Diffusion of Organic Solvents in Rubber Membranes Measured Via a New Permeation Cell

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SYNOPSIS

An experimental method based on a gravimetric permeation cell was designed and successfully used in measuring the diffusivities, permeabilities, and the breakthrough times of several rubber–solvent systems. The experimental results for four organic solvents: benzene, o-xylene, ethylbenzene, and chloroform in silicone, natural, and bromobutyl rubbers, respectively, are reported along with a description of the experimental method. The relations between the diffusivities measured by a permeation method and a sorption uptake method are discussed. This permeation cell provides a simple and reliable mean to determine the diffusional transport properties of a polymer–solvent system. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A quantitative knowledge of the diffusion rates for polymer–solvent systems is required for the design of the polymer membrane-based separation processes. For polymeric materials used as packaging and protective clothing, the breakthrough times of a given penetrant through the membrane as well as the diffusion coefficients are the most important data reflecting the barrier properties of the polymer. Various experimental methods are available for measuring polymer diffusion properties.[1,2] Few methods, however, combine the advantages of simplicity, reliability, and low cost in terms of the experimental measurements. In this contribution, we present an experimental method based on a gravimetric permeation cell that can be used to determine the breakthrough times and diffusion coefficients of polymer–solvent systems. Experimental results for benzene, o-xylene, and ethylbenzene diffusing in silicone, natural, and bromobutyl rubbers are also discussed.

EXPERIMENTAL

Permeation Cell

This method was developed during our study of the barrier properties of polymeric membranes. For the characterization of the barrier properties, one needs to determine the diffusion coefficients (D), permeabilities (P), and the breakthrough times (BRT) of a given penetrant (liquid or vapor) in a polymeric membrane. A simple and inexpensive experimental method that can yield reliable results was required, especially in the case where a large number of tests were needed. The method developed is centered on a gravimetric permeation cell, referred to as the G-cell. Figure 1 shows a photograph of the cell. This cell, completely made of Teflon, is basically a liquid container with a polymeric membrane sealed on its top. The use of Teflon ensures that the liquid in the cell does not react with the surfaces of the cell. The cell consists of two parts. The bottom part is essentially a liquid container. The inside diameter of the container is 1.79×10^{-3} m and its depth is about 1.0×10^{-3} m. The top part, which has the same inside diameter as the bottom container, helps to seal the polymeric membrane on the liquid container. The inside diameter of the cell accurately defines the permeation area of the polymeric membrane. The
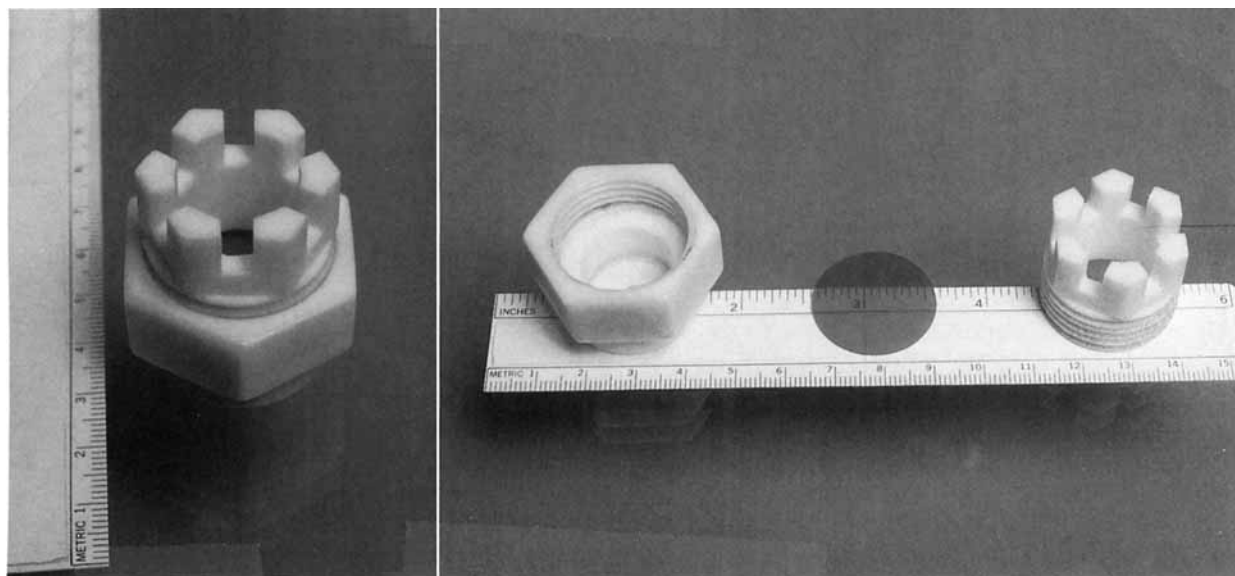
Figure 1   Photograph of the G-cell.

