

# Polymeric Alloys of Polyphosphonates and Acetyl Cellulose. I. Sorption and Diffusion of Benzene and Cyclohexane

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## Synopsis

The solubility of benzene in the polymeric alloys (P/A) consisting of polyphosphonates (PPN) and acetyl cellulose (AC) is nearly two orders of magnitude larger than that of cyclohexane. The preferential absorption of benzene by P/A membranes is also maintained upon its dilution with cyclohexane, though the solubility of the latter in the P/A membranes is affected by their swelling with benzene. Absolute values of solubilities increase exponentially with increase in the weight fraction of PPN in P/A membranes. They are also affected by the thermal and solvent "history" of a membrane. For the sorption of benzene by a P/A-50 membrane

$$\Delta H_{\text{app}} \simeq -0.3 \text{ kcal/mole}$$

The diffusion coefficients of benzene in the solvent-swollen membranes are strongly concentration dependent and increase exponentially up to  $\sim 10^{-6}$  cm<sup>2</sup>/sec with the increase in the volume fraction of benzene. Values of  $D_0$  are of the order of  $10^{-11}$  to  $10^{-10}$  cm<sup>2</sup>/sec. Sorption experiments indicate a pronounced time dependence of the diffusion coefficients. Self-diffusion experiments conducted with <sup>14</sup>C-labeled benzene revealed that values of  $D^*$  derived from the steady-state permeation measurements are in certain membranes much larger than those derived from the "time-lag." It was observed that the discrepancies between the two sets of values depend strongly upon the thermal "history" of the membranes and vanish when the membranes are swollen to a high degree at elevated temperatures. The above phenomenon is discussed in terms of differences in the membrane structure; a model is proposed. The apparent energy of activation of diffusion of benzene at 10–40°C in the swollen P/A-50 membrane  $E_B^D = 14.4$  kcal/mole was derived from the temperature dependence of the self-diffusion coefficients. For the same temperature range at  $C_{(B)} \rightarrow 0$ ,  $E_B^{D_0} = 8.3$  kcal/mole was derived from the final slopes of the desorption curves. The small difference between the energies of activation in a swollen and in an unswollen system is due to the fact that at room temperature it remains below  $T_g$  even upon extensive swelling with benzene.

## INTRODUCTION

During the last two decades, various polymeric membranes were investigated as to their selective permeability to organic liquids.<sup>1-11</sup> The separation of azeotropic mixtures of aromatic and aliphatic hydrocarbons or close-boiling isomers was of particular interest to many research groups

because of the industrial importance of such processes. Thus, the performance of polyethylenes and of cellulose as selective membranes for such separations was quite extensively studied by several workers in the field.<sup>3,6,7</sup> Separation factors which were achieved with polyethylene membranes were, however, rather low. On the other hand, fluxes of the permeants which were observed for the nonporous membranes, based on acetyl cellulose, were very slow.

The permeation of a liquid through a nonporous film is usually described in terms of sorption and molecular diffusion. The flux of a given permeant depends, therefore, both on its concentration profile in the membrane and on the values of the diffusion coefficients at conditions which prevail during the permeation experiment. The driving force for the diffusion is provided by gradients of concentrations maintained in the case of the so-called "pervaporation technique" by evaporating the permeated liquid from the membrane surface.

Absolute values of the diffusion coefficients of the permeating liquids may strongly depend on the membrane structure and composition<sup>12</sup> as well as on the concentration of the permeant in the membrane.<sup>13,14</sup> In a design of a membrane system suitable for separation of a solvent mixture, one should, therefore, pay close attention to the respective solubilities in the polymeric phase of the components to be separated.

The solubility of polymers in various solvents may be fairly accurately predicted by comparing their "solubility parameters space" with the solubility parameters  $\delta$  of the solvents.<sup>15</sup> For a polymer which is prevented from being dissolved in the adjoining liquid phase, a similar approach may also be fruitful in predicting its degree of swelling by the solvents. Insolubility of a polymeric system is usually attained by chemical crosslinking. Such treatment may, however, lead to a considerable restriction of the mobility of the polymeric segments. Hence, the diffusion of the permeating molecules in the crosslinked matrix may be severely hindered. A polymer can also be prevented from being dissolved by having its chains entangled within another polymeric network. Only a few polymeric blends in which the mixing of their components was sufficiently intimate to provide the required high degree of the molecular entanglement of the two networks were previously described in the literature.<sup>16,17</sup> Such blends were referred to as interpolymers or polymeric alloys.

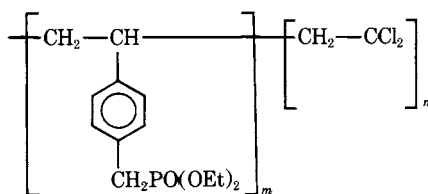
Studies conducted recently in this laboratory revealed that polymeric polyphosphonates are capable to form polymeric alloys with a large number of polymeric systems.<sup>18</sup> The examination of properties of polymeric alloys consisting of polyphosphonates and of acetylcellulose indicated<sup>19</sup> that, though polyphosphonates are highly soluble in aromatic hydrocarbons, they cannot be extracted by them from such blends. Instead, a significant swelling of the polymeric alloy seems to occur under such conditions. Hence, one could expect that membranes constructed from such materials may be highly permeable to aromatic hydrocarbons, while at the same time they may remain impermeable to aliphatic hydrocarbons in which both polyphosphonates (PPN) and acetyl cellulose (AC) are insoluble. We decided, therefore, to conduct a quantitative study of the sorption of ben-

zene and of cyclohexane by membranes constructed from polymeric alloys of PPN and AC of varying compositions. In the present paper we wish to report the results of such experiments together with those of self-diffusion of  $^{14}\text{C}$ -labelled benzene, and we hope that they may contribute to the understanding of the mechanisms involved in the membrane separation processes and outline useful guidelines for the preparation of efficient membrane systems for separation of solvent mixtures.

## EXPERIMENTAL

### Materials

Polyphosphonate (PPN) of the general formula



was synthesized as described elsewhere.<sup>19</sup> PPN used in the experiments had a phosphorous content of 6.5%,  $[\eta]^{25^\circ}_{\text{benzene}} = 0.14 \text{ dl}^{-1} \text{ g}$  and  $T_g = 47^\circ\text{C}$ . Acetyl cellulose (AC) (Eastman 394-45) was used as the second component of the polymeric alloys. The two polymers were dissolved in dry dioxane, and their solutions which contained 10% CA and from 1% up to 10% PPN were cast on glass plates. Uniform 20 to 100- $\mu$ -thick films were formed after excess of the solution was removed with a "doctor blade" and solvent was allowed to evaporate slowly at room temperature. Thus obtained membranes were conditioned by immersion for 2 hr in a 1:1 benzene-cyclohexane mixture kept at reflux.

Benzene (Frutarom, Analytical),  $^{14}\text{C}$ -labelled benzene (The Radiochemical Centre, Amersham), and cyclohexane (Frutarom Analytical) dried over calcium chloride were used in all permeation and sorption experiments.

