and y_B and y_C are in the permeate, respectively. After the initial transient operation, a steady-state permeation was maintained for at least 16 h, and at least five samples were collected at each run to determine the total flux as well as the composition of the permeate.

Liquid sorption for mixture of benzene and cyclohexane

The equilibrium swelling properties of the membrane in the benzene/cyclohexane mixture were measured gravimetrically. Preweighed dry PPOP membranes were equilibrated with the mixture at 35°C. After 24 h of immersion, the swollen membranes were taken out of the mixture, blotted dry quickly, and reweighed, by which process the equilibrated sorbed amount of liquid in the membranes was determined. The sorbed liquid in the membrane was then extracted by acetone (about 50-fold of the amount of sorbed liquid was added) for 1 day and analyzed by gas chromatography to determine the composition of benzene and cyclohexane. In comparison with the method of distillation under vacuum (Mulder and Smolders, 1985; Huang and Feng, 1992), only a small sample size is needed for the procedure outlined here. Even when the sorbed amount of liquid in the membrane is as little as 0.005 g, both an accurate composition and the total amount (with a standard added into the extract) of liquid extracted can be determined. The accuracy of the analysis was checked by spike experiments, and the error was generally within 3% if the samples were handled properly in the extraction step. Larger errors can occur only when too much or too little acetone is added for extraction. The sorption selectivity (α_S) can be defined similarly to Eq. 5:

$$\alpha_S = \frac{(w_B/w_C)}{(x_b/x_C)}, \tag{6}$$

where x_B and x_C are the weight fraction of benzene and cyclohexane in the solution, and w_B and w_C are in the sorbed liquid in the membrane, respectively.

Vapor sorption and desorption experiments

The sorption–desorption kinetics of the benzene and cyclohexane vapors at various activities in a PPOP membrane at 25–55°C were determined gravimetrically using the method suggested by Crank and Park (1968). A continuous microbalance (Cahn, C-1000) was used to monitor the vapor gain or loss in the sample during the sorption and desorption experiments. In a sorption experiment, a uniform flat membrane initially placed in vacuum was suddenly exposed to a vapor while pressure p was kept constant. The vapor activity was determined by the ratio of actual vapor pressure (p) to the saturated vapor pressure (p^0) at the experimental temperature. The gain in weight of the membrane as a function of time was recorded until sorption equilibrium was established. In the subsequent desorption experiment, the full equilibrium membrane was suddenly brought to vacuum and the loss in weight was recorded vs. time. Because the kinetics of the sorption and desorption were close to Fickian, either the half-time method or the initial slope method would give similar results for the corresponding diffusivities (Crank, 1975). In this study, we reported the average of the sorption and desorption diffusivities. Detailed descriptions of the apparatus, the experimental procedure, and the data analysis were given elsewhere (Sun and Chen, 1994).

Computation scheme

Equation 4 can be solved by using $C_1 = C_2 = 0$ at the downstream surface ($z = 1$) as initial conditions and assuming a pair of A_{12} and A_{21}. A Runge-Kutta algorithm was used to solve the equation. The upstream concentrations at $z = 0$ can be obtained in the calculation. Proper values for A_{12} and A_{21} were determined by the ZSCNT routine (a nonlinear system equation solver) from IMSL to fit the calculated upstream concentrations with the concentrations determined from liquid sorption data. The concentration profiles and the local diffusivities for benzene and cyclohexane were obtained as well.

Results and Discussion

Effect of feed composition on the pervaporation characteristics

Figures 1 and 2 show, respectively, the benzene concentration in the permeate and the normalized permeation fluxes as a function of feed composition for the mixture of benzene and cyclohexane through the PPOP membrane by pervaporation at 35°C. The effect of feed composition on the pervaporation selectivity (α_{PV}) for benzene/cyclohexane is shown in Figure 3. The results showed that PPOP membranes were more permselective torward benzene than cyclohexane, as the benzene concentration in the feed was lower than 73%. There was a maximum pervaporation selectivity of 3 when the benzene concentration in the feed was between 35 and 50%. The flux of benzene was more sensitive to the benzene concentration in the feed than to that of cyclohexane. It increased almost linearly and dominated the total flux when the benzene concentration feed was greater than 35%. It was suspected that sorption of benzene could swell the membrane significantly so the total flux increased and the pervaporation selectivity would drop to unity (no separation) eventually as the benzene concentration increased.

Effect of temperature on the pervaporation characteristics

By increasing the operating temperature, the permeation fluxes through the membrane increased, as the benzene concentration in the feed was kept at 41% (see Figure 4). At higher temperatures, the permeants have greater kinetic energy in order to cross the diffusion barrier, which is created by the bundles of polymer chains, and the polymer matrix has a larger available free volume for diffusion, therefore the permeation fluxes are higher. The activation energies of the pervaporation flux ($E_{F,i}$) for benzene and cyclohexane were 22.9 and 28.6 kJ/mol, respectively. The pervaporation energy barrier for benzene is lower than that of cyclohexane. This explains the better permselectivity toward benzene than cyclohexane. The increase of the permeation flux for cyclohexane with temperature is greater than that for benzene, how-

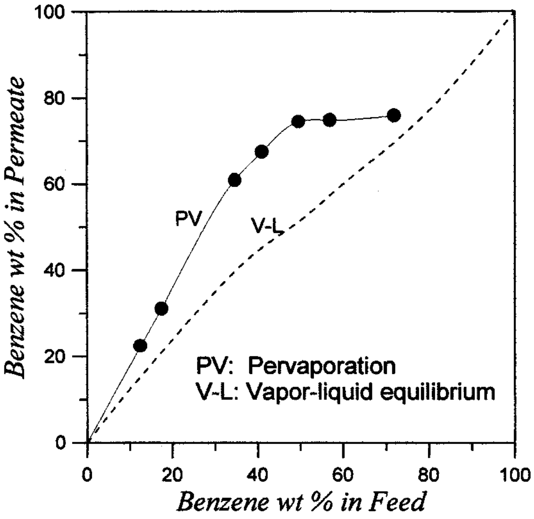

Figure 1. **Effect of the feed composition on the benzene concentration in the permeate for the mixture of benzene and cyclohexane through the PPOP membrane by pervaporation at 35°C.**

