Separation of Liquid Mixtures by Using Polymer Membranes. I. Permeation of Binary Organic Liquid Mixtures through Polyethylene*

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Synopsis

The permeation characteristics and the separation behavior of 25 combinations of binary liquid mixtures through low-density polyethylene membrane have been investigated. The organic compounds studied were members of the homologous series of liquid aliphatic hydrocarbons between n-pentane and n-nonane as well as some aromatic and cyclic compounds. A special permeation cell was designed in order to study permeation rates at different temperatures ranging from 25 to 45°C. The rate of permeation increased with temperature, and it was found that the temperature dependence of the permeation rate for both pure compounds and mixtures could be expressed by Arrhenius-type relationships. The efficiency of separation, however, decreased with increasing temperature. Activation energies of permeation ranged from 16–22 kcal/mol for pure compounds and binary mixtures of benzene, n-hexane, cyclohexane, and 2-2-dimethyl-butane. The effects of chemical nature, molecular size, and molecular shape of the diffusing species on the permeation and separation were studied and qualitative guidelines were suggested. The effect of the composition of the binary mixtures on the permeation rate has been investigated for several systems. Permeation enhancement effects were observed in which the mixtures permeate considerably faster than either of the pure components. Maximum permeation rates occurred at about 50 wt-% mixtures for the systems benzene–n-hexane and benzene–cyclohexane. This phenomenon is explained in terms of a combined internal plasticizing and solubility effect.

INTRODUCTION

The permeation of gases and liquids through polymer films has been the subject of extensive research during the past two decades. In recent years, there has been considerable interest in the potential uses of polymer films or membranes for separating mixtures of chemical compounds. The basis of a membrane separation process is the selective permeation of the permeating molecule or permeant through the membrane. In this way, the composition of a mixture may be changed by passage through a selective membrane. The mechanism of a liquid permeation process can be described as consisting of dissolution of the liquid into the membrane, diffusion through it, and evaporation from the membrane surface. The rate of

permeation and the efficiency of separation are governed by a number of factors, including the chemical nature, molecular size, and molecular shape of the diffusing species, the composition of the permeating mixture, and the physicochemical properties of the polymer. In comparison with work on gas permeation through polymer membranes, relatively little work on liquid permeation has been reported in literature. In particular, few detailed studies have been published on the permeation of liquid mixtures through polymer membranes. Binning et al.[1] studied the separation of organic mixtures by a liquid permeation process, by use of polymer films. Long[2] studied the transport properties of some selected hydrocarbons through polypropylene film. Liquid permeation was considered a special case of ordinary diffusion which could be explained by a classical diffusion model. The exponential concentration dependence of diffusivity led to equations which were very sensitive to the concentration of liquid in the upstream side of the film.

Michaels et al.[3,4] studied the separation of xylene isomers and other organic liquid mixtures through preconditioned polyethylene films. They reported that higher permeabilities of liquids through polyethylene could be achieved by annealing the polymer. They also presented a model based on the polymer acting as a simple molecular sieve or screen, wherein the amorphous region constituted the holes and the interconnected crystalline regions constituted the mesh. A qualitative study was made by Sweeny et al.[5] on the separation of organic mixtures using polymer films. They found that hydrogen bonding played an important role in the separation process. Krewinghaus[6] investigated the transport of binary mixtures of organic liquids through stretched and annealed polyethylene films. He found that orientation and annealing of the polyethylene film resulted in significant changes in the diffusivities and also in the permeation selectivity of the film. Carter et al.[7] studied the separation of organic mixtures of different concentrations through polymer films. They suggested that the selective permeation of one liquid from the mixture consisted of two mechanisms: (1) preferential absorption in the upstream face of the film of the liquid in contact with it and (2) differing rates of transport through the film itself.

It is the purpose of this study to examine the permeation behavior of selected organic mixtures through polymer membranes. Attempts will be made to relate the physicochemical properties of the permeating liquids and the polymer membrane to the separation and permeation processes.

THEORY

Liquid Permeation

The permeation rate of a liquid through a polymer membrane depends on the solubility of the liquid and its diffusivity in the polymer. The steady state permeation process may be described by a form of Fick's law,

$$Q = -D \, (dc/dx) \tag{1}$$

where Q is the permeation rate, D is the diffusivity, and dc/dx is the concentration gradient across the membrane.

The values of diffusivity depend strongly on the concentration of liquid in the polymer membrane. Many expressions have been proposed to relate D to the solubility of liquid in the membrane and to a diffusivity D_0 obtained at zero concentration of liquid. An equation which is commonly used[8,9] is

$$D = D_0 e^{\gamma c} \tag{2}$$

where D_0 and γ are constants at a given temperature. The constant γ, is a measure of the plasticizing action of liquid on the polymer membrane; the concentration c of liquid in the polymer is the amount of sorption of liquid in the polymer, which is essentially determined by the solubility of the liquid in the polymer. Therefore, eq. (2) shows that in the permeation process the diffusivity of liquid is actually a function of its solubility in the polymer membrane.