### Solubility Determinations

Membrane strips ( $\sim 100 \mu$  thick and  $\sim 3 \text{ cm}$  wide) were dried under vacuum ( $\sim 1 \text{ torr}$ ) at  $50^\circ\text{C}$  to constant weight and were immersed in appropriate mixtures of dry solvents kept over calcium chloride. The hermetically closed containers were placed for one week in a constant-temperature bath thermostated within  $\pm 0.2^\circ\text{C}$ . An equilibrated membrane strip was transferred quickly to a weighing bottle after solvent was blotted from its surface with tissue paper, and the increase in its weight was determined on a Mettler semimicrobalance with an accuracy of  $\pm 0.05 \text{ mg}$ . Afterwards, the membrane was placed in a flask connected to a vacuum line, and solvents removed from it were trapped at  $-77^\circ\text{C}$  in 20 ml of toluene which contained 0.5% ethyl benzene as an internal standard for the subsequent VPC determinations. (In some experiments, the swollen

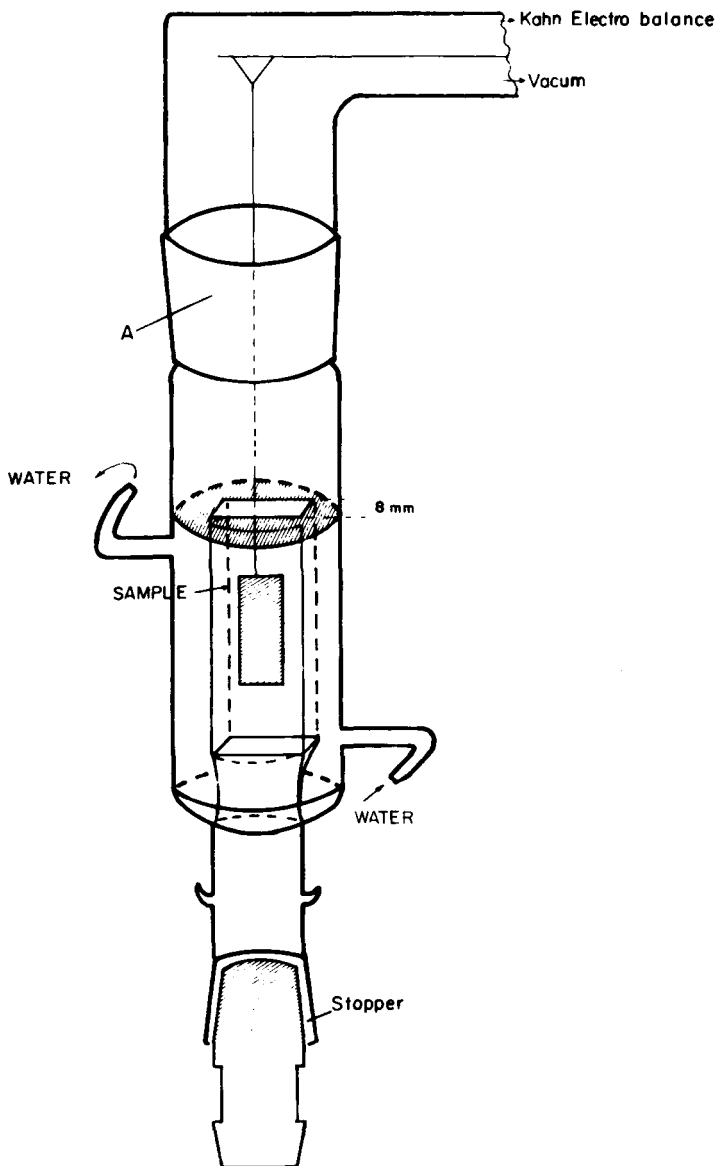


Fig. 1. The thermostated desorption chamber: (A) ground joint connecting the desorption chamber with the Perkin-Elmer TGS-1 thermobalance.

membrane was again immersed and the equilibration procedure was repeated at a different temperature or in a solvent mixture of a different composition.) Toluene solutions were analyzed on a Hewlett Packard 7620D gas chromatograph equipped with a 10-ft column packed with the 20% DEGA polyester (with 2% phosphoric acid) on Chromosorb W. The ratios of benzene to cyclohexane were determined with an accuracy of  $\pm 5\%$ .

### Diffusion Coefficient Determinations

**Desorption Experiments.** Membrane strips (2 cm  $\times$  1 cm) equilibrated as described in the preceding section were inserted into a specially designed desorption chamber thermostated within  $\pm 0.1^\circ\text{C}$  (cf. Fig. 1) and were attached to the arm of a Perkin-Elmer TGS-1 thermobalance. The desorption chamber was evacuated to 0.01 torr, and the loss of weight was continuously recorded with an accuracy of  $\pm 1 \gamma$ . The temperature near the surface of the membrane was checked during the desorption experiment with a copper-Constantan thermocouple inserted into the chamber. It initially decreased because of rapid evaporation of the solvent at the onset of desorption, but returned within  $0.2^\circ\text{C}$  to the equilibrium value after 20–30% of the solvent was removed from the membrane.

The desorption was considered to be completed when the weight of the membrane remained constant for 5 hr. From the tail portion of thus obtained desorption curves, the diffusion coefficients  $D_0$  corresponding to very low solvent concentrations in the membrane ( $C \rightarrow 0$ ) were computed by plotting  $\ln [(w_t - w_d)/(w_s - w_d)]$  versus time, where  $w_d$  and  $w_s$  denote the weight of dry and solvent saturated membrane, respectively, and  $w_t$  denotes its weight after time  $t$ . In such a case, the relationship between the diffusion coefficient and the rate of desorption is given<sup>20</sup> by the expression

$$\frac{w_t - w_d}{w_s - w_d} = \frac{8}{\pi^2} \exp\left(\frac{\pi^2 D t}{l^2}\right) \quad (1)$$

where  $l$  is the membrane thickness.

