

## Difficulties Associated with the Measurement of the Diffusion Coefficient of Solvating Liquid or Vapor in Semicrystalline Polymer. I. Permeation Methods

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### Synopsis

The diffusion coefficients  $D$  for solvating liquids and vapors in membranes can be measured in a number of ways. The effectiveness of permeation methods for systems involving semicrystalline polymers at near-ambient temperatures has been assessed, and new experiments have been performed using *p*-xylene and high-density polyethylene. The conclusions are likely to apply to any semicrystalline polymer where the diffusant concentration is not zero. Stresses induced in the downstream side of the membrane by solvent sorption at the upstream surface during the nonsteady period are shown to lead to underestimation of  $D$ . The rate of attainment of a steady state is controlled primarily by the rate at which these stresses relax. The extremely slow rate of stress relaxation in polyethylene implies that, under many experimental conditions, a true steady state of permeation is not attained within an experimentally accessible time, a conclusion supported by experimental evidence. Diffusion coefficients calculated in the usual way from apparently steady-state permeation rates may be grossly underestimated. In liquid permeation experiments, some of the polymer may dissolve in the upstream permeant, and this may lead to overestimation both of the time to reach an apparently steady state and of the steady-state permeation rate itself.

### INTRODUCTION

Studies of the diffusion of penetrant molecules in a semicrystalline polymer offer some scope for investigating both the molecular nature of the noncrystalline regions and the overall morphology of the polymer. They also provide information about the permeability of the polymer and are of relevance to the packaging industry and to the development of membrane separation processes. The diffusion coefficient  $D$  of a penetrant in a polymeric material has been determined most commonly<sup>1</sup> from (i) the rate of attainment of a steady state of permeation (time-lag procedure), (ii) measurements of the steady-state permeability and equilibrium solubility of the penetrant in the polymer, or (iii) a study of the kinetics of sorption and desorption of the penetrant by the polymer.

A prerequisite for any study of diffusion is to ensure that the measured diffusion coefficients have a known physical significance. In each of the above methods,  $D$  is defined in terms of equations derived from Fickian

laws for boundary conditions relevant to the particular experiment. The derivation of these equations involves assumptions regarding the dependence or independence of  $D$  on variables such as concentration and time. If one or more of these assumptions is invalid, diffusion will be apparently non-Fickian, and the calculated values for  $D$  will have little or no physical significance.

The diffusion of permanent gases, and of other slightly soluble penetrants for which  $D$  is independent of concentration, has been found<sup>2</sup> to obey these Fickian laws and attendant assumptions in all polymers. Similar conclusions are believed<sup>3</sup> to apply to diffusion of solvating vapors in amorphous polymers well above the glass transition temperature  $T_g$ , even though  $D$  is concentration dependent in these systems. This paper offers an assessment of the validity of the assumptions underlying the application of methods (i) and (ii) above to the diffusion of solvating liquids and vapors in semicrystalline polymers above  $T_g$ . Method (iii) will be treated similarly in another paper.

Diffusion of solvating vapors in semicrystalline polymers has received little attention in the literature. The available data refer solely to polyethylene at or near ambient temperature and suggest that the process displays certain apparently non-Fickian anomalies. In a study of liquid xylene permeation through high-density polyethylene membranes, Baddour et al.<sup>4</sup> found that the time to reach a steady rate of permeation was 4 hr at 50°C. The equilibration time calculated from the diffusion coefficient appropriate to the steady state was about 1 min. The discrepancy was attributed to slow changes in the crystalline regions of the polymer resulting from the sorption of a good solvent at elevated temperatures. In the same study, the permeation rate was observed to pass through a maximum on the way to the attainment of a steady state, an effect attributed to stresses induced at the underside of the film as a result of a sudden uptake of solvent in the upstream surface. For high- and low-density polyethylene at ambient temperature, Rogers et al.<sup>5</sup> found that  $D$  values for benzene and other good solvents determined by method (ii) were generally higher, except at very low concentrations, than those determined by method (iii). Using similar materials, McCall and Slichter<sup>6</sup> found that  $D$  was lower by method (i) than by method (iii). The apparently non-Fickian characteristics of these systems were again attributed to slow changes in the crystalline regions of the polymer.