Substituting eq. (2) in eq. (1), rearranging, and integrating with boundary conditions gives

$$Q \int_0^L dx = - D_0 \int_{c_3}^{c_2} e^{\gamma c}\, dc \tag{3}$$

where L is thickness of the membrane, c_1 and c_2 are the concentrations of permeant in the polymer at the upstream and downstream, respectively. At steady state, the permeation rate can be expressed as

$$Q = (D_0/\gamma L)(e^{\gamma c_1} - e^{\gamma c_2}) \tag{4}$$

where c_1 can be determined by the equilibrium sorption of liquid in the polymer and c_2 is essentially zero, provided the downstream is maintained at a low pressure and the rate of evaporation of permeate is not controlled by diffusion. Equation (4) can then be simplified to

$$Q = (D_0/\gamma L)(e^{\gamma c_s} - 1) \tag{5}$$

where c_s is the solubility of liquid in the polymer. This equation shows that the permeation rate of a liquid through a polymer membrane depends not only on its diffusivity but also on its solubility in the membrane.

Polymer morphology has a strong affect on permeation characteristics. The degree of crystallinity and size of crystallites within the polymer affect both the rate of transport and the efficiency of separation. Since only amorphous regions in the polymer take part in the transport process, in highly crystalline polymers any factor which disrupts the order of these regions can have an effect on the liquid permeation process.

Binary Liquid Permeation

The membrane selectivity of a binary system consisting of two liquids A and B can be expressed in terms of a separation factor α, defined as the

concentration ratio B/A in the permeate (downstream) divided by the ratio B/A in the permeant (upstream).

$$\alpha_{B/A} = (Y_B/Y_A)/(X_B/X_A) \tag{6}$$

where X_B is the weight fraction of B in the permeant, Y_B is the weight fraction of B in the permeate, etc.

The total permeation rate of a mixture through a membrane Q is

$$Q = q_A + q_B \tag{7}$$

where the subscripts A and B indicate the permeation rates of components A and B. If the permeation is ideal, the rates in the mixture can be expressed in terms of the pure component permeation rate as

$$q_A^0 = X_A q_A \tag{8}$$

$$q_B^0 = X_B q_B \tag{9}$$

where Q is the permeation rate of pure component permeation and the superscript zero refers to the ideal permeation rate. The total ideal permeation rate Q^0 is thus given by

$$Q^0 = X_A Q_A + (1 - X_A)Q_B \tag{10}$$

and the selectivity for a system which exhibits ideal behavior is simply the ratio of the pure component permeation rates.

$$\alpha_{B/A}^0 = Q_B/Q_A \tag{11}$$

Permeating permanent gas mixtures exhibit such ideal behavior.[10,11] Nonideal behavior results when one component of the permeating mixture plasticizes the membrane more than the other. Organic vapors or liquids do not exhibit ideal permeation behavior because the permeants swell the membrane to different degrees.

The measure of the nonideal behavior of liquid permeation can be expressed by a permeation ratio θ, defined as the ratio of the actual permeation rate Q and its ideal permeation rate Q^0:

$$\theta = Q/Q^0 \tag{12}$$

The permeation ratios for the individual components can be expressed as

$$\theta_A = q_A/q_A^0 \tag{13}$$

and

$$\theta_B = q_B/q_B^0 \tag{14}$$

Thus the permeation ratio should be equal to unity when a system exhibits ideal permeation behavior. The value of the permeation ratio may be higher or lower than unity for nonideal permeation. If the permeation ratio of a system is higher than unity, the system can be said to exhibit a permeation enhancement effect, while a value lower than unity indicates a permeation depression effect.

EXPERIMENTAL

Apparatus

An apparatus for measuring liquid permeation through polymer membranes was designed and built.   It consisted of the following three main sections: (1) permeation cell with temperature-control system; (2) sample-collecting system and pressure gauge; (3) vacuum pumping system.

A schematic diagram of the apparatus is shown in Figure 1, and a cross section showing details of the permeation cell is given in Figure 2.

Permeation Cell with Temperature-Control System.   The permeation cell was made of two pieces of glass joints having an inside diameter of 4 in.   The membrane was supported on a sintered brass disk, which in turn was held in place by a piece of glass tubing (3 in. in diameter) sitting on the bottom of the lower compartment.   A Teflon gasket was placed on the membrane before the upper part of the cell was matched with the lower one.   The whole unit was tightened up by bolting together the flanges holding the glass compartments.

