

A Study of Permeation of Organic Solvents Through Polymeric Membranes Based on Polymeric Alloys of Polyphosphonates and Acetyl Cellulose.

II. Separation of Benzene, Cyclohexene, and Cyclohexane

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Synopsis

Membranes prepared from polymeric alloys of polyphosphonates and acetyl cellulose are highly permeable to benzene and to cyclohexene, but practically impermeable to the aliphatic hydrocarbons cyclohexane and decalin. Pervaporation and osmotic distillation techniques were used in order to achieve separation of the benzene-cyclohexane mixtures. The flux of the permeate increases sharply with increasing temperature, concentration of benzene in the feed solution, and fraction of polyphosphonate in the membrane. The increase of permeate flux is accompanied by a slight decrease of the separation factors. The permeation characteristics of the membranes were compared with those predicted from the results of sorption experiments. The agreement between the observed and the predicted fluxes and separation factors indicates that the permeation mechanism can be described in terms of molecular diffusion. The high selectivity of the membranes makes possible the development of a novel "osmotic distillation" technique. Such a technique, which combines osmotic permeation of organic liquids with conventional distillation, may be advantageous in the separations of azeotropic mixtures.

INTRODUCTION

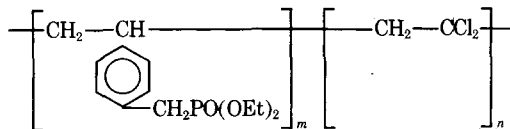
It has recently been reported¹ that the polymeric alloys (P/A) of polyphosphonates and acetyl cellulose selectively absorb benzene from its mixtures with cyclohexane. It was also noted that the diffusion coefficients of benzene in the solvent-swollen polymeric alloys are remarkably high. It was suggested,¹ therefore, that membranes made of such polymeric alloys may be particularly useful as selective barriers for the separation of aromatics and naphthenes.

In the present paper, we wish to report results of permeation studies designed to achieve such separations. Permeability of P/A membranes to benzene, cyclohexane, and cyclohexene was tested by the so called "pervaporation" (liquid permeation) method.²⁻⁵ Liquid-liquid permeation under osmotic conditions was also investigated as an alternative to the "pervaporation" technique.

EXPERIMENTAL

Materials

Analytical-grade benzene, cyclohexane, cyclohexene, and decalin were used in all experiments. Polyphosphonate (PPN) of the general formula



was synthesized as described elsewhere.⁶ PPN used in the experiments had $[\eta]_{\text{benzene}}^{25^\circ} = 0.14 \text{ dl}^{-1} \text{ g}$, $T_g = 47^\circ\text{C}$, and a phosphorous content of 6.5%. Acetyl cellulose (AC) (Eastman 394-45) was used for the preparation of the alloys. Polymeric alloys of PPN and AC (P/A) comprising 10%, 30% and 50% of PPN were prepared as described in the first part of this work.¹ Films 20 μ thick were cast from dioxane solutions.

Membranes were dried at room temperature and conditioned by immersion for 2 hr in an 1:1 benzene-cyclohexane mixture at reflux temperature.

Pervaporation Experiments

Membranes 5 cm in diameter and 20 μ thick were inserted, after conditioning, into the pervaporation cell shown schematically in Figure 1. Membranes were supported by a Jena D sintered-glass disk.⁸ Feed solution, 250 ml, was introduced into the upstream compartment (1) and brought to an appropriate temperature while being vigorously stirred. The downstream compartment was evacuated to 20 ± 5 torr, and the permeate was collected in the vacuum trap (A) cooled by liquid air. Composition of the permeate was determined by checking its refractive index against a calibration curve. For experiments conducted at 30–51°C, when the permeation rates were rather slow, the vacuum trap (A) was filled with a 0.5% solution of ethylbenzene in toluene cooled to -77°C with Dry Ice. The permeate was trapped by the toluene solution. Ethylbenzene served as the internal standard for the subsequent VPC determination of the permeated benzene and cyclohexane. A Hewlett-Packard 7620 D gas chromatograph equipped with a 10-ft column packed with 20% DEGA polyester (with 2% phosphoric acid) on Chromosorb W was used in these determinations.

Membrane performance was measured in terms of permeate flux and separation factors. The separation factor $\alpha_{n,m}$ was defined as

$$\alpha_{n,m} = \frac{X_n^P \cdot X_m^F}{X_n^F \cdot X_m^P}$$

where X_n^F , X_m^F , X_n^P , and X_m^P denote the weight fraction of component n and component m in the feed solution and in the permeate, respectively.

