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Dioxane-Water Transport through Nylon 6 Membranes

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Abstract

An experimental study was made of the permeation of water, paradioxane, and water-paradioxane mixtures through nylon 6 membranes. Laminated films were utilized to determine actual liquid permeate concentration profiles within the membrane structure. Knowledge of these profiles permitted the investigators to measure the concentration-dependent diffusivities and to characterize the mechanism of mass transfer. Since water plasticizes nylon, the behavior of the water-dioxane mixture could not be accurately predicted from pure component performance. Thus the transfer of water was enhanced and the dioxane depressed for equimolar feed mixtures. Moreover, it was demonstrated that a simple, acid surface-treatment of the separative membrane can greatly enhance the transfer of both components. Concentration profiles measured during the unsteady state leading to equilibrium suggested that the nylon polymer matrix was in the process of undergoing structural changes.

INTRODUCTION

Liquid phase separations produced by selective permeation through polymer membranes are now popular in several commercial areas. A prime example is the increased utilization of liquid Permasep columns for water purification. Additional applications include the separation of azeotropes and close boiling mixtures, the removal of trace organics from aqueous solutions, and the recovery of heat-sensitive compounds such as enzymes. In these cases the separations are difficult to effect by more conventional means and liquid permeation provides an alternative solution. However, these unique unit operations are frequently based on empirical correlations since the actual liquid permeation phenomena are not fully understood. This study attempts to add to the present state of the art.

In developing an analytical approach the assumption of Fickean behavior provides an adequate model for many diffusional processes. This is certainly the case for most liquids as they permeate through plastic barriers. Crank (*1*) has supplied the mathematical expressions to describe many of these situations. Even so, a realistic solution is not always obtained and information beyond the basic model must be sought. It is at this point that most investigations resort to empirical relationships (*2–7*).

The basis for all separations by liquid permeation is the selective absorption and permeation of one component over another due to the inherent properties of the separating membrane. For each component this is viewed as a three-step process which consists of sorption of the permeate into the membrane, diffusion of the permeate through the membrane, and desorption of the permeate on the downstream side of the membrane. The driving force for net mass transfer is the concentration gradient across the membrane. The three steps of this transfer model occur in series, and each can act as the rate-controlling mechanism. However, if vacuum conditions exist on the downstream side of the membrane, the desorption rate is relatively fast, and it is the permeate's sorption and diffusion rates which remain potentially rate controlling. By simultaneously applying vacuum and reducing the membrane to a very thin barrier, the diffusion rate may also become a relatively fast process (*8,9*). At this point, only the rate of absorption remains as the single controlling step. By proper manipulation, then, it should be possible to reduce liquid permeation phenomena to a more simple subsystem. Experiments of this sort were attempted in this study in an effort to both improve the efficiency of liquid permeation separations and to obtain more knowledge of the liquid–polymer interactions which affect membrane selectivity and permeate diffusion.

THE EXPERIMENT

In the area of mixture separation by liquid permeation the literature is especially lacking in treated and/or altered membrane surface characteristics. This is probably due to the complexity of such systems and to proprietary reasons, at least in commercial applications. For, if a film can be surface-treated so that the permeation of one component through the membrane is enhanced while that of another is decreased. then the selectivity of that separative barrier must also increase. This gives an added dimension of flexibility to the designer; it is necessary only to tailor the surface of the membrane to a specific separation rather than attempt to completely restructure the polymer membrane on a molecular scale. Therefore, in this study a procedure was sought whereby the surface of a membrane could be modified (*10*).

One possibility for surface modification was provided by the investigations of Sweeney and Rose (*11*), where the permeation rates of a variety of organic liquids through polymer membranes were reported. They observed that polar liquids dissolved faster than nonpolar liquids in polar membranes and vice versa. In addition it is also known that polymer films exposed to oxidizing atmospheres will exhibit increased polar behavior on their surface. Therefore, the already somewhat polar nylon 6 membranes were selected as separative barriers for testing, and their surfaces were etched with nitric acid to hopefully increase their sorption of polar liquids even more. Solutions of water and paradioxane were next chosen as the permeates to be studied. There were several reasons for the selection. First, water is a polar liquid whereas paradioxane is much less so. This implies that their relative absortivities should be affected by the polarity of the membrane. Second, the two liquids are miscible for all mixture compositions and have similar specific gravities (*12*). Finally, their boiling points differ by only 1.5 °C which makes distillation inefficient and separation via liquid permeation more attractive.