**Absorption Experiments.** Strips of dry membranes (100  $\mu$  thick and  $\sim 150$  mg in weight) were immersed in solvents at  $30^\circ \pm 0.2^\circ\text{C}$ . After a period of between 1 and 80 hr, the increase in weight due to solvent absorption was determined on a Mettler semimicrobalance. It took 10–15 sec to blot the solvent from the membrane surface and to put it on the scale. The first reading was taken 20 sec after the membrane was removed from the solvent, and it was followed by three to four additional readings at 30-sec intervals. The initial portion of the experimental curve was extrapolated to zero time if a decrease in the membrane weight was noted in readings subsequent to the first one. The necessary corrections were usually very small and never exceeded 5% of the calculated solvent content. Every point of the absorption curve was calculated as an average of two to three determinations. From the initial slopes of absorption curves thus obtained, values of  $D_0$  were calculated from the relationship<sup>20</sup>

$$\frac{w_t - w_d}{w_s - w_d} = \left(\frac{16 D t}{\pi l^2}\right)^{1/2} \quad (2)$$

**Self-Diffusion Experiments.** Connectors, size 20 (Kontes Glass Corp., Vineland, N.J.) were used to build permeation cells (I.D. = 4.15 cm<sup>2</sup>) shown schematically in Figure 2. The two compartments of the cell were separated by a  $\sim 100\text{-}\mu$ -thick P/A membrane, and the cell was filled to

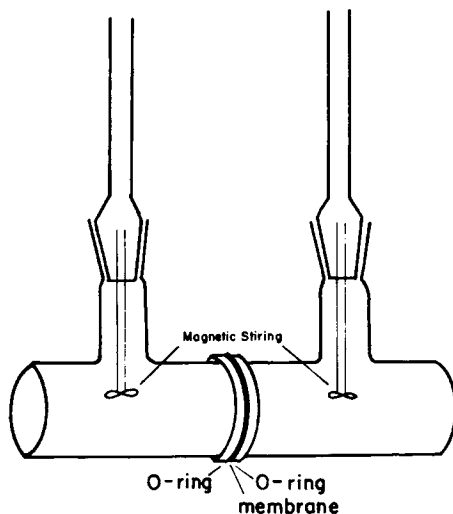


Fig. 2. Permeation cell.

capacity with a benzene-cyclohexane solution ( $2 \times 20$  ml). The solution in the compartment (II) was replaced by another one identical in composition but containing  $^{14}\text{C}$ -labelled benzene after the cell was equilibrated at a constant temperature for at least 24 hr. Vigorous stirring by two magnetically operated stirrers located close to the two sides of the membranes was started, and  $250\text{-}\mu$  samples were removed with H. E. Pedersen analytical micropipets at constant time intervals. Samples were transferred to a standard scintillation solution (DPPH in toluene), and their activity was counted with a Packard liquid scintillation spectrometer. Values of the self-diffusion coefficients  $D^*$  were calculated from the expressions

$$D^* = \frac{\Delta R_t}{R_I \Delta t} \frac{l \cdot V_{\text{II}}}{S \cdot \alpha} \quad (3a)$$

or

$$D^* = \frac{l^2}{6\theta} \quad (3b)$$

where  $\Delta R_t$  is the radioactivity (in cpm) of solution II after time  $\Delta t$ ;  $R_I$  is the radioactivity (in cpm) of solution I (during the experiment, its initial value was decreasing by less than 1%);  $V_{\text{II}}$  is the volume of solution II;  $\alpha$  is the partition coefficient of benzene between membrane and solution;  $S$  is the membrane area; and  $\theta$  is the lag time of the steady-state permeation of radioactive benzene.

## RESULTS AND DISCUSSION

Benzene is a good solvent of PPN, while cyclohexane is a nonsolvent for both AC and PPN. It was expected, therefore, that the solubilities of

TABLE I  
Sorption of Benzene and Cyclohexane by P/A Membranes Exposed  
to Benzene-Cyclohexane Mixtures at 30°C

Membrane designation <sup>b</sup>		0 <sup>a</sup>	0.25	0.50	0.75	1.00
P/A-10	Volume fraction of benzene in the membrane ( $f_B^V$ )	—	.047	.100	.135	.160
P/A-20		—	.054	.116	.146	.175
P/A-30		—	.073	.140	.174	.200
P/A-40		—	.090	.160	.205	.245
P/A-50		—	.106	.175	.225	.315
P/A-10	Volume fraction of cyclohexane in the membrane ( $f_B^V$ )	<0.002	~.002	.007	.006	—
P/A-20		<0.002	~.003	.008	.007	—
P/A-30		~0.002	~.004	.010	.008	—
P/A-40		~0.002	~.005	.012	.01	—
P/A-50		~0.003	~.0055	.013	.011	—

<sup>a</sup> Weight fraction of benzene in the benzene-cyclohexane solution.

<sup>b</sup> The number in the membrane designation denotes the weight-% of PPN in the alloy. P/A membranes which contained more than 50% of PPN were not used in the present experiments, as it was shown<sup>19</sup> that a fraction in excess of 50% may be removed from the blend by its prolonged extraction with benzene.

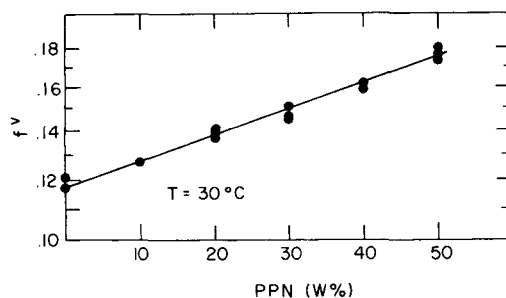


Fig. 3. Semilog plot of the volume fraction of the adsorbed solvent ( $f^V$ ) vs. weight fraction of PPN in the P/A membranes. Membranes equilibrated at 30°C with 1:1 (w/w) benzene/cyclohexane.

these solvents in the alloys of the two polymers will differ considerably. Inspection of data summarized in Table I reveals that this is indeed the case; the solubility of benzene is nearly two orders of magnitude larger than that of cyclohexane. A strong dependence of solubilities upon the composition of polymeric alloys (P/A) is also evident from these data. An exponential relationship is indicated by the nearly straight line obtained for a semilog plot of the volume fraction  $f^{(V)}$  of the absorbed solvent versus fraction of PPN in PA (see Fig. 3). A similar trend for cyclohexane is consistent with the fact that the values of the solubility parameters of cyclohexane are more remote from AC than from PPN.

A highly preferential absorption of benzene by the P/A membranes is also maintained when they are exposed to the binary mixtures of the two solvents. However, in this case the solubility of cyclohexane is somewhat

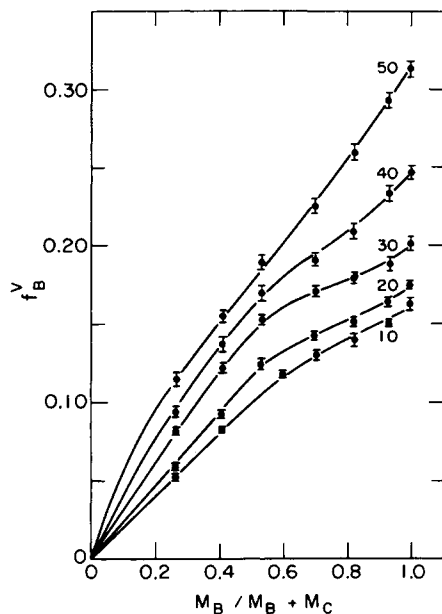


Fig. 4. Volume fraction of benzene in the membranes as function of the molar fraction of benzene in the benzene-cyclohexane mixture; temp. 30°C. Numbers above the four upper curves and below the lowest curve indicate the weight fraction in per cent of PPN in the respective P/A alloys.

increased as result of swelling of the P/A membrane by benzene, while that of benzene is decreased because of the reduction in its activity in the liquid phase due to dilution with cyclohexane (cf. Fig. 4 and Table I). The quantities of benzene adsorbed under such conditions by the P/A membranes are still 10–20 times larger than those of cyclohexane, whose concentrations in all investigated solvent swollen membranes were low.