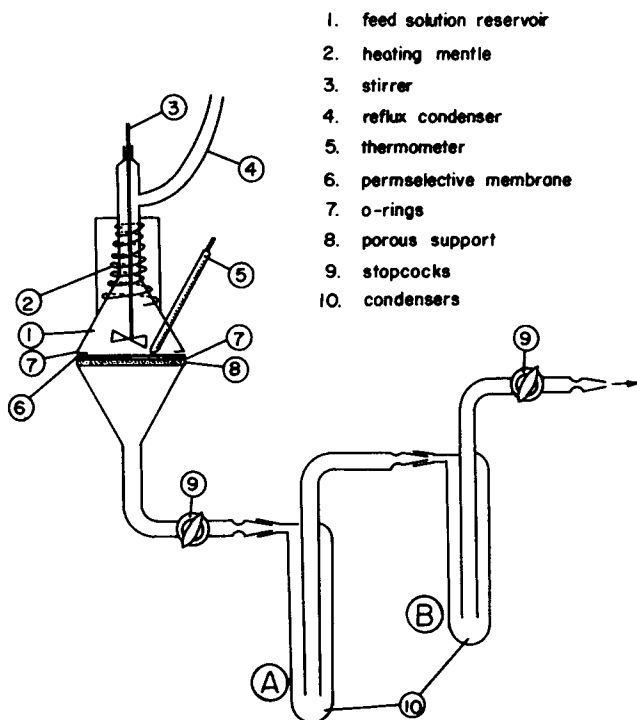


Fig. 1. "Pervaporation" cell.

The volume of permeate collected during a given test was small compared with the volume of the feed. Hence, composition of the feed was assumed to remain constant throughout a run.

Permeation Under Osmotic Gradient

A permeation cell of construction similar to that described in reference 1 was used in all osmotic permeation experiments. The cell was thermostated for 100 hr. The solutions in the two compartments were replaced by fresh ones and filled up to the 25-cm marks of the two capillaries (50 cm long and 3 mm I.D.) connected with the cell. The flow of permeate was determined from the increase in the liquid level on the decalin side of the membrane and by VPC determinations of the concentration of benzene and of cyclohexane in the decaline solution. (Ethylbenzene was used as internal standard.)

RESULTS AND DISCUSSION

The permeation of benzene and cyclohexane through polymeric alloys (P/A), comprising from 10% to 50% of the polymeric polyphosphonate (PPN), was investigated in the temperature range of 30–80°C. Membranes containing more than 50% of PPN were not used in the present study because of their limited resistance to benzene.

Effect of Membrane Composition

According to the results of sorption experiments described in the first part of this study,¹ it was expected that the permeation rates will increase sharply with increasing fraction of PPN in the membranes. "Pervaporation" experiments summarized in Table I fully confirm this expectation. Thus, a flux of 820 g/m²·hr is obtained when a 20- μ -thick P/A-50 membrane is exposed to a 1:1 mixture of benzene and cyclohexane at a reflux-temperature of 77.8°C. (number in membrane designation indicates wt-% of PPN in the alloy). The permeates contains 90.0% of benzene and only 10% of cyclohexane ($\alpha_{BC} = .9$).

It is interesting to note that, for benzene-cyclohexane separations with poly(vinyl fluoride) membranes,⁷ fluxes were obtained two orders of magnitude lower than in our system at separation factors similar to the presently attained ones. On the other hand, in permeation experiments in which the high-flux polyethylene or polypropylene membranes were used,⁸⁻¹⁰ only very mediocre separations have been achieved ($\alpha_{BC} < 2$).

The separation factors for P/A membranes increase slightly with decrease of the fraction of PPN in the membranes (cf. Table I). The experimentally determined separation factors were compared with values computed from the solubility data of reference 1, by assuming that membrane selectivity is determined by the ratio of the respective solubilities of benzene and cyclohexane in the membrane. The agreement between the measured and calculated values is remarkably good. Thus, $\alpha_{BC}^{30} = 13.3$ is measured and $\alpha_{BC}^{30} = 13.5$ is calculated for a P/A-50 membrane in contact with a 1:1 (w/w) benzene-cyclohexane mixture at 30°C. The agreement between selectivity under permeation conditions and solubility at equilibrium seems to indicate that the coupled diffusion coefficients of benzene and cyclohexane in the solvent-swollen P/A membranes have nearly identical values.