Experimental runs were made for the pure component liquids and for 50 vol-% mixtures of the two. Sorption characteristics were determined from the pure component runs, while the diffusional properties were measured with the aid of concentration profiles. The profiles were established experimentally with multilayer membranes. These could be dissected into the individual layers. Gravimetric analysis of each section produced an accurate indication of the permeate's concentration as a function of distance along the diffusional path (*8*, *13*).

THEORETICAL CONSIDERATIONS—UNICOMPONENT PERMEATION

When flat membranes are used as separative barriers, all concentration gradients can be assumed to be zero except the one which is perpendicular to the membrane and in the same direction as the net mass transfer. The result is unidirectional diffusion in which the permeation flux for a single component is expressed by:

$$J = D\frac{dC}{dx} \tag{1}$$

In a like manner the rate of change in permeate concentration within the membrane becomes a function of the flux and the distance through the membrane:

$$\frac{dC}{dt} = -\frac{dJ}{dx} \tag{2}$$

For steady-state operation, however, the concentration is invariant with time so that Eq. (2) reduces to

$$\left.\frac{dJ}{dx}\right|_{\text{s.s}} = 0 \tag{3}$$

Now the most widely accepted mathematical expression for diffusivity as a function of concentration is:

$$D = D_0 e^{\alpha C} \tag{4}$$

Substituting Eq. (4) into Eq. (1) gives:

$$J = D_0 e^{\alpha C}\frac{dC}{dx} \tag{5}$$

Let $x_f = (x/L)$, where x_f is the fraction of total thickness. Substitution of this quantity into Eq. (5) gives:

$$J = \frac{D_0}{L} e^{\alpha C}\frac{dC}{dx_f} \tag{6}$$

For steady-state operation, Eq. (6) can be substituted into Eq. (3) such that

$$\frac{d}{d_{xf}}\left(\frac{D_0}{L} e^{\alpha C}\frac{dC}{dx_f}\right) = 0 \tag{7}$$

Using the boundary conditions $x_f = 0$, $C = C_1$ and $x_f = 1$, $C = C_2$, Eq. (7) can be integrated twice and reduced to give

$$e^{\alpha C} = (e^{\alpha C_2} - e^{\alpha C_1})x_f + e^{\alpha C_1} \tag{8}$$

Solving for C:

$$C = \frac{1}{\alpha}\ln[(e^{\alpha C_2} - e^{\alpha C_1})x_f + e^{\alpha C_1}] \tag{9}$$

Differentiating with respect to x_f gives

$$\frac{dC}{dx_f} = \frac{1}{\alpha}\frac{(e^{\alpha C_2} - e^{\alpha C_1})}{[(e^{\alpha C_2} - e^{\alpha C_1})x_f + e^{\alpha C_1}]} \tag{10}$$

Substituting Eqs. (4), (8), and (10) into Eq. (6) gives a new expression for flux:

$$J = \frac{D_0}{L\alpha}(e^{\alpha C_2} - e^{\alpha C_1}) \tag{11}$$

If a vacuum is used downstream, then C_2 approaches zero and Eq. (11) reduces to

$$J = \frac{D_0}{L\alpha}(1 - e^{\alpha C_1}) \tag{12}$$

In this equation, values of α and C_1 can be obtained from a plot of C vs x_f for the experimental data. These values, together with the experimentally measured values for J and L, are substituted into Eq. (12) in order to determine values of diffusivity, D_0 (*8*, *13*).

BINARY MIXTURE SEPARATION

A separation factor, γ, can be used to describe the selectivity of a membrane when a mixture is permeated through it. For a binary mixture of liquids, A and B, it can be defined by

$$\gamma_{AB} = (y_A/x_A)/(y_B/x_B) \tag{13}$$

The total permeation rate of the mixture through the membrane, Q, becomes equal to the sum of the components:

$$Q = q_A + q_B \tag{14}$$

If the permeation is ideal, the rates should follow pure component permeation rates:

$$q_A = x_A q_A{}^\circ \tag{15}$$

$$q_B = x_B q_B{}^\circ = (1 - x_A)q_B{}^\circ \tag{16}$$

The total ideal permeation rate is then

$$Q^\circ = x_A q_A{}^\circ + (1 - x_A) q_B{}^\circ \tag{17}$$

and the ideal separation factor is simply

$$\gamma_{AB}{}^\circ = q_A{}^\circ / q_B{}^\circ \tag{18}$$

Permeating gas mixtures often exhibit this ideal behavior (*14*). However, ideal behavior is rarely observed in liquid separations since one of the liquids will tend to plasticize the membrane thus changing its diffusive characteristics. The nonideality of the system can be represented by the ratio of the actual permeation rate to the ideal permeation rate (*1*):

