

Sorption and Transport of Benzene in Poly(ethylene Terephthalate)

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Synopsis

The kinetics and equilibria of benzene sorption in poly(ethylene terephthalate) were measured at 40°C, 50°C, and 60°C, with benzene activities ranging from 0.02 to 0.3. At most experimental conditions, diffusion was found to be Fickian; however, evidence of non-Fickian transport was found at the highest activity levels. Values of the diffusion coefficient of benzene range from 10^{-14} cm²/s at 40°C to 10^{-12} cm²/s at 60°C in the limit of low concentrations. Nonlinear isotherms observed for benzene sorption were successfully interpreted in terms of the dual mode model for sorption in glassy polymers, whereby the sorbed penetrant exists as two populations: one sorbed according to Henry's law and the other following a Langmuir isotherm. Non-Fickian transport data were correlated with a model that superimposes diffusion of both the Henry's law and Langmuir populations (the "partial immobilization" model) upon first-order relaxation of the polymer matrix.

INTRODUCTION

A common method of monitoring ambient air pollution levels involves trapping an air sample in a bag made of a relatively impermeable glassy polymer, and subsequently subjecting the sample to gas chromatographic analysis. The fraction of the collected sample which is lost by sorption into the bag wall is seldom considered, due in part to a scarcity of data regarding the sorption and transport characteristics of pollutants in bag materials. The focus of the present study is the demonstration of a method for obtaining such data. Benzene was chosen as the representative pollutant and poly(ethylene terephthalate) (PET) was selected as the representative sample bag material.

The study of the sorption and transport of large condensable penetrants such as benzene in glassy polymers is complicated by the prohibitively long times that are often required to reach equilibrium at ambient and near ambient temperatures. To overcome this problem, a gravimetric sorption rate measurement technique was adopted,¹ using extremely thin film samples of PET. Even under these conditions, transport rates at ambient temperatures were too slow to permit the acquisition of the desired data in a reasonable period of time. Consequently, data were obtained at temperatures in the range 40–60°C. The resulting sorption, transport, and equilibrium parameter values may be extrapolated to ambient temperatures with a reasonable degree of accuracy.

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EXPERIMENTAL

Materials. All PET film samples used in this study, other than 1.0-mil films, were provided by the DuPont Co. The 1.0-mil films were National Bureau of Standards reference materials. The benzene used was obtained from Fisher Scientific Co., and contained less than 1% impurities. The as-received benzene was frozen in liquid nitrogen, placed under vacuum for several minutes, and then allowed to thaw. Three such freeze-thaw cycles were carried out to remove any noncondensable contaminants before the benzene was used in the sorption experiments.

Sorption Apparatus and Procedure. The sorption system used was a quartz spring balance enclosed in a fluid-jacketed glass cell. Details of the cell construction and operating procedures are given by Felder et al.² The polymer films were degassed for 24–48 h. before use.

Koros et al.³ have shown that the previous history of glassy polymers can affect their sorption characteristics. To insure consistent sorption behavior and avoid possible anomalies due to slow relaxation, the PET samples were equilibrated at the highest benzene activity to be studied and thoroughly evacuated before any sorption data were taken. Experiments at 60°C indicated that such pre-swelling protocols were not necessary at the low activities used in this study, but they were, nevertheless, followed as insurance against any subtle conditioning effects which might otherwise confound results at the lowest experimental temperature. Runs were carried out at 60°C, 50°C, and 40°C, in that order.

Sorption runs were performed in an "integral" fashion. After the preconditioning treatment discussed above, the films were systematically exposed to lower benzene activities, and the sorption kinetics and equilibria were measured. Equilibrium was assumed to occur when no uptake of penetrant by the film was observed for at least 96 h. Desorption data were also routinely obtained following each sorption run, and care was taken that all the benzene sorbed was subsequently desorbed before further experiments were performed.

SORPTION EQUILIBRIA

Data and Model. Sorption isotherms for benzene in PET are shown in Figure 1. The isotherms are concave to the pressure axis. This behavior may be interpreted in terms of the so-called dual mode sorption model, which postulates that the sorbed penetrant exists in two populations: one dissolved according to Henry's law (concentration = C_D), and the other held in unrelaxed gaps between polymer chains and sorbed according to a Langmuir isotherm (concentration = C_H). This model has been found by several authors to provide a satisfactory description of the equilibrium sorption of gases and low activity vapors in glassy polymers.⁴⁻⁷ Vieth⁸ gives a detailed review of systems described by the dual sorption model.

The dual mode sorption isotherm is given by

$$C = C_D + C_H = k_D p + C'_H b p / (1 + b p) \quad (1)$$

where k_D [cc (STP)/cc polymer·atm] is the Henry's law constant, p (atm) is the penetrant partial pressure at equilibrium, b (atm⁻¹) is the affinity constant of

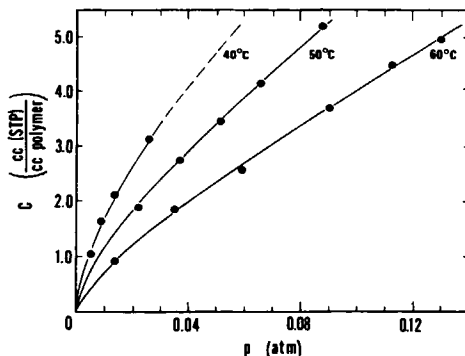


Fig. 1. Sorption isotherm for benzene in 0.10 mil poly(ethylene terephthalate).

the gas for the Langmuir sites, and C'_H [cc (STP)/cc polymer] is the maximum capacity of the polymer for the penetrant in the Langmuir sorption mode.