The upper compartment of the cell had a capacity of about 600 cm^2 for holding the liquid feed and a membrane area of 83.3 cm^2 for permeation.   The entire permeation cell was immersed in water in a glass water bath having a diameter of 12 in. and a height of 12 in.   The temperature of the water in the bath was maintained within 0.1°C of the preset temperature by a Fisher temperature controller.   An auxiliary 800 W heater was used to change to higher temperature settings rapidly.   A $^1/_8$-in. diameter circulation coil was placed into the upper compartment and water was circulated from a submerged pump in the bath to keep the temperature of the liquid feed constant.   A speed-adjustable mechanical stirrer was used in the upper compartment to eliminate any concentration or temperature gradients in the liquid feed.   A thermometer was placed in the cell to determine the temperature reading of the liquid feed.
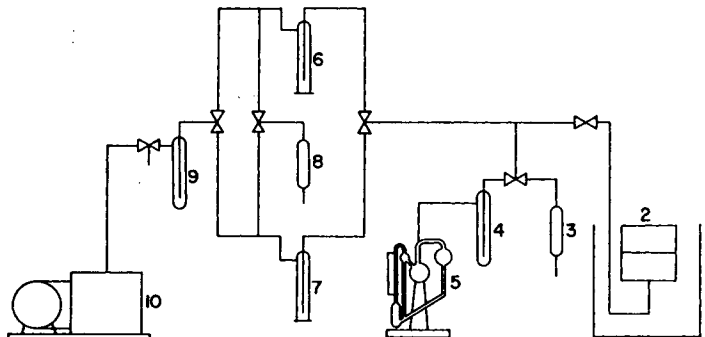

Fig. 1. Diagram of the permeation apparatus: (1) constant temperature bath; (2) permeation cell; (3, 8) drying tubes; (4) trap; (5) McLeod-Lippincott vacuum gauge; (6, 7) cold traps (for collecting samples); (9) cold trap; (10) vacuum pump.
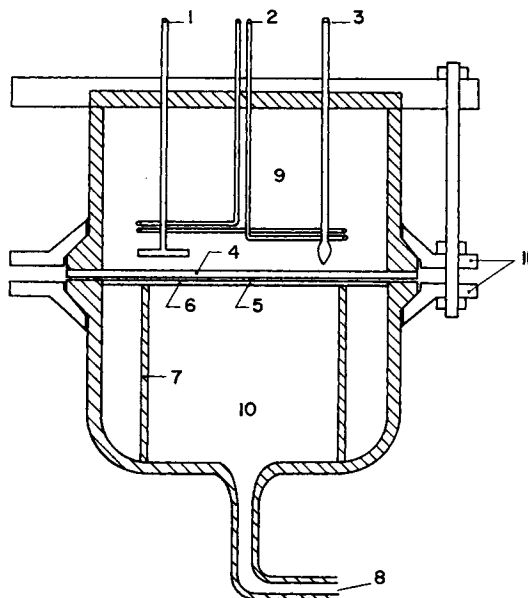
Fig. 2. Cross section of the permeation cell: (*1*) mechanical strirrer; (*2*) circulation coil; (*3*) thermometer; (*4*) Teflon gasket; (*5*) polyethylene membrane; (*6*) sintered brass disk; (*7*) supporting glass tubing; (*8*) outlet of the lower compartment; (*9*) upper compartment; (*10*) lower compartment; (*11*) aluminum flanges.

Sample-Collecting System and Pressure Gauge. The outlet tube from the bottom of the permeation cell was connected to a McLeod-Lippincott vacuum gauge having a measuring range of 0–1 mm Hg pressure. A trap was connected before the gauge in order to prevent any liquid from contaminating the mercury in the gauge, in case of membrane leakage. The system was connected to two traps in parallel and then to another in series with them. A three-way stopcock linking the former to a drying tube exposed to the atmosphere provided a passage for releasing vacuum from the system. During an experiment, the traps were cooled by liquid nitrogen. A pneumatic liquid nitrogen level controller was designed to carry out the feeding procedure automatically.

Vacuum Pumping System. The preceding system was connected to a vacuum pump having a free-air capacity of 150 l/min. Vacuums of up to 1 mm Hg were maintained during the experiments. A three-way stopcock was placed before the pump to allow the releasing of vacuum from the system.

Analysis of Binary Mixtures

For binary permeation studies the compositions of the samples collected in the traps were determined with a precision refractometer (Bausch and Lombe Optical Inc.), which enabled measurement of the refractive index of a sample up to the fifth decimal place. The refractometer was maintained at

20 ± 0.1°C by circulating water through it from a Haake circulating bath. A calibration curve of refractive index versus the composition of binary mixtures was prepared for each set of organic liquid mixtures.

Materials

Polyethylene Membrane. The low-density (0.9199 g/cc) polyethylene membrane was kindly supplied by the Plastic Film Division, Canadian Industries Limited, Toronto, Ont. It had a melt index of 2.0 g/10 min. Membranes of 1 mil thickness (0.001 in.) were specially prepared by the tubular blow extrusion process without any additive. Membranes were cut into 13.5-cm circles before use.