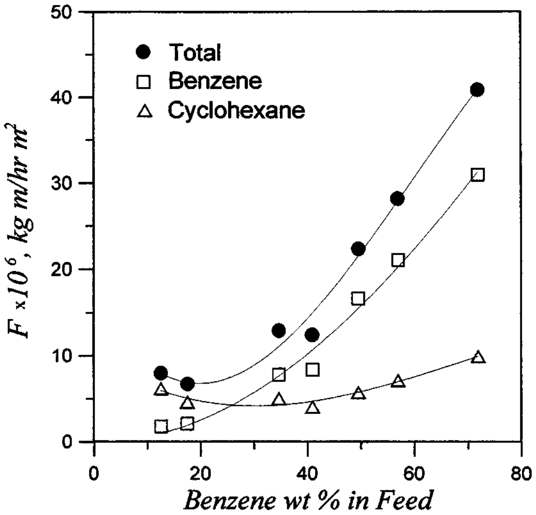

Figure 2. **Effect of the feed composition on the normalized permeation fluxes (F) for the mixture of benzene and cyclohexane through the PPOP membrane by pervaporation at 35°C.**

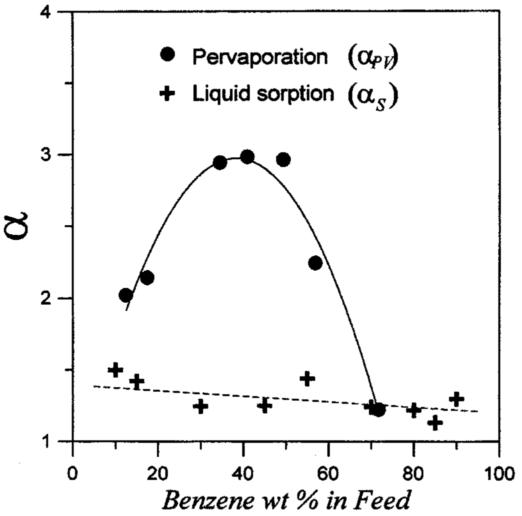

Figure 3. Effect of the feed composition on the pervaporation selectivity (α_{PV}) for the mixture of benzene and cyclohexane through the PPOP membrane at 35°C.

ever, so the pervaporation selectivity (α_{PV}) decreased slightly with temperature. The measured values of α_{PV} were 2.94, 2.69, and 2.61 for benzene/cyclohexane at 35, 45, and 55°C, respectively.

Liquid sorption for mixture of benzene and cyclohexane

In a pervaporation operation, one side of the membrane is in contact with the liquid mixture. It is assumed that the concentration of each permeant within the membrane surface is in equilibrium with the liquid-phase mixture. Preferential sorption occurs when the composition of the mixture within the polymer membrane differs from that in the feed solution.

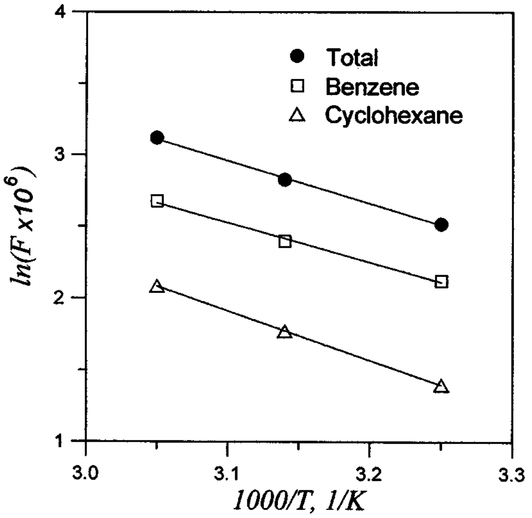

Figure 4. Arrehenius plots for the effect of operating temperature on the pervaporation fluxes (F), as the benzene concentration in the feed was kept at 41%.

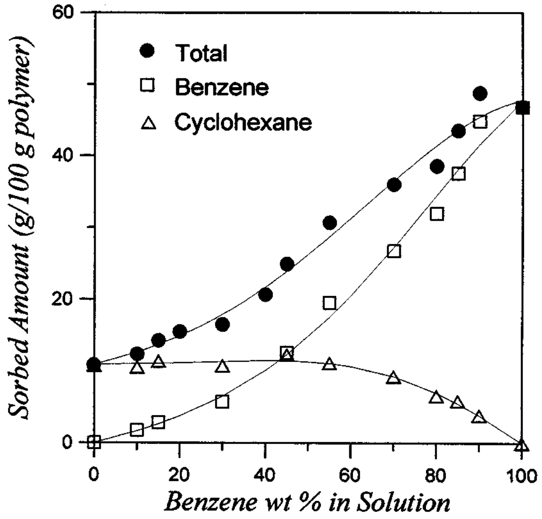

Figure 5. Amount of benzene, cyclohexane, and total liquid sorbed in the PPOP membrane as a function of benzene concentration in the solution in the liquid sorption experiment at 35°C.

The liquid sorption experiment was performed to study the preferential sorption of the benzene/cyclohexane system in the PPOP membrane at 35°C. The effect of the solution composition on the total sorption amount and the sorption amount for each individual component are shown in Figure 5.

The total amount sorbed in the PPOP membrane increases as the benzene concentration increases. This amount indicates that benzene has a higher solubility in PPOP than does cyclohexane. The sorption selectivity for benzene/cyclohexane is shown in Figure 3 along with the pervaporation selectivity. The sorption selectivity is fairly constant, and it ranges from about 1.5 to 1.2 in low to high benzene concentration. Although it contributes positively to the pervaporation selectivity, it is not the dominant factor for better permselectivity toward benzene in the middle concentration range in the pervaporation operation. The diffusion selectivity should account for the large variation in pervaporation selectivity shown in Figure 3.