However, there appears to be no direct experimental evidence to support this view. On the contrary, a dilatometric study of the *p*-xylene/high-density polyethylene system at temperatures in the range 20° to 130°C indicated<sup>7</sup> that measurable dissolution of crystalline material did not occur below 40°C, even when the *p*-xylene concentration exceeded the equilibrium sorptive capacity of the polymer. Very recently, Udagawa and Keller<sup>8</sup> concluded that the addition of excess *p*-xylene, decalin, or octane (all good solvents for polyethylene) to polyethylene single crystals at room temperature caused no dissolution of the crystalline regions.

Anomalies precisely analogous to those described above have been observed in studies of the diffusion of solvating molecules in wholly amorphous polymers below and just above  $T_g$ . Meares<sup>9</sup> found that when one face of an initially solvent-free poly(vinyl acetate) membrane was contacted with allyl chloride vapor at a temperature a few degrees above  $T_g$ , there was a rapid flow of vapor through the film. The flux quickly fell to a very low value and then slowly rose to its steady-state value. Similar behavior has been observed by Kishimoto<sup>10</sup> for the system methanol-poly(vinyl acetate) just above  $T_g$ , and by Park<sup>11</sup> for the system methylene chloride-polystyrene well below  $T_g$ . These maxima in permeation rate occurred much earlier, lasted for a shorter time, and were more pronounced than the maximum observed by Baddour et al.<sup>4</sup> for the xylene-polyethylene system.

For the polymers near or below  $T_g$ , the high initial flux has been attributed<sup>9,12</sup> to an increase in the diffusion coefficient consequent upon the strain induced in the underside of the membrane by solvent swelling of the upper surface. The permeation rate is believed to have fallen from the maximum as the equilibrium chain density was restored by a redistribution of the polymer segments.<sup>12</sup> The rate of increase in permeation rate, after the initial maximum and minimum, was found by Meares<sup>12</sup> to be lower than predicted from the diffusion coefficient appropriate to the steady state. In other words,  $D$  determined from steady-state measurements was higher than that calculated from the permeation time lag. The origins of these non-Fickian characteristics are not yet fully understood. They are generally believed<sup>13</sup> to be associated with the relatively slow relaxation of stresses set up in the membranes as a result of unequal swelling of the polymer during the sorption process. The diffusion coefficient obtained from steady-state permeation data is generally taken to be the true value of  $D$  because it is uncomplicated by these time-dependent effects.<sup>14</sup>

Even in steady-state data, however, anomalies have been observed in respect of the dependence of the permeability coefficient and, by inference of  $D$ , on the thickness of the membrane. The plot of permeability coefficient against thickness has been found experimentally to be of positive<sup>15,16</sup> or negative<sup>17,18</sup> slope, and may even be parabolic in shape.<sup>19,20</sup> There is some debate as to whether all such data constitute a violation of the Fickian laws for steady-state permeation. Crank<sup>19</sup> has shown that an increase in permeability coefficient with membrane thickness could result from failure to ensure that the concentrations of permeant in the membrane surfaces correspond to the equilibrium concentrations appropriate to the existing vapor pressures. Furthermore, structural effects which are a function of film thickness may arise during processing.<sup>1,20</sup>

## THEORY

### Steady-State Method

Consider diffusion through a plane, isotropic membrane of thickness  $l$ , whose surfaces  $x = 0$  and  $x = l$  are maintained at constant concentrations

$C_0'$  and 0. In the steady state, the permeation rate or flux  $F$  of diffusant per unit area of membrane surface may be expressed as<sup>19</sup>

$$F = -D \frac{\partial C}{\partial x} = \frac{1}{l} \int_0^{C_0'} D \cdot dC = \frac{\bar{D}C_0'}{l} \quad (1)$$

where  $D$  is the (concentration-dependent) diffusion coefficient of the diffusing species and  $\bar{D}$  is the integral diffusion coefficient which is related to  $D$  by

$$\bar{D} = \frac{1}{C_0'} \int_0^{C_0'} D \cdot dC. \quad (2)$$

Measurement of the steady-state permeability coefficient  $P$  (defined here as  $F$ ), and the concentration  $C_0'$  of permeant in the upstream surface of the membrane, permits evaluation of  $\bar{D}$  by means of eq. (1). If  $\bar{D}$  is determined as a function of  $C_0'$ ,  $D$  may be calculated by means of eq. (2) expressed in the form

$$D = \bar{D} \left\{ 1 + C_0' \frac{d(\ln \bar{D})}{dC_0'} \right\}. \quad (3)$$

