

The Measurement of the Permeability of Polymer Membranes to Solvating Molecules

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Synopsis

Methods previously used to measure the permeability of polymer membranes to solvating liquids and vapors have been reviewed. Experiments with polyethylene and several liquids, notably *p*-xylene, indicate that the various methods are not necessarily equivalent. The medium over which the membrane is supported and, more particularly, the nonpermeant pressure differential during permeation are shown to influence the permeation rate. Failure to appreciate this latter fact is believed to be the cause of previously reported anomalies concerning the effect of preswelling on permeation rate and the difference in permeation rate between a liquid and its saturated vapor.

INTRODUCTION

The measurement of the permeability of polymer membranes to solvating liquids and vapors has received considerable attention in the past two decades. The aims of such measurements have been to collect information of relevance to the packaging industry, to develop liquid-liquid separation processes, or to study diffusion mechanisms in, and the morphology of, the membranes themselves.

The motivation for obtaining experimental data obviously influences the experimental procedure adopted. It is not surprising, therefore, that liquid and vapor permeation rates have been measured by nonuniform experimental techniques using inadequately characterized membranes. In consequence, direct comparison of results from different laboratories cannot be attempted with any confidence.

It was decided to examine the methods by which liquid and vapor permeation rates have been measured, with the aims of establishing their equivalence or otherwise of explaining, if possible, some reported anomalies and of assessing the significance of information derived from such measurements. For reasons which become apparent in subsequent sections, most of the new data refer to liquid penetrants. High-density polyethylene membranes were used exclusively, but the results will be applicable to all polymers.

For all published steady-state measurements of liquid solvent permeability, the apparatus was similar in principle to that used in this work and

described below. Liquid was placed in the upper compartment of a permeation cell, and the lower compartment was maintained at or near zero pressure of permeant. The flux was calculated from the measured rate of loss of solvent from the upstream side,¹⁻³ from the rate of collection of solvent in downstream cold traps,^{4,5} or from the rate of increase in permeant pressure on the downstream side of the membrane.^{6,7}

The total pressure difference across the membrane during liquid permeation was normally about 1 atmosphere,^{3,4,8,9} the solvent on the upstream side being open to the atmosphere and the downstream side being under high vacuum. In the experiments of Yasuda and Stannett,^{6,7} both sides of the membrane were maintained at a nonpermeant pressure of zero. In experiments conducted by the cup method,^{2,10} both the liquid surface on the upstream side and the downstream surface of the membrane were exposed to air at 1 atmosphere. Recently, Michaels et al.³ used an adaptation of the cup method to study the permeation of liquid *p*-xylene through polypropylene. Unfortunately, no comparative measurements were reported between this procedure and the method used previously^{1,4} by the same group of workers. The effect of the pressure drop across films during liquid permeation was investigated by Binnings et al.⁵ With the downstream pressure maintained at zero, the flux of liquid *n*-heptane through an unspecified (polyolefin?) film was found to be independent of upstream pressures in the range of 1 to 8 atmospheres of nitrogen.

Four groups of workers^{1,4,8,11} have stated that vacuum was applied to the underside of the films before addition of permeant to the upstream face. Baddour et al.¹ found that films equilibrated with *p*-xylene *before* the application of vacuum exhibited permeabilities to *p*-xylene approximately double those observed when vacuum was applied before introduction of the solvent. They also found that preswelling increased the tendency of the films to rupture, an observation supported by Sweeney and Rose.¹¹ The increased flux rate and the tendency to rupture were attributed to permanent structural damage in the film, caused by the rapid removal of imbibed solvent on application of vacuum to the underside of the film.

The existence of a pressure differential requires that the underside of the film be adequately supported during permeation. The supports employed include metal gauzes, metal and glass sinters, and filter paper resting on perforated metal plates. In converting measured fluxes to a unit area basis, the question arises as to whether the upstream area of film should be reduced to allow for the contact area between the membrane and its support. A correction of this type does not appear to have been applied previously in gas, vapor, or liquid permeability studies.