It is also of interest to note in Figure 5, that the concentration of cyclohexane within the membrane is kept relatively constant when the outside cyclohexane concentration is reduced from 100% to about 50%. The interaction of benzene and cyclohexane, as well as benzene and polymer and cyclohexane and polymer, accounts for the effect. The benzene concentration within the membrane increases with its outside concentration in a concave shape to the axis. The cyclohexane concentration within the membrane slowly drops in a convex shape to zero when its outside concentration is further reduced from 50% to 0%. Better understanding of the interaction in the ternary system can be analyzed by Flory–Huggins thermodynamics for the liquid sorption data (Mulder et al., 1985).

Vapor sorption isotherms for benzene and cyclohexane

The sorption isotherms for benzene and cyclohexane vapors at various temperatures are shown in Figures 6 and 7,

Table 1. Solubility and Interaction Parameter for Benzene and Cyclohexane in the PPOP Membrane

Temp. °C	Solubility (S) cm^3(STP)/cm^3(polymer)(cm Hg)		Interaction Parameter (χ)	
	Benzene	Cyclohexane	Benzene	Cyclohexane
25	4.73	1.96	1.15	1.67
35	3.23	1.26	1.03	1.60
45	1.73	0.99	1.01	1.38
55	1.18	0.68	0.98	1.34

respectively. The concentration of sorbed vapor in the membrane increases with vapor pressure. The isotherms can be well described either by Henry's law or by Flory–Huggins theory. The correlation by the Flory–Huggins theory is fundamentally sound, but that by Henry's law is simple, and an explicit relationship between the sorption concentration and vapor activity is readily available. Both approaches were used to analyze the sorption isotherm data.

By Henry's law, the solubility (S_i) of a vapor in the polymer was treated as constant and could be determined from the slope of the isotherm plot by using the following relationship

$$S_i = \frac{C_i}{p_i} \tag{7}$$

where C_i is the concentration of the sorbed vapor in the polymer and p_i is the external vapor pressure.

By the Flory–Huggins equation for a binary vapor–polymer system, the external vapor pressure and the volume fraction of the sorbed vapor (ν_i) in the polymer matrix can be correlated with an interaction parameter (χ_i) (Flory, 1953):

$$\ln a_i = \ln\left(\frac{p_i}{p_i^0}\right) = \ln \nu_i + (1-\nu_i) + \chi_i(1-\nu_i)^2, \tag{8}$$

where ν_i was calculated by assuming that the sorbed vapor was in liquid form and the volume additivity law was valid in the polymer matrix.

The values of S_i and χ_i by using Eqs. 7 and 8 were determined from the experimental results and are given in Table 1. The curve fittings by using these two models with the parameters obtained are shown along with the experimental data in Figures 6 and 7.

The solubility of benzene vapor is greater than that of cyclohexane vapor, and the interaction parameter for benzene is smaller than that for cyclohexane in the temperature range studied. The selectivity toward benzene is obvious for vapor-phase sorption in this kind of system. Sorption involves the condensation of vapor and the mixing of the condensate and polymer. Because the enthalpy change of condensation is negative and its absolute value is much larger than that of mixing, the solubility decreases with temperature. The temperature dependence of the solubility obeys the Clausius–Clapeyron equation written in the form

$$\Delta H_{S,i} = -R\frac{d \ln S_i}{d(1/T)}, \tag{9}$$

which allows for the evaluation of the heat of sorption (Figure 8). The sorption heats of benzene and cyclohexane are -39.0 and -27.9 kJ/mol, respectively. However, these values are doubtful if sorption is considered to be the combination of vapor condensation and the mixture of condensed liquid and polymer, that is,

$$\Delta H_{S,i} = \Delta H_{C,i} + \Delta H_{\text{mix},i}, \tag{10}$$

where $\Delta H_{C,i}$ is the heat of condensation, and $\Delta H_{\text{mix},i}$ is the heat of mixing. The heat of condensation equals the negative of the heat of vaporization ($\Delta H_{V,i}$), $\Delta H_{C,i} = -\Delta H_{V,i}$, and the heat of vaporization can be determined by the Clausius–Clapeyron equation in the form

$$\Delta H_{V,i} = -R\frac{d \ln p_i^0}{d(1/T)}. \tag{11}$$

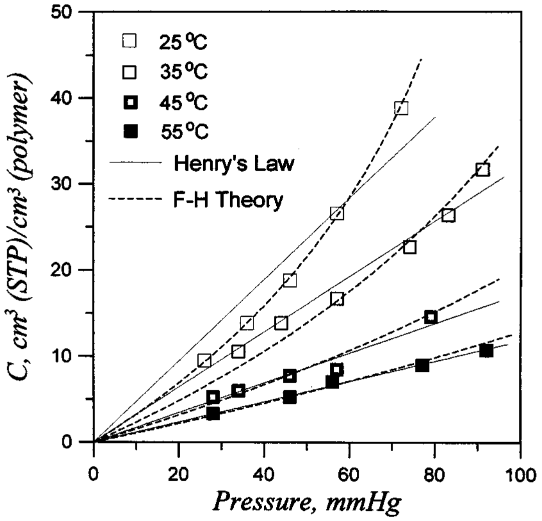

Figure 6. Vapor sorption isotherms for benzene in the PPOP membrane at various temperatures.

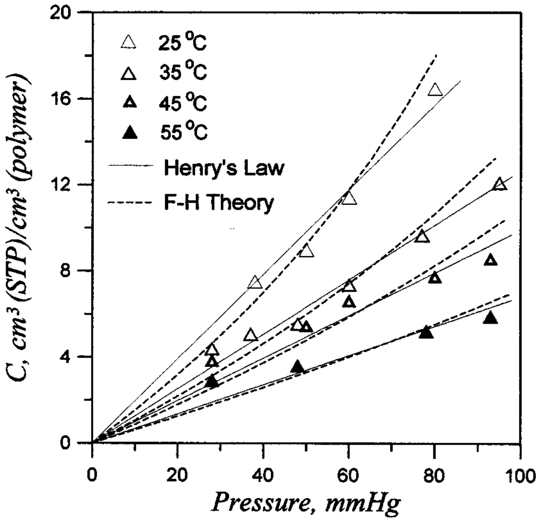

Figure 7. Vapor sorption isotherms for cyclohexane in the PPOP membrane at various temperatures.

