Differential Sorption in Glassy Polymers

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ABSTRACT: Anomalous sorption curves have often been observed for differential sorption experiments in glassy polymers. A model is proposed to describe this non-Fickian behavior. This model is based on the presence of interfacial resistance caused by slow rate processes at the phase boundary. Predictions of the model are compared with general experimental observations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1431–1440, 1999

Key words: differential sorption; interfacial resistance

INTRODUCTION

The mutual diffusion process in concentrated polymer-solvent mixtures is often studied using a sorption experiment. For sorption in glassy polymers, non-Fickian behavior is often observed, and, therefore, it is useful to examine the mechanism for the diffusion process using differential sorption experiments. In an idealized differential sorption experiment, the difference in the final and initial equilibrium concentrations is kept as small as possible so that the properties of the system can be adequately characterized by an average concentration, by a single value of the mutual diffusion coefficient, and by a single value of the diffusion Deborah number.¹ Most differential sorption experiments are carried out using thin polymer films (<0.003 cm) with solvent mass fraction changes of the order of 0.01.

Comprehensive differential sorption experiments have been carried out by Odani et al.^{2–4} and by Billovits and Durning.⁵ More limited experimental results have been reported by Vrentas et al.¹ and by Gao and Ogilby.⁶ The characteristics of these experiments are summarized in Ta-

Contract grant sponsor: Dow Chemical Company. Journal of Applied Polymer Science, Vol. 71, 1431-1440 (1999) ble I. Only the shape of the sorption curve at the lowest penetrant concentrations is included in this table. Non-Fickian behavior was observed in refs. 2-5, and Fickian behavior was reported in refs. 1 and 6. In addition, Odani et al.²⁻⁴ reported sigmoidal sorption curves for all five of their sorption experiments, whereas Billovits and Durning⁵ characterized the sorption behavior at low ethylbenzene mass fractions as being pseudo-Fickian. However, the two lowest sorption experiments reported by Billovits and Durning (R1 and R2 in their identification system) are somewhat suspect, because their time scales are not consistent with their other experiments. The next three experiments (R3, R4, and R5) were classified as being two stage, but the initial stage in each case is very short, and its existence depends on the accuracy of a small number of data points at small weight gains. Indeed, if one ignores the first few data points, it is evident that all of the sorption curves of Billovits and Durning can be classified as either sigmoidal or Fickian.

All of the experiments reported in Table I are at temperatures significantly below the glass transition temperature of the pure polymer. Hence, for small penetrant concentrations, the diffusion Deborah number should be high, and there should be an elastic diffusion process which is Fickian.¹ For example, for the ethylbenzene– polystyrene system at 40°C, Billovits and Durn-

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Polymer	Penetrant	$ \begin{array}{c} \text{Temperature} \\ ^{\circ}\text{C} \end{array} $	Type of Sorption Curve	Reference
Polystyrene	Benzene	25	Sigmoidal	2
Polystyrene	Benzene	35	Sigmoidal	2,3
Polystyrene	Ethyl acetate	25	Sigmoidal	3
Polystyrene	Ethyl methyl ketone	25	Sigmoidal	4
Polystyrene	Ethylbenzene	40	Pseudo-Fickian	5
Polystyrene	Methanol	70	Fickian	1
Polystyrene	Oxygen	25	Fickian	6

 Table I
 Summary of Differential Sorption Experiments

ing⁵ estimate that there should be an elastic Fickian response for solvent mass fractions ranging from 0 to 0.07 (we estimate that elastic Fickian behavior should persist until a solvent mass function of about 0.09.). However, only for two of the eight experiments presented in Table I is a Fickian diffusion process actually observed. Billovits and Durning suggested that relaxation processes with time scales shorter than the terminal relaxation time are involved in the diffusion process at low solvent mass fractions. Hence, they proposed that viscoelastic diffusion actually takes place because the true diffusion Deborah number is lower than the Deborah number calculated previously.⁷ Billovits and Durning⁸ have thus used viscoelastic models to describe their differential sorption experiments.