$$\Phi = Q/Q^\circ \tag{19}$$

Permeation ratios for the individual components can then be expressed as

$$\Phi_A = q_A / q_A{}^\circ x_A \tag{20}$$

$$\Phi_B = q_B / q_B{}^\circ (1 - x_A) \tag{21}$$

If the ratio of a system is higher than unity, the system is said to exhibit a permeation enhancement effect. A value lower than unity indicates a permeation depression effect (*13*).

DISCUSSION OF THE RESULTS

Pure Component Behavior

Tables 1, 2, and 3 summarize the results of the experiments, while Figs. 1 through 6 depict the membrane concentration profiles for each subsystem investigated. Alpha values were obtained for each system by a least squares technique using Eq. (9) and the experimentally determined profiles. Values of C_1 were extrapolated from the concentration curves. This was an arbitrary choice which appeared to give the best correspondence with the mathematical model. In the most ideal case C_1 should equal C^*, the equilibrium concentration. However, with thin barriers and vacuum conditions downstream, this will rarely occur and the mathematical model fails to accurately describe the system. Equation (9) also assumes a value for C_2 of zero. Here again this is not quite correct since there must be some finite concentration of permeate at the downstream surface. Of the two assumptions, the value of C_1 most critically affects the determination of α. This is especially so for the surface-treated films. As shown in Figs. 2 and

TABLE 1

Permeation Parameters. Pure Component Systems, Temperature; 35 °C, Nylon 6 Barrier-Capran, Type 77-C, Allied Chemical Corp.

	Permeate			
	Water		Paradioxane	
Parameter	Untreated film	Treated film	Untreated film	Treated film
J, mass flux	3.305×10^{-7}	5.901×10^{-7}	1.144×10^{-8}	1.181×10^{-8}
P, permeability	1.799×10^{-9}	3.227×10^{-9}	7.686×10^{-11}	6.297×10^{-11}
α, exponent	33.8	53.6	−40.7	−117.6
D_0, diffusivity	2.911×10^{-9}	1.714×10^{-9}	1.002×10^{-8}	9.047×10^{-7}
C^*, equilibrium concentration	0.096	0.119	0.074	0.113
Film thickness, cm	5.11×10^{-3}	5.11×10^{-3}	5.11×10^{-3}	5.11×10^{-3}
C_1, concentration	0.0913	0.086	0.0092	0.0144

TABLE 2

Permeation Parameters: Mixtures. Feed: Water and Paradioxane Mixture (50:50). Temperature: 35 °C. Nylon 6 Barrier

	Total permeate mixture	
	Untreated film	Treated film
J, total mass flux	5.023×10^{-7}	11.210×10^{-7}
P, total permeability	2.679×10^{-9}	6.042×10^{-9}
α, exponent	10.3	32.8
D_0, diffusivity	1.690×10^{-8}	1.724×10^{-8}
C^*, equilibrium concentration	0.116	0.163
Film thickness, cm	5.11×10^{-3}	5.11×10^{-3}
C_1, concentration	0.094	0.077

TABLE 3

Separation Parameters: Mixtures. Permeate: Water and Paradioxane Mixture (50:50). Temperature: 35 °C. Film: Nylon 6.

	Untreated film	Treated film
$\gamma_{\text{water-paradioxane}}$	58.6	44.9
Feed (mole fraction)		
Water	0.50	0.50
Paradioxane	0.50	0.50
Permeate (mole fraction)		
Water	0.983	0.978
Paradioxane	0.017	0.022
q_{water}	4.939×10^{-7}	10.965×10^{-7}
$q_{\text{paradioxane}}$	0.084×10^{-7}	0.244×10^{-7}
q^0_{water}	1.653×10^{-7}	2.951×10^{-7}
$q_{\text{paradioxane}}$	0.072×10^{-7}	0.059×10^{-7}
J^0	1.725×10^{-7}	3.010×10^{-7}
$\gamma^0_{\text{water-paradioxane}}$	22.9	50.0
θ	2.91	3.72
θ_{water}	1.49	1.85
$\theta_{\text{paradioxane}}$	0.58	2.07

4, the concentration profiles are seemingly discontinuous in this region. This suggests significant structural changes in the polymer to the extent that crystallinity in this region has been greatly reduced (*15*).