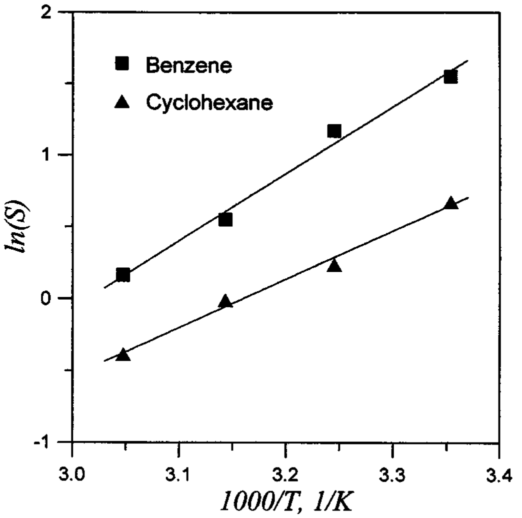

Figure 8. Clausius–Clapeyron plots for the effect of temperature on the solubilities of benzene and cyclohexane in the PPOP membrane.

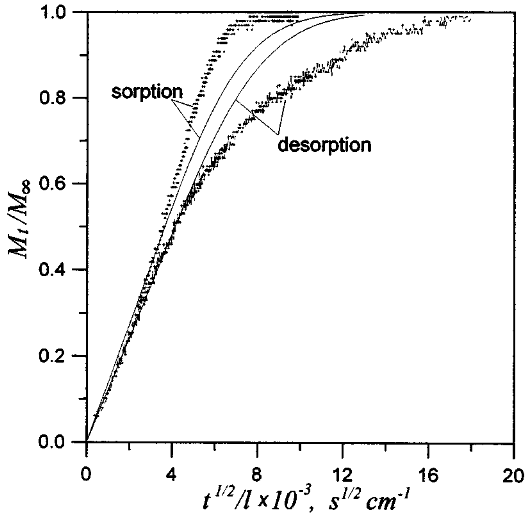

Figure 9. Typical vapor sorption–desorption conjugate pair (symbols: experimental data; solid lines: calculated data by Fickian model for benzene vapor activity of 0.39 at 35°C).

By using the saturated vapor pressure (p_i^0) data at various temperatures, the values of the heat of vaporization can be obtained: they are 33.6 and 32.9 kJ/mol for benzene and cyclohexane, respectively, in the temperature range of this study. According to Eq. 10, the heat of mixing could be negative for benzene in this case, but it cannot be true due to the theory in thermodynamics of polymer solution. The deficiency of the simple Henry's law model may account for the error. Henry's law might overestimate the solubility of benzene at lower temperature (such as 25 or 35°C), where the Flory–Huggins equation may give a better correlation as the sorbed amount becomes larger.

Alternatively, the sorption heat can be estimated by assuming Eq. 10 is valid. The heat of mixing can be calculated from the interaction parameter according to the Flory–Huggins theory (Flory, 1953):

$$\Delta H_{\text{mix},i} = RT\nu_p \chi_i \tag{12}$$

where ν_p is the volume fraction of the polymer. Assuming that the penetrant is at infinite dilution, the volume fraction of polymer approaches unity. The calculated temperatures of mixing are 2.7 ± 0.1 and 3.9 ± 0.3 kJ/mol for benzene and cyclohexane, respectively, in the temperature range of this study. The heats of sorption are estimated to be -30.9 and -29.0 kJ/mol for benzene and cyclohexane, respectively. Both methods gave reasonably close results for the sorption heat for cyclohexane, but the second method might give a value of the sorption heat for benzene that is more theoretically correct. Energetically, the larger magnitude of the sorption heat (negative value) for benzene favors the vapor sorption of benzene than cyclohexane, and the smaller heat of mixing (positive value) for benzene favors liquid sorption of benzene.

Moreover, benzene is smaller in size than cyclohexane, as the molar volumes of benzene and cyclohexane are 89.4 and 108.7 cm^3/mol, respectively. Even the volume fraction given by Eq. 8 can be the same, the polymer still absorbs a higher number of moles of benzene than cyclohexane, and it results in a higher solubility for benzene than that for cyclohexane.

It was also noted that the interaction parameter given by vapor sorption did not match the one obtained from pure liquid ($a = 1$) sorption. The interaction parameters obtained from liquid sorption were 0.84 and 1.39, respectively, for benzene and cyclohexane. The concentration-dependent interaction parameter could be one of the reasons for the difference.

Diffusivities for benzene and cyclohexane

Figure 9 shows a typical reduced plot for the sorption and desorption kinetics in this study. The first 50% of weight gain or loss was linear, and the conventional Fickian model was assumed to estimate a constant diffusivity for sorption or desorption. Both the half-time method and the initial slope method (Crank, 1975) gave similar results. However, the later half of the sorption or desorption kinetic data deviated from those predicted by the Fickian model. The experimental data were higher than those predicted for sorption and lower than those predicted for desorption. The results indicate that the diffusivity may be an increasing function of the sorbed vapor concentration in the polymer matrix. Nevertheless, the averaged diffusivity of sorption and desorption was used in subsequent calculations as suggested by Crank (1975).