Chemicals

The organic liquids used in the permeation process were pure compounds and binary mixtures. The liquids and the sources were as follows: *n*-pentane (Chromatoquality, Matheson, Coleman & Bell Co.); *n*-hexane (A.C.S. grade, Fisher Scientific Co.); *n*-heptane (Chromatoquality, Matheson, Coleman & Bell Co.); *n*-octane (Chromatoquality, Matheson, Coleman & Bell Co.); *n*-nonane (Chromatoquality, Matheson, Coleman & Bell Co.); 2,2-dimethylbutane (Reagent grade, Matheson, Coleman & Bell Co.); cyclohexane (Chromatoquality, Matheson, Coleman & Bell Co.); benzene (A.C.S. grade, Fisher Scientific Co.); dichloromethane (Chromatoquality, Matheson, Coleman & Bell Co.); chloroform (A.C.S. grade, Fisher Scientific Co.); carbon tetrachloride (A.C.S. grade, Fisher Scientific Co.); acetone (A.C.S. grade, Fisher Scientific Co.); methanol (A.C.S. grade, Fisher Scientific Co.); ethanol (Absolute alcohol, Consolidated Alcohols, Toronto, Ont.); isopropanol (A.C.S. grade, Fisher Scientific Co.); ethyl acetate (A.C.S. grade, Fisher Scientific Co.). These compounds were used as obtained without further purification.

Procedure

The polyethylene membrane was cut into a circle 13.5 cm in diameter then mounted in the permeation cell. The vacuum pump was turned on to evacuate the system for about 30 min, and the pressure of the vacuum system was measured with the McLeod-Lippincott vacuum gauge. Adequate sealing of the system was indicated when the pressure was lower than 0.1 mm Hg in the system. A 200 ml portion of a prepared liquid of known composition was charged into the upper compartment through the opening for inserting the thermometer. The water level in the water bath was adjusted by adding additional water until the level of the liquid in the cell was about one inch below that of water outside. The temperature for consecutive runs of the same system was then raised to 30, 35, 40, and 45°C, respectively, by controlling the temperature of the water bath. A fresh membrane was used for each new system.

Liquid permeation through the membrane was allowed to proceed for about five hours to assure attainment of steady-state flow conditions. The second trap in parallel was then connected to the system and cooled with liquid nitrogen. In the meantime, the first trap which had become filled with solidified liquid was removed from the system and warmed up to the temperature of the liquid in the permeation cell. The sample was then fed back into the cell to keep the composition of the liquid constant. For the experimental runs, the permeation was carried out for measured time intervals ranging from 10 to 350 min, depending upon the permeation rates of the samples. At the end of the required time the second trap was isolated from the system, allowed to warm to room temperature and weighed to determine the amount of liquid permeate. If the liquid was a mixture, the sample was analyzed with respect to composition, using a precision refractometer.

RESULTS AND DISCUSSION

Experimental results are presented in Figures 3–14. They are arranged in the order in which they appear in the discussion which follows. The results of the temperature dependence of permeation rate and selectivity are presented first, followed by those of the effect of molecular size, shape, and chemical nature. The experimental results of the concentration dependence on the binary permeations are presented next, followed by the results of further detailed investigations into this phenomena.

Effect of Temperature

Steady-state measurements of the permeation of organic liquids through 1-mil low-density polyethylene membranes were made. Permeation runs were carried out at 25, 30, 35, 40, and 45°C. It was found that the temperature dependence of the permeation rate can be expressed by Arrhenius-type relationships not only for pure components, but also for binary mixtures. These relationships are shown in Figures 3–5. The activation energies of permeation for pure compounds and binary mixtures of benzene, n-hexane, cyclohexane and 2,2-dimethylbutane were calculated and ranged from 16 to 22 kcal/mol. In most of the systems studied, the permeation rates increased by a factor of about 1.6 for every 5 degree increment in temperature

The effect of temperature on the selectivity of the membrane is shown in Figure 6. It was found that the separation factor for benzene relative to cyclohexane, $\alpha_{B/C}$, decreased from 1.632 at 25°C to 1.439 at 45°C for a mixture of 50% benzene and 50% cyclohexane. This can be explained by the increase in agitational energy or motions of the polymer chains at higher temperatures. According to Eyring's hole theory of diffusion, the formation of "holes" in the polymer requires enough energy to break down a number of secondary valence bonds. At low temperature there are more smaller holes than larger holes in the amorphous regions. These holes

allow more benzene than cyclohexane to go through, because the benzene
molecule has a smaller diffusional cross section than the cyclohexane mole-
cule (as shown in Table I).   At higher temperatures, larger holes are pro-
duced as a result of the higher agitational energy of the polymer chains.
More cyclohexane molecules can therefore diffuse through the larger holes
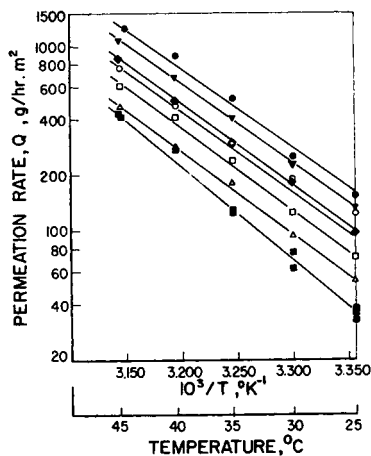and thus the separation factor, $\alpha_{B/C}$, decreases at higher temperatures.