There has been debate in the literature regarding the relative permeation rates through polymer films of a liquid and its saturated vapor. For low-density polyethylene at 30°C, Michaels et al.⁴ claimed that the steady-state permeation rate of liquid xylene was more than ten times that of the saturated vapor. This result was attributed largely to reduced solubility of the vapor in the polymer. Long¹² has stated that the equilibrium solu-

bilities of saturated vapor and liquid are equal and that the lower permeation rate for saturated vapor was caused by a lower rate of replenishment of surface permeant during vapor permeation experiments. In a study of the rates of loss of ten liquids and their saturated vapors from aluminum cups sealed with low-density polyethylene membranes, Pinsky et al.¹⁰ found that liquid fluxes were between one and two times as great as corresponding vapor flux rates. Yasuda and Stannett,^{6,7} on the other hand, have reported good agreement between liquid and saturated vapor permeation rates for benzene, cyclohexane, and water through low-density polyethylene and rubber membranes. These results were obtained from an apparatus in which the nonpermeant pressure differential across the film was zero.

In summary, there appear to be inconsistencies in the literature with regard to the influence of membrane support, nonpermeant pressure differential, and preswelling on the permeation rate, and with regard to the relative permeation rates of a liquid and its saturated vapor. An understanding of these inconsistencies is a prerequisite for confidence in experimental permeation rate data and forms the basis for the work described in the following sections.

EXPERIMENTAL

Materials

Rigidex 50 polyethylene film of thickness 75 μm and density 955 kg/m^3 was supplied by B.P. Chemicals and used as received. With the exception of 99% *p*-xylene supplied by I.C.I. Ltd., all liquids were A.R. or spectroscopic grade and were used as received.

Permeation Rates

The apparatus used for measuring permeation rates for liquids and vapors is depicted schematically in Figures 1 and 2. The permeation cell (Fig. 1) consisted of two hemispherical glass compartments each having a 2-cm ground-glass flange (A). The membrane (M) was mounted over a flat porosity-3 sinter (S) having a diameter of 6.5 cm. The upper face of the sinter was flush with the flange in the lower compartment. A Teflon gasket (G), 0.05 cm thick, was placed on the upper surface of the membrane before

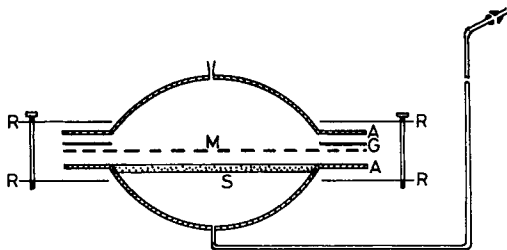


Fig. 1. Schematic diagram of permeation cell.

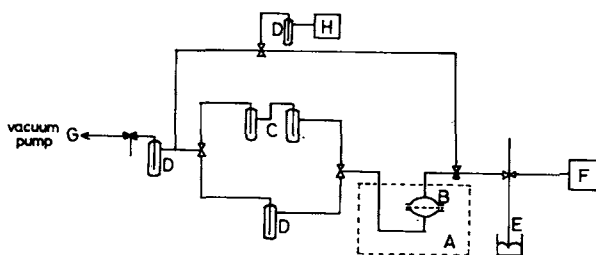


Fig. 2. Schematic diagram of permeation apparatus.

the two halves of the cell were clamped together by means of brass clamping rings (R).

The entire permeation cell (B, Fig. 2) was mounted in a thermostatted ($\pm 0.1^\circ\text{C}$) water bath (A), and the outlets from the upper and lower compartments were connected, via ground-glass ball-and-socket joints, to the vacuum pumping system. All connecting tubing was constructed of glass having a bore of 1 to 2 cm. The outlet from the lower chamber led through measuring traps (C) connected in parallel with "waste" traps (D) to the pumps (G). The traps were cooled in liquid nitrogen. The vacuum at the measuring gauge (H) was below 13 N/m^2 (0.01 cm Hg) during the experiments.

Liquid Permeation Experiments. Liquid was placed in the upper chamber of the cell, in contact with the film. Except where stated to the contrary, vacuum was applied to the underside of the film *before* the liquid was contacted with the membrane. The nonpermeant pressure above the liquid could be varied between zero and 1 atmosphere by means of the connection between the pumping system and the outlet from the upper chamber of the cell. Permeation rates were calculated from the mass (measured to $\pm 1 \text{ mg}$) of permeate collected in the first measuring trap over a timed ($\pm 5 \text{ sec}$) period. The mass of permeate collected in each run was in the range of 100 to 1500 mg. Permeation rates were measured 8–12 hr after solvent was first contacted with the film.