A study of the temperature dependence of the equilibrium swelling of P/A membranes reveals some peculiarities in their behavior which seem to indicate that their properties may depend to a certain extent upon their thermal history. The volume fraction of the solvent absorbed by a membrane increases in a monotonous fashion with the decrease in temperature, if a series of sorption experiments are started from higher toward lower temperatures. Under such conditions the system seems to be completely reversible, since, if the direction of the experiment is reversed and the temperatures are raised, the equilibrium swelling decreases again along the same curve (see  $E'E''$  in Fig. 5). One may conclude, therefore, that the sorption process is exothermic. For a P/A-50 membrane, a semilog plot of volume fractions of the absorbed solvent versus reciprocals of absolute temperatures yields  $\Delta H_{app} \simeq -0.3$  kcal/mole (cf. Fig. 6). However, if the membrane is dried under vacuum and a series of sorption experiments is started from lower toward higher temperatures, the solubilities increase with the increase in the temperature, all values being lower than in the previous experiment,



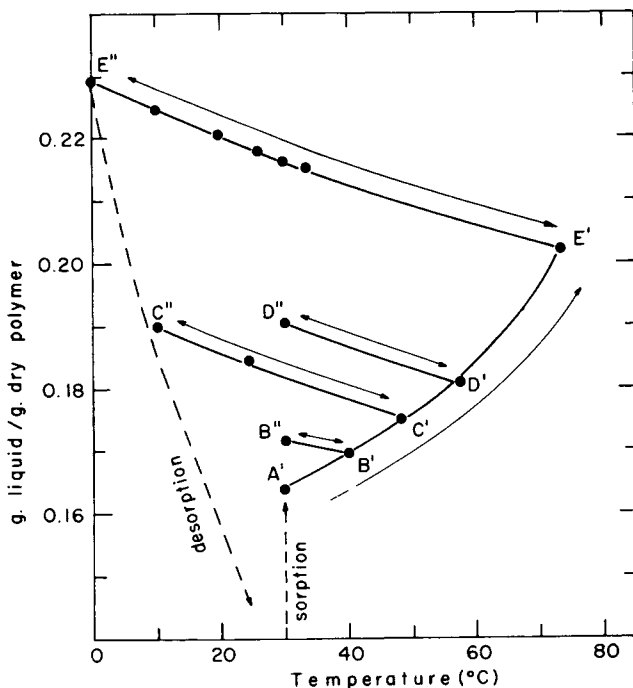


Fig. 5. A typical hysteresis curve of the equilibrium sorption of benzene by P/A membranes as function of temperature. P/A-50 membrane equilibrated with 1:1 (w/w) benzene-cyclohexane; the initial equilibration of the *dry* membrane at  $t'_{(A')} = 30^\circ\text{C}$ . Line  $A'E'$  represents the irreversible part of the cycle due to the increase of the equilibration temperature from  $t'_{(A')}$  to  $t'_{(E')}$ . Lines  $B'B''$ ,  $C'C''$ ,  $D'D''$ , and  $E'E''$  represent the reversible path corresponding to the decrease and increase of the temperature between  $t'$  and  $t''$  after the initial equilibration at  $t'_{(B')}$ ,  $t'_{(C')}$ ,  $t'_{(D')}$ , or  $t'_{(E')}$ , respectively.

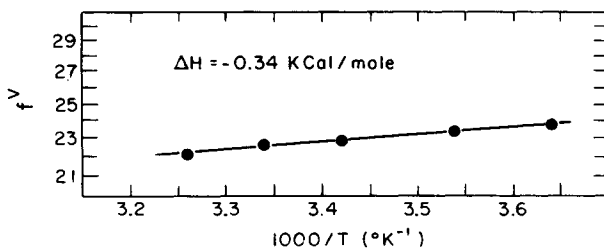


Fig. 6. Semilog plot of the volume fraction of the absorbed solvent ( $f^V$ ) vs. reciprocals of the absolute temperature. P/A-50 membrane equilibrated with 1:1 (w/w) benzene-cyclohexane. Membrane was conditioned at the onset of the experiment for 30 min at  $78^\circ\text{C}$  in the same solvent.

until the starting temperature of the earlier experiment is reached (see  $A'E'$ ). If at this point the direction of the experiment is reversed and the temperatures are decreased, the solubilities continue to increase along the same path  $E'E''$  as in the earlier experiment. The resulting hysteresis curves are shown in Figure 5. Inspection of Figure 7 reveals that a history-

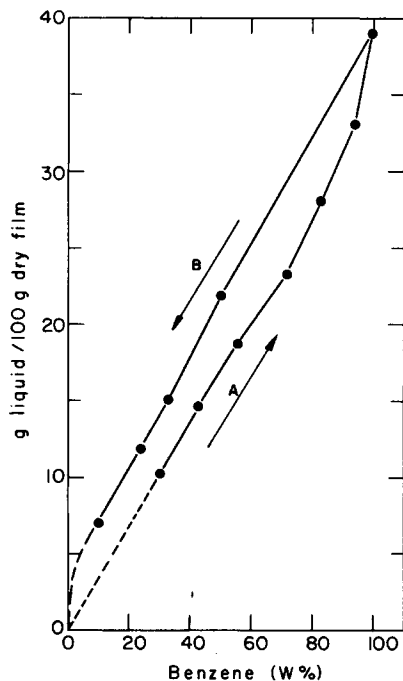


Fig. 7. A typical hysteresis curve of the equilibrium sorption of benzene by P/A membranes as function of the weight fraction of benzene in the equilibrating solutions; temp., 30°C; P/A-50 membrane. Part A corresponds to the increase in the concentration of benzene in the equilibrating solutions; part B corresponds to the decreasing concentrations of benzene in the equilibrating solutions.

dependent behavior is also observed when the composition of the solvent mixtures is changed, while the temperature is kept constant. Apparently, in a swollen membrane configurational changes may occur which lead to its quasi-permanent expansion. The expanded matrix will not contract as long as the membrane is swollen with the solvent; however, after its removal the tighter structure may be again restored.