### Nonsteady-State (Time-Lag) Method

The time lag  $\theta$  for permeation is defined as the intercept on the time axis of the steady-state portion of a permeation curve. Consider a plane isotropic membrane of thickness  $l$  which is initially free of permeant throughout. At time  $t = 0$ , the upstream face is suddenly contacted with permeant at constant activity, while the permeant activity at  $x = l$  is maintained at zero. When  $D$  is a function of concentration only, and the concentration of permeant in the upstream surface of the membrane attains its equilibrium value  $C_0'$  instantaneously at  $t = 0$ , the time lag is given by<sup>3</sup>

$$\frac{\theta}{l^2} = \frac{\int_0^{C_0'} CD(C) \int_0^{C_0'} D(u) du dC}{\left\{ \int_0^{C_0'} D(C) dC \right\}^3}. \quad (4)$$

Values of  $D$  obtained by means of eqs. (1) to (4) are the diffusion coefficients of the liquid or vapor relative to the stationary membrane, if concentrations are expressed on a dry polymer basis.

## EXPERIMENTAL

### Materials

*p*-Xylene, 99%, was supplied by I.C.I. Ltd. and used as received.

**Polyethylenes.** Sample 1 was commercial Rigidex 50 film, supplied by B. P. Chemicals, having a thickness of 75  $\mu\text{m}$  and a density of 955  $\text{kg}/\text{m}^3$ .

Sample 2 was prepared by holding sample 1 in a large volume of liquid *p*-xylene at 50°C for one week before air drying to constant weight at room temperature.

Sample 3 was prepared by holding sample 1 in a large volume of liquid *p*-xylene for one week at 85°C, air drying at room temperature, and recrystallizing the dried film to a density of 955 kg/m<sup>3</sup> and thickness of 84 μm by quenching from 145°C into cold water.

Sample 4 was prepared by recrystallizing Rigidex Type 3 film, of nominal thickness of 50 μm, as supplied by B.X.L., to a density of 957 kg/m<sup>3</sup> by cooling from 145° to 50°C at 5°C/hr.

### Apparatus and Procedures

**Permeation Rate Measurements.** The apparatus and procedure have been described elsewhere.<sup>21</sup> The film was mounted over a sintered glass support in a glass permeation cell immersed in a thermostat. The upper surface of the membrane was exposed to permeant at constant activity, while the underside, or downstream surface, was exposed to high vacuum. When the permeant was in the liquid state, the liquid was contacted directly with the upstream surface of the membrane. The total pressure drop across the film during liquid permeation experiments could be varied by applying a nonpermeant (air) pressure of between 0 and 1 atm to the upper surface of the liquid in the permeation cell. Permeation rates were determined by weighing the permeate collected, over timed periods, in downstream cold traps. Measurements of permeation rate in the nonsteady period were made by collecting permeate for periods of at least 30 min. The minimum mass of permeate collected was 60 mg. Measured rates were identified with the middle of the collection period.

**Film Thicknesses.** These were calculated from the mass, density, and area of circular pieces of film.

**Densities.** A carbon tetrachloride/*p*-xylene gradient column was maintained at 25°C.

**Film Recrystallization.** In any study of diffusion through polymer membranes, it is obviously desirable that the membranes be of uniform structure throughout. The existence in some polyethylenes of a surface layer in which the spherulites are oriented perpendicular to the plane of the sheet<sup>22,23</sup> is fairly widely known. Eby<sup>23</sup> found that the diffusion coefficient of ethane in the 25-μm surface layer of a quenched polyethylene film was about twice as high as that in the central core. Kwei et al.<sup>24</sup> found that the thickness of the surface layer depended upon the materials between which the polyethylene was crystallized, and increased with the rate of crystallization.