Vapor Permeation Experiments. The entire apparatus was outgassed for 2 to 4 hr before vapor, supplied at the required vapor pressure by the generator (F), was introduced to the upper compartment. When the saturation temperature of the vapor, T_s , was above ambient, all exposed glassware between the generator and the upper surface of the thermostat was maintained at a temperature about 20°C above T_s by means of insulated resistance wire wound externally. Permeation rates were measured after at least 20 hr of equilibration.

The vapor generator is shown schematically on Figure 3. Outgassed liquid (L) was placed in the inner tube (A), and circulating water from an external thermostat ($\pm 0.1^\circ\text{C}$) was pumped through the surrounding jacket (B). The liquid surface was broken continuously by a rotating magnetic stirrer (S). The vapor pressure of the liquid was calculated from the temperature

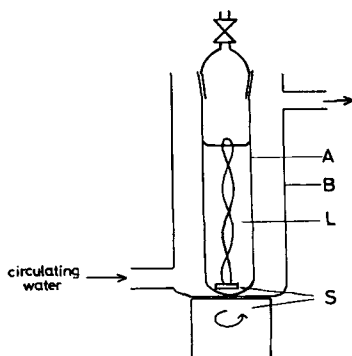


Fig. 3. Vapor generator.

of the circulating water and tabulated vapor pressure-temperature data for the permeants used. The vapor pressure of *p*-xylene as measured by means of the mercury manometer (E, Fig. 2) agreed very well with literature data.^{13,14} The vapor pressure-temperature data used for benzene was that of Fiock et al.¹⁵ reported by Timmermans.¹⁶

RESULTS AND DISCUSSION

The Membrane Support

Table I shows the permeation rates, at 30°C, of liquid *p*-xylene through the 75- μm Rigidex 50 film mounted over five different supports. The applied nonpermeant pressure differential was 1 atmosphere in all experiments. The results demonstrate that the choice of support can influence the permeation rate. The high rates observed for films mounted over screens having the larger mesh sizes (experiments 1 and 3) are at least partly attributable to stretching of the membrane during permeation. This is indicated by experiment 2, in which the film used for experiment 1 was re-permeated, after vacuum drying, while supported on the sinter used for experiment 4. Comparison of the permeation rates observed in experi-

TABLE I
Steady-State Permeation Rates for *p*-Xylene at 30°C Through 75 μm Rigidex 50
Films Mounted Over Various Supporting Media

Experiment	Description of support	Flux, ($\text{kg hr}^{-1} \text{m}^{-2}$) $\times 10^2$
1	30-mesh copper gauze ^a	3.96
2	porosity-3 glass sinter ^a	3.39
3	8-mesh polyethylene screen	6.15
4	porosity-3 glass sinter	2.66
5	filter paper (Whatmans No. 1)	2.67
6	120-mesh brass gauze	2.61

^a Conducted in numerical order, using the same membrane.

TABLE II
Permeation Rates for Liquid *p*-Xylene Through Polyethylene Film Mounted at
30°C Over Punctured Aluminum Sheets^a

Experiment	A_f , cm ²	A_s , cm ²	Flux, (kg hr ⁻¹ m ⁻²) × 10 ²	
			A_f basis	A_s basis
5	30.0	30.0 ^b	2.67	2.67
8	30.0	6.28	2.61	12.5
9	30.0	3.14	2.09	20.0
10	30.0	1.26	0.82	19.6
11	30.0	0.38	0.28	22.3

^a A_f = area of film exposed to solvent; A_s = area of holes in support. ^b Film mounted on filter paper, data from Table I.

ments 2 and 4 indicates that the film was permanently damaged during experiment 1.