### Analysis of Sorption Curves

Absorption and desorption experiments are often used as a tool in the study of diffusion in polymeric films.<sup>12,20</sup> The  $D$  value can be computed from eq. (1) or from eq. (2) (see experimental section) if its value is little affected by concentration changes. Such behavior is, however, rather unusual for the diffusion of solvents in polymeric systems. Nevertheless, eqs. (1) and (2) can be used for the calculation of the limiting values  $D_0$  and  $D_s$  corresponding to the zero and to the saturation concentration, respectively. An exact analysis of the entire sorption curve may become very complex if the diffusion coefficients depend strongly on concentration, and their mean values  $\bar{D}$  (integral diffusion coefficients) are often used<sup>20,21</sup> where

$$\bar{D} = \frac{1}{C_s} \int_0^{c_s} D_{(c)} dc.$$

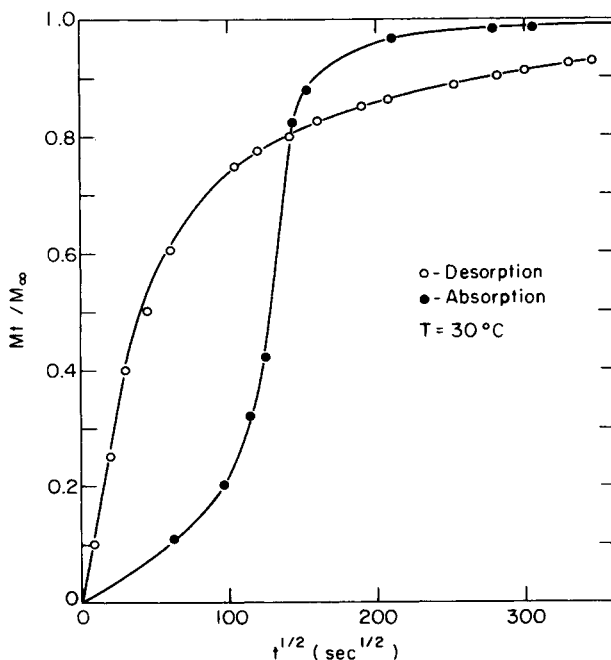


Fig. 8.  $M_t/M_\infty$  vs. square root of the absorption or of the desorption time for a P/A-50 membrane; temp., 30°C: (●) absorption from 1:1 (w/w) benzene-cyclohexane; (○) desorption after equilibration with the same solvent mixture.

A well-established technique for the determination of diffusion coefficients, sensitive to concentration changes, is based on self-diffusion measurements at steady-state permeation in which a constant concentration of the solvent may be maintained during the entire experiment.<sup>22</sup> Such an approach seems to be especially advisable for the study of systems in which the diffusion coefficients may also depend on their "history."

A comparison between the absorption curve obtained for sorption of benzene by a P/A-50 membrane immersed in a binary 1:1 mixture of benzene and cyclohexane and its desorption after equilibration with the same solution indicates that the values of  $D$  depend very strongly on the concentration of the permeant (cf. Fig. 8). A plot of  $M_t/M_\infty$  versus  $t^{1/2}$  yields a sigmoid curve which sharply deviates from linearity nearly at the onset of the absorption. Similar behavior is also noted for P/A membranes which contain less than 50% of PPN, though their curvatures become somewhat milder as the PPN fraction in the membrane is decreased (see Fig. 9). Values of  $D_0$  computed from the initial slopes of these lines and from the final slopes of the semilog plots of the desorption curves shown in Figure 10 are summarized in Table II. For the P/A-50 membrane; both methods yield  $D_0^{30^\circ} \simeq 5.5 \times 10^{-11}$  cm<sup>2</sup>/sec, if measurements are taken on membranes exposed to a 1:1 mixture of benzene with cyclohexane.

A value of  $D_0^{30^\circ} = 8 \times 10^{-11}$  cm<sup>2</sup>/sec is, however, obtained from the desorption experiments on the same membrane equilibrated with undiluted

TABLE II  
Initial Diffusion Coefficients of Benzene ( $D_0$ ) and Its Self-Diffusion Coefficients ( $D_j^*$ ) in Solvent-Swollen P/A membranes Exposed to 1:1 (w/w) Benzene-Cyclohexane

Polymer alloy designation	$D_0 \times 10^{11}, \text{cm}^2/\text{sec}^a$						$D_j^* \times 10^9, \text{cm}^2/\text{sec} \text{ } 30^\circ$
	30°C		40°C		50°C	56°C	
	a	d	a	d	d	d	
Acetyl cellulose	0.8	—	4.4	—	—	—	1.2
P/A-20	1.0	—	—	—	—	—	3.8
P/A-30	2.0	—	—	5.8	—	—	12.0
P/A-40	4.1	—	—	—	—	—	26.0
P/A-50	5.4	5.8	—	8.4	11.0	14.7	80.0

<sup>a</sup> The "a" values were calculated from the initial slopes of the absorption experiments; the "d" values were calculated from the final slopes of the desorption experiments.

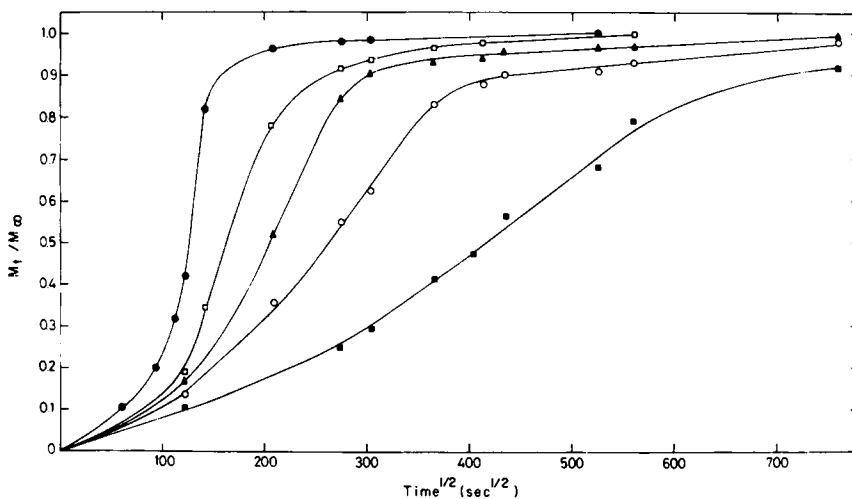


Fig. 9.  $M_t/M_\infty$  vs. square root of time for various P/A membranes and for acetyl cellulose; temp., 30°C; absorption from 1:1 (w/w) benzene-cyclohexane: (●) P/A-50; (□) P/A-40; (▲) P/A-30; (○) P/A-20 (□) acetyl cellulose.

benzene. Differences in the values of  $D_0$  reflecting on the previous treatment of the membrane seem to indicate that changes induced in the highly swollen membrane may still affect its structure after the solvent is removed at relatively low temperatures.