The data shown in Figure 1 were fit by nonlinear regression, using a Fletcher-Powell function minimization algorithm⁹ to minimize the sum of squares of the unweighted residuals at each temperature. The model parameters determined in this manner are listed in Table I. The solid curves shown in Figure 1 were generated from eq. (1) using these parameters.

Henry's Law Constant and Langmuir Affinity. The values of the Henry's law constant k_D and the Langmuir affinity constant b , shown in Table I, are much larger than corresponding values found for CO₂ in PET over the same temperature range.¹⁰ This seems reasonable, since at 50°C, CO₂ is at a reduced temperature of 1.06 while benzene has a reduced temperature of only 0.57. Clearly, benzene has a much greater tendency than CO₂ to exist in a condensed phase due to its significantly higher critical temperature.

The solubility parameters b and k_D are each amenable to standard van't Hoff analysis, as shown in Figure 2. The van't Hoff formulas determined by fitting the data are given in Table I. The slopes of these semilogarithmic plots multiplied by $-R$, where R is the gas constant, equal the enthalpy changes for transferring one mole of benzene from the gas phase into the dissolved Henry's law (ΔH_D) and Langmuir (ΔH_b) populations, respectively. The values of ΔH_D and ΔH_b determined in this manner are -32.8 kJ/mol and -34.1 kJ/mol. The enthalpy of benzene in the Henry's law mode is thus approximately 1300 J/mol

TABLE I
Dual Mode Sorption Parameters for the PET/Benzene System

Temp (°C)	k_D^a [cc (STP)/cc polymer-atm]	C'_H [cc (STP)/cc polymer]	b^b (atm ⁻¹)	$K^c = C'_H b / k_D$
40	67.33	1.73	150.1	3.85
50	44.42	1.42	100.2	3.20
60	31.57	1.00	68.2	2.17

^a $k_D = 2.275 \times 10^{-4} \exp[3945/T (\text{°K})]$, $\Delta H_D = -32.8$ kJ/mol.

^b $b = 3.079 \times 10^{-4} \exp[4102/T (\text{°K})]$, $\Delta H_b = -34.1$ kJ/mol.

^c $C'_H = 0.043 [83.0 - T (\text{°C})]$.

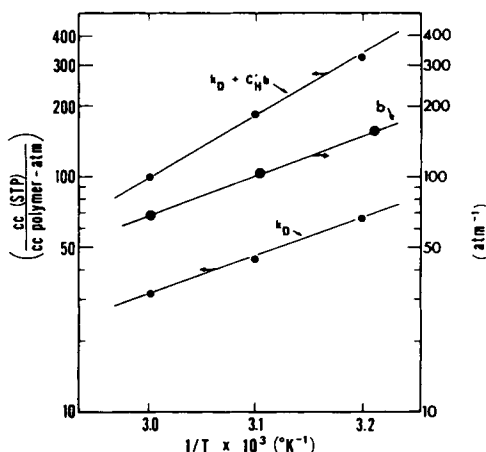


Fig. 2. Van't Hoff plots of the true Henry's law equilibrium sorption parameter (k_D), the Langmuir affinity parameter (b), and the apparent Henry's law parameter ($k_D + C'_H b$) for benzene in poly(ethylene terephthalate).

higher than that of benzene sorbed in the molecular gaps between chains. The difference is less than that reported by Koros et al.¹⁰ for CO₂ in PET (5020 J/mol).

The latter results may be interpreted in light of a suggestion of Michaels et al.⁴ that more energy is needed for a molecule to enter the Henry's law mode since separation of polymer chains is needed for dissolution by this mechanism, whereas molecules in the Langmuir mode sorb in preexisting gaps. This accounts for the positive difference between ΔH_D and ΔH_b . The argument also implies that as the size of the penetrant molecule increases, the energy needed to sorb into the gaps should increase correspondingly, since an expansion or coalescence of existing gaps may be necessary to accommodate the larger penetrant molecules. Thus, the magnitude of the difference in enthalpies of the sorbed molecules in each environment should decrease with increasing molecular size, in agreement with the results given above.

The apparent Henry's law constant k_D^* , which equals the low-pressure limiting slope of the sorption isotherm, is from eq. (1) equal to $k_D + C'_H b$, and can also be represented by an effective van't Hoff expression, as shown in Figure 2. The apparent sorption enthalpy at low pressures, ΔH_D^* , was determined to be -51.2 kJ/mol. This quantity does not have a simple physical interpretation, since it includes temperature-dependent contributions from C'_H which are not truly energetic in nature.¹⁰

Langmuir Capacity. Information about the "gaps" in the polymer in which the Langmuir population is sorbed is provided by the magnitude and temperature dependence of the Langmuir capacity C'_H . Koros¹¹ proposed that regions of localized lower density are frozen in glassy polymers when the polymers are quenched to a state below T_g from the rubbery region. They further asserted that the difference between the actual specific volume of the glass, v_g , and the limiting specific volume, v_l , obtained by extrapolating the v vs. T curve from the rubbery region through T_g , provides a direct measure of the volume of the gaps