It was found that there was a linear relationship between the logarithm of the averaged diffusivity and the vapor activity for benzene and cyclohexane at various temperatures, as shown in Figures 10 and 11, respectively. When Eq. 2 was used, the diffusivity at infinite dilution and the plasticization parameter can be determined as follows:

$$D_i = D_{i0} \exp(\alpha_i a_i) = D_{i0} \exp(A_i C_i), \tag{13}$$

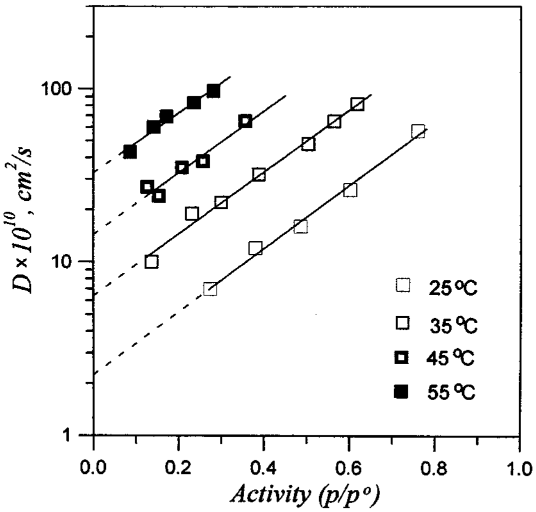

Figure 10. Diffusivity vs. vapor activity for benzene in the PPOP membrane at various temperatures.

Table 2. Diffusivity at Infinite Dilution D_{i0}, Slope α_i for Curves in Figures 10 and 11, and Plasticization Coefficient A_i (or A_{ii} in Eq. 3) for Benzene (1) and Cyclohexane (2)

T (°C)	D_{10} (cm²/s)	α_1	A_1 (or A_{11})*	D_{20} (cm²/s)	α_2	A_2 (or A_{22})*
25	2.24×10^{-10}	4.189	0.0934	8.10×10^{-11}	1.963	0.1030
35	6.38×10^{-10}	4.119	0.0867	2.00×10^{-10}	2.062	0.1093
45	1.44×10^{-9}	4.115	0.1072	6.06×10^{-10}	1.931	0.0874
55	3.27×10^{-9}	3.994	0.1036	1.51×10^{-9}	1.916	0.0865

*Unit for A_i (or A_{ii}) is cm^3 (polymer)/cm^3 (STP), as the unit for C_i is cm^3 (STP)/cm^3 (polymer).

where α_i is the slope obtained from the semilogarithm plot of D_i with a_i in Figure 7 and $\alpha_i = A_i S_i p_i^0$ if Henry's law is valid for the system. The data of D_{i0}, α_i, and A_i (or A_{ii}) are tabulated as a reference in Table 2.

The diffusivity of benzene is about twofold to one-order of magnitude higher than that of cyclohexane, depending on the vapor activity and temperature. The effect of molecular size presumably accounts for the difference in the magnitudes of their diffusivities. The diffusion selectivity may be the prime reason for the permselectivity toward benzene in the pervaporation operation.

It is of interest to note that the log $D - a$ plot for benzene has similar slopes at various temperatures, and so does cyclohexane, as shown in Figures 10 and 11. The ratio of the slopes for benzene and cyclohexane is about $2.0 \sim 2.1$ at various temperatures. It appears that each component has its own characteristic activity dependence for diffusivity in the temperature range studied. The resulting plasticization parameters in this temperature range showed similar values [0.097 ± 0.01 cm^3 polymer/cm^3 (STP)] for both benzene and cyclohexane if the sorbed vapor volume concentration was used for Equation 2. This indicates that benzene and cyclohexane may have a similar plasticization effect on PPOP membrane.

The diffusion activation energies ($E_{D,i}$) for benzene and cyclohexane were evaluated according to the Arrhenius equation for the temperature dependence of their diffusivity at infinite dilution (D_{i0}); these were 72.1 and 80.3 kJ/mol, respectively (Figure 12). The diffusional energy barrier for benzene is smaller than that for cyclohexane in the PPOP membrane. The molecular-size effect accounts for the difference, because smaller molecules require lower energy for a diffusion jump within the polymer matrix.

Mass transport within the membrane in the pervaporation operation

Equation 4 was solved by the procedure outlined in the subsection on the computation scheme. The concentration

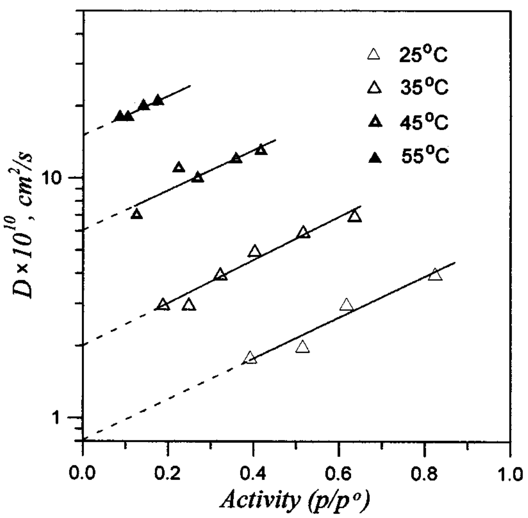

Figure 11. Diffusivity vs. vapor activity for cyclohexane in the PPOP membrane at various temperatures.

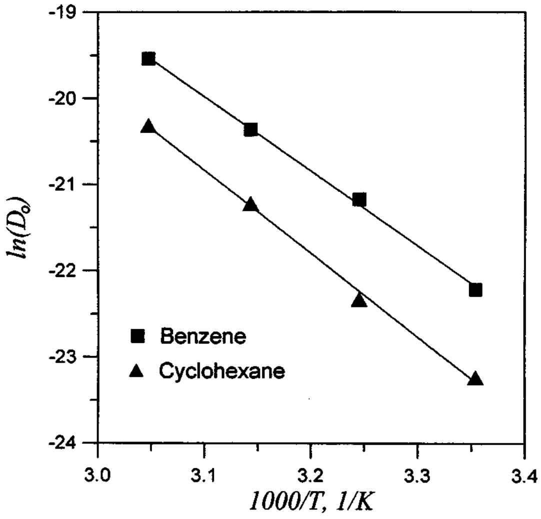

Figure 12. Arrhenius plots for the effect of temperature on the diffusivities at infinite dilution (zero activity) for benzene and cyclohexane in the PPOP membrane.