Fig. 3. Effect of temperature on the permeation rate of cyclohexane–2,2,-dimethyl-
butane: (■) 100% D (2,2-dimethylbutane); (△) 20% C + 80% D; (□) 35% C + 65%
D; (O) 50% C + 50% D; (♦) 65% C + 35% D; (▼) 80% C + 20% D; (●) 100% C
(cyclohexane).
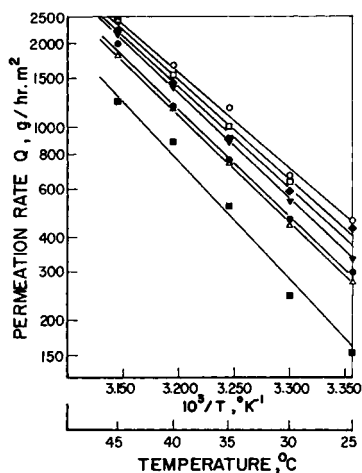
Fig. 4. Effect of temperature on the permeation rate of benzene–cyclohexane mix-
ture; (■) 100% C (cyclohexane); (△) 20% B + 80% C; (♦) 35% B + 65% C; (O)
50% B + 50% C; (□) 65% B + 35% C; (▼) 80% B + 20% C; (●) 100% B (ben-
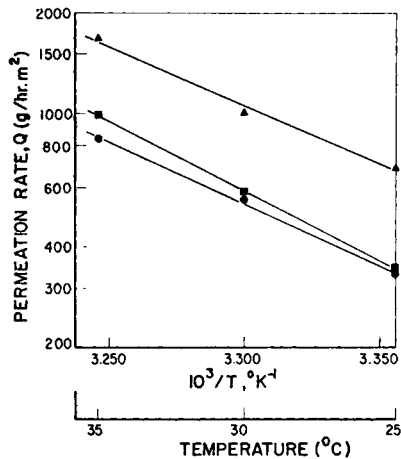zene).

Fig. 5. Effect of temperature on the permeation rate of chlorides of methane: (●) dichloromethane; (▲) chloroform; (■) carbon tetrachloride.
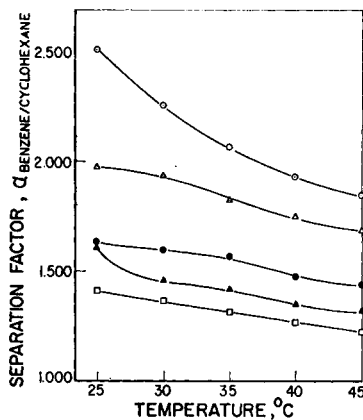

Fig. 6. Effect of temperature on the selectivity of low-density polyethylene to benzene–cyclohexane mixtures: (⊙) 20% B (benzene) + 80% C (cyclohexane); (△) 35% B + 65% C; (●) 50% B + 50% C; (▲) 65% B + 35% C; (□) 80% B + 20% C.

TABLE I
Effect of Molecular Shape and Size on the Permeation Rate

Permanent	$\bar{L}$, Å	$\bar{V}/\bar{L}$, Å^2	Permeation rate (at 25°C), g/hr-m^2
Benzene	5.96	24.8	301
n-Hexane	9.10	23.9	203
Cyclohexane	5.74	31.3	152
2,2-Dimethylbutane	6.58	33.8	35

Effect of Molecular Size, Molecular Shape, and Chemical Nature

Since the first two steps of the permeation process are dissolution of molecules into the polymer membrane and the diffusion of these molecules through it, differences in either the solubility or the diffusivity can result in separation. The solubility difference depends primarily on the difference in the chemical nature of the permeating species. On the other hand, the diffusivity difference is determined largely by the size and shape of these molecules and by the degree of aggregation among the diffusing species within the polymer. For molecules with similar shape and chemical nature, the permeation rate was found to decrease with increasing molecular length. The permeation rates of a homologous series of aliphatic hydrocarbons from n-pentane to n-nonane are presented in Figure 7. The permeation rate was found to decrease with increasing number of carbons in the molecule. Experimental results also showed that when molecules of similar chemical nature were compared, the permeation rate increased with decreasing $\bar{V}/\bar{L}$, the diffusional cross section of the molecule, where $\bar{V}$ is the molecular volume and $\bar{L}$ the maximum molecular length. These results are presented in Table I. It can also be noted that n-hexane has a lower permeation rate than benzene although its diffusional cross section is slightly smaller than that of benzene. This discrepancy may be caused by the length of the n-hexane molecule when compared to the other molecules.