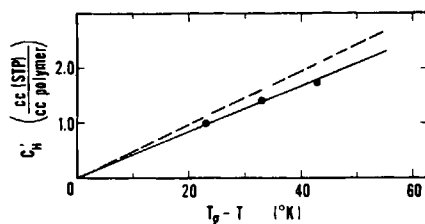


Fig. 3. Comparison of experimentally measured points of the Langmuir capacity parameter, C'_H , with predicted values (.....) calculated using eq. (2).

between chain segments. The latter quantity is in turn related to the Langmuir capacity, as follows:

$$C'_H = \frac{[(v_g - v_l)]}{v_g} \rho^* \quad (2)$$

where ρ^* is the molar density of the sorbate at the saturation point of the Langmuir isotherm. The amount of unrelaxed volume, and thus C'_H , should decrease with increasing temperature, finally disappearing near the glass transition.

If the specific volumes of the polymer in both the rubbery and glassy regions each vary approximately linearly with temperature, then, from eq. (2), over a reasonably small temperature interval, C'_H should vary linearly with the difference between the actual temperature T and the glass transition T_g .¹⁰ A plot of C'_H vs. $(T_g - T)$ for benzene in PET, shown in Figure 3, confirms this expectation. The equation of the line that fits the data is given in Table I.

Values of C'_H were predicted from eq. (2), using the density of pure liquid benzene for ρ^* , values for dilatometric expansion coefficients for PET from the literature,¹² and a value $T_g = 83^\circ\text{C}$ obtained from differential scanning calorimetry measurements.¹³ The results are shown as the dotted line along with the measured values in Figure 3. The agreement between the predicted and measured values is gratifying.

SORPTION RATES

Uptake Rates and Diffusion Coefficients. Figures 4 and 5 show plots of the cumulative mass of benzene sorbed, $M_t(t)$, normalized by the uptake at equilibrium, M_∞ vs. \sqrt{t} for a 1.0-mil and a 0.1-mil film, respectively. Effective Fickian diffusion coefficients were determined from the formula

$$\bar{D} = 0.04919 h^2/t_{1/2} \quad (3)$$

where h is the polymer thickness and $t_{1/2}$ is the time required for the sorption of half the equilibrium uptake of penetrant.¹ The coefficients determined in this manner were substituted into the solution of the diffusion equation for sorption into flat membranes¹⁴:

$$M_{t,F} = M_{\infty,F} \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-\bar{D}(2n+1)^2\pi^2t/h^2]}{(2n+1)^2} \right\} \quad (4)$$

The results are shown as the solid curves through the data in Figures 4 and 5.

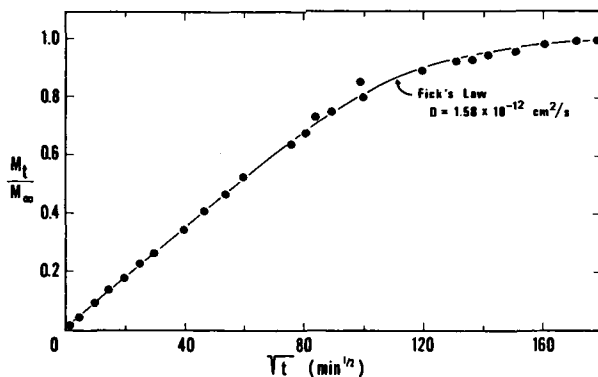


Fig. 4. Sorption kinetic run for benzene sorption in 1.0 mil thick poly(ethylene terephthalate) at 60°C for a vapor activity equal to 0.25; $l = 1.0$ mil.

The model of purely Fickian diffusion is seen to provide an excellent representation of the sorption of benzene into a 1.0-mil PET film at 60°C, but deviations from this ideal model appear for the thinner (0.1-mil) membrane at the same and a lower temperature, even at lower vapor activities. For the thin film, the Fickian model describes the data well only at 40°C for the lowest activity studied ($p/p_0 = 0.02$).

The above observations suggest that a relaxation process is superimposed on the Fickian diffusion process. At very low vapor activities, penetrant-induced relaxations are relatively minor, explaining why the sorption curves are described most effectively by the Fickian model at low activities. In fact, any small relaxational effects present in the low activity case ($p/p_0 = 0.02$) at 40°C cannot be distinguished from experimental error.

This interpretation is consistent with the ability of the pure Fickian diffusion model to correlate the kinetic data for the thicker (1.0-mil) film. Since the diffusion and relaxation processes superimpose (no distinct two-stage sorption is observed) in the 0.1-mil film, the characteristic relaxation time of the polymer under the conditions studied is presumably of the same magnitude as the characteristic diffusion time (h^2/D) for this film. For the thick film, the characteristic diffusion time is 100 times larger than that of the thin film, while the characteristic relaxation times are about the same for both films. It follows that the diffusion process in the thick film is roughly 2 orders of magnitude slower than the relaxation process, so that a model which neglects relaxation effects in this film should provide a good correlation of sorption kinetic data, as is, in fact, the case.