Table 3. Coupling Coefficients for Diffusivities of Benzene (1) and Cyclohexane (2) for Various Benzene Feed Concentrations at 35°C

Benzene %	A_{12}	A_{21}
13	0.1452	0.5386
17	0.1333	0.3179
35	0.1102	0.1118
41	0.0863	0.0779
50	0.0651	0.0639
57	0.0326	0.0565
72	−0.0621	0.0499

*Unit for A_{12} or A_{21} is cm^3 (polymer)/cm^3 (STP), as the unit for C_i is cm^3 (STP)/cm^3 (polymer).

profiles, coupling coefficients, and local diffusion coefficients could be obtained for each set of experimental flux data (Figure 2), as the upstream concentrations of benzene and cyclohexane at the membrane surface were determined from the correlation of liquid mixture sorption data (Figure 5). For each set of data, the optimal coupling coefficients for benzene and cyclohexane are listed in Table 3. An example of the concentration profiles for benzene and cyclohexane is shown in Figure 13, and its corresponding diffusion coefficient profiles and the ratio of them are shown in Figure 14.

In a pervaporation separation process, one side of the membrane is in contact with liquid and the other side with reduced pressure. The membrane is presumed to have two kinds of layers: one is swollen with the penetrants and exists at the upstream side, and the other is a dry layer at the downstream side (Nakagawa, 1992; Neel, 1995), although there is no distinct boundary between these two layers. In the dry layer, the sorbed concentration of penetrants is sufficiently low, the diffusion approaches to the same situation created in the vapor sorption experiments. The correlation obtained previously, as in the form of Eq. 2, can be applied to estimate the diffusivity for each individual penetrant if the effect from other penetrants is neglected. In this case, it is assumed that the penetrant will diffuse as if it is only aware of itself and the polymer, and that the existence of the other penetrant is negligible. However, Eq. 3 will give a better correlation for the diffusivity if the coupling effect from the other penetrant cannot be neglected. Nevertheless, the sorbed concentration of each penetrant is low in the dry layer, as is the corresponding diffusivity for each of them, as predicted by Eq. 2 or Eq. 3. On the other hand, the sorbed concentration in the upstream swollen layer is high, and the corresponding diffusivity is high. In a steady-state operation, the flux should be the same at any position within the membrane. Therefore, according to Eq. 1, the concentration gradient at the dry layer is much steeper than that in the swollen layer. The concentration profiles shown in Figure 13 demonstrate the phenomena exactly, while Figure 14 shows the corresponding diffusivity for benzene and cyclohexane along the transport distance.

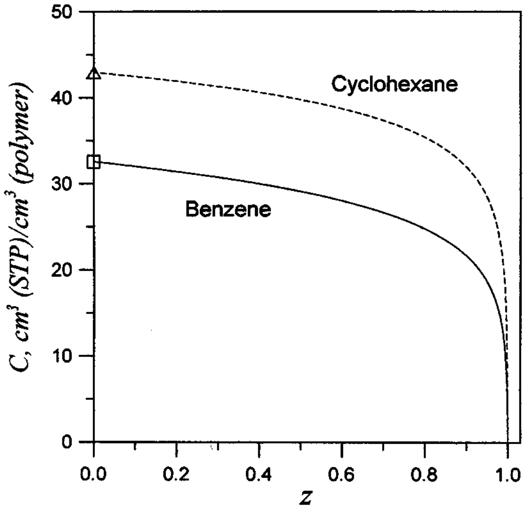

Figure 13. Example of the concentration profiles for benzene and cyclohexane within the PPOP membrane in the pervaporation.

The run is with 35% benzene in feed solution and operated at 35°C; symbols at $z = 0$ are computed data with the correlation obtained in Figure 5.

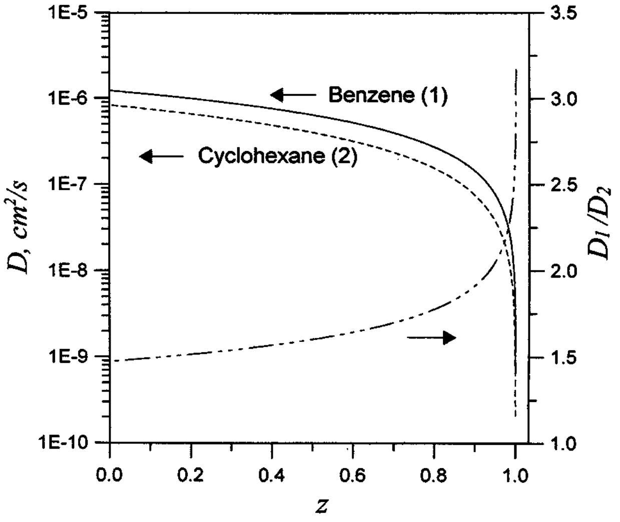

Figure 14. Example of the diffusivity and diffusion selectivity profiles for benzene and cyclohexane within the PPOP membrane in the pervaporation.

The run is with 35% benzene in feed solution and operated at 35°C.

The diffusivity for benzene and cyclohexane changes dramatically with the position within the membrane. At the swollen layer, the change is rather mild and the order of the diffusivity is about 10^{-7} to 10^{-6} cm^2/s. In contrast, the diffusivity can drop to the order of 10^{-10} cm^2/s within the last few percent of the membrane thickness, where the "dry layer" may exist. The ratio for the diffusivities of benzene and cyclohexane or the diffusion selectivity between the two also changes with position. It is generally the lowest at the upstream surface, rises slowly in the swollen layer and much quicker in the dry layer, and then reaches the highest at the downstream surface. It is the dry layer that may account for the better pervaporation selectivity. The behavior coincides with the hypothesis that the dry layer is the "active layer" for separation (Nakagawa, 1992).