D_0 values were obtained with Eq. (12) and the experimentally determined values of J, L, and C_1 and the calculated α's. The diffusivity coefficients can also be plotted as a function of the experimentally determined concentrations. Sekita and Kawasaki (*16*) have reported that the percentage of absorbed water in nylon 6 films has a tremendous influence on diffusivity. They attributed this to the plasticizing effect of the sorbed water and its disruption of interchain bonding. In the 2 to 4% sorbed water region the diffusion coefficient of water vapor for nylon 6 increases exponentially with increasing water content. The experimental evidence of this investigation supports this interpretation, since the concentration gradient is steepest on the downstream side which was subjected to vacuum conditions. Hence it also has the lowest permeate concentration.

Mixture Behavior

Table 3 shows the permeation ratio, θ, obtained for an equimolar feed. This quantity was defined as the ratio of the actual permeation rate to the

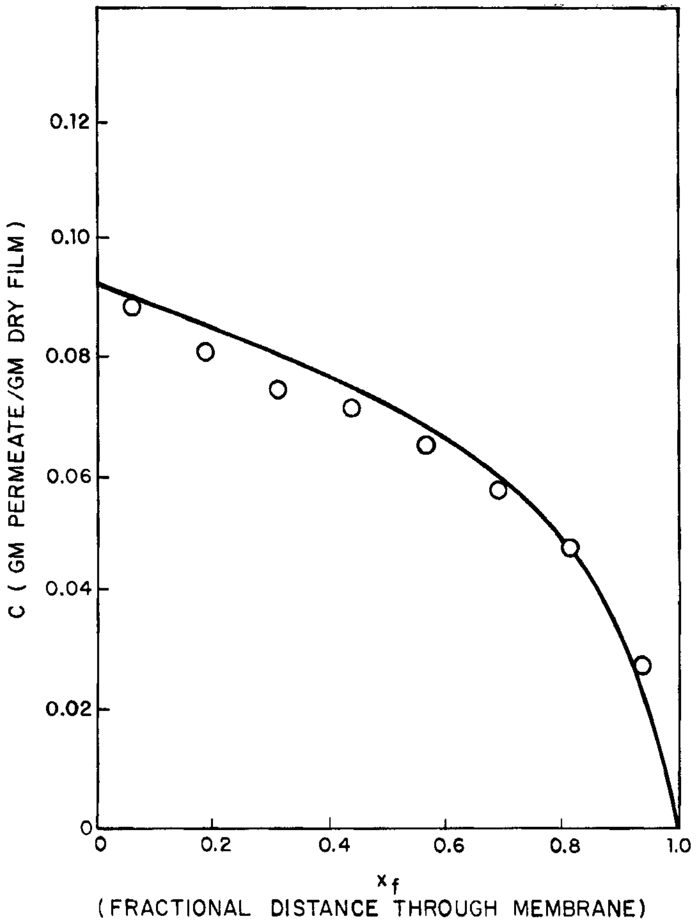

FIG. 1. Concentration profile for pure water as a function of fractional distance through an eight-layered nylon 6 membrane.