The results of experiments 4, 5, and 6 were confusing in that they indicated that the effective areas of filter paper, porosity-3 glass sinter, and 120-mesh brass screen were very similar, although their physical appearance strongly suggested this was not so. Accordingly, further experiments were conducted, using supporting media of known effective area. These supports were prepared by punching varying numbers of uniformly spaced holes, each 1.8 mm in diameter, in 50- μ m aluminum sheet. The total area of these holes is denoted by A_s , while that of the film is A_f . All other experimental conditions were as described above, and the results are given in Table II. Comparing experiments 5 and 8, it is seen that a fivefold reduction in the free area of the support had a negligible effect on the total flux. Furthermore, as the ratio A_f/A_s increased from unity, the flux per unit free area of support at first increased rapidly and then leveled off (experiments 9, 10, and 11) at a value about eight times that appropriate to the same film when mounted over filter paper. These results can be interpreted in terms of a funneling effect, involving three-dimensional diffusion, by which the area of a hole in the membrane support is effectively enhanced by a factor whose limiting value is 8 under the conditions of these experiments. The magnitude of the enhancement obviously will depend, for a particular film, on the size of the holes and the distance between them and on the solvent power of the permeant.

The latter effect is clearly demonstrated by a study of the temperature dependences of the permeation rates through films mounted over filter paper, porosity-3 glass sinter, and the punctured aluminum sheet used for experiment 9 in Table II. The results are given on Figure 4. The apparent activation energy for permeation, $E_{F,a}$, through the film mounted over the aluminum sheet was strongly dependent on temperature and lower than that for a film mounted over filter paper. Comparison of the calculated apparent activation energies for permeation through films mounted over filter paper (52 kJ/mole) and over the glass sinter (47 kJ/mole) demon-

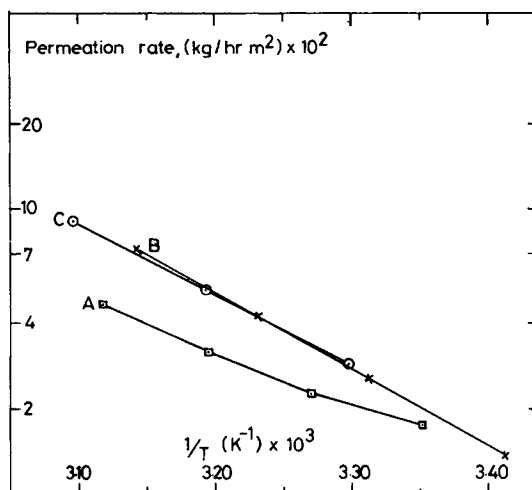


Fig. 4. Temperature dependence of liquid *p*-xylene permeation rates through 75 μm films mounted over punctured aluminium foil (A), filter paper (B), and glass sinter (C). (Nonpermeant pressure differential = 1 atm.)

strates also that the type of contact between the sinter and film gives rise to a small funneling effect.

For the purpose of studying unidirectional permeation, the support should therefore be one having only point contacts between film and support. The closest practical approach to this is a filter paper which provides a support composed of fibers of microscopic size. The use of other supports, such as sinters and fine metal gauze, may lead to erroneous results.

The Effect of Nonpermeant Pressure Difference

A film mounted in a permeation cell and held to its support by a pressure drop of 1 atmosphere may be significantly restricted as to radial swelling. The concentration of solvent in the upstream surface of the film will correspond to the equilibrium static swelling only if the potential radial swelling can be accommodated by increased swelling in the axial direction. Such a possibility seems to be precluded by the following experiments. Three cylindrical sections (approximately 10 mm in diameter and 20 mm long) were cut from a rod of Rigidex 50 polyethylene of density 955 kg/m^3 . Before immersion in *p*-xylene at 45°C , one piece was placed inside a tightly fitting brass tube so that expansion could occur only in the axial direction. The second piece was clamped at each end, thereby permitting only radial swelling. The third piece was not restricted. The rate of uptake of solvent decreased with increasing restriction, but for all blocks was virtually zero after four weeks, and the data refer to sorption for six weeks. The unrestricted block swelled isotropically and imbibed 10.7% by weight of solvent, of which 7.2% was attributable to radial swelling and 3.5% to axial swelling. These weight increases are only slightly lower than those

for the blocks restricted axially (8.1%) and radially (4.5%). It is concluded, therefore, that restriction of swelling in one or more directions substantially reduces the total solvent uptake and results in only a small increase in the solvent uptake in the unrestricted dimensions. The reductions in solvent uptake by the restricted blocks agree qualitatively with those predicted by Treloar's^{17,18} expressions (suitably modified for semicrystalline polymer) for the solvent swelling of strained, crosslinked rubbers. The predicted uptakes, 9.4% for axially restricted and 6.9% for radially restricted blocks, are somewhat higher than the experimental values, an observation in accord with the view¹⁹ that crystallites in semicrystalline polymers impose greater restrictions on noncrystalline chain segments than do chemical crosslinks in wholly amorphous polymers.