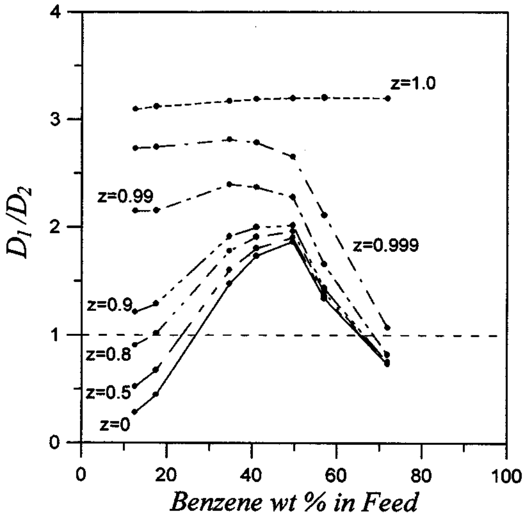

Figure 15. Diffusion selectivity as a function of the benzene concentration in feed solution at different positions within the PPOP membrane in the pervaporation at 35°C.

The coupling coefficients were chosen to meet the concentration of penetrant at the upstream membrane surface. It has been found that those coefficients are decreasing functions of the benzene concentration in the feed solution. The more the coupling coefficient deviates from zero, the more the diffusivity of the penetrant will be affected by the other penetrant. A positive coupling coefficient would enhance the diffusivity, and a negative coupling coefficient would reduce the diffusivity. For cyclohexane, the coupling effect caused by the presence of benzene is greatest at lower benzene concentration and becomes less at higher benzene concentration. For benzene, the effect due to the presence of cyclohexane is relatively mild, and the corresponding coefficient even becomes a small negative value at a higher benzene concentration. The interaction among the penetrant−penetrant and penetrant− polymer should be responsible for the variation in the coupling coefficients caused by the change in concentration. It has been noted that the coupling coefficients for benzene and cyclohexane have similar values with feed solution from 35 to 50 wt. % of benzene; this is also the range in which the maximum pervaporation selectivity has been found. It is suggested that the coupling effect determines the variation in the diffusion selectivity, and hence the pervaporation selectivity.

Figure 15 shows the ratio of the diffusivities between benzene and cyclohexane, that is, the diffusion selectivity toward benzene vs. cyclohexane, at different positions within the membrane as a function of the feed concentration of benzene. It is rather interesting to evaluate the pervaporation selectivity (Figure 3) and the change in the diffusivity ratio or the diffusion selectivity along the position within the membrane for each feed condition. When the benzene feed concentration is 13 or 17%, about 80% or more of the traveling distance within the membrane (swollen layer) favors the diffusion of cyclohexane, and only the last 10% of the membrane (dry layer) has a diffusion selectivity toward benzene larger than 1.2. While for benzene feed concentration is 35, 41, and 50%, the whole membrane has a diffusion selectivity greater than 1.5 toward benzene. For the preceding feed concentration, the last 1% of membrane can have a diffusion selectivity greater than 2.2, and the pervaporation selectivity increases with benzene feed concentration, as the overall diffusion selectivity becomes less impaired by the swollen layer. For the benzene feed concentration is 57%, an active layer with diffusion selectivity higher than 2 is less than 0.1% of the membrane thickness. Finally, when the benzene feed concentration is 72%, there is not a great deal of diffusion selectivity toward benzene or cyclohexane for 99.9% of the membrane thickness. As a result, in the last two cases, the pervaporation selectivity falls with increasing feed benzene concentration. In summary, the lower pervaporation selectivity at lower benzene feed concentration is due to the unfavorable diffusion selectivity in the swollen layer, and that at higher benzene feed concentration is caused by the narrow thickness of the active layer with high diffusion selectivity. The pervaporation selectivity reaches the maximum of about 3 at medium benzene feed concentration.

Strictly speaking, the coupling coefficient should depend on the local concentrations of benzene and cyclohexane, and it may change with position within the membrane. In this study, the coupling coefficient was treated as a ''bulk'' property and only a single value was obtained for each penetrant for each set of experimental conditions. Nevertheless, the validity of the relationship between the coupling coefficient and the upstream feed concentration is not jeopardized very much, because the penetrant concentrations are not too far away from the upstream surface concentrations in most of the thickly swollen layer within the membrane, and it really does not matter a great deal in the dry layer, where the penetrant concentrations are low.

Activation energy consideration

In the pervaporation operation, the flux equation can also be written phenomenologically, like gas permeation, as (Wijmans and Baker, 1995; Feng and Huang, 1996, 1997):

$$J_i = \frac{P_i}{l}(p_{i0} - p_{i1}), \tag{14}$$

where p_{i0} and p_{i1} are the partial vapor pressure of the penetrant i in, respectively, the upstream and the downstream, and P_i is the permeability for the penetrant i through the membrane with respect to the driving force expressed in terms of partial vapor pressure, and is related to the solubility (S_i) and diffusivity (D_i):

$$P_i = D_i S_i. \tag{15}$$

The temperature dependence for P_i is commonly described by an Arrhenius-type equation, and the permeation activation energy $(E_{P,i})$ can be determined. According to Eqs. 9 and 15, the permeation activation energy $(E_{P,i})$ can be calculated by adding the diffusion activation energy $(E_{D,i})$ and the sorption enthalpy $(\Delta H_{S,i})$ (Feng and Huang, 1996, 1997),

$$E_{P,i} = E_{D,i} + \Delta H_{S,i}. \tag{16}$$

Wijmans and Baker (1993) proposed visualizing the sorption in pervaporation as the evaporation of liquid feed to

Table 4. Energy Parameters Obtained in This Study (kJ/mol)

	E_F	ΔH_V	E_{PV}	E_D	ΔH_S^*	E_P^*	ΔE_{P-PV}^*
Benzene	22.9	33.6	−10.7	72.1	−30.9	41.2	−51.9
Cyclohexane	28.6	32.9	−4.3	80.3	−29.0	51.3	−55.6