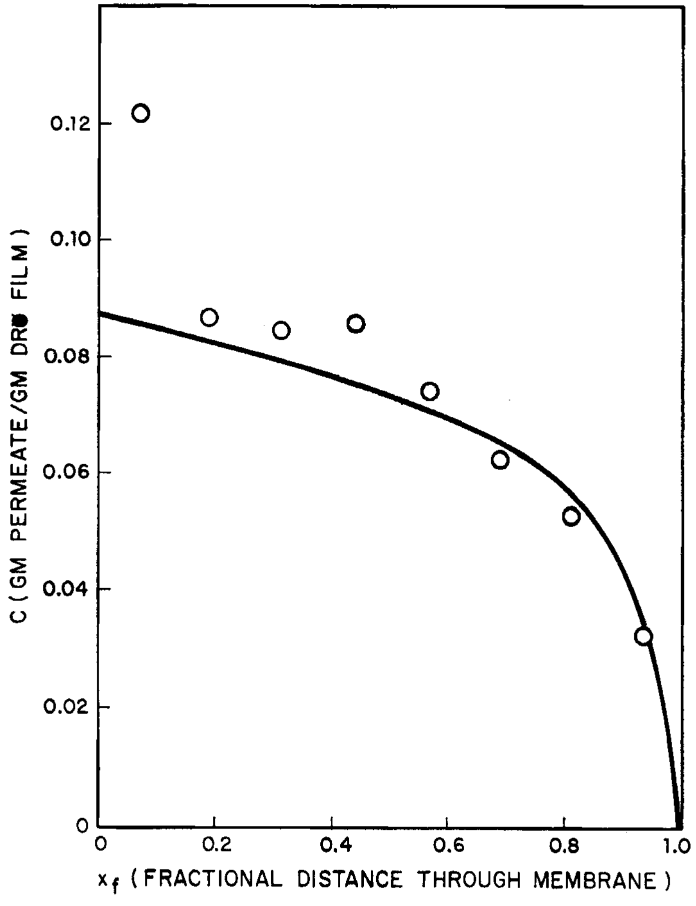

FIG. 2. Concentration profile for pure water and a surface-treated nylon 6 membrane.

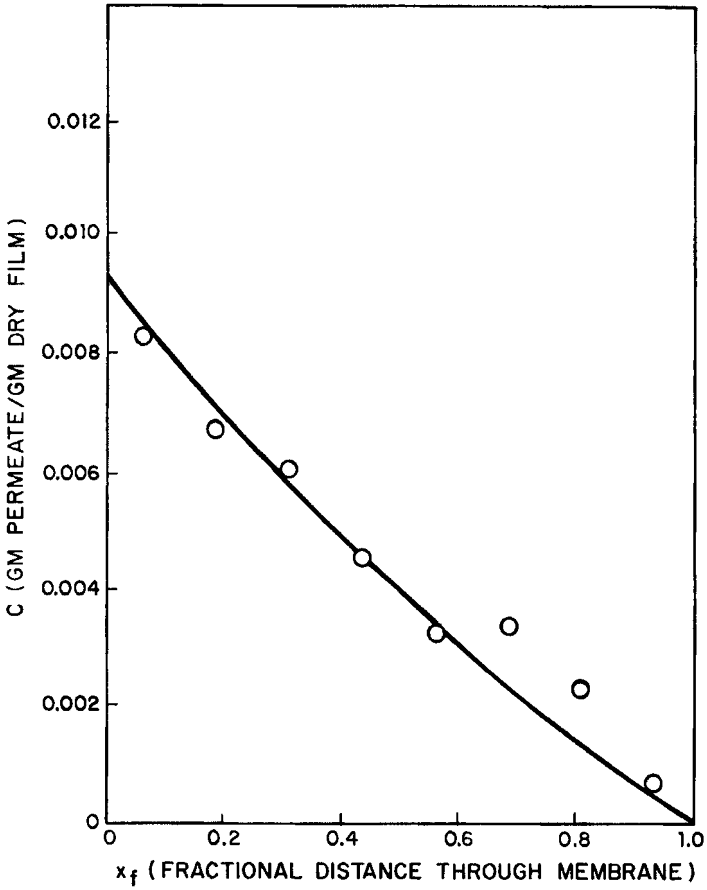

FIG. 3. Concentration profile for pure paradioxane as a function of fractional distance through a nylon 6 membrane.