#### Self-Diffusion of Benzene in Solvent-Swollen P/A Membranes

A plot of  $\Delta R_{II}/R_I$  versus time, shown in Figure 11, is typical for the permeation of  $^{14}\text{C}$ -labelled benzene across solvent-swollen P/A membranes. Its initial curvature indicates that a relatively long time elapses before steady-state conditions are reached. The time lag  $\theta$  is given by the cut-off point on the time coordinate of the straight line corresponding to the steady-state permeation. From the slopes of such straight lines or from their cut-

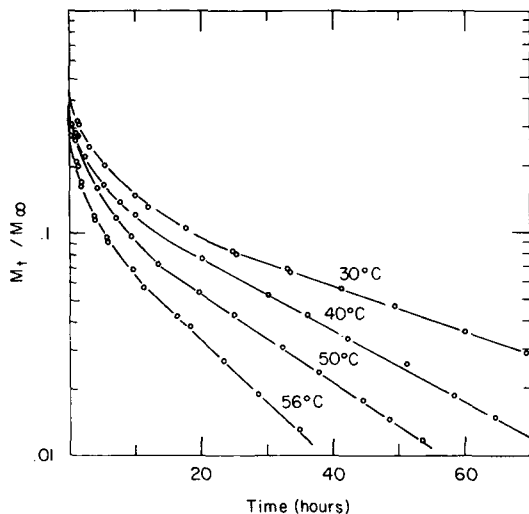


Fig. 10. Semilog plots of  $M_t/M_\infty$  vs. time for desorption experiments; P/A-50 membranes after equilibration with 1:1 (w/w) benzene-cyclohexane. Numbers above the curves indicate temperature of the experiment.

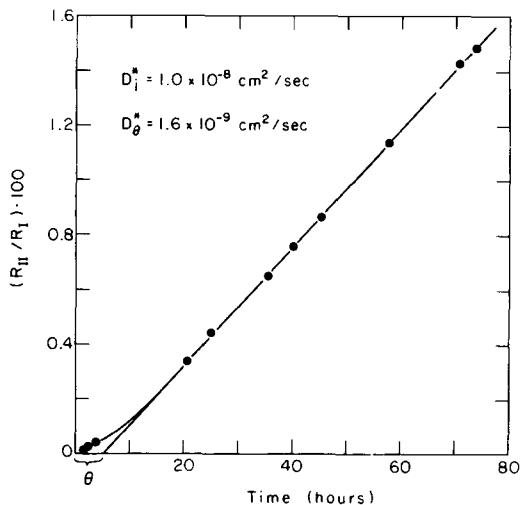


Fig. 11. Permeation of the  $^{14}\text{C}$ -labelled benzene across a P/A-50 membrane after its initial equilibration with the non-radioactive solution of the same composition; 1:4 (w/w) benzene-cyclohexane solutions; temp., 30°C; ( $R_I$ ) radioactive count for the solution in compartment I; ( $R_{II}$ ) radioactive count after time  $t$  for the solution in compartment II.

off points, the self-diffusion coefficients were calculated using eq. (3a) or (3b), respectively (see experimental section). Values of  $D^*$  derived from the two equations were not identical, and in the forthcoming discussion we will use the notation  $D_j^*$  and  $D_\theta^*$ , respectively. Though the experimental accuracy of determinations of  $D_\theta^*$  is not as high as that of  $D_j^*$  (cf. Fig. 11),

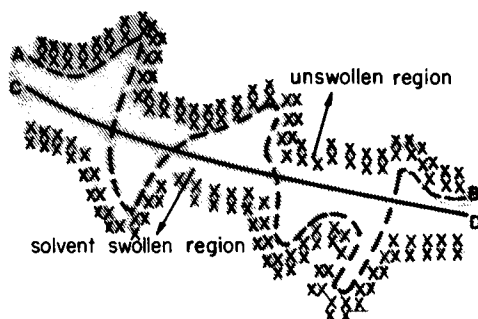


Fig. 12. Schematic representation of the structure of a segment of the solvent-swollen P/A membrane.

the differences between the calculated values of  $D_\theta^*$  and  $D_j$  cannot be attributed to the experimental scatter. Our measurements with  $^{14}\text{C}$ -labelled benzene yield a wide range of the  $D_j^*/D_\theta^*$  ratios in various systems, namely,  $0.7 < D_j^*/D_\theta^* < 15$ . The ratio  $D_j^*/D_\theta^*$  seems to be extremely sensitive to the thermal and solvent "history" of the investigated membrane. For example,  $D_j^*/D_\theta^* = 6.6$  is obtained for a P/A-50 membrane which was equilibrated at  $30^\circ$  with a 1:4 benzene-cyclohexane mixture after being dried under vacuum. However, if the same membrane is refluxed for 1 hr with 1:1 benzene-cyclohexane and then equilibrated with this solvent mixture at  $30^\circ\text{C}$ ,  $D_j^*/D_\theta^* \simeq 1$ . After a subsequent drying under vacuum and equilibration in 4:1 benzene-cyclohexane at  $30^\circ$ , the ratio  $D_j^*/D_\theta^*$  increases again to 2.8.

In all experiments, the discrepancy between  $D_j^*$  and  $D_\theta^*$  becomes less pronounced as result of swelling at higher temperatures and by more concentrated benzene solutions. Variations in  $D_j^*/D_\theta^*$  are mainly due to changes in  $D_\theta^*$  while values of  $D_j^*$  are affected only if the fraction of benzene in the swollen membrane is considerably changed as result of the pretreatment. The discrepancies between  $D_j^*$  and  $D_\theta^*$  may be accounted for by assuming that crystalline or semicrystalline regions essentially unpenetrable to the solvent are intermingled with the solvent swollen regions in the membrane. In such a system, the structure of a segment of a solvent-swollen membrane can be schematically represented by Figure 12. Thus, the value of  $D_\theta^*$  will depend on the length of the path "AB" marked as a dotted line in Figure 12, while value of  $D_j^*$  depends on the length "CD" of the open "channel." Hence,

$$D_j^*/D_\theta^* = \frac{(\Sigma''\text{AB})_{\text{av}}^2}{1(\Sigma''\text{CD})_{\text{av}}}$$

The number and size of the unswollen regions responsible for the difference between  $(\Sigma''\text{AB})_{\text{av}}$  and  $(\Sigma''\text{CD})_{\text{av}}$  may be expected to decrease when a membrane is conditioned in concentrated benzene solutions at elevated temperatures. Thus, the above representation explains the relation between the  $D_j^*/D_\theta^*$  ratio and the thermal and solvent history of a membrane.

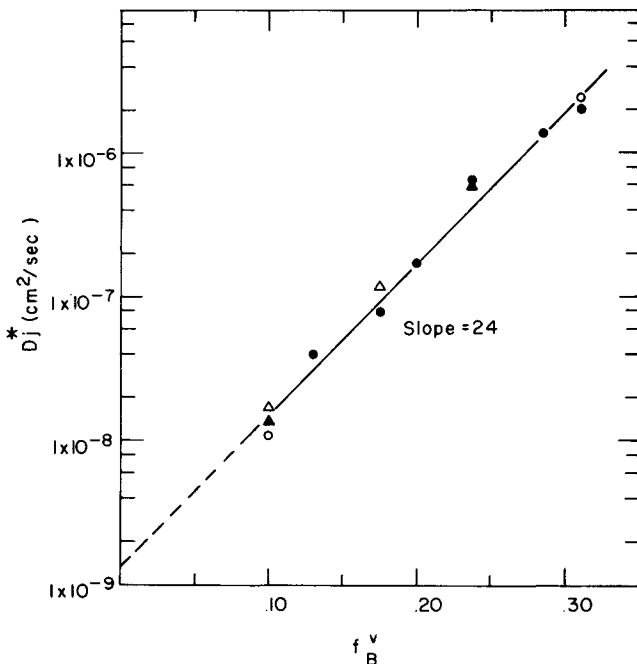


Fig. 13. Semilog plot of  $D_j^*$  vs. volume fraction of benzene ( $f_B^V$ ) in the solvent swollen membrane; P/A-50 membrane; temp, 30°C;  $f_B^V$  adjusted by changing the concentration of benzene in the equilibrating solutions.