These observations lead to the view that the formation of a surface layer is dependent on a surface nucleation mechanism, and it was therefore desirable that the films used in this work should be crystallized between materials that had no nucleating effect on polyethylene. One such material, readily available in film form, is poly(ethylene terephthalate).<sup>25</sup> Accordingly, the press used to form membranes was lined with 50-μm films of this polymer. The press consisted of two brass plates, each 9 cm in diameter and 1.5 mm thick, lined on their inner surfaces with 50-μm Melinex

film. The press was clamped around the circumference by four equally spaced fold-back bulldog clips. The film in the press was melted for 2 hr in a large evacuated steel vessel mounted in a thermostated ( $\pm 0.1^\circ\text{C}$ ) oil bath, after which the polymer and press were cooled at the desired rate. Membranes prepared in this press by quenching into iced water were microtomed and examined under a polarizing microscope. No surface layer was observed. Measurements of the specific viscosities of suitable samples indicated that the film preparation procedures resulted in no significant degradation of the polymers.

**Soluble Fraction.** This is defined as the percentage by weight of the whole polymer leached out during immersion for one week in a large volume of liquid *p*-xylene. Before and after this solvent pretreatment, the specimen was vacuum dried, either to constant weight or for two days, whichever period was the greater.

## RESULTS AND DISCUSSION

### Nonsteady State

Figure 1 shows permeation rate against time curves for *p*-xylene permeation at  $40^\circ\text{C}$  through several polyethylene films under nonpermeant pres-

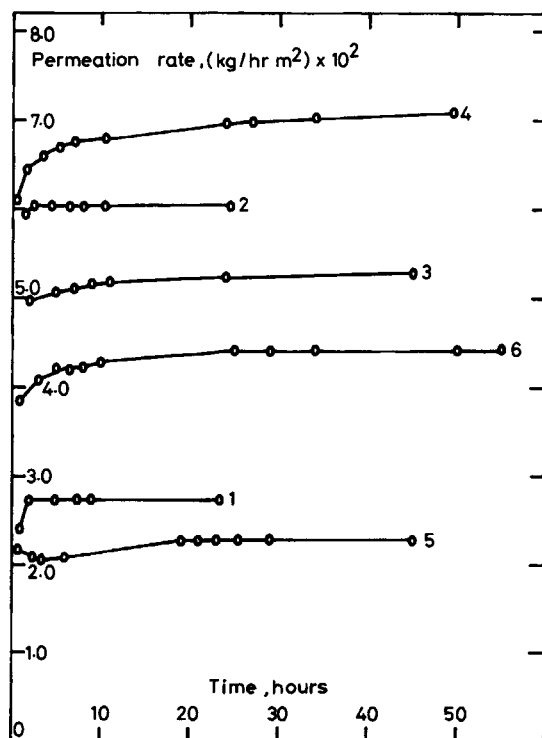


Fig. 1. Permeation rate vs. time curves for *p*-xylene and polyethylene film at  $40^\circ\text{C}$  (see Table I).

TABLE I  
Approximate Times Required for Establishment of Steady-State Permeation at 40°C for  
*p*-Xylene-Polyethylene System under a Range of Experimental Conditions

Experiment no.	Sample no. (see text)	Pressure of non-permeant, atm	Upstream permeant phase	Time to reach steady state, hr	Soluble fraction in <i>p</i> -xylene at 40°C, % w/w
1	3	1	liquid	<3	0.00
2	2	1	liquid	<3	0.00
3	1	1	liquid	>24	0.66
4	1	0	liquid	>48	0.66
5	1	0	vapor, 0.85 <sup>a</sup>	8-24	(0.00)
6	3	0	liquid	8-24	0.00

<sup>a</sup> Vapor activity =  $p/p_0$ .

sure differentials of zero and 1 atm. The experimental technique does not lend itself to accurate assessments of equilibration times, but rough values of this parameter are shown in Table I. The equilibration times show considerable variation, but it is possible to divide them into three groups. An apparently steady state was attained within 3 hr for experiments 1 and 2, within 8 to 24 hr for experiments 5 and 6, and in more than 24 hr for experiments 3 and 4. The variations between groups may be interpreted in terms of two effects:

(i) Loss of soluble material to the upstream solvent during permeation experiments in which the membrane was contacted with liquid *p*-xylene. (Loss of soluble material is shown elsewhere<sup>26</sup> to result in an increase in the sorptive capacity of the polymer, and thereby to cause an increase in the diffusion coefficient and permeation rate of a solvating molecule.) Such loss would be a relatively slow process, involving diffusion of low molecular weight polymer molecules.