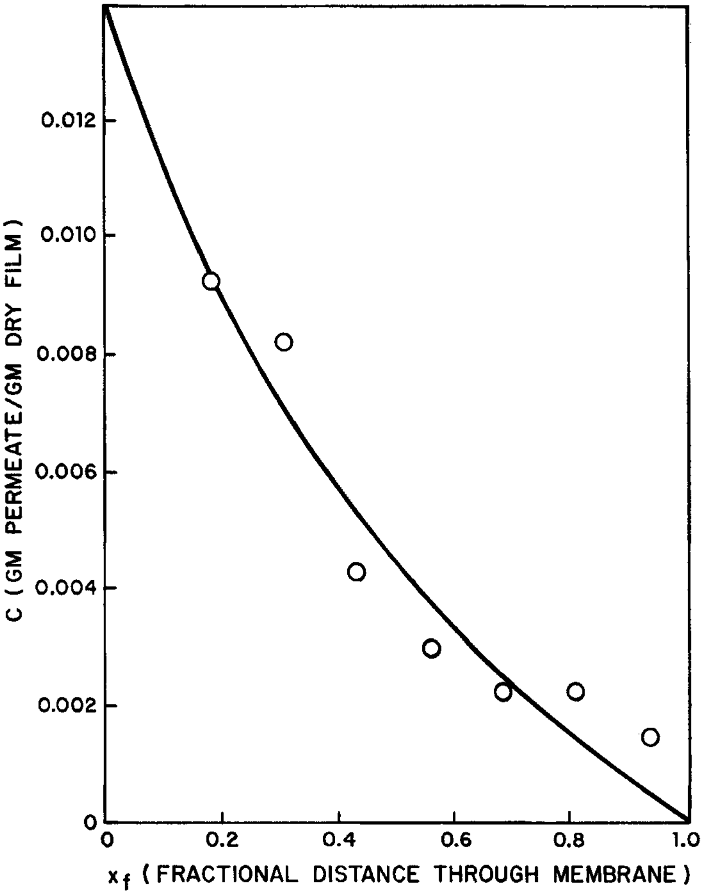

FIG. 4. Concentration profile for pure paradioxane and a surface-treated nylon 6 membrane.

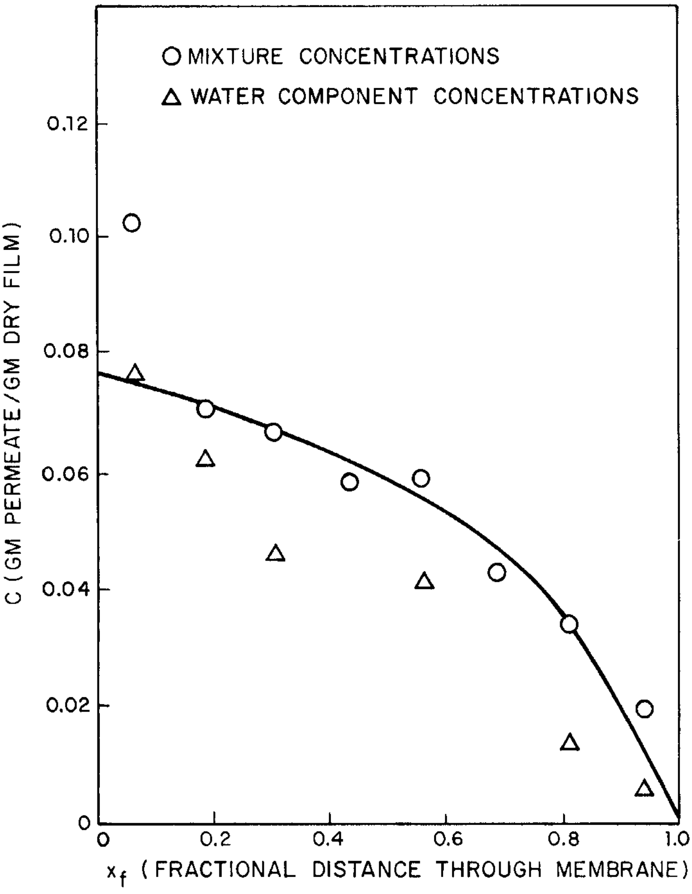

FIG. 5. Concentration profile for an equimolar mixture of water and para-dioxane through a nylon 6 membrane.

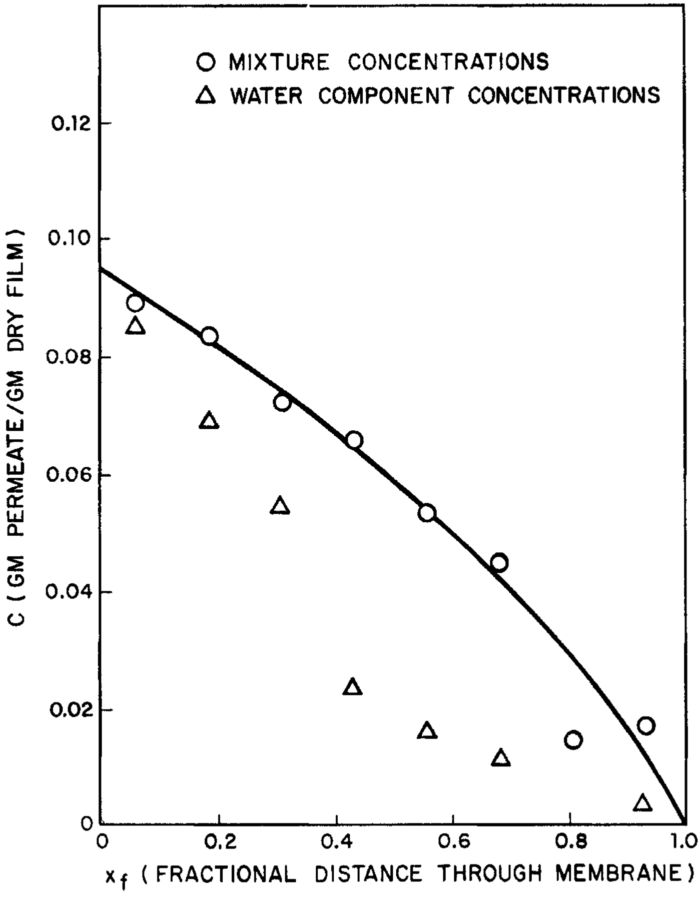

FIG. 6. Concentration profile for an equimolar mixture of water and paradioxane through a surface-treated nylon 6 membrane.