Although a viscoelastic analysis is a plausible explanation for the differential sorption data, we believe that there exists an alternative explanation, namely the presence of interfacial resistance caused by slow rate processes at the phase boundary. It is, thus, proposed that the shape of the sorption curves is affected by a time-dependent surface concentration in the polymer film, and the molecular origin of this time dependence is simply the presence of finite rate processes at the polymer-gas interface. There is no conceptual inconsistency in having a retarded surface response under conditions when an elastic response is present inside the polymer film. The proposed model is presumably applicable at the lowest penetrant concentrations when the Deborah number should be large.

The equations for the proposed model are formulated in the second section of the article, and methods for calculating the properties of the polymer-solvent system are discussed in the third section. Predictions of the model are presented and discussed in the fourth section of the article.

FORMULATION OF MODEL

The model proposed for differential sorption in glassy polymers is based on the following assumptions: (1) The diffusion process is isothermal. (2) The gas phase of a vapor sorption experiment is essentially pure. (3) The liquid phase is a binary liquid mixture of penetrant and polymer. (4) The diffusion process is a one-dimensional transport process. The polymer film has a dry, initial thickness L_0 . For each sorption experiment, the diffusion field extends from a solid wall at x = 0 to the moving phase boundary at x = L(t). Here, x is the distance variable in the diffusion direction, t is time, and L is the thickness of the polymer film at time t. (5) There are no chemical reactions in the liquid phase. (6) The effect of pressure on liquid density is negligible. (7) The weight gain of penetrant is small enough for each differential sorption experiment so that there is a negligible change in sample thickness for that particular experiment. (8) The polymer-solvent system is in the glassy state during the entire sorption process. The diffusion Deborah number is sufficiently high so that the diffusion process is an elastic, Fickian diffusion process.¹ The analysis of this article is thus limited to differential sorption experiments for which the penetrant concentration is small enough so that the diffusion Deborah number is significantly greater than unity. Differential sorption experiments at higher penetrant concentrations with Deborah numbers near unity must be analyzed using a viscoelastic analysis. (9) The concentration change for the differential sorption experiment is small enough so that the mutual diffusion coefficient D is effectively a constant for each sorption experiment. (10) For a differential sorption experiment with effectively constant D, it can be shown⁹ that the x component of the volume average velocity is very small

and can be neglected. (11) The rate process at the polymer-gas interface can be characterized by a mass transfer coefficient k.

For the above set of assumptions, the differential sorption process can be described by the following set of equations:

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \xi^2} \tag{1}$$

$$C(\xi, 0) = 0$$
 (2)

$$\left(\frac{\partial C}{\partial \xi}\right)_{\xi=0} = 0 \tag{3}$$

$$\left(\frac{\partial C}{\partial \xi}\right)_{\xi=1} = \frac{kL}{D} \left[1 - C(1, \tau)\right] \qquad (4)$$

$$C = \frac{\rho_1 - \rho_{10}}{\rho_{1E} - \rho_{10}} \tag{5}$$

$$\tau = \frac{Dt}{L^2} \tag{6}$$

$$\xi = \frac{x}{L} \tag{7}$$

Here, ρ_1 is the mass density of the solvent, ρ_{1E} is the equilibrium solvent mass density, and ρ_{10} is the initial solvent mass density. In addition, the weight gain in the sample can be calculated using the expression

$$\frac{M}{M_{\infty}} = \int_{0}^{1} C \, d\xi \tag{8}$$

where M is the mass of solvent per unit area that has entered the polymer film at time t, and M_{∞} is the value of M at infinite time. The solution to eqs. (1)–(4) is well known,¹⁰ and the result for the fractional weight gain is given by the expression

$$\frac{M}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\left(\frac{kL}{D}\right)^2 \exp\left[-\beta_n^2 \tau\right]}{\beta_n^2 \left[\beta_n^2 + \frac{kL}{D} + \left(\frac{kL}{D}\right)^2\right]}$$
(9)

where the β_n are the positive roots of the following equation:

$$\beta_n \tan \beta_n = \frac{kL}{D} \tag{10}$$

The fractional weight gain could be calculated as a function of dimensionless time from eq. (9) if an expression for the mass transfer coefficient kwere available. An equation for k can be derived by considering the actual mechanisms for molecular interchange between a liquid and a gas. The interfacial boundary condition, eq. (4), is derived using the following expression for n_1 , the mass flux of solvent at the phase boundary:

$$-n_1 = k[\rho_{1E} - \rho_1(L, t)] \tag{11}$$

The quantity n_1 can be related to the rate processes at the interface by the expression

$$-n_1 = \Gamma_C - \Gamma_E \tag{12}$$

where Γ_C is the mass flux of gas molecules that condense, and Γ_E is the mass flux of penetrant molecules that evaporate from the liquid surface. The mass of gas striking the interface per unit area per unit time, Γ , is given by the following expression for a gas in thermal equilibrium.¹¹

$$\Gamma = \frac{p_1 M_1^{1/2}}{(2\pi RT)^{1/2}} \tag{13}$$

Here, p_1 is the penetrant pressure in the gas phase, M_1 is the molecular weight of the penetrant, T is temperature, and R is the gas constant. If only a fraction of the molecules, θ , penetrates into the liquid because of some restraint at the interface, the rate of transport of matter from gas to liquid is

$$\Gamma_{C} = \theta \Gamma = \frac{\theta p_{1} M_{1}^{1/2}}{(2\pi RT)^{1/2}}$$
(14)

In addition, if it is assumed that the evaporation of penetrant molecules from the liquid surface is proportional to the concentration of dissolved penetrant at that point, then we can write

$$\Gamma_E = \beta \rho_1(L, t) \tag{15}$$

where β is a proportionality constant. This constant can be evaluated by using the fact that the condensation and evaporation rates must be equal at equilibrium. Thus, combination of eqs.

(12), (14), and (15) produces the following expression for the mass flux:

$$-n_{1} = \frac{\theta p_{1} M_{1}^{1/2}}{(2 \pi R T)^{1/2} \rho_{1E}} \left[\rho_{1E} - \rho_{1}(L, t) \right] \quad (16)$$

Comparison of eqs. (11) and (16) produces the following equation for k:

$$k = \frac{\theta p_1 M_1^{1/2}}{(2\pi RT)^{1/2} \rho_{1E}}$$
(17)

A gas molecule that strikes the liquid surface will penetrate into the liquid only if space is made available by the movement of a surface molecule into the bulk liquid. Hence, θ is equal to the probability that a surface molecule will jump because there is sufficient energy to overcome attractive forces and because there is a hole of sufficient size that is available. Consequently, from the free-volume theory of transport

$$\theta = \frac{D_1}{\bar{D}_0} \tag{18}$$

where D_1 is the self-diffusion coefficient for the solvent and \overline{D}_0 is the preexponential factor in the equation for D_1 . Hence, the dimensionless group kL/D can be calculated using the following equation:

$$\frac{kL}{D} = \frac{M_1^{1/2}L}{\bar{D}_0(2\pi RT)^{1/2}} \left(\frac{p_1}{\rho_{1E}}\right) \left(\frac{D_1}{D}\right)$$
(19)

A comprehensive analysis of interphase mass transfer has been given by Schrage.¹²

EVALUATION OF PROPERTIES

The calculation of the time dependence of M/M_{∞} for a glassy polymer–solvent system can be carried out using eqs. (9) and (19) if the properties of the polymer–solvent system can be estimated. The following properties must be evaluated: p_1/ρ_{1E} (sorption) \bar{D}_0 , D_1 (self-diffusion), D (mutual diffusion), and L (volumetric behavior).