TABLE I
Pervaporation Experiments with P/A Membranes^a

Temp., °C	Flux, (g/cm ² ·hr) $\times 10^4$			Separation factor α_{BC}	
	P/A-10 ^b	P/A-30	P/A-50	P/A-30	P/A-50
30	—	—	40	—	13.3
35	—	—	56	—	13.1
39	—	—	73	—	12.8
44	—	12.5	125	14.0	—
49	—	—	146	—	12.0
51	10.0	18.7	—	—	—
60	20.0	33.0	320	12.9	11.0
70	—	55.5	482	11.7	10.5
73	35.5	72.0	565	10.7	10.1
77.8	61.1	118.0	810	10.8	9.0

^a Feed solution: benzene-cyclohexane; membrane thickness: 20 μ .

^b Membrane designation: number denotes the wt-% of PPN in the membrane.

Effect of Temperature

Increase in the temperature causes a slight decrease of separation factors (see Table I, columns 5 and 6). Such behavior could again be predicted from the solubility results of reference 1. The sorption of benzene is slightly exothermic, while the absorption of cyclohexane from its mixtures with benzene is probably isothermal or even slightly endothermic; hence, the higher benzene-cyclohexane ratios in the permeate at lower temperatures.

Semilog plots of flux versus reciprocals of absolute temperatures are shown in Figure 2. From the slopes of the resulting straight lines the apparent "energy of activation" of permeation, $E_{app} \approx 14$ kcal/mole, is calculated.

Permeability in polymeric nonporous membranes is determined by the solubility and by the diffusivity terms.⁴ The solubility of benzene in P/A

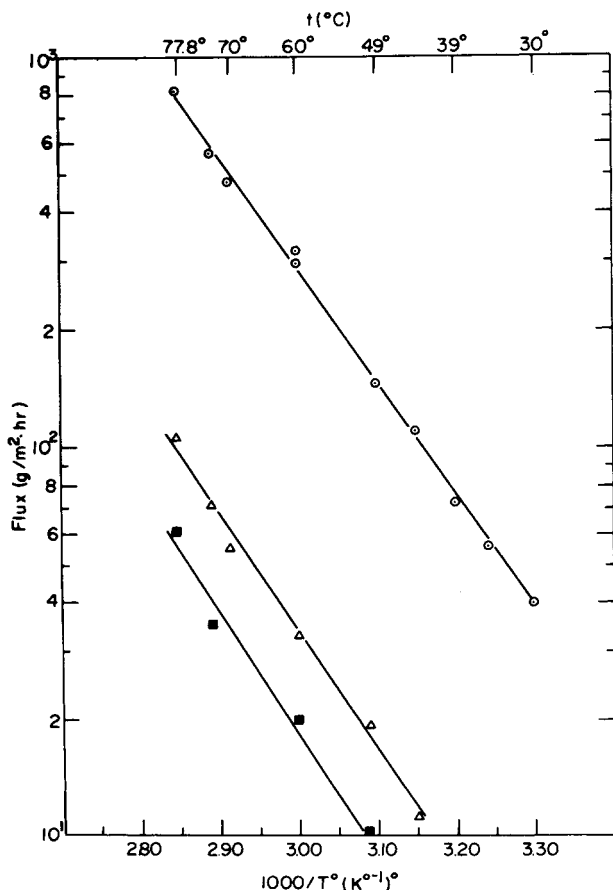


Fig. 2. Semilog plots of flux vs. reciprocals of absolute temperatures: (○) P/A-50 membrane; (△) P/A-30 membrane; (■) P/A-10 membrane.

membranes was shown¹ to be little affected by temperature ($\Delta H_{\text{app}} = -0.3$ kcal/mole). The apparent "energy of activation" of permeation derived from the steady-state permeation experiments should, therefore, be attributed to the effect of temperature on the diffusion coefficients. $E_{\text{app}} \sim 14$ kcal/mole is, indeed, nearly identical with the energy of activation of diffusion of benzene in the solvent swollen P/A membranes¹ ($E_D^{D*} = 14.2$ kcal/mole). On the other hand, this value is significantly larger than $E_B^0 = 8.3$ kcal/mole derived from desorption experiments for [benzene] $\rightarrow 0$.