The effect of the chemical nature of the molecule on permeation was studied by comparing the permeation rates of the chlorides of methane as shown in Table II. Sweeny[5] has found that polar compounds tended to permeate polar membranes faster than nonpolar compounds, and *vice versa*. As can be seen from the experimental data, the less polar compound, chloroform, permeates faster than dichloromethane, in spite of the fact that chloroform has a larger molar volume than dichloromethane. Solubility effects play an important part in liquid permeation. Solvents with solubility parameters δ close to that of the polymer sorb to a greater extent than
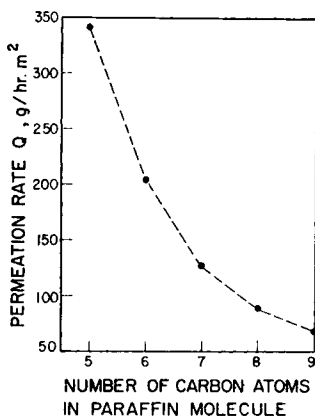

Fig. 7. Effect of molecular size on the permeation rate of normal paraffins at 25°C.

TABLE II
Effect of Chemical Nature on the Permeation Rate

Permeant	Molar volume (at 25°C), cc/mol	Fractional polarity	Solubility parameter $\delta_{1/2}$, polarity	Permeation rate (at 25°C), g/hr-m²
Dichloromethane	65	0.120	9.7	328
Chloroform	81	0.017	9.3	681
Carbon tetrachloride	97	0.000	8.6	344

solvents which have values of δ which are far from that of the polymer. On this basis chloroform ($\delta = 9.3$) would be expected to permeate polyethylene ($\delta = 7.9$) faster than dichloromethane ($\delta = 9.7$).

From the experimental results the following three general trends have been observed.

(1) For single component permeation, when comparing members of a given homologous series of compounds, those with lower molecular weight permeate faster than the higher molecular weight members. In binary permeation, for a given binary mixture containing two members of a homologous series, the lower molecular weight member permeates preferentially.

(2) For single component permeation, molecules with a smaller cross section permeate faster, when comparing molecules of similar molecular weight and chemical nature. For binary liquid permeation, molecules with smaller cross sections will permeate at a faster rate than the other.

(3) In liquid permeation, shape and size effects predominate for molecules with small differences in chemical nature. However, molecules with large differences in chemical nature are not as affected by their shape and size, but depend more on parameters such as solubility, etc., which are related to the chemical nature of the molecule.

Effect of Liquid Composition

The permeation and separation of binary mixtures were investigated over the full range of compositions at temperatures varying from 25 to 45°C. It is interesting to note that the curve obtained by plotting the per cent weight of one component in the permeant versus that in the permeate somewhat resembles a liquid and vapor composition curve for distillation. This is shown in Figure 8. Plots of the concentration in permeant versus the separation factor α are also included in this figure. As can be seen, higher separation was obtained at concentrations in which the preferentially permeating component was less than the other. For example, for a mixture of benzene and n-hexane, the membrane selectivity decreased with increasing concentration of benzene. This can be explained on the basis that benzene has a higher solubility and consequently has more plasticizing effect on polyethylene than n-hexane. An increase in plasticizing effect tends to loosen up the amorphous region and decreases the ability of
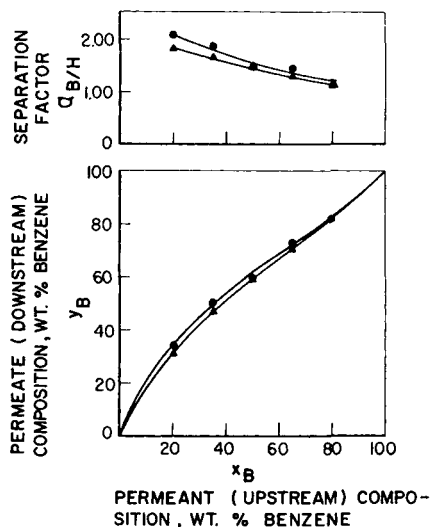
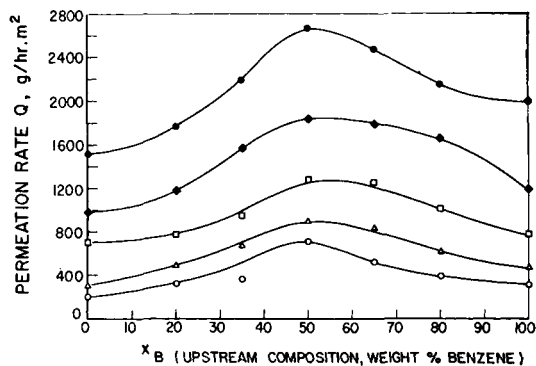Fig. 8. Separation of benzene–n-hexane mixture at 25°C and 45°C: (●) 25°C; (▲) 45°C.

Fig. 9. Effect of composition on the permeation rate of benzene–n-hexane mixtures: (●) 45°C; (◆) 40°C; (□) 35°C; (△) 30°C; (○) 25°C.

the polymer membrane to selectively permeate benzene faster than n-hexane. Thus an increase in concentration of benzene results in a decreased selectivity and *vice versa*.