Sorption

The sorption process for polymer–solvent systems can be described by the following equations^{13,14}:

$$\frac{p_1}{p_1^0} = \phi_1 \exp[\phi_2 + \chi \phi_2^2] e^F$$
(20)

$$F = \frac{M_1 \omega_2^2 (\hat{C}_p - \hat{C}_{pg}) A}{RT} \left(\frac{T}{T_{gm}} - 1 \right) \quad T < T_{gm} \quad (21)$$

$$F = 0 \quad T \ge T_{gm} \tag{22}$$

$$\phi_1 = \frac{\omega_1}{\omega_1 + q \,\omega_2} \tag{23}$$

$$\phi_2 = \frac{q\,\omega_2}{\omega_1 + q\,\omega_2} \tag{24}$$

$$q = \frac{\hat{V}_2^0}{\hat{V}_1^0} \tag{25}$$

$$T_{gm} = T_{g2} - A\omega_1 \tag{26}$$

Here, ϕ_I is the volume fraction of component *I*, ω_I is the mass fraction of component I, \hat{V}_1^0 is the specific volume of pure penetrant in the liquid state, \hat{V}_2^0 is the specific volume of the pure equilibrium liquid polymer, p_1^0 is the vapor pressure of the pure liquid penetrant at *T*, and χ is the interaction parameter of the Flory-Huggins theory. Also, \hat{C}_p is the specific heat capacity at constant pressure for the equilibrium liquid polymer, $\hat{C}_{n\sigma}$ is the specific heat capacity at constant pressure for the glassy polymer, T_{g2} is the glass transition temperature of the pure polymer, and T_{gm} is the glass transition temperature of the polymer-penetrant mixture at a particular penetrant mass fraction. The concentration dependence of T_{gm} can be approximated using eq. (26). The value of the coefficient A depends on the nature of the penetrant that is used to depress the glass transition temperature of a particular polymer.

It is evident that the combination of eqs. (20) and (21) produces the sorption isotherm for a glassy polymer–solvent system ($T < T_{gm}$), and the combination of eqs. (20) and (22) yields the equation for a sorption isotherm for a rubbery polymer–solvent system ($T \ge T_{gm}$). In addition, eq. (20) can be rewritten as follows

$$\frac{p_1}{\rho_{1E}} = p_1^0 \hat{V}_1^0 \exp[\phi_2 + \chi \phi_2^2] e^F$$
(27)

and this form can be used in eq. (19) to evaluate kL/D. The input parameters for the sorption cal-

culation, \hat{V}_1^0 , \hat{V}_2^0 , T_{g2} , A, \hat{C}_p , \hat{C}_{pg} , p_1^0 , and χ , are usually available or can be estimated.

Volumetric Behavior

The total volume of a glassy polymer-penetrant mixture, V_m , can be determined using the equation^{13,14}

$$\frac{V_m}{V_0} = \frac{\omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_{2g}^0(\omega_1)}{\omega_2 \hat{V}_{2g}^0(\omega_1 = 0)}$$
(28)

where V_0 is the volume of the pure polymer and \hat{V}_{2g}^0 is the specific volume of the glassy polymer used to form the nonequilibrium mixture at a given temperature below T_{gm} . The concentration dependence of \hat{V}_{2g}^0 can be calculated from the following equation¹⁴

$$\hat{V}_{2g}^{0}(\omega_{1}) = \hat{V}_{2}^{0}(T_{g2})[1 - \alpha_{2}A\omega_{1} + \alpha_{2g}(T - T_{g2} + A\omega_{1})] \quad (29)$$

where $\hat{V}_2^0(T_{g2})$ is the specific volume of the polymer at T_{g2} , α_2 is an average thermal expansion coefficient for the equilibrium liquid polymer, and α_{2g} is the thermal expansion coefficient for the glassy polymer. Thus, because the ratio of L, the sample thickness at ω_1 , to L_0 , the thickness of the dry polymer film, is given by the expression

$$\frac{L}{L_0} = \frac{V_m}{V_0} \tag{30}$$

it is evident that the quantity L/L_0 can be calculated using eqs. (28)–(30). The input parameters for the volumetric calculation, α_2 , α_{2g} , \hat{V}_1^0 , A, T_{g2} , and $\hat{V}_2^0(T_{g2})$, are usually known.