top part of the cell is cut in the form of a gear to reduce the weight so that a more sensitive weighting range of a balance can be utilized; and allow the permeated vapor to leave the cell quickly. This is especially useful for the liquid permeation case, where gear teeth are in contact with the balance pan. The two parts of the cell are screwed together with a polymeric membrane in between. The weight
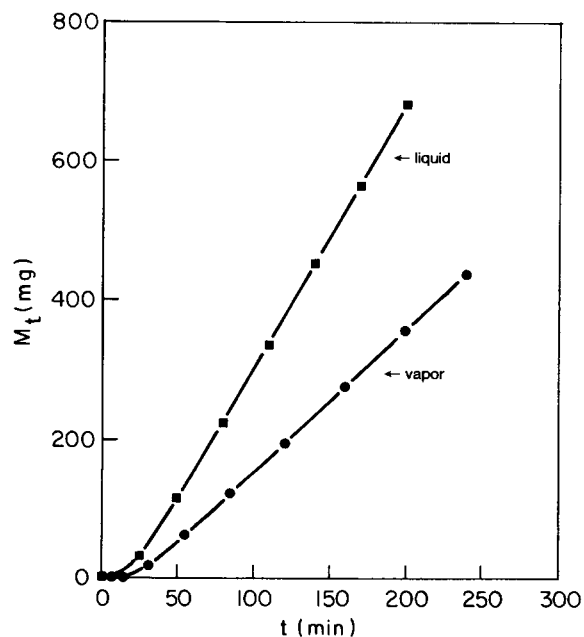

Figure 2   Permeation curves of p-xylene in natural rubber at 303 K.

of the cell is designed such that the total mass of the cell including the membrane and liquid to be within the most accurate range of the balance. The use of Teflon adds another advantage in this aspect compared to a cell made of steel.

The principle underlying the design of this diffusion cell is the following. As a penetrant liquid is placed inside the cell, there is a concentration gradient across the polymeric membrane because the outgoing side of the membrane is at zero penetrant concentration. The liquid (or vapor) inside the cell permeates the polymeric membrane and molecules that penetrated the membrane will evaporate to the air. The penetration is reflected by the decrease in the overall weight of the cell. The weight decrease as a function of time allows one to obtain the breakthrough time, and the diffusion coefficient as well as the permeability for a given polymer–penetrant system by a time-lag plot as the steady state of the permeation process is reached.

In an actual permeation experiment, the cell is dried by hot air to ensure there is no excess liquid or vapor on its surfaces. A "cleaned" empty cell shows no weight change on the balance in the sensitivity of 1×10^{-5} g. A polymeric membrane with a known thickness is cut into a 2.54×10^{-2} m diameter disk. The penetrant liquid is then put into the bottom container and the membrane is put on the top of the container. The two parts of the cell are quickly assembled to allow the polymeric membrane to seal the pathway of the liquid. The sealed

cell is immediately put on an analytical balance that is in a constant temperature chamber. In the present study, a Mettler AE 240 balance with an RS232C interface device is used for weighting. The mass of the cell as a function of time is recorded by a computer with a data acquisition program through this interface device. This balance has two weighting ranges: 205 mg with readability of 0.1 mg and 41 mg with readability 0.01 mg. The total weight of the cell is about 37 mg so that the most sensitive weight range can be used.