(ii) Time-dependent buildup of the permeant concentration in the upstream surface of the membrane. This results from noninstantaneous relaxation of stresses induced in the underside of the film by absorption of solvent at the upstream surface. The stresses restrict radial expansion of the film, and such restrictions have been shown<sup>21</sup> to reduce the sorptive capacity of polyethylene.

Experiments 3 and 4, in which the equilibration time was longer than 24 hr, were those where the membranes contained material soluble in the permeant. Sample 2 film (obtained by removal of the soluble material from sample 1) reached steady state in less than 3 hr when permeated under a nonpermeant pressure differential of 1 atm (experiment 2). Under the same experimental conditions, sample 3, also devoid of soluble material, reached steady state within 2 hr (experiment 1). When the nonpermeant pressure differential was zero, however, sample 3 required 8-24 hr to reach steady state (experiment 6). In experiment 5, sample 1 could lose no

soluble material because the upstream permeant was in the vapor phase, but also required 8–24 hr to reach steady state.

A difference in equilibration time for the same sample when permeated under nonpermeant pressure differentials of zero and 1 atm may be explained as follows. In a previous paper,<sup>21</sup> it was stated that films permeating under a pressure differential of zero rose away from the support, whereas those permeating under a pressure drop of 1 atm did not. The inference is that the underside of the film, in which the permeant concentration is zero for either pressure drop, expands in the former case but not in the latter. In any event, the underside of the membrane will not expand to the same extent as the upper surface, because the membrane adopts a curved profile during permeation. Calculations indicate, however, that the difference in area between the upper and lower surfaces will be less than 1% for the present experiments.

The driving force for the biaxial expansion of the membrane during permeation under a zero nonpermeant pressure differential is the tendency for the polymer to swell to an equilibrium level in the presence of a swelling solvent. Expansion of the upstream surface of the membrane will be impeded by a retractive stress exerted by the lower, solvent-free layer of the membrane. Obviously, the extent to which the upper surface of the membrane is expanded will not become constant until the retractive stress exerted by the lower portion of the membrane is also constant with time. This means that the rate of attainment of a constant degree of expansion at the upstream surface will be dependent on the rate of stress relaxation in the membrane. Such relaxation processes have been reported to be very slow in semicrystalline polymers, the original stress decreasing at a uniform rate of 5–12% per decade of time in polyethylene. In films permeating under a zero nonpermeant pressure differential, the rate of attainment of a constant concentration of permeant in the upstream surface, and hence of a steady state permeation rate, will therefore be controlled by the rate of stress relaxation in the lower regions of the film. During permeation under a nonpermeant pressure differential of 1 atm., radial expansion of the membrane was not observed. Stress relaxation effects should thus be absent, and the rate of attainment of steady-state permeation should be much greater, as was observed.

### **Evidence for Stress Effects in Steady-State Permeation**

In the preceding section, it was concluded that the rate of relaxation of stress in the underside of a membrane could, in certain circumstances, control the rate of attainment of a steady-state flux across the membrane. Reported studies on stress relaxation in polyethylene indicate that an imposed stress does not decay to zero in any experimentally accessible time. For example, Turner<sup>27</sup> studied the rate of relaxation of an unspecified (small) stress imposed, presumably at ambient temperature, on polyethylenes covering a wide range in crystallinity. He found that the stress



decayed to about 20% of its original level in  $10^8$  sec (3 years). Becher and Rademacher<sup>28</sup> observed the rate of stress relaxation at 40°C, as a function of initial strains in the range 0.2 to 12%, in a polyethylene of crystallinity 0.74. They found that the rate of stress relaxation was independent of initial strain and that, after  $10^4$  sec, the stress had decayed to 40% of its original value. Even in the presence of swelling solvents, the rate of stress relaxation is very low, a characteristic time of 63 hr having been reported by Nisizawa<sup>29</sup> for polyethylene swollen to equilibrium with liquid *p*-xylene at 30°C.