It was pointed out by Crank and Hartley<sup>23</sup> that the chemical diffusion and self-diffusion coefficients in solvent swollen membranes should be related as follows:

$$D^* = D(1 - f_B^V)^{-3} d \log f_B^V / d \log a_B \quad (4)$$

where  $a_B$  denotes the activity of the solvent and  $f_B^{(V)}$  denotes the volume fraction of solvent in the membrane. All other symbols retain their previous meaning.

The diffusion coefficients  $D_s$  derived from desorption experiments are also determined by the path "AB" as is the case of  $D_\theta^*$ . The  $D_s$  values estimated from the initial slopes of the desorption lines agree within  $\pm 20\%$  with the corresponding  $D_\theta^*$ . Taking into account the experimental uncertainties in determining both  $D_s$  and  $D_\theta^*$ , such agreement is quite satisfactory and reflects on the self-consistency of our results.

Values of  $D_j^*$  at 30°C in the solvent-swollen P/A-50 membranes are summarized in Table III. Volume fractions of benzene,  $f_B^{(V)}$  in the range of 0.10–0.32 were attained by adjusting the benzene activity in the liquid phase, used for membrane equilibration, by dilution with cyclohexane. Inspection of the tabulated results reveals a very strong dependence of  $D_j^*$  on  $f_B^{(V)}$ . A semilog plot of  $D_j^*$  versus  $f_B^{(V)}$  shown in Figure 13 yields a straight line with a slope  $\gamma = 24.2$ . According to the relationship  $D^* =$

TABLE III  
Self-diffusion Coefficients ( $D_j^*$ ) of Benzene at 30°C in P/A-50 Membranes Equilibrated  
with Benzene-Cyclohexane Solutions

Weight fraction of benzene in solution	Volume fraction of benzene in the membrane ( $f_V^B$ )	$D_j^* \times 10^8$ , cm <sup>2</sup> /sec
0.20	0.10	1.1-1.7
0.30	0.13	4.0
0.50	0.175	8-12
0.58	0.20	17.5
0.75	0.23	60
0.90	0.285	140
1.00	0.315	200-250

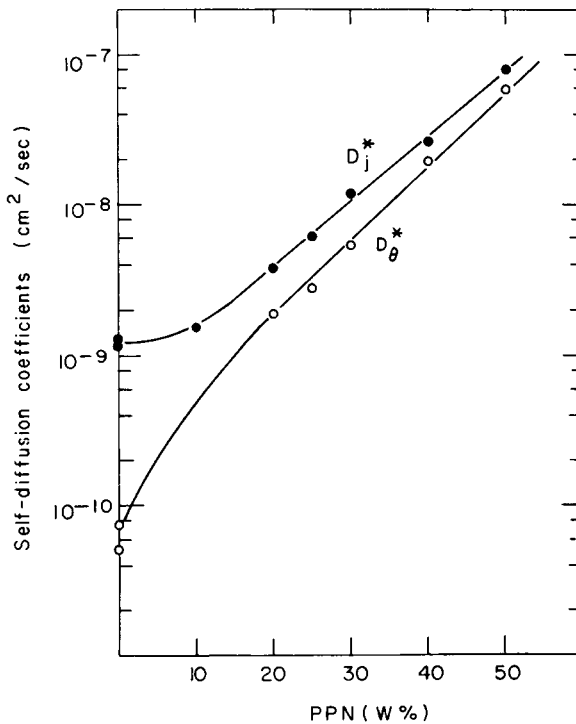


Fig. 14. Semilog plots of  $D_j^*$  and  $D_0^*$  vs. weight fraction of PPN in the P/A membranes. Equilibrating solution, 1:1 (w/w) benzene-cyclohexane; temp., 30°C.

$D_0 \exp \gamma f_B^{(V)}$ , the intercept of such a plot should yield  $D_0$ . The extrapolated value is, however, more than one order of magnitude larger than  $D_0$  experimentally determined from sorption experiments (cf. Table II). This suggests a discontinuity in the  $D^*$ -versus- $f_B^{(V)}$  relationship at very low benzene concentrations.

In a second series of experiments, the dependence of the self-diffusion coefficients in the swollen membranes upon the weight fraction of PPN in the



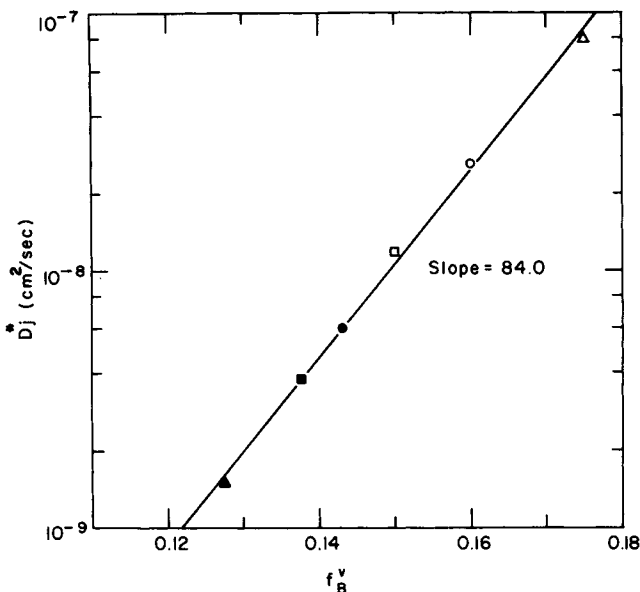


Fig. 15. Semilog plot of  $D_j^*$  vs. volume fraction of benzene ( $f_B^V$ ) in the solvent swollen P/A membranes of varying PPN content; equilibration with 1:1 (w/w) benzene-cyclohexane; temp., 30°C: (▲) P/A-10; (■) P/A-20; (●) P/A-25; (□) P/A-30; (○) P/A-40; (△) P/A-50.

polymeric alloys was investigated. Dry membranes were equilibrated at 30° with a 1:1 solution of benzene in cyclohexane. Thus, both  $f_B^{(V)}$  and the composition of the P/A membranes were changed simultaneously. Semilog plots of  $D_j^*$  and  $D_\theta^*$  in thus equilibrated membranes versus weight fraction of PPN (calculated per dry membrane) are shown in Figure 14. In this series of experiments, the ratio  $D_j^*/D_\theta^*$  was more or less constant down to a PPN content of 20%. However, in pure acetyl cellulose the ratio  $D_j^*/D_\theta^*$  was as large as 15. A plot of  $D_j^*$  versus  $f_B^{(V)}$  for P/A membranes containing 10–50% PPN is shown in Figure 15. An exponential relationship is again observed. Slope of the line obtained by changing  $f_B^{(V)}$  simultaneously with the composition of the membranes is, however, four times steeper than that obtained from the semilog plot of  $D_j^*$  versus  $f_B^{(V)}$  in a P/A-50 membrane shown in Figure 13. This indicates that the increase in the value of  $D_j^*$  with the increase in fraction of PPN cannot be simply explained in terms of concentration effect, but is also due to differences in the free volume parameter of the respective polymeric alloys.