As mentioned earlier, this cell can be used to measure either vapor or liquid permeation through a polymeric membrane. When the gear teeth are resting on the balance, liquid is in contact with the membrane and liquid permeation can be measured. Otherwise, when the container in the cell is put upward, the saturated vapor of the solvent contacts the membrane and vapor permeation is measured. There was no condensate observed on the outside surface of the membrane in all the tests.

The organic liquids (with purity > 99%) used in this study were all purchased from the Aldrich Chemical Co. They were used without further treatment. The permeation cell and the balance were all kept in a constant temperature chamber during the experiment. A thermocouple inside the balance was used to monitor the system temperature.

Time-Lag Equation

It is well known that in a permeation test of a polymer–solvent system with a constant diffusion coefficient, for a polymeric membrane of original thickness l and initially free of solvent, the amount of solvent permeated through the membrane at time $t(M_t)$, is related to the permeation time t at the steady state as follows:

$$M_t = \frac{Dc_1}{l}\left(t - \frac{l^2}{6D}\right). \tag{1}$$

As M_t is plotted against t, the intercept of the steady-state straight line on the t-axis, or the time lag, $l^2/6D$, yields the diffusion coefficient of the polymer–penetrant system. If the diffusion coefficient is concentration dependent, the expression of the time lag involves the integration of the concentration dependence relation of the diffusion coefficient and the concentration profile across the membrane.[3] An accurate mathematical function for the concentration dependence of the diffusion coefficient for the organic liquids in these rubbers is not avail-

able. The reliability of diffusivity determinations is not improved by using the experimentally determined $D \sim c$ relation. Therefore, the present method determines the diffusion coefficient of a polymer–penetrant system using eq. (1) with the original thickness of the rubber membranes. This results in a diffusion coefficient of the solvent relative to the stationary polymer component (D). The relation of this diffusion coefficient with concentration in the system and with the diffusivities obtained from a sorption uptake method will be discussed in the next section.

RESULTS AND DISCUSSION

Figures 2–4 illustrate typical permeation curves for three rubber–solvent systems at 303 K measured by the G-cell method. Table I summarizes the diffusion coefficients and breakthrough times for all the rubber–solvent systems tested. In these figures and in Table I, "liquid permeation" and "vapor permeation" refer to the saturated liquid and saturated vapor constant contact with the challenging side of the membrane, respectively. The breakthrough time is defined as the time at which the first 1×10^{-5} g of the solvent is evaporated from the outgoing side of the membrane of thickness 0.75 mm, as indicated by the balance recording.
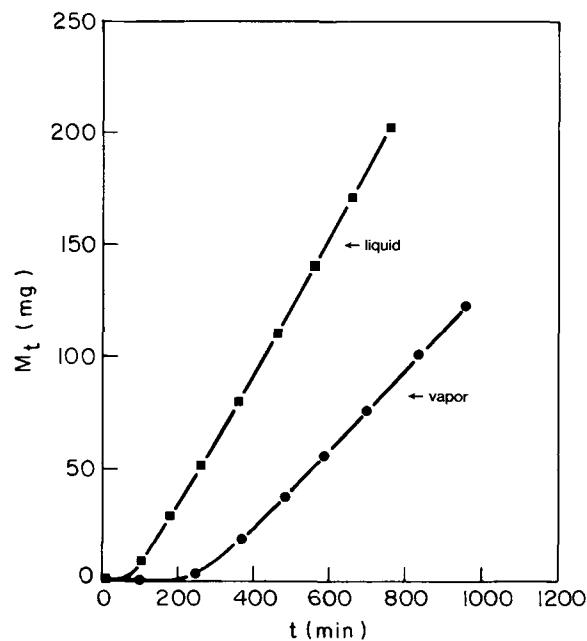