The effect of composition of the upstream liquid on the permeation rate at different temperature is shown in Figures 9–12. Interesting "permeation enhancement" and "permeation depression" effects were observed. It was found that for certain cases, mixtures permeated faster than either of the pure components. For the binary systems, benzene–n-hexane and benzene–cyclohexane, maximum permeation rates of the mixtures were found at a concentration of about 50 wt-%. In contrast to this, the maximum permeation rate of the mixture was found at 100 wt-% of cyclohexane
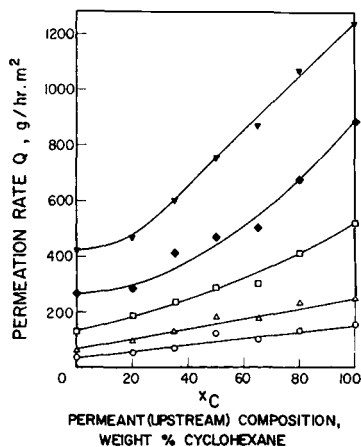
Fig. 10. Effect of composition on the permeation rate of cyclohexane-2,2-dimethyl-butane mixtures: (O) 25°C; (△) 30°C; (□) 35°C; (◆) 40°C; (▼) 45°C.
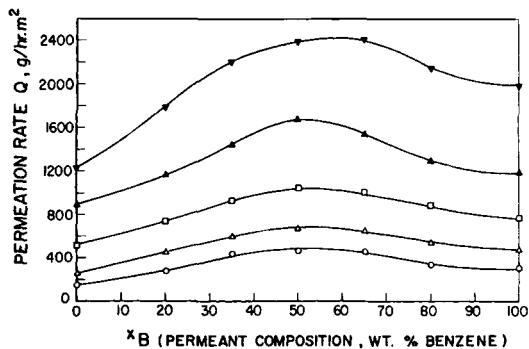
Fig. 11. Effect of composition on the permeation rate of benzene-cyclohexane mixtures (▼) 45°C; (▲) 40°C; (□) 35°C; (△) 30°C; (O) 25°C.

for the binary system, cyclohexane-2,2-dimethylbutane and at 100 wt-% of n-hexane for the binary system, n-hexane-2,2-dimethylbutane. The experimental data for the binary permeation rates for the systems benzene-n-hexane and cyclohexane-2,2-dimethylbutane are plotted against the binary liquid composition in Figures 13 and 14. The relationship between the permeation ratio θ and the upstream binary liquid composition is shown in the same figures. In Figures 13 and 14, the dotted lines indicate the permeation rates q_A and q_B, respectively, of the individual components. The permeation ratio of a component can be interpreted as a measure of the effect of the other component on its permeation rate. Permeation enhancement refers to a permeation ratio higher than unity, while permeation depression refers to a permeation ratio less than one. For benzene-n-hexane mixtures, both components had a permeation ratio higher than one in all ranges of concentration, which indicates that the permeation rates of both components
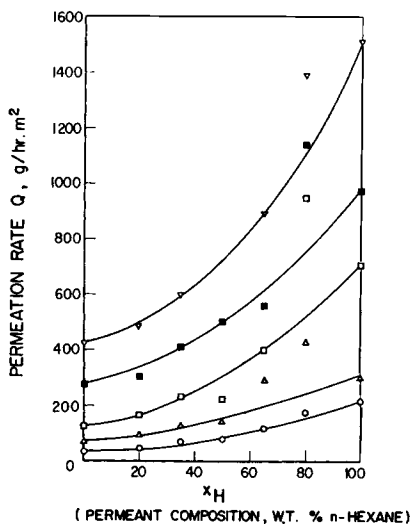
Fig. 12. Effect of composition on the permeation rate of n-hexane–2,2-dimethylbutane: mixtures: (O) 25°C; (△) 30°C; (□) 35°C; (■) 40°C; (▽) 45°C.

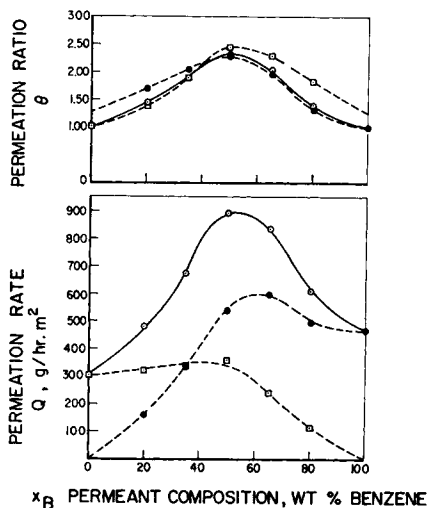Fig. 13. Permeation enhancement effect in the binary system benzene–n-hexane: (⊙) benzene + n-hexane; (●) benzene; (□) n-hexane.