Self-Diffusion

The solvent self-diffusion coefficient, D_1 , for diffusion in a polymer–solvent mixture can be determined using the following equation^{15–18}

$$D_{1} = \bar{D}_{0} \exp\left[-\frac{E^{*}}{RT}\right] \exp\left[-\frac{\omega \hat{V}_{1}^{*} + \omega_{2}\xi \hat{V}_{2}^{*}}{\hat{V}_{FH/s}}\right]$$
(31)

where \hat{V}_{I}^{*} is the specific hole free volume of component *I* required for a jump, \hat{V}_{FH} is the average hole free volume per gram of mixture, and 8 rep-

resents an average overlap factor for the mixture that is introduced because the same free volume is available to more than one jumping unit. Also, E^* is the effective energy per mol that a molecule needs to overcome attractive forces, and ξ is an effective ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. For glassy polymer–solvent systems, the quantity $\hat{V}_{FH/s}$ can be calculated using the following set of equations:

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1} \left(K_{21} + T - T_{g1} \right) + \omega_2 \frac{\hat{V}_{FH2g}}{\gamma_2}$$
(32)

$$\hat{V}_{FH2g} = \hat{V}_{2}^{0}(T_{g2}) \left[f_{H2}^{G} - \int_{T_{gm}}^{T_{g2}} (\alpha_{2} - \alpha_{C2}) dT' - \int_{T}^{T_{gm}} (\alpha_{2g} - \alpha_{C2g}) dT' \right] T \leq T_{gm} \quad (33)$$

Here, \hat{V}_{FH2g} is the specific hole free volume of the glassy polymer for $T \leq T_{gm}$; α_{C2} and α_{C2g} are the thermal expansion coefficients for the sum of the specific occupied volume and the specific interstitial free volume for the equilibrium liquid polymer and the glassy polymer, respectively; γ_2 is the overlap factor for free volume of pure polymer; K_{11}/γ_1 and $K_{21} - T_{g1}$ are solvent free-volume of the polymer at T_{g2} . The determination of the input parameters for the calculation of D_1 has been discussed in detail elsewhere.^{15–18}

Mutual Diffusion

For a glassy polymer–solvent system, the following relationship between D and D_1 has been proposed¹⁸:

$$\frac{D}{D_{1}} = 1 + \frac{\omega_{1}}{\omega_{1E}} \left[\frac{D}{D_{1}} \left(\omega_{1} = \omega_{1E} \right) - 1 \right]$$
(34)

Here, ω_{1E} is the mass fraction at which the glassy polymer becomes rubbery at temperature *T*. The quantity ω_{1E} at any temperature *T* can be calculated from the following equation if eq. (26) is used for the concentration dependence of T_{gm} :

$$\omega_{1E} = \frac{T_{g2} - T}{A} \tag{35}$$



Figure 1 Dependence of film thickness on solvent mass fraction for the ethylbenzene–polystyrene system at 40°C.

The quantity D/D_1 at $\omega_1 = \omega_{1E}$ can be determined from the mutual diffusion calculation for rubbery polymer-solvent systems. A general procedure for the calculation of D/D_1 for rubbery polymer-solvent systems has been given elsewhere.¹⁸ For cases where ω_1 is small (as is the case here), $D/D_1(\omega_1 = \omega_{1E})$ can be approximated using the following expression:

$$\frac{D}{D_1}(\omega_1 = \omega_{1E}) = \frac{1 - 2\chi\phi_{1E}}{1 + 2\phi_{1E}}$$
(36)

Here, ϕ_{1E} is the solvent volume fraction when $\omega_1 = \omega_{1E}$.

It is important to note that there are no adjustable parameters in the model because either known values or reasonable estimates for all input parameters exist. However, in some cases, measured values rather than reasonably good estimates must be used to provide accurate values for self-diffusion coefficients. It can be easily shown that a 20% change in α_{2g} can lead to nearly an order of magnitude change in D_1 . The small hole free volumes in glassy polymers make the predicted diffusion coefficients quite sensitive to the volumetric properties of the glass. Therefore, meaningful comparisons between experiment and theory can be carried out only if actual values rather than reasonable estimates of some of the glassy volumetric properties are available.

RESULTS AND DISCUSSION

Calculations were primarily carried out for the ethylbenzene–polystyrene system at 40°C, and a

few results were obtained at 70 and 100°C. The input parameters for this system have been reported previously^{15,16} or are generally available. A value of 0.35 was used for χ , and our best estimate for *A* is 550 K. Most of the predictions at 40°C were carried out for the glassy region ($\omega_1 = 0$ to $\omega_{1E} = 0.109$).