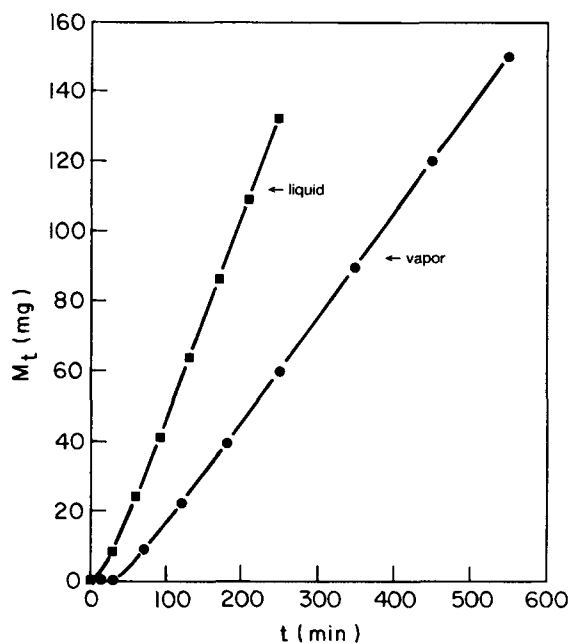**Figure 3** Permeation curves of benzene in butyl rubber at 303 K.

Figure 4 Permeation curves of o-xylene in silicone rubber at 303 K.

It can be seen from Figures 2–4 that all the permeation curves follow the same pattern: zero permeation before a breakthrough point followed by a transient permeation during which the amount permeated in a given time interval increases with time; after that a straight line appears, characterizing the establishment of a steady state. The breakthrough time and the steady state are well defined by these permeation curves. The diffusion coefficients and the permeabilities are obtained from the steady-state permeation lines. The permeabilities of these systems are given in Table II.

The results in Table I indicate that for the four solvents diffusing in the same rubber, the diffusion coefficients follow the order:

$$D_{chloroform} > D_{benzene} > D_{ethylbenzene} > D_{o\text{-}xylene}.$$

This is consistent with the effect of molecular geometry suggested in our recent study.[4] That is, for molecules that jump in a single unit during a diffusive displacement, as the three dimensions of a diffusant are combined according to a given weighting function ($d_{eff} = 0.6d_{min} + 0.3d_{mid} + 0.1d_{max}$), the molecule with a greater effective diameter shows a slower diffusion rate in a given polymer. For the diffusion in different rubbers, all the systems show that $D_{silicone} > D_{natural} > D_{bromobutyl}$. This may be related to the differences in fractional free volumes and polymer chain flexibilities in these rubbers.

Applying eq. (1) to the steady-state permeation curves results in the solvent diffusion coefficients relative to the stationary rubber component. This diffusion coefficient characterizes the mass transport process of the solvent molecules through a polymeric matrix with a given concentration distribution across the membrane. This is different from the conditions in a sorption uptake experiment where the diffusion proceeds in a system with an essentially uniform concentration, especially when the concentration interval in each successive sorption step is small. A comparison between the diffusion coefficients from the present permeation method and from a sorption uptake method shows that the diffusion coefficients from a permeation method correspond to that from a sorption method at a relatively low solvent concentration. Such correspondence for benzene, o-xylene, and ethylbenzene in natural rub-