Binning et al.⁴ predicted that the concentration profile for the steady-state permeation is such that essentially all the resistance to permeation is due to resistance to diffusion at the unswollen "downstream" interface of the membrane. Predictions of Binning et al. were confirmed experimentally by Long.¹⁰ However, from the presently determined values of the activation energies it is evident that this prediction does not apply to the system investigated by us. Actually, the very existence of the completely unswollen layer at the "downstream" interface seems to be questionable. Recent "pervaporation" experiments of Kim and Kammermayer¹¹ with "stack" membranes indicated that the limiting conditions $C_1 = C^*$ and $C_2 = 0$ are realized only for very thick membranes (subscripts 1 and 2 indicate the upstream and the downstream interface of the membrane, and C^* denotes the equilibrium concentration of the solvent in the membrane). In the case of P/A membranes, it may also be argued that the condition $C_2 = 0$ cannot be maintained in the steady-state permeation because of the discontinuity in the D -versus- C dependence at $C \rightarrow 0$ (see ref. 1).

Effect of Feed Composition

The effect of feed composition of the benzene-cyclohexane mixtures on the selectivity and flux characteristics of a P/A-50 membrane is shown

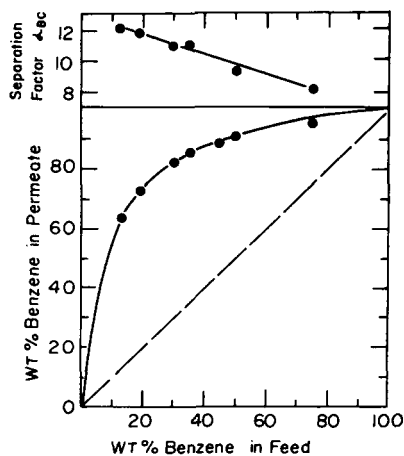


Fig. 3. Wt % of benzene in permeate vs. wt % of benzene in feed. P/A-50 membrane. Feed at reflux temperature.

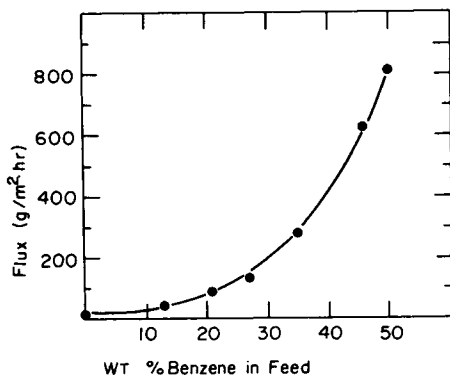


Fig. 4. Flux vs. wt-% of benzene in feed. P/A-50 membrane. Feed at reflux temperature.

in Figure 3 and 4, respectively. These data were taken at the reflux temperature of the benzene-cyclohexane azeotrope (77.8°C).

The permeation rates show an exponential dependence on the fraction of benzene in the feed. This is apparently due to the superposition of the exponential dependence of the diffusion coefficients on the fraction (ϕ) of benzene in the solvent-swollen polymeric alloy¹ with a nearly linear dependence of ϕ on the concentration of benzene in the feed.

The selectivity decreases with increase in benzene concentration in the feed. However, it may be seen from Figure 3 that the separation factors remain high even at much higher feed concentrations of benzene than the azeotropic one (55% of benzene and 45% cyclohexane).

Tests of Other Systems

Various combinations of cyclohexane, cyclohexene, and benzene were tested using a P/A-50 membrane to determine its separation characteristics at 80°C. The results are summarized in Table II. The separation factors for the benzene-cyclohexene and cyclohexene-cyclohexane mixtures are lower than those for benzene-cyclohexane. The selectivity between aromatics and aliphatic hydrocarbons is apparently much better than that between aromatics and olefins. Flux of the permeate in the case of a

TABLE II
Pervaporation Experiments with a P/A-50 Membrane at 0°C^a

Feed solution	Flux, g/m ² ·h	Separation factors		
		α_{12}	α_{23}	α_{13}
Benzene-cyclohexene-1:1 (w/w)	1350	2.8	—	—
Benzene(1)-cyclohexene(2)- cyclohexane (3) 1:1:1 (w/w/w)	1150	2.8	1.9	5.4
Cyclohexene-cyclohexane	60	2.7	—	—

^a Membrane thickness: 20 μ .

benzene-cyclohexene feed is, however, even higher than that of the benzene-cyclohexane mixture.