Enscore¹⁵ measured rates of sorption of *n*-hexane in polystyrene microspheres, and found that the uptake after long times proceeded more slowly than the Fickian model predicted. The measured responses were similar to those observed in most of the sorption runs for the thin film presented in Figure 5. Enscore analyzed his data in terms of a phenomenological model proposed by Berens and Hopfenberg¹⁶ that permits separation of diffusion and relaxation effects. A similar approach will be used in the present study for the thin film samples.

Berens-Hopfenberg Model. According to the Berens-Hopfenberg model, penetrant uptake can be described as the linear superposition of a Fickian dif-

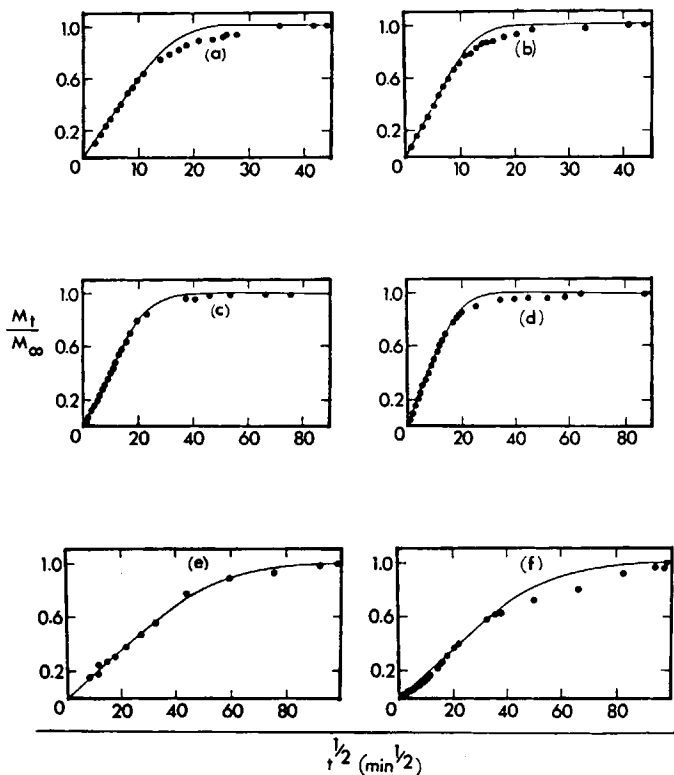


Fig. 5. Sorption kinetic runs for benzene in 0.10 mil PET under a variety of conditions. The lines are the Fickian model [(eq. (4))] using diffusion coefficients estimated from the half-time formula [(eq. (3))]: (a) $p/p_0 = 0.07$, 60°C ; (b) $p/p_0 = 0.22$, 60°C ; (c) $p/p_0 = 0.06$, 50°C ; (d) $p/p_0 = 0.30$, 50°C ; (e) $p/p_0 = 0.02$, 40°C ; (f) $p/p_0 = 0.11$, 40°C .

fusion term and a first-order relaxation term.¹⁶ The total uptake at a given time is given by

$$M_t = M_{t,F} + M_{t,R}, \quad (5)$$

where $M_{t,F}$ is the amount that would be sorbed by the Fickian process proceeding alone, given by eq. (4), and $M_{t,R}$ is the corresponding term for the relaxation process. The uptake due to relaxation is

$$M_{t,R} = M_{\infty,R}[1 - \exp(-kt)] \quad (6)$$

where k is a first-order rate constant for the relaxation process, and $M_{\infty,R}$ represents the equilibrium uptake due to relaxation.

Substitution of eqs. (4) and (6) into eq. (5) and division by the total quantity of dissolved penetrant at equilibrium, M_∞ , yields

$$\frac{M_t}{M_\infty} = \varphi_F \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-\bar{D}(2n+1)^2\pi^2t/h^2]}{(2n+1)^2} \right\} + (1 - \varphi_F)[1 - \exp(-kt)] \quad (7)$$

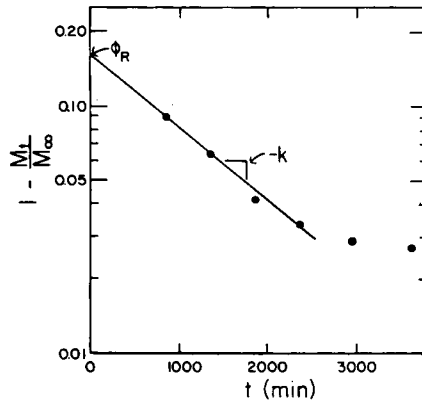


Fig. 6. Illustration of approximate graphical method for evaluation of the Berens-Hopfenberg model parameters for use in eq. (7); $p/p_0 = 0.11$, 60°C .

where

$$\varphi_F = M_{\infty,F}/M_\infty \quad (8)$$

is the fraction of the equilibrium sorption contributed by the diffusion process.