Table I Diffusion Coefficients and Breakthrough Times

Solvents	State of Solvent Contacting Rubber	Natural Rubber $D \times 10^{-11}$ (m²/s)	Natural Rubber BRT (min)	Butyl Rubber $D \times 10^{-11}$ (m²/s)	Butyl Rubber BRT (min)	Silicone Rubber $D \times 10^{-11}$ (m²/s)	Silicone Rubber BRT (min)
Benzene	Liquid	6.3	9.0	3.7	38.5	23.0	1.0
	Vapor	5.2	16.0	1.0	71.0	9.8	4.0
o-Xylene	Liquid	4.9	26.0	1.3	76.5	9.7	1.5
	Vapor	1.7	78.0	.55	205.0	3.9	25.0
Ethylbenzene	Liquid	6.2	12.5	5.1	37.0	8.7	4.5
	Vapor	2.0	64.0	1.1	139.0	2.7	25.0
Chloroform	Liquid	8.7	9.0				

Values are for the solvent–rubber systems at 303 K measured via the G-cell.

Table II   Permeabilities of Rubber-Aromatics Systems at 303 K

	Permeabilities (mmol-cm/cm^2-s)		
	Silcone	Natural	Bromobutyl
Liquid permeation			
Benzene	2.27×10^{-5}	2.21×10^{-5}	7.04×10^{-6}
o-Xylene	1.41×10^{-6}	1.50×10^{-6}	1.34×10^{-6}
Ethylbenzene	2.73×10^{-6}	2.83×10^{-6}	2.37×10^{-6}
Vapor permeation			
Benzene	9.88×10^{-6}	1.14×10^{-5}	4.68×10^{-6}
o-Xylene	7.77×10^{-7}	1.11×10^{-6}	8.12×10^{-7}
Ethylbenzene	1.31×10^{-6}	1.53×10^{-6}	1.56×10^{-6}

ber is given in Table III. These results indicate that in a permeation test, although the overall solvent concentration in the system may be quite high (0.27–0.3 mass fraction in these rubber–aromatics systems), the solvent concentration near the outgoing membrane surface (where the mass fraction = 0) is very low. The constant mass flux in the steady state and the increase of the diffusion coefficient with concentration may result in a steady-state concentration profile concave to the t-axis. The diffusion coefficient obtained by the permeation method may be an averaged value over the concentration distribution across the membrane. The comparison shows, however, that the average is heavily weighted in the low concentration region of the membrane. The present result shows that this low concentration region is 5–15% for liquid diffusion and 1–5% for vapor diffusion of the membrane thickness near the outgoing side of the membrane. Therefore, although one can obtain an approximate overall solvent concentration at steady state by integrating the concentration profile across the membrane, the diffusion

Table III   Solvent Mass Fraction (ω_1) at Which $D_{\text{adsor}} = D_{\text{perm}}$ for Natural Rubber–Aromatics Systems

	ω_1		% of L	
Solvents	Liquid	Vapor	Liquid	Vapor
Benzene	0.075	0.062	7.29	5.83
o-Xylene	0.052	0.016	5.47	1.3
Ethylbenzene	0.15	0.020	15.0	3.2

% of L is the percentage of the membrane thickness adjacent to the outgoing membrane surface that has the ω_1 at which diffusivities from both methods match.

coefficients obtained from the permeation tests characterize the diffusion rate in the low concentration region. An approximate value for the mutual diffusion coefficient can be obtained using the solvent volume fraction in this low concentration region. This is given by

$$D_{\text{mut}} = D/(1 - \phi_1)^2 \qquad (2)$$

where ϕ_1 is the volume fraction of the solvent.

The proposed method produces realistic breakthrough time data. Such information is particularly important for polymers used as barrier materials, because the experimental conditions are very close to those in real world applications. The breakthrough times are mainly affected by the diffusion rate as can be seen from their relation to the diffusion coefficients of the systems. The liquid permeation tests indicate shorter breakthrough times than the vapor permeation case because of the larger concentration gradient in the former case. The higher solvent concentration in the liquid permeation case also contributes to the short breakthrough times through the concentration dependence of the diffusion coefficient on concentration (usually by an exponential function for polymer–organic systems).