Liquid-Liquid Permeation Under Osmotic Conditions

The "permselective" character of P/A membranes can be utilized in osmotic permeations of benzene or of other aromatics dissolved in aliphatic hydrocarbons. The solubility of decalin, a high-boiling aliphatic hydrocarbon, in P/A membranes was found to be even lower than that of cyclohexane, and it was chosen as a medium for the osmotic experiment. The difference in the osmotic pressures of benzene in its diluted and concentrated solutions in decalin is immediately revealed by a build-up of a hydrostatic pressure in the dilute solution compartment. Actual permeation experiments were conducted by using benzene-cyclohexane mixtures as feed solutions and decalin as a downstream diluent for the permeate. Benzene was distilled off from the decalin solutions. In analogy with the so called "extractive distillation," we propose to call such a process "osmotic distillation." A schematic representation of an "osmotic distillation" cell is given in Figure 5.

A semilog plot of fluxes of benzene versus benzene concentrations in the feed solution for an "osmotic permeation" experiment at 30°C is shown in Figure 6. In this experiment, the concentration of benzene in the decalin compartment was kept below 1%. Comparison of osmotic and pervaporation experiments at 30°C (cf. Fig. 6 and Table I) reveals that the flux of permeate is considerably higher in the osmotic liquid-liquid permeation experiment than in the parallel pervaporation experiment. This may be due to differences in the concentration profiles of permeate in the P/A-50 membrane during the two experiments. Cooling of the downstream interface of the membrane in the pervaporation cell, as result of the evaporation of the permeating benzene, may also play some role.

The flux of the permeate can be calculated from the steady-state integration of Fick's first law

$$Jl = \int_{c_2}^{c_1} D_{(c)} dc \quad (1)$$

where c_1 and c_2 are, respectively, the concentrations in the upstream ($X = 0$) and downstream ($X = 1$) faces of the membrane.

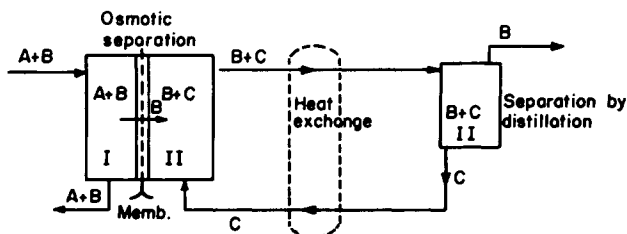


Fig. 5. Schematic representation of an "osmotic distillation" set up.

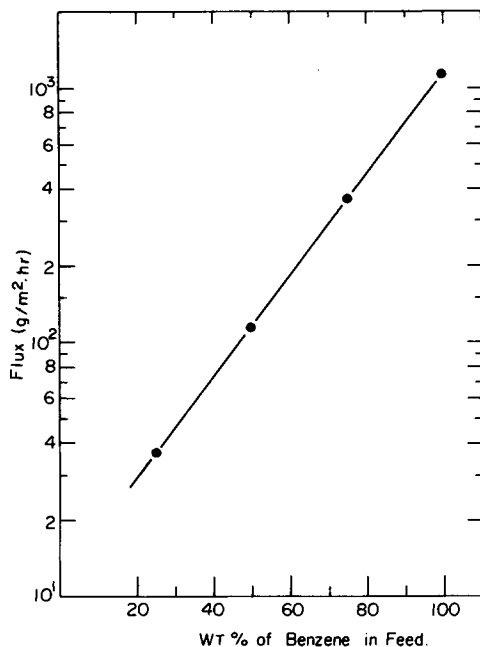


Fig. 6. Semilog plot of flux vs. wt % of benzene in feed. P/A-50 membrane. Osmotic permeation at 30°C.

The solution of the diffusion problem is given by the equation¹¹

$$J = \frac{D_0(e^{\gamma c_1} - e^{\gamma c_2})}{\gamma l} \quad (2)$$

if the concentration dependence of the diffusion coefficients may be expressed by the exponential equation

$$D_{(c)} = D_0 e^{\gamma c} \quad (3)$$

where γ is a constant characteristic for a given system.

It was shown in the preceding paper that in solvent-swollen membranes, eq. (3) describes satisfactorily the concentration dependence of D , but it breaks down at $C \simeq 0$.

It seems, however, that in the system under investigation, $C_2 > 0$. Hence, it is reasonable to expect that eq. (2) may be adopted for the calculation of fluxes in these systems, by replacing the term D_0 by D_s , where D_s is an extrapolated value of D for $C_2 = C_s > 0$.