*Values of ΔH_S are obtained from the calculation based on Eqs. 10, 11, and 12, and they are more theoretically correct than those obtained from Eq. 9, although Eq. 9 is a prerequirement for Eq. 16.

produce a saturated vapor phase, followed by sorption by the membrane, although there is actually no vapor on the feed side of the membrane. This treatment assumed that the liquid−membrane and the liquid−vapor−membrane systems were thermodynamically equivalent and that the membrane permeation properties in pervaporation could be analyzed the same way as those of the vapor-phase permeation process. Consequently, in this treatment the permeation activation energy ($E_{PV,i}$) through the membrane can be determined by subtracting the heat of vaporization ($\Delta H_{V,i}$) from the activation energy of pervaporation flux (Feng and Huang, 1996, 1997)

$$E_{PV,i} = E_{F,i} - \Delta H_{V,i}. \tag{17}$$

The $E_{PV,i}$ could be evaluated from our experimental results using Eq. 17 if the temperature dependence of the activity coefficient for each component in the system was minimal.

In theory, the values of $E_{P,i}$ and $E_{PV,i}$ should be the same if the interaction among the penetrants and the polymer membrane is weak and the swelling of the membrane is not significant. Our data show, however, that there are significant differences between $E_{P,i}$ and $E_{PV,i}$ (Table 4), where the $E_{P,i}$ obtained by Eq. 16 is for permeation of a single penetrant without the interference by other penetrants, and $E_{PV,i}$ by Eq. 17 is for pervaporation where two penetrants permeate the membrane simultaneously. The coupling effect of the multicomponent transport could play an important role in the difference. In addition, the penetrant is expected to encounter a much smaller diffusion barrier when it permeates the swollen layer, as the free volume within the polymer matrix increases significantly, and thus the activation energy for diffusion can be reduced. The heat of sorption can also be affected due to the situation of a ternary system in pervaporation. The coupling effect, the reduction of activation energies for diffusion, and the change of sorption enthalpy due to swelling create the difference between the values of $E_{P,i}$ and $E_{PV,i}$, that is,

$$\Delta E_{P-PV,i} = E_{PV,i} - E_{P,i} \tag{18}$$

where $\Delta E_{P-PV,i}$ is the difference between the activation energies for pervaporation and single-vapor permeation.

In the vapor sorption experiment, the diffusivity (at infinite dilution) for benzene was about 3.2 times larger than that for cyclohexane, and the solubility for benzene was about 2.5 times larger than that for cyclohexane at 35°C. According to the solution−diffusion model, the ideal permselectivity (α_P^{ideal}) between benzene and cyclohexane was expected to be 8 as was implied by Eq. 15:

$$\alpha_P^{\text{ideal}} = \frac{P_{10}}{P_{20}} = \left(\frac{D_{10}}{D_{20}}\right)\left(\frac{S_1}{S_2}\right). \tag{19}$$

However, due to the thermodynamic interaction among the penetrants and the polymer in the ternary system, the sorption selectivity was reduced when the liquid mixture came in contact with the membrane. The diffusion selectivity was influenced by the coupling effect as discussed earlier. The activation energy for diffusion can be reduced because of the swelling effect at the swollen layer. The value of $\Delta E_{P-PV,i}$ indicates the degree of these effects in a pervaporation operation. Our results show that cyclohexane ($\Delta E_{P-PV} = -55.6$ kJ/mol) was affected slightly more than benzene ($\Delta E_{P-PV} = -51.9$ kJ/mol). The difference between the values of ΔE_{P-PV} for benzene and cyclohexane may be caused by the slightly different coupling effect in pervaporation experienced by each permeant. The difference in the activation energy between benzene and cyclohexane in single vapor permeation ($E_{P,2} - E_{P,1}$) is 10.1 kJ/mol while that in pervaporation ($E_{PV,2} - E_{PV,1}$) is 6.4 kJ/mol. As a result, the ability to differentiate in pervaporation becomes less than is expected for vapor permeation. The permselectivity is therefore less in pervaporation than what we expected based on the single-vapor sorption results and the solution−diffusion model.

Conclusions

In this study, the pervaporation for the mixture of benzene and cyclohexane by using PPOP membranes was investigated. As expected, the membrane was more selective toward benzene than cyclohexane. The maximum pervaporation selectivity α_{PV} was 3 when the feed concentration of benzene was in the range between 35 and 50% at 35°C. Transport through the membrane has been clearly understood by the solution−diffusion model with an exponential form of diffusivity that takes the plasticization and the coupling effects of the penetrants into consideration. The model used the information obtained from independent liquid mixture and vapor sorption experiments. Using the proposed computation scheme, the concentration and diffusivity profiles were obtained for benzene and cyclohexane within the membrane. The activation energy analysis showed that the energy barrier for permeation in the pervaporation is largely reduced due to membrane swelling, the coupling effect, and the interaction between the penetrants and the polymer membrane when compared to the transport of a single-vapor permeation through an unswollen membrane.

With the independently obtained exponential relationship between the diffusivity and the concentration for each individual penetrant, the model allows the diffusivity of penetrants in the binary transport of a pervaporation operation to be determined. The proposed computation method is considered much simpler and more straightforward than the other existing methods for modeling the pervaporation process. This approach works well for the system where the sorption isotherms of penetrants in the membrane are not too far from an ideal Henry's law and the degree of the coupling effect is similar for both penetrants but should not be limited to it. The application of such an approach to other systems is worth studying.

Analysis of the activation energy consideration provides a useful tool to characterize the effects of membrane swelling, coupling phenomena, and thermodynamic interaction for membrane transport in pervaporation. Different components can have different values of ΔE_{P-PV} in a similar system due to the difference in the coupling effect for each permeant. The value of ΔE_{P-PV} can be very different if the coupling effect to each penetrant is significantly different, and the pervaporation selectivity would change a great deal as well. However, the analysis relies on accurate experimental data of heat of sorption, activation energy of diffusion through the unswollen membrane, and the activation energy of permeation in the pervaporation operation.

Acknowledgments

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