The permeabilities given in Table II were also obtained from the steady-state permeation curves. In the case of permanent gas permeation, the absolute pressure difference of the gas is the driving force for permeation. In the present tests, the saturated liquid or vapor is contacting the challenging side of the membrane and the concentration in the outgoing side is essentially zero. It is the relative vapor pressure (P/P_s) or the relative density of the solvent that characterizes the driving force. The permeabilities in Table II represent the amount of

solvent (mmol) that permeates through a unit area (cm^2) of membrane of unit thickness (1 cm) per second under the driving force of a saturated liquid (for liquid permeation) or a saturated vapor (for vapor permeation). Table II shows that for a given system, the liquid permeation always has a greater permeability than the vapor permeation as a result of greater driving force. However, the difference in permeabilities for a given solvent in different rubbers is not as clear as in the case of the diffusion coefficients. This reflects the effect of solubilities of these solvents in different rubbers. Table IV lists the solubilities of the three aromatic solvents in different rubbers as obtained by liquid immersion tests. It is evident that the solubilities of a given solvent in the three rubbers are quite different. For the aromatics, the solubilities in the silicone rubber are the lowest, those in bromobutyl rubber are the highest, with those in natural rubber in between. This is the reverse of the order in the diffusion coefficient values. As a result, mixed values for solubilities are observed because $\bar{P} = \bar{D} \times \bar{S}$.

The mass transport properties of water in silicone rubber were also measured using the G-cell. Although water molecules are very small, which should have a relatively high diffusion rate according to molecular geometry considerations, no breakthrough was observed during a period of 48 h for the liquid on an 0.8-mm silicone rubber membrane. This is due to very small solubilities of the water–silicone rubber system. The solubility of this system is also given Table IV. The large differences in the permeabilities of the organic solvents and water in silicone rubber membranes indicates the great potential of silicone rubber for separating organic solvents from contaminated waters.

CONCLUSIONS

1. A simple experimental method based on a gravimetric permeation cell was presented. This method can be used to make reliable measurements of diffusion coefficients, permeabilities, and breakthrough times of various liquid or vapor solvents through polymeric membranes of various thickness (from 0.01 to 3 mm).
2. The diffusion coefficients, permeabilities, and breakthrough times of benzene, ethylbenzene, o-xylene, and chloroform in silicone, natural, and bromobutyl rubbers at 303 K were determined.

Table IV   Solubility Data at 298 K

Solvents	Solubilities (g Solvent/ g Dry Rubber)		
	Silicone	Natural	Bromobutyl
o-Xylene	0.9605	1.6837	2.1256
Ethylbenzene	0.9401	1.5217	1.7158
Water	0.0014		

3. The permeation method yields the diffusion coefficient of a polymer–solvent system at low solvent concentrations. This concentration is an average concentration in approximately 10% of the total membrane thickness adjacent to the outgoing surface of the membrane. This helps to interpret the relation between the diffusion coefficients obtained from a permeation method and a sorption uptake method.
4. The significant difference in permeabilities of organic solvents and water in silicone rubber as obtained in this study indicates the great potential of applications of silicone rubber membranes in the separation of organic components from water.

NOMENCLATURE

BRT	Breakthrough time (min)
c	Solvent concentration in a polymer–solvent system ($mmol/cm^3$)
D	Diffusion coefficient (m^2/s)
D_{adsor}	Diffusion coefficient measured by adsorption method (m^2/s)
D_{mut}	Mutual diffusion coefficient (m^2/s)
D_{perm}	Diffusion coefficient measured by permeation method (m^2/s)
d_{eff}	Effective molecular diameter (m)
l	Polymer membrane thickness (m)
M_t	Amount of solvent permeated through the membrane (g)
$P, \bar{P}$	Permeability, average permeability ($mmol\text{-}cm/cm^2\text{-}s$)
$S, \bar{S}$	Solubility, average solubility (g solvent/g rubber)
t	Time (min)
ω_1	Mass fraction of solvent in a polymer–solvent system
ϕ_1	Volume fraction of solvent in a polymer–solvent system

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