The expression of eq. (7) is seen to contain three adjustable parameters: the effective diffusion coefficient \bar{D} ; the relaxation rate parameter k ; and the fraction of the equilibrium sorption due to diffusion, φ_F . The values of k and φ_F are first estimated by analyzing the uptake data at times sufficiently long for the summation in eq. (7) to be negligible. When this is the case, the simplified equation may be rewritten as

$$1 - M_t/M_\infty = (1 - \varphi_F) \exp(-kt) \quad (9)$$

In view of eq. (9), it might be anticipated that a semilogarithmic plot of $(1 - M_t/M_\infty)$ vs. t would be linear over some intermediate range of times—long enough for the summation of eq. (7) to be negligible, but not long enough for the closeness of the approach to equilibrium to make the data imprecise. The slope of the line would equal $-k$, and the intercept would equal $(1 - \varphi_F)$. A representative plot of this type is shown in Figure 6. The plot is indeed close to linear for times in the range 800–2000 min, thus allowing the estimation of k and $\varphi_R = 1 - \varphi_F$.

Once the two relaxation process parameters have been estimated, it is a straightforward matter to estimate the effective Fickian diffusion coefficient \bar{D} . The asymptotic limit of the uptake due to diffusion alone is by definition φ_F . If $t_{1/2}$ is the time required for the fractional uptake (M_t/M_∞) to reach half of this limiting value, the effective diffusion coefficient \bar{D} may be estimated from eq. (3).

While the above procedure yields reasonable estimates of the three parameters of the Berens-Hopfenberg model, its neglect of the interactions between the diffusion and relaxation processes must inevitably lead to estimation errors. Improved parameter estimates were obtained by applying nonlinear regression to the sorption rate data, simultaneously determining the values of k , φ_F , and

TABLE II
Optimum Parameter Values of D , k , and φ_F Determined from Experimental Data for Benzene Sorption in PET

p/p_0	$D \times 10^{13}$ (cm ² /s)	$k \times 10^6$ (s ⁻¹)	φ_F
$T = 40^\circ\text{C}$			
0.02	0.67	—	1.00
0.06	1.70	0.36	0.51
0.11	2.00	0.36	0.44
$T = 50^\circ\text{C}$			
0.06	4.67	1.31	0.85
0.10	5.04	1.43	0.85
0.14	5.70	1.43	0.79
0.19	5.90	0.90	0.85
0.25	6.50	1.00	0.87
0.30	6.80	0.90	0.88
$T = 60^\circ\text{C}$			
0.03	10.70	4.04	0.89
0.07	12.0	3.20	0.80
0.11	14.5	4.59	0.84
0.17	14.9	3.57	0.65
0.22	15.5	2.05	0.88

\bar{D} . A pattern search (Hooke-Jeeves) function minimization algorithm⁹ was used to determine the parameter values that minimized the unweighted sum of squares of residuals between the data points and the predictions of eq. (7).¹³ The procedure described in the preceding paragraphs was used to obtain the initial parameter estimates provided as input to the search routine, and convergence was usually quite rapid.

Values of the three model parameters determined for the sorption of benzene into 0.1-mil PET film at 40°C, 50°C, and 60°C are given in Table II. Correlations of the sorption data for several representative runs (corresponding to those of Fig. 5) are shown in Figure 7, which illustrates both the adequacy of the Berens-Hopfenberg model and the inadequacy of the simple Fickian model to represent the sorption of benzene in thin PET films at the higher penetrant activities considered in these thin films.

As shown by the results given in Table II, the diffusion coefficient \bar{D} increases with increasing concentration (or vapor activity), as is often observed in glassy polymer systems. The relaxation rate parameter k appears to increase significantly with increasing temperature, but at a given temperature little systematic variation of k with penetrant activity is observed. The fraction of sorption controlled by diffusion, φ_F , did not vary systematically with either temperature or penetrant activity under the conditions studied. However, it is quite likely that significant variations in both k and φ_F would be observed if a broader range of conditions were examined.

The value of the true Fickian diffusion coefficient for a given temperature and penetrant activity should be independent of film thickness. Results obtained in two runs carried out at 60°C confirm this expectation. In one run, performed with a 1.0-mil film and a benzene activity of 0.25, transport was almost entirely

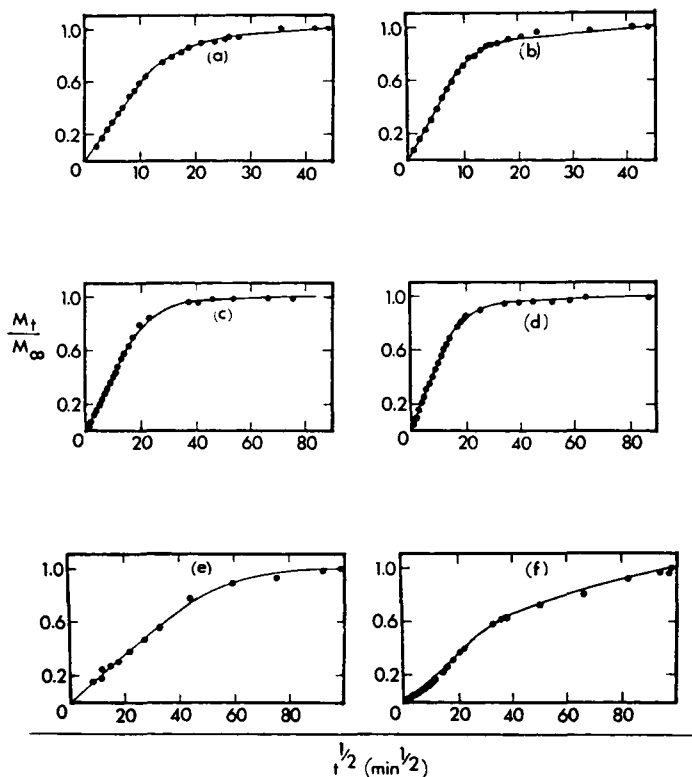


Fig. 7. Sorption kinetic runs for benzene shown in Figure 5. The lines are the Berens-Hopfenberg equation fit to the data using the parameters in Table II: (a) $p/p_0 = 0.07$, 60°C ; (b) $p/p_0 = 0.22$, 60°C ; (c) $p/p_0 = 0.06$, 50°C ; (d) $p/p_0 = 0.30$, 50°C ; (e) $p/p_0 = 0.02$, 40°C ; (f) $p/p_0 = 0.11$, 40°C .