permeation rate predicted from pure component behavior. Thus a ratio of *one* indicates that a mixture behaves ideally in that its behavior can be predicted from that of its components. The values shown in Table 3 suggest that for this binary mixture and approach, such predictions are not possible. Barriers which were not surface-treated displayed a greater permeability for the mixture than expected. On a component basis the water transfer was enhanced by as much as 50% by the presence of the dioxane while dioxane's behavior was depressed. Thus the potential for separation of a water–dioxane mixture by permeation through nylon 6 is greater than expected. As yet there is no substantiated hypothesis to explain such behavior.

Mixture permeation through barriers with surface treatments is even more anomalous. Here the flux increased 123% over that of the untreated film. However, separation of the two components changed little. Both components increased their individual permeation fluxes when in the presence of the other. The causes of such behavior must reside at the molecular level.

Unsteady State Behavior

Prior to obtaining steady-state permeation, the rates of transfer for both the water and paradioxane passed through a maximum. Li et al. (*17*) noted the same effect when measuring permeation rates of xylene through polyethylene. They attributed the initial increase with time to fragmentation of crystallites due to osmotic pressure build-up. This was followed by a decline to steady state as the polymer underwent stress relaxation and recrystallization in the swollen state. Their maximum usually occurred within the first hour for the polyethylene. With the nylon in this investigation, the maximum was not reached until the twentieth hour of operation. Figure 7 is a representative plot of this phenomenon. A chromatographic analysis of the permeate revealed no indication that this change occurred as the result of components being leached from the film. A study by Cheung attempted to clarify this unsteady-state phenomenon (*18*). He employed layered nylon 6 membranes to determine concentration profiles in the manner of Cook (*13*) and Kim (*8*) as a function of time up to equilibrium. A typical plot is shown in Fig. 8. From these data it is evident that some form of molecular rearrangement is occurring within the polymer. Otherwise it would not be possible, thermodynamically, to have membrane concentrations greater than the equilibrium concentration. Cheung's data show that this does happen. Furthermore, if $(C_1 - C_2)$ values from

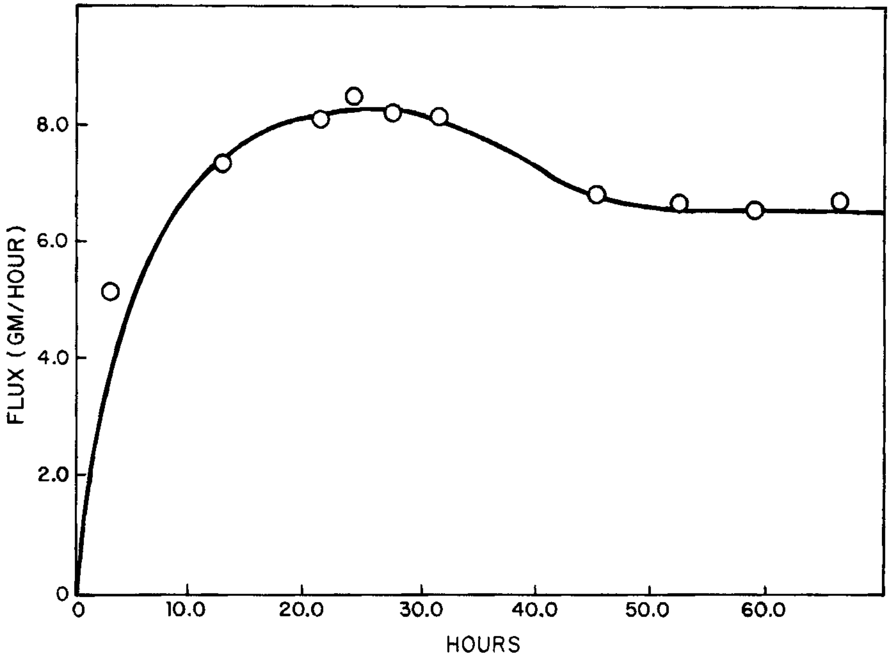

FIG. 7. Behavior of permeation flux with time for the water–nylon 6 system.