Diffusion coefficients in the solvent-swollen P/A-50 membrane were calculated from the relationship¹²

$$D = D_j^*(1 - \phi)^3 d \log a/d \log \phi \quad (5)$$

where D_j^* , ϕ , and a denote, respectively, the self-diffusion coefficient of benzene, the corresponding volume fraction of benzene in the solvent swollen-membrane, and benzene activity in its cyclohexane solutions.

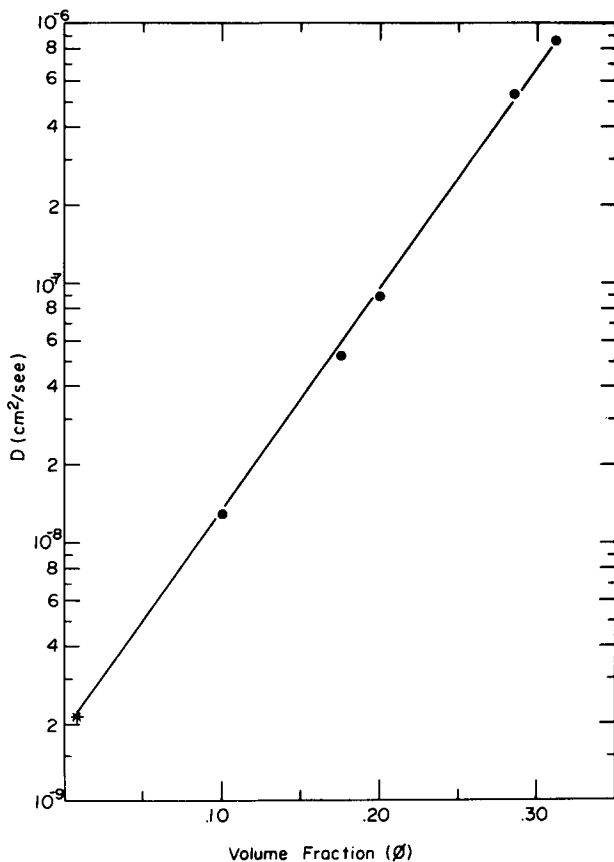


Fig. 7. Semilog plot of D vs. volume fraction of solvent (ϕ) in a P/A-50 membrane at 30°C: (*) extrapolated value; (●) values calculated from data given refs. (1) and (13).

Values of D_j^* and ϕ were taken from reference 1, and values of a were taken from the results of Scatchard et al.¹³ The resulting semilog plot of D versus ϕ shown in Figure 7 yields $\gamma = 19.8$. Let us express concentrations of benzene in the membrane in terms of its volume fractions and assume $C_2 \simeq 0.01$ – 0.005 . Thus, one derives from the plot in Figure 7 $D_s = 2.2 \times 10^{-9}$ cm²/sec.

The equilibrium values of ϕ at 30° for a preconditioned P/A-50 membrane at reflux are $\phi_{\text{eq}}^{BC} = 0.215$ for 1:1 (w/w) benzene–cyclohexane feed and $\phi_{\text{eq}}^B = 0.325$ for pure benzene. Assuming $C_1 \simeq \phi_{\text{eq}}$, one calculates from eq. (2) $J_{BC} = 115$ g/m²·hr and $J_B = 1026$ g/m²·hr, respectively. Thus calculated J values are in good agreement with the experimental values of the osmotic permeation runs shown in Figure 6.

CONCLUSIONS

Membranes made of polymeric alloys of PPN and acetyl cellulose comprising 50% of the PPN component are selectively permeated by benzene.

Preliminary experiments conducted in this laboratory indicated that *asymmetric* membranes characterized by similar selectivity and by fluxes which are orders of magnitude higher than the presently reported ones can also be prepared from P/A alloys.

No change in the performance of membranes with time was noted in the present study. However, the total time of exposure to permeation conditions was relatively short (up to 100 hr). Long-term tests designed to evaluate the lifetime of P/A membranes have been started, and their results will be reported elsewhere.

The permeation characteristics of P/A membranes agree well with those predicted from the previously reported solubility and diffusivity data. This indicates that the permeation mechanism can, indeed, be described in terms of sorption and molecular diffusion.

Flux characteristics of membranes under the osmotic liquid-liquid permeation conditions seem to be superior to those attained under "pervaporation" conditions. The osmotic permeation technique can be easily coupled with conventional distillation and may, therefore, offer a more practical solution to the problem of separation of azeotropic or closely boiling mixtures than the "pervaporation" technique.

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