It seems probable, therefore, that stresses induced in the lower portions of a membrane during the approach to steady-state permeation will not decay to zero in any experimentally accessible time. Measured steady-state permeation rates will correspond to a quasi-equilibrium under which the lower regions of the film will be exerting a retractive stress equal to about one third of the maximum stress attained during the nonsteady-state period. This retractive force will exert a compressive force on the upper regions of the film and may lead to an upstream permeant concentration  $C_0'$ , that is, below the equilibrium value  $C_0$ , for a freely swollen sample. The effect of the residual stress on the average free volume in the upper and lower portions of the membrane, and hence on its intrinsic sorption-diffusion characteristics, is likely to be small.

If incomplete relaxation of stress in the lower regions of the membrane does in fact lead to an upstream surface concentration that is below the equilibrium value, an experiment in which the magnitude of such stress is diminished should give rise to a higher permeation rate. The steady-state permeation rate for a single film of thickness,  $l$ , may be compared with that for a sandwich of films whose total thickness is  $l$ . In the sandwich, the upper surface of the uppermost film will be compressed only by the stress in the underside of the same film, where the permeant concentration will be greater than zero. The lower retractive stress so caused should manifest itself as a lower compressive stress on the upper regions of the film and, consequently, as a higher upstream surface concentration. The concentration gradient, and the permeation rate, across a sandwich of films should therefore be greater than across a single film of the same thickness.

Experimental data in support of this hypothesis are provided in Table II. The data refer to permeation of liquid *p*-xylene through membranes of sample 4 at 30°C. The slow cooling rate, 5°C/hr, used in the preparation of these samples would be expected to produce separate films of highly uniform structure, both in different parts of the same film and in different films. The densities all lay between 956.8 and 957.2 kg/m<sup>3</sup> when measured in the same column. The constancy of the permeability coefficient  $P$  for single films of different thicknesses (Table II, experiments 7-12) provides further evidence that the preparative technique produced films of uniform structure. The absence of any dependence of  $P$  on film thickness in these carefully prepared specimens contrasts with the previously mentioned data of other workers.

In Table II, the average permeability coefficient for single films may be compared with the values obtained for sandwiches of films. Since measurements did not begin until after at least 16 hr of permeation, they may be regarded as giving (apparent) steady-state values, the amount of soluble polymer being in any case very small (0.2% in *p*-xylene at 30°C). In experiments with sandwich films, a small quantity of air was unavoidably trapped between the separate films during assembly. Sudden application of vacuum to both parts of the permeability cell would have caused stretching of the upper films, and this was avoided by lowering the upstream pressure gradually from atmospheric to the permeant vapor pressure over a period of 6 hr.

TABLE II  
Liquid *p*-Xylene Permeability Coefficients at 30°C for Polyethylene Films, Sample 4

Experiment no.	Total thickness, $\mu\text{m}$	$P \times 10^6$ , <sup>a</sup> kg/hr	$P$ sandwich/ $P$ single film
7 (single film)	35.8	1.54	
8 (single film)	68.8	1.56	
9 (single film)	109	1.56	
10 (single film)	140	1.55	
11 (single film)	221	1.55	
12 (single film)	301	1.57	
		average	1.56
13 (2-film sandwich)	$2 \times 35.8 = 71.6$	1.63	1.04
14 (2-film sandwich)	$2 \times 68.8 = 138$	1.76	1.13
15 (3-film sandwich)	$3 \times 35.8 = 107$	1.82	1.17
16 (4-film sandwich)	$4 \times 35.8 = 143$	2.18	1.40

<sup>a</sup> Calculated on basis of dry film area and thickness.