were higher than the calculated ideal permeation rates. This suggests that the plasticizing actions of benzene and n-hexane operate more or less independently to supplement each other, resulting in permeation rate enhancement. For example, at 30°C and 50 wt-% composition, the permeation ratio of benzene is 2.30 and that of n-hexane is 2.39. These ratios indicate that the actual permeation rates of the components are over twice those of ideal single component permeation rates. In the cyclohexane–2,2-dimethyl-
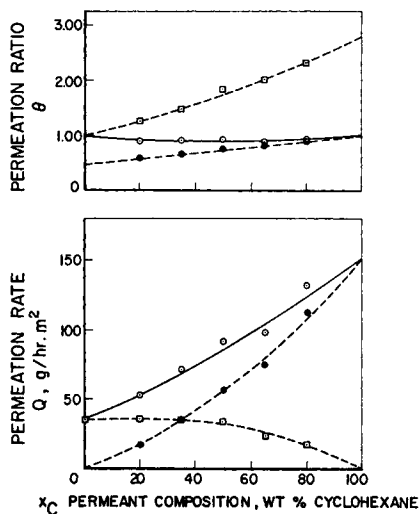
Fig. 14. Permeation enhancement and permeation depression effects in the binary system cyclohexane–2,2-dimethylbutane: (○) cyclohexane + 2,2-dimethylbutane; (●) cyclohexane; (□) 2,2-dimethylbutane.

butane system, it was found that cyclohexane had permeation ratios lower than unity, while those of 2,2-dimethylbutane were higher than one. The plasticizing action of cyclohexane appears to have increased the permeation rate of 2,2-dimethylbutane. However, the reverse does not hold for this case. The presence of 2,2-dimethylbutane decreases the permeation rate of cyclohexane, which is reflected in a depression in the permeation ratio. This may be explained on the basis that the hindrance caused by the bulky molecular volume of 2,2-dimethylbutane predominates over any plasticizing action that it may have on the polymer membrane.

The permeation rate of pure components through a polymer membrane can be described according to eq. (5):

$$Q = (D_0/\gamma L)(e^{\gamma c} - 1)$$

While no attempt will be made to propose a mathematical model for binary permeation, it is helpful to use eq. (5) to interpret the present experimental binary permeation data in a qualitative manner. The plasticizing constant γ is a measure of the plasticizing action of the liquid on the polymer membrane in an actual steady-state permeation process. This plasticizing action plays an important role in the separation of liquid mixtures, since permeation and separation result from differences in either solubilities or diffusivities of the components. Separation can also result from a change in the combination of solubility and diffusivity parameters of the components. In eq. (5), if γ is large, then there is a strong plasticizing effect which can result in a large change in diffusivity. In the binary system benzene–n-hexane, it can be said that the individual values of γ for each -component in binary permeation are higher than those in pure component

permeation.   In other words, in this binary system both components exert a stronger plasticizing effect on the polyethylene membrane than they would if they had been present alone in pure component permeation.   This increased plasticizing action results in larger diffusivities which explains the permeation enhancement effect.   On the other hand, a permeation depression effect, as observed in the system cyclohexane–n-hexane, can be explained in terms of a lowering of the plasticizing parameter γ, relative to pure component permeation.

From the above discussion, it can be seen that there is a complex interaction between diffusing species and the polymer membrane, which manifests itself in changes in the permeation rates and separation efficiencies. The present interpretation in terms of the plasticizing parameter γ is admittedly a semiempirical approach to this complex problem.   However, a systematic study would require detailed measurements of sorption and diffusivities, in order to separate the solubility and diffusivity parameters. Such investigations are currently in progress and will form the subject of a separate paper.[12]

References

1. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, **53**, No. 1, 45 (1961).

2. R. B. Long, *Ind. Eng. Chem. Fundamentals*, **4**, 445 (1965).

3. A. S. Michaels, R. F. Baddour, H. J. Bixter, and C. Y. Choo, *Ind. Eng. Chem., Proc. Design Devel.*, **1**, 14 (1962).

4. R. F. Baddour, A. S. Michaels, H. J. Bixter, R. P. de Phillippi, and J. A. Barrie, *J. Appl. Polym. Sci.*, **8**, 897 (1964).

5. R. F. Sweeny and A. Rose, *Ind. Eng. Chem., Prod. Res. Devel.*, **4**, 248 (1965).

6. A. B. Krewinghaus, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.

7. J. W. Carter and B. Jagannadhaswamy, *Brit. Chem. Eng.*, **9**, 523 (1964).

8. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).

9. H. W. Chandler and E. J. Henley, *A.I.Ch.E. J.*, **7**, 295 (1961).

10. V. Stannett, *Permeability of Plastic Films and Coated Paper to Gases and Vapors*, TAPPI Monograph Series No. 23, Technical Association of the Pulp and Paper Industry, New York, 1962.

11. C. E. Rogers, in *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Labes, and A. Weissberger, Eds., Interscience, New York, 1965, Vol. II, Chap. 6.

12. R. Y. M. Huang and M. Fels, in preparation.