The dependence of the film thickness on solvent mass fraction for the ethylbenzene-polystyrene system at 40°C is presented in Figure 1. The addition of solvent obviously leads to an increase in the sample thickness, but this increase is moderated somewhat by the decrease in the specific volume of the polymer. The polymer specific volume decreases from $0.9627 \text{ cm}^3/\text{g}$ to $0.9411 \text{ cm}^3/\text{g}$ as the polymer goes from the solvent-free state at $\omega_1 = 0$ to the rubbery state at $\omega_1 = \omega_{1E}$. Below T_{g2} , the glassy polymer is in a nonequilibrium liquid configuration, and there is extra hole free volume that is effectively frozen into the polymer. As penetrant is added to the system, there is a change in the molecular structure of the polymer and an elimination of the extra hole free volume of the system. The dependence of D/D_1 on solvent mass fraction for the ethylbenzene-polystyrene system at 40°C is presented in Figure 2. For concentrations in the glassy region, there is about a 30% decrease in D/D_1 from the value of unity at $\omega_1 = 0$. The sorption isotherm for the ethylbenzene–polystyrene system at 40°C is presented in Figure 3. The shape of the isotherm in the glassy region (the solid line going from $\omega_1 = 0$ to $\omega_1 = \omega_{1E} = 0.109$ is significantly different than the isotherm shape in the rubbery region (dotted line for $\omega_1 > 0.109$). The predicted isotherm is in reasonably good agreement with experimental data reported by Billovits and Durning.⁵ The solid circles in Figure 3 represent approximate average values



Figure 2 Dependence of D/D_1 on solvent mass fraction for the ethylbenzene–polystyrene system at 40°C.



Figure 3 Sorption isotherm for the ethylbenzene– polystyrene system at 40°C. The solid line represents the isotherm for the glassy region, and the dotted line is the isotherm for the rubbery region. The solid circles represent data collected by Billovits and Durning.⁵

for the sorption data set of Billovits and Durning, which has a considerable amount of scatter.

The dependence of the mutual diffusion coefficient on solvent mass fraction for the ethylbenzene-polystyrene system at 40°C is presented in Figure 4. The mutual diffusion coefficient changes



Figure 4 Dependence of mutual diffusion coefficient for the ethylbenzene–polystyrene system at 40°C on solvent mass fraction.



Figure 5 Dependence of kL/D for the ethylbenzene– polystyrene system at 40°C on solvent mass fraction.

by nearly five orders of magnitude as the solvent mass fraction goes from 0 to 0.109. This very strong concentration dependence for D means that, in general, very small mass fraction changes must be utilized if true differential sorption experiments are to be carried out. This is particularly true at the lower ethylbenzene mass fractions. Consequently, some of the sorption experiments reported by Billovits and Durning⁵ may not have been good approximations to an ideal differential sorption experiment. The dependence of kL/D on solvent mass fraction for the ethylbenzene-polystyrene system at 40°C is presented in Figure 5. This dimensionless group changes by a factor of about 3.35 as ω_1 goes from 0 to 0.109. From a graph presented by Crank,¹⁰ it is evident that the curve of fractional weight gain in a plane sheet vs. the square root of time has a sigmoidal shape for low values of kL/D and proceeds toward the curve with a constant surface concentration (the so-called Fickian limit) as kL/D increases. The Fickian limit is effectively achieved when kL/D > 10. Consequently, the increase of kL/Dwith increasing solvent concentration means that sorption curves at constant temperature can have sigmoidal shapes at low solvent mass fractions, and that the shape should change toward the Fickian limit as the solvent concentration increases.