It will be seen from Table II that  $P$  was higher for a sandwich of films than for a single film. (This is equivalent to saying that the actual permeability of a given sandwich was greater than that of a single film of similar total thickness.) Furthermore, the extent of the increase in  $P$  was enhanced by increasing subdivision within a fixed total thickness. This behavior agrees qualitatively with the arguments presented above. From experiment 16, in particular, it would seem that stresses in the underside of a membrane may so reduce the upstream surface concentration that the permeability coefficient and permeation rate are reduced by at least 40%. Further research would be required to establish the detailed concentration profiles through sandwich films in these very striking experiments.

In deriving integral diffusion coefficients from permeation data, it has been customary to assume that during steady-state permeation the concentration of permeant in the upstream surface of the membrane is equal to the concentration of permeant in an unstrained sample of the same polymer swollen to equilibrium with permeant at the same activity. In the present work, such an assumption would be clearly erroneous and would lead to gross underestimation of integral diffusion coefficients.

### The Effect of Soluble Material

Experiments <sup>21</sup> have shown that the soluble fraction of a particular polymer sample varies as expected with both solvent and temperature. For sample 1, the soluble fraction in *p*-xylene was 0.33% at 30°C, 0.66% at 40°C, and 1.06% at 50°C. Viscosity determinations before and after solvent pretreatment indicated that the soluble fraction consisted largely of low molecular weight polymer.

It was shown earlier that loss of soluble material during liquid permeation experiments leads to overestimation of steady-state permeation rates. The mechanism by which this increase occurs is discussed in detail elsewhere<sup>26</sup> and has been outlined in a previous section. Further evidence for losses of soluble material leading to an increase in permeability is provided by the data in Table III. Fluxes reported in this table were determined after 6 to 10 hr of permeation under a nonpermeant pressure drop of 1 atm. Soaking in *p*-xylene for three days at 40°C is seen to have had a negligible effect on the permeability of sample 3 (which contained no soluble material), but increased the permeability of sample 1 (0.66% soluble material) by about 10%. This increase is attributable to complete loss of soluble material from sample 1 during its long immersion in *p*-xylene.

TABLE III  
Liquid *p*-Xylene Permeation Rates at 40°C Before and  
After Soaking in *p*-Xylene for Three Days at 40°C

Experiment no.	Condition of film	Flux, (kg/hr m <sup>2</sup> ) × 10 <sup>2</sup>	
		Sample 1	Sample 3
17	New film	5.21	2.73
18	Film from expt. 17 soaked in <i>p</i> -xylene for 3 days, then dried before use	5.72	2.76

For the system investigated here, therefore, the maximum error in permeation rate attributable to soluble material would be in the vicinity of 10%. It should be emphasized, however, that the magnitude of the error will depend on the experimental conditions. The thickness, composition, and preparation of the film, the solvent, the temperature, and the permeation history are the prime determinants of these errors. These factors, together with the accuracy required in a particular study, will determine whether the soluble material should be removed from the polymer before the membranes are prepared.

### CONCLUSIONS

Sorption of a solvating vapor or liquid at the upstream side of a membrane induces stresses in the solvent-free lower regions of the membrane.

These stresses impede radial expansion of the membrane and thereby restrict sorption of permeant at the upstream surface. The rate at which the stresses decay controls the rate at which the upstream surface concentration approaches its steady-state value. Stress relaxation rates can be the major determinant of the time required for the system to attain a steady state of permeation.

In the case of polyethylene membranes, these stresses do not decay to zero in any experimentally accessible time. The residual stress may reduce the upstream permeant concentration, at a quasi-steady state, below that corresponding to equilibrium between the upstream permeant and the polymer. Diffusion coefficients calculated in the usual way, from apparently steady-state permeation rates and equilibrium solubilities, will be grossly underestimated as a result of these stress effects. The degree of underestimation will be a function of the stress relaxation characteristics of the polymer and the solubility of the penetrant in the polymer. It seems reasonable that such stress effects will operate, to varying extents, in all other semicrystalline polymers and, perhaps, in chemically crosslinked amorphous polymers.

When the upstream permeant is in the liquid phase, loss of material from the membrane to the upstream solvent may occur. Such losses lead to overestimation of liquid permeation rates compared to those of vapor. The magnitude of such errors, although dependent on polymer, temperature, and solvent, is likely to be fairly small in most instances.

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