by pure Fickian diffusion (see Fig. 4), with $\bar{D} = 1.58 \times 10^{-12}$. In another run, performed with a 0.1-mil film and a benzene activity of 0.22 (see Fig. 7), the value of \bar{D} determined by fitting the data with the Berens-Hopfenberg model was 1.55×10^{-12} , statistically indistinguishable from the first value.

From Table II, the characteristic time scale for the relaxation process (k^{-1}) is 5×10^4 s, and the characteristic times for the diffusion process (h^2/D) are 10^5 s and 10^7 s for the 0.1-mil and 1.0-mil films, respectively. These results are completely consistent with the previous discussion about the relative importance of the diffusion and relaxation processes in the two films. It is clear that, in the thicker film, the 200-fold greater characteristic time scale for diffusion relative to relaxation precludes direct observation of the relaxation process.

In short, the Berens-Hopfenberg model provides an excellent phenomenological description of the sorption process. It is also worth noting, however, that the model does not by itself provide insight into the molecular source of the apparent differences between the "diffusion" and "relaxation" processes. Additional experimentation beyond the scope of the present study, possibly involving dilatometric measurements, and the formulation and validation of a nonequilibrium statistical model of the glassy state will be required to obtain such insight.

Dual Mobility (Partial Immobilization) Model. It is clear from consideration of the data in Table II that the phenomenologically determined average diffusion coefficients tend to increase with penetrant activity (or sorbed concentration). The observed diffusivities of penetrants in glassy polymers often increase with increasing penetrant concentration, even in the absence of plasticization by the penetrant.¹⁷ Fick's law, given by eq. (10), is traditionally used to describe the migration of penetrant at low activities:

$$N = -D_{\text{eff}} \frac{\partial C}{\partial x} \quad (10)$$

where N is the observed flux, D_{eff} is an effective local concentration-dependent diffusion coefficient, C is the local sorbed concentration, and x is the direction of migration.

Paul and Koros¹⁸ formulated a transport model based on the dual mode sorption concept, which explicitly assigns a separate mobility to penetrants in the Henry's law and Langmuir populations. This model, termed the dual mobility or partial immobilization model, expresses the flux as

$$N = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (11)$$

where D_D and D_H are the respective diffusion coefficients of the Henry's law (C_D) and Langmuir (C_H) populations. A similar model expressed in terms of gradients in chemical potential has been discussed by Petropoulos.¹⁹

The relationship between the effective local diffusion coefficient [D_{eff} of eq. (10)] and the dual mobility model parameters is as follows¹⁷:

$$D_{\text{eff}} = D_D \left[\frac{1 + FK/(1 + \alpha C_D)^2}{1 + K/(1 + \alpha C_D)^2} \right] \quad (12)$$

where $K = C_H' b/k_D$, $F = D_H/D_D$, and $\alpha = b/k_D$. Clearly, if $F \neq 1$ ($D_D \neq D_H$), the local effective diffusion coefficient of all sorbed species is a function of the local penetrant concentration.

Since the value of D_{eff} in eq. (12) changes from the beginning of a sorption run (at which point the concentration is defined to be a uniform C_1 , usually 0) to the end of the run (when the concentration is C_2), the actual diffusion coefficient determined from the curve-fitting procedure previously described is appropriately defined as²⁰

$$\bar{D} = \frac{\int_{C_1}^{C_2} D_{\text{eff}} dC}{C_2 - C_1} \quad (13)$$

Substitution of eq. (12) for D_{eff} into this equation yields²¹

$$\bar{D} = D_D \left[\frac{1 + FK/(1 + bp_1)(1 + bp_2)}{1 + K/(1 + bp_1)(1 + bp_2)} \right] \quad (14)$$

where p_1 and p_2 are the equilibrium partial pressures at $t = 0$ and $t = \infty$, respectively. If p is the constant penetrant partial pressure surrounding the

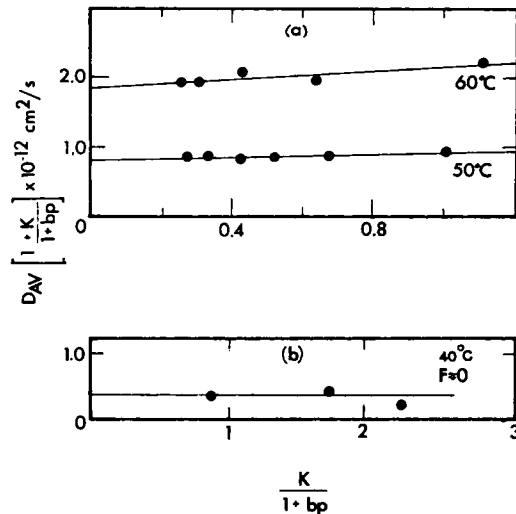


Fig. 8. Average diffusion coefficient values (see Table II) plotted according to eq. (15).