These results suggest that the mean concentration of a swelling solvent in a film during permeation under a high nonpermeant pressure drop will

TABLE III
Liquid Permeation Rates Under High and Low Nonpermeant Pressure Differentials^a

Permeant	Temp., °C	C, kg/kg	Flux, (kg hr ⁻¹ m ⁻²) × 10 ²		Ratio (ii)/(i)
			$\Delta p = 100$		
			$\Delta p = 100$ kN/m ² (i)	$\Delta p = 0$ (ii)	
dioxane	30	0.02	0.13	0.13	1.0
benzene	30	0.06	2.4	3.0	1.3
<i>p</i> -xylene	20	—	1.4	2.3	1.6
<i>p</i> -xylene	30	0.08	2.7	4.6	1.7
<i>p</i> -xylene	40	—	5.5	9.1	1.7
dekalin	30	0.11	0.24	0.78	3.2

^a C is the equilibrium solubility of permeant in the polymer at the permeation temperature, expressed on a dry polymer basis; Δp is the (approximate) nonpermeant pressure difference during permeation.

be lower than that in an unrestricted film. This should manifest itself as a lower solvent permeation rate in the restricted film, because reduced sorption at the upstream face will reduce, at constant film thickness, the mean concentration gradient across the film. A test of this hypothesis is provided by the data in Table III which shows the permeation rates of four liquids through the polyethylene membrane under each of the following pressure conditions: (i) the liquid above the film was exposed to the atmosphere ($\Delta p \approx 100$ kN/m²), (ii) the liquid above the film was maintained under its own vapor pressure ($\Delta p \approx$ zero).

The permeation rate for *p*-xylene through the unrestricted film ($\Delta p \approx 0$) was 60% to 70% higher than that through the restricted film ($\Delta p \approx 100$ kN/m²) at all temperatures examined. Furthermore, the ratio of permeation rates at 30°C increased with increasing permeant solvent power, as judged by the equilibrium solubility of the permeant in the membrane at the temperature of permeation. Such a trend would be expected on the

grounds presented above and is in line with the predictions of the theory of rubber elasticity.

Visual examination of the membranes during permeation also indicated a difference in swelling behavior between the two pressure conditions. Films permeated under a low nonpermeant pressure drop adopted a curved profile, whereas those permeated under the higher pressure difference remained flush with the support.

Preswelling

Table IV shows the effect of preswelling on *p*-xylene permeation rates determined under high and low nonpermeant pressure differentials.

TABLE IV
Permeation Rates Through Polyethylene Films Under High and Low Nonpermeant Pressure Differentials, With and Without Preswelling at 30°C^a

Experiment	Δp , kN/m ²	Preswelling ^b	Flux, (kg hr ⁻¹ m ⁻²) × 10 ²
12	100	no	2.8
13	0	no	4.6
14	100	yes	5.1
15	0	yes	5.0

^a Δp = Nonpermeant pressure differential. ^b Swollen in *p*-xylene for 16 hr before permeation started.

The film used for experiment 14 was preswollen while out of the permeation cell to prevent the radial swelling being taken up as creases on application of the pressure drop. The formation of these creases often results in film failure of the type reported previously.^{1,11} Radial expansion of the membrane, resulting from solvent sorption in the upstream surface, introduces stresses into the (virtually) solvent-free underside of the membrane. The influence of these stresses on permeation rates in the steady and nonsteady state is considered elsewhere.²⁰

Comparison of experiments 12 and 14 indicates that, for permeation under a pressure differential of 1 atmosphere, preswelling increases the flux by a factor of about 2, in accord with the observations of Baddour et al.¹ However, an effect of the same magnitude is not observed for permeation under a low pressure differential. In this case, the observed increase of about 10% is explicable in terms of losses of solvent-soluble material from the membrane during the preswelling period. The effects of solvent-soluble material on liquid permeation rates is considered in more detail elsewhere.²⁰

Of direct interest here is the result that the flux through preswollen films was independent of pressure drop (experiments 14 and 15). Therefore, the observed effect of nonpermeant pressure drop on permeation rates is attributable solely to a difference in swelling behavior.