A sequence of five sorption curves for the ethylbenzene-polystyrene system at 40°C is presented in Figure 6. The solvent concentrations range from $\omega_1 = 0.01$ to 0.08, and the sorption



Figure 6 Differential sorption predictions for the ethylbenzene–polystyrene system at 40°C at five solvent concentrations. Curve A, $\omega_1 = 0.08$; Curve B, $\omega_1 = 0.06$; Curve C, $\omega_1 = 0.04$; Curve D, $\omega_1 = 0.02$; Curve E, $\omega_1 = 0.01$.

curves proceed from sigmoidal shapes toward a Fickian shape. At low solvent concentrations, Odani et al.^{2–4} reported sigmoidal sorption curves and a change to pseudo-Fickian curves as the solvent mass fraction increased. Furthermore, if experiments R1 and R2 and the very early portions of some of the other experiments are discounted, then the sorption curves of Billovits and Durning⁵ effectively have a sigmoidal shape at low concentrations and a change to Fickian behavior at higher concentrations. Consequently, the proposed model predicts sorption behavior that is roughly in agreement with what is observed experimentally, particularly when consideration is taken of two experimental difficulties with differential sorption experiments. The first difficulty is that the accuracy of the sorption curves for differential sorption experiments is compromised somewhat by the small weight gains that are often utilized. The second difficulty is that it is not easy to perform a valid differential sorption experiment because of the type of concentration dependence for D exhibited in Figure 4. Thus, it is often not meaningful to compare experimental differential sorption results with theoretical results based on the utilization of a constant value for *D*. It is of course, in principle, possible to derive theoretical results based on the utilization of a concentration-dependent diffusivity, but this can be done only if actual volumetric properties are available for the glassy polymer used in the differential sorption experiments. These actual volumetric properties are needed because the calculation of diffusion coefficients in the glassy state from free-volume theory is sensitive to the amount of available free volume.

Although direct comparison between theory and experiment for the ethylbenzene-polystyrene system is not possible because of insufficient knowledge about the glassy volumetric properties of the polymer used in the experiments, it is still possible to carry out a rough comparison of the shapes of sorption curves. The shape of the sorption curve for the R3 experiment of Billovits and Durning⁵ at 40°C (solvent mass fractions ranging from about 0.016 to 0.04) is compared in Figure 7 with the shape of a predicted sorption curve at 40°C for $\omega_1 = 0.01$. It is clear that the shapes are comparable, particularly when it is noted that the theoretical prediction is based on a constant value of D, whereas it is unlikely that the mutual diffusion coefficient is a constant for the R3 experiment.

The temperature dependence of the sorption process for the ethylbenzene-polystyrene system is illustrated in Figure 8, where sorption curves are presented for 40, 70, and 100°C for $\omega_1 = 0$ (sorption of a trace of solvent into the polymer). It is a clear that an increase in temperature produces a change in the sorption curves from sigmoidal shapes to an effectively Fickian shape. The model thus predicts that sorption curves proceed from sigmoidal shapes toward a Fickian shape either by increasing the solvent concentration at fixed temperature or by increasing the temperature at fixed solvent concentration.

From the above discussion, it appears fair to conclude that the proposed model provides a rea-



Figure 7 Comparison of shapes of experimental and theoretical sorption curves for ethylbenzene–polystyrene system at 40°C. Dotted line is experimental curve for R3 experiment of Billovits and Durning,⁵ and solid line is theoretical curve for $\omega_1 = 0.01$.



Figure 8 Differential sorption predictions for the ethylbenzene-polystyrene system at $\omega_1 = 0$ (trace of solvent) at three temperatures. Curve A, 100°C; Curve B, 70°C; Curve C, 40°C.

sonable explanation for the anomalous sorption curves usually observed at low solvent concentrations for glassy polymer-penetrant systems. It remains to explain why Fickian behavior is observed for the last two systems presented in Table I (methanol-polystyrene and oxygen-polystyrene). For the ethylbenzene-polystyrene system at 40°C, the highest value of kL/D for systems presented in Figure 6 was 1.83 at $\omega_1 = 0.08$, and, therefore, there was only an approach toward a Fickian shape, which is effectively achieved for kL/D > 10. Similarly, in Figure 8, the highest value of kL/D was 5.61 at 100°C, and the sorption curve at this temperature is very close to achieving a Fickian shape. On the other hand, for the methanol-polystyrene and oxygen-polystyrene systems