membrane during an integral sorption experiment, then $p_1 = 0$ and $p_2 = p$, and eq. (14) reduces to

$$\bar{D} = D_D \left[\frac{1 + FK/(1 + bp)}{1 + K/(1 + bp)} \right] \quad (15)$$

The last equation indicates that a plot of

$$\bar{D} \left(1 + \frac{K}{1 + bp} \right) \text{ vs. } \frac{K}{1 + bp}$$

should produce a straight line with slope $D_H (= FD_D)$ and intercept D_D . Figure 8 shows such plots for the benzene-PET system at 40°C, 50°C, and 60°C, with the value of K and b taken from Table I and those of \bar{D} from Table II. The values of D_D and D_H determined in this manner are listed in Table III.

The results show that the Langmuir-sorbed species is between 10% and 20% as mobile as the Henry's law population at 50°C and 60°C, and therefore that neglecting the mobility of the former species (as was routinely done in early analyses of dual-mode transport in glassy polymers) could lead to substantial errors in data correlation. At 40°C, on the other hand, it appears that, within the accuracy of the data available, the assumption $F \approx 0$ is a reasonable *mathematical* approximation. Physically, of course, $D_H \neq 0$, or else the assumption

TABLE III
Kinetic Parameters D_D , D_H , and F for Benzene in 0.10 mil PET Film

Temp (°C)	$D_D^a \times 10^{13}$ (cm ² /s)	$D_H \times 10^{13}$ (cm ² /s)	$F = D_H/D_D$
40	3.5	$\ll D_D$	≈ 0
50	8.14	1.06	0.13
60	18.5	3.43	0.185

^a $D_D = 0.395 \exp[-8691/T (\text{°K})]$, $E_D = 72.3 \text{ kJ/mol}$.

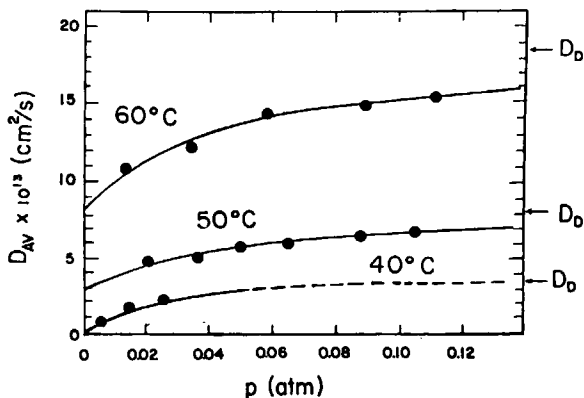


Fig. 9. Comparison of observed average diffusion coefficients (see Table II) to the values calculated from eq. (15) using the parameters in Tables I and III.

of local equilibrium between the two sorption modes could not be satisfied.

The values of D_D shown in Table III are well correlated by an Arrhenius formula. The formula is also given in Table III; the activation energy for diffusion of the Henry's law-sorbed species is 72.7 kJ/mol. Since the diffusion coefficient of the Langmuir-sorbed species is negligible at the lowest of the three temperatures studied, a similar analysis for D_H cannot meaningfully be done.

A direct illustration of the variation of the effective diffusion coefficient with penetrant partial pressure is given in Figure 9, which plots \bar{D} vs. p for the three temperatures studied. Also shown on this figure are the curves predicted from eq. (15), using the dual mobility model parameters given in Table III.

Since the glassy polymer matrix undergoes swelling at the same time diffusive transport is occurring, the Henry's law solubility coefficient k_D and diffusion coefficient D_D change slightly during a sorption run, so that application of the given equations for \bar{D} is not rigorously justified. However, the excellent correlation of the \bar{D} vs. p data shown in Figure 8 indicates that, at the conditions of the present experiments, swelling was slight enough for its effect on the calculated value of \bar{D} to be neglected.

Prediction of Permeabilities and Time Lags. The transport properties reported thus far can be determined by either sorption rate measurements, as was done in this study, or by permeation experiments.¹ The latter approach involves the determination of the steady-state permeability and diffusion time lag.

Koros and Paul¹⁸ derived analytical expressions for the permeability and time lag for systems described by the partial immobilization model. Substitution of the parameters for the benzene/PET system given in Tables I and II into these expressions yields the plots of permeability and time lag vs. penetrant partial pressure shown in Figures 10 and 11. In the absence of non-Fickian effects, both the permeability and the time lag are seen to be decreasing functions of upstream partial pressure.