Liquid and Saturated Vapor Permeation Rates

Figure 5 shows permeation rate–vapor activity (p/p_0) relationships for permeation of benzene at 45°C and *p*-xylene at 40°C and 30°C. Also shown are the liquid permeation rates determined at these temperatures under a zero nonpermeant pressure drop. Before plotting, these liquid permeation rates were reduced by 10% to allow for the overestimating effect of solvent-soluble material. These rates correspond, therefore, to those of the liquid solvents through films from which no solvent-soluble material had been removed and may be compared validly with the results of experiments in which the upstream permeant was in the vapor phase.

It is readily seen that extrapolation of the permeation rate (P) versus vapor activity curve to unit vapor activity leads to a value for P that is in very good agreement with the liquid permeation rate determined under a zero nonpermeant pressure drop. These results are in agreement with those of Yasuda and Stannett^{6,7} and are consistent with the thermodynamic argument that the activity, and hence equilibrium sorption, of saturated vapor and liquid are necessarily equal.

The failure of other workers to obtain agreement between the permeation rates of liquids and their saturated vapors may be explained, at least in part, by qualitative observations made during this work. It has been found that the rate at which a polymer film absorbs vapor emanating from a liquid surface, situated at some distance from the film, is drastically re-

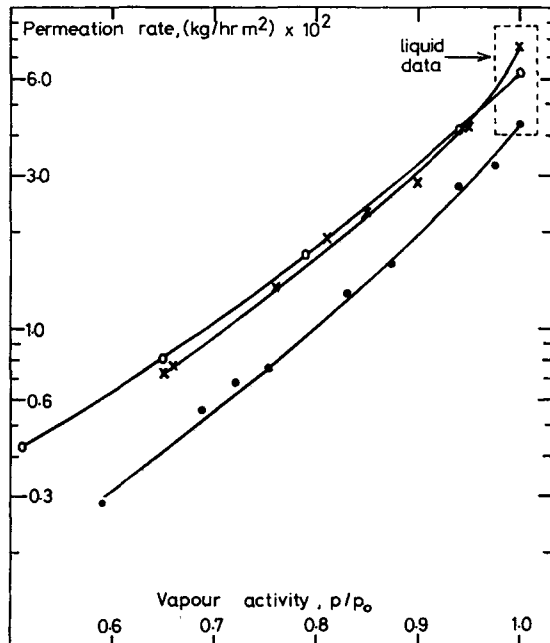


Fig. 5. Comparison of liquid and vapor permeation rates through 75 μm films for benzene at 45°C (O), *p*-xylene at 40°C (X), and *p*-xylene at 30°C (●).

duced by the presence of relatively small amounts (2–5 kN/m²) of air in the system. If air, or other nonpermeant vapor, were present in sufficient amount, diffusion of permeant to the membrane surface could become rate controlling. This would be particularly likely in the experiments of Pinsky et al.¹⁰ and, more recently, of Laine and Osburn²¹ in which no attempt was made to eliminate the air between the liquid and membrane surfaces.

CONCLUSIONS

The medium over which a membrane is supported during permeation experiments needs to be chosen with care. This is particularly important when the membrane is held to the support by a high applied pressure differential. Filter paper resting on a rigid porous material is recommended as a suitable support.

The diffusion coefficients of organic molecules in polymer membranes are frequently calculated from independently measured values of the steady-state permeability and equilibrium solubility of the permeant. The assumption implicit in these calculations is that the measured equilibrium solubility is equal to the concentration of permeant in the upstream surface of the membrane during permeation. The data presented here show clearly that this may not be so. The conclusions, valid for both liquid and vapor permeation, may be stated broadly as follows. When the permeant has a low solubility at the temperature of measurement, the nonpermeant pressure drop across the membrane is unimportant. When the permeant has an appreciable solubility in the polymer and a low vapor pressure at the temperature of measurement, the nonpermeant pressure drop should be zero. When the permeant has an appreciable solubility and high vapor pressure, the total pressure differential across the membrane should be maintained close to zero by means of a back pressure of "inert" gas; alternatively, the membrane could be preswollen in the permeant vapor.

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