### Temperature Dependence of Diffusion Coefficients

Arrhenius plots of  $D_0$  and  $D_j^*$  (benzene in a P/A-50 membrane) versus reciprocals of absolute temperatures yield apparent energies of activation of the diffusion processes:  $E_{\text{app}}^{(D_0)} = 8.3$  kcal/mole and  $E_{\text{app}}^{D^*} = 14.2$  kcal/mole (see Fig. 16). The relatively small difference between the energy

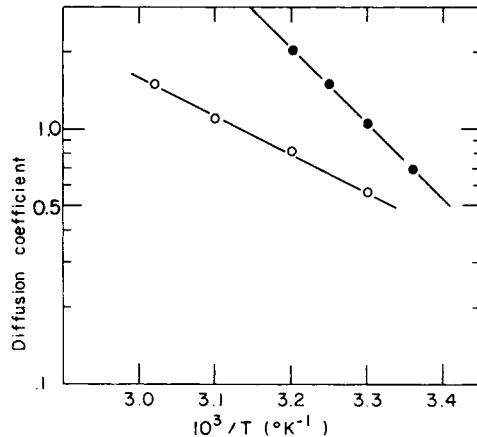


Fig. 16. Semilog plot of diffusion coefficients vs. reciprocals of absolute temperatures: (●)  $D_j^* \times 10^7$   $\text{cm}^2/\text{sec}$  for a P/A-50 membrane equilibrated with 1:1 (w/w) benzene-cyclohexane; (○)  $D_0 \times 10^{10}$  ( $\text{cm}^2/\text{sec}$ ) for a P/A-50 membrane.

of activation of diffusion in the swollen and in the unswollen P/A membrane supports our belief that in the investigated temperature range, swelling of the P/A does not induce a glass transition in the system. It was reported by Kanamaru et al.<sup>12</sup> that in polymer-penetrant systems in which hydrogen bonding is not involved,  $E^D$  increases sharply above the  $T_g$ , since it is then related to the viscous flow of the polymer and represents an energy of activation of segmental movements of polymeric chains, while below  $T_g$ , in a frozen network, it is related to solvent-polymer or solvent-solvent interactions.

### Time Dependence of Diffusion Coefficients

The anomalous character of the absorption curves shown in Figures 9 and 10 may be due to a non-Fickian character of the diffusion or to time-dependent changes in the membrane structure. In many glassy polymers, solvent penetration was found to be represented by the case II diffusion.<sup>24-27</sup> The definition of case II diffusion given by Alfrey et al.<sup>24</sup> is as follows: As the solvent penetrates into the polymer, a sharp boundary advancing at a constant speed separates the inner glassy core from the outer swollen, rubbery shell in which the swollen gel is essentially in an equilibrium state of swelling. Thus, plots of  $M_t/M_\infty$  versus time yield a straight line going through the origin ( $M_t$  and  $M_\infty$  being the weight of penetrant at time  $t$  and at equilibrium, respectively).

A sharp boundary of the advancing solvent implies a discontinuity in the  $D$ -versus-concentration relationship. Such discontinuity is, however, not a sufficient condition for a case II diffusion. Crank<sup>25</sup> analyzed a theoretical case of diffusion involving a discontinuous change of  $D$  with concentration and predicted a Fickian diffusion in which the boundary of the swollen polymer advances with a rate proportional to  $t^{1/2}$ . This type

of behavior was indeed observed experimentally<sup>26</sup> for the diffusion of methylene chloride in crosslinked epoxy polymers, while sorption of benzene exhibited characteristics of case II diffusion. Frish et al.<sup>27</sup> discussed the superposition of Fickian and case II diffusion in a system in which two different driving forces for penetration are operating. They pointed out that in such a case the solution of the diffusion problem yields the following expressions:

$$X = at^{1/2} + bt \quad (5)$$

$$M_i/M_\infty = a't^{1/2} + b't \quad (5a)$$

$$(M_i/M_\infty)/t^{1/2} = a' + b't^{1/2} \quad (5b)$$

where  $X$  denotes the depth of penetration while  $a$ ,  $a'$ ,  $b$ , and  $b'$  are proportionality coefficients.

In the presently investigated polymeric alloys, a discontinuity in the  $D$ -versus-concentration curve is implied by the analysis of the experimentally determined diffusion coefficients, and the existence of a sharp boundary during a sorption experiment seems to be indicated by the fact that the increase in the thickness of a membrane is directly proportional to the fraction of the adsorbed solvent, while no change in dimensions perpendicular to the penetration is noted. Such behavior is easily understood, if the swollen and unswollen layers are separated by a sharp boundary, since in such a case the unswollen layer prevents a longitudinal expansion of the membrane, while the swollen layer may freely increase its thickness.<sup>28</sup> One could, therefore, consider the possibility that a case II diffusion or a superposition of Fickian and case II may represent the diffusion of benzene in the P/A membranes. Accordingly, curves given in Figure 9 were replotted to test the validity of eq. (5b). Their inspection indicated, however, that the dependence of  $M_i/M_\infty$  on time is closer to the power 3/2 than to linearity. A power higher than one in the time dependence of absorption must be attributed to a time dependence of the diffusion coefficients. It was recently suggested by Kwei<sup>29</sup> that systems in which time dependent coefficients were postulated should be reassessed in terms of a non-Fickian diffusion. The case presently investigated provides, however, an example of a system in which a pronounced time dependence of  $D$  is evident. This may be due to the fact that, in spite of  $f_B^{(V)}$  being large, the swollen polymeric material remains rigid. Thus, the rearrangement of the polymeric chains required to accommodate the absorbed solvent must take place stepwise and rather slowly. The slow relaxation rates are reflected by the time dependence of diffusion coefficients. Such behavior may perhaps be attributed to the dual character of the system in which segments of PPN and of cellulose acetate may be characterized by different relaxation times.

## CONCLUSIONS

Polymeric alloys of PPN and acetyl cellulose selectively absorb benzene from its mixtures with cyclohexane. This is in agreement with predictions

based on the analysis of relevant solubility parameters. The diffusion coefficients of benzene depend strongly on its concentration in the polymer and are very high in the solvent-swollen polymeric membranes in which the PPN content is in the range of 40–50%. Hence, they may be useful as selective barriers for separations of aromatics from their mixtures with aliphatic hydrocarbons. Results of permeation measurements in which P/A membranes were tested under dialytic and pervaporation conditions will be discussed in the second part of this work.

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