Cheung's graphs are plotted vs time, they pass through a maximum at essentially the same point in time as that reported for this study (~20 hr) for flux as a function of time.

SUMMARY

This study demonstrated that water can be separated from paradioxane by selective permeation through nylon 6 membranes. However, this separation could not be predicted from the pure component behavior in terms of degree of separation. It was also shown that a simple surface treatment will greatly enhance the permeability of thin membranes. This treatment appeared to destroy the crystallinity of the barrier's surface and thereby increase its sorptive capacity. Unsteady-state measurements of fluxes and concentration profiles indicated that stress relaxation and perhaps recrystallization phenomena were both occurring prior to steady-state operation.

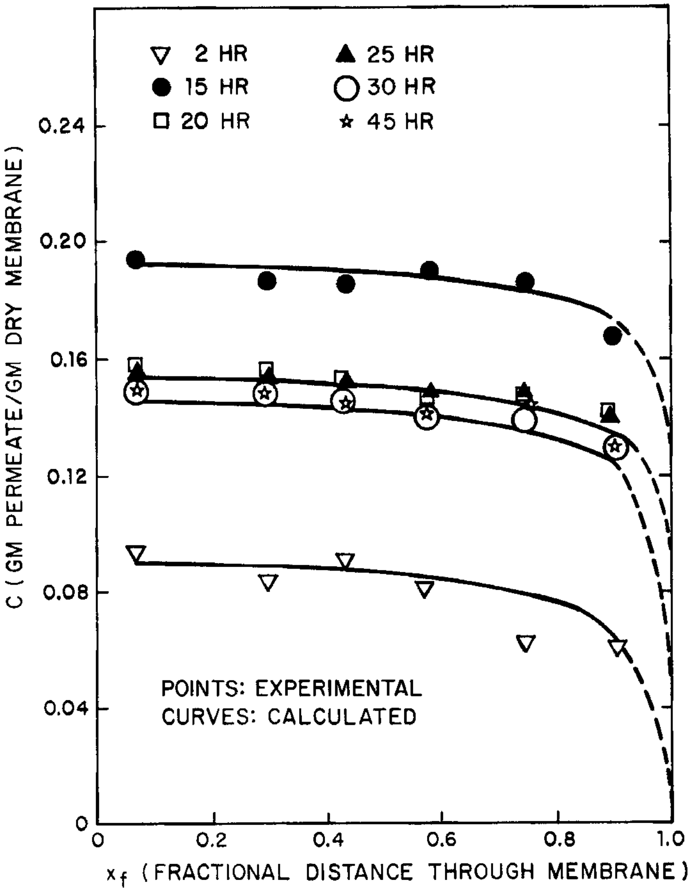

FIG. 8. Concentration profiles for pure water in a nylon 6 membrane during unsteady-state operation leading up to dynamic equilibium.

SYMBOLS

C	concentration of permeate in membrane (g permeate/g dry film)
C_1	concentration of permeate in membrane at upstream interface (g permeate/g dry film)
C_2	concentration of permeate in membrane at downstream interface (g permeate/g dry film)
C^*	equilibrium concentration of permeate in membrane(g permeate/g dry film)
D	diffusivity coefficient (cm^2/sec)
D_0	diffusivity coefficient at zero concentration (cm^2/sec)
J	permeation flux (g/cm^2-sec)
L	total membrane thickness (cm)
Q	total permeation rate (g/cm^2-sec)
Q°	ideal permeation rate (g/cm^2-sec)
q_A	permeation rate of component A (g/cm^2-sec)
q_B	permeation rate of component B (g/cm^2-sec)
$q_A{}^\circ$	pure component permeation rate of Component A (g/cm^2-sec)
$q_B{}^\circ$	pure component permeation rate of Component B (g/cm^2-sec)
t	time (sec)
x	thickness (cm)
x_f	fraction of total membrane thickness
y_A	mole fraction of A in the bulk permeate
y_B	mole fraction of B in the bulk permeate
x_A	mole fraction of A in the bulk feed
x_B	mole fraction of B in the bulk feed
α	constant determining the shape of concentration profile
γ_{AB}	separation factor
$\gamma_{AB}{}^0$	ideal separation factor
Φ	nonideality ratio for total mixture
Φ_A	nonideality ratio for Component A
Φ_B	nonideality ratio for Component B

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