The effects of relaxational contributions to the transport process should be relatively unimportant in the case of the steady-state permeability, and so the accuracy of the predictions in Figure 10 is expected to be quite satisfactory, even

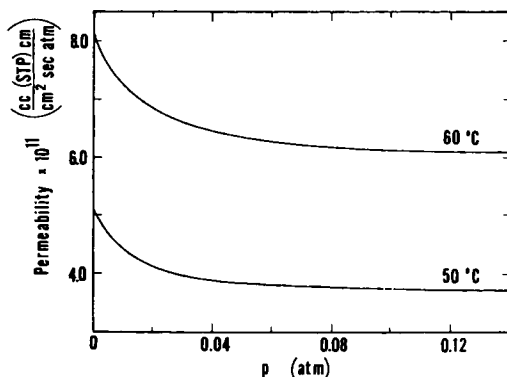


Fig. 10. Prediction of the steady state permeability of benzene for poly(ethylene terephthalate) at 50°C and 60°C.

for thin films. On the other hand, time-dependent relaxations during the transient period could protract the approach to steady-state, thereby causing the predictions of θ to be underestimated for the 0.1-mil film except at very low vapor activities. For the thicker film, time lags should be 100 times greater than those shown in Figure 11, since the lags vary as the square of the film thickness.

For the same reason that the Fickian model successfully described sorption in the thick film but failed to do so for the thin film, one would expect the predictions of time lags determined by scaling the results of Figure 11 to describe the behavior of thick films, but to fail for thin films. This is a fortunate result, in that it suggests that the behavior of thick barrier films (≥ 1 mil) can be deduced by studying thin films over more convenient time scales. This is the topic of a current study in our laboratory.

Desorption Kinetics. Desorption rates were measured routinely after benzene sorption had reached equilibrium. Data from a representative desorption run at 50°C are shown in Figure 12. The line shown in this figure is the

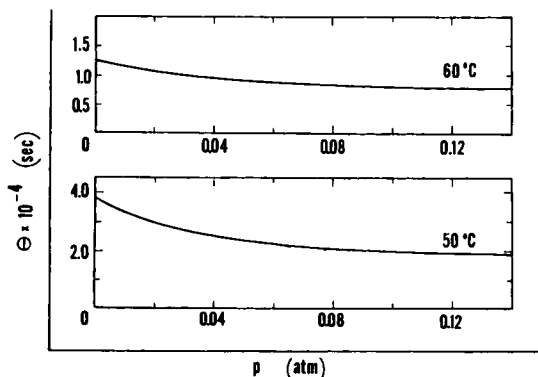


Fig. 11. Prediction of the diffusion time lag for benzene in a 0.10 mil thick film of poly(ethylene terephthalate) at 50°C and 60°C.

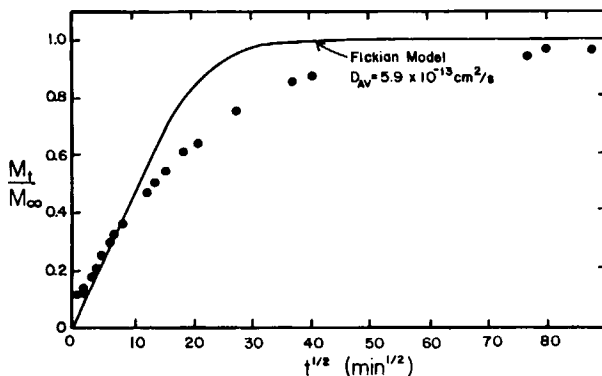


Fig. 12. Comparison of the experimentally observed normalized desorption kinetic run for benzene in poly(ethylene terephthalate) with the simple Fickian model line [eq. (4)]. The average diffusion coefficient for this system, determined from the Berens-Hopfenberg analysis of the sorption data (see Table II), was used in the calculation: $T = 50^\circ\text{C}$, $p/p_0 = 0.19$, $l = 0.1$ mil.

prediction of the Fickian transport model using the diffusion coefficient determined from the corresponding sorption run.

The results indicate that rapid desorption occurs initially, followed by a slower desorption process. Such non-Fickian behavior is presumably due to consolidation of distended polymer chains over the same time scale as that of the diffusion process for the thin film samples. Due to equipment failure, a formal desorption experiment was not performed on the 1.0-mil film. One would expect, however, that desorption from the thicker film would more closely approximate Fickian behavior, again because the characteristic time scale for diffusion is substantially longer than for chain relaxation in the thick sample.

CONCLUSIONS

The dual mode sorption and partial immobilization models provide good correlations of data for benzene sorption in PET at low vapor activities. This result is particularly significant in that these models have heretofore been used primarily for noncondensable gases. The occurrence of relaxation in the polymer during sorption was treated successfully with the Berens-Hopfenberg model.

The diffusional mobility of the Langmuir-sorbed component is significantly lower than the mobility of the Henry's law component for benzene in PET. This result is consistent with previous results which suggest that the relative mobility of penetrants in the Langmuir and Henry's law environments ($F = D_H/D_D$) decreases as the critical temperature of the penetrant increases.² Benzene has a high critical temperature²² (562K), so that low values of F were anticipated and observed.

The temperature dependence of the Langmuir capacity, C'_H , was qualitatively and quantitatively consistent with the interpretation of this parameter in terms of unrelaxed volume frozen in the polymer below T_g . The predictions of C'_H from dilatometric data for PET and the density of liquid benzene were gratifyingly accurate.

The results also indicate that the sorption anomalies seen in this study are less

apparent when dealing with the thicker films. This suggests that these anomalies will be of minor consequence in the prediction of benzene sorption into air bags (3–5 mils thick), even through significant quantities of benzene may in fact be sorbed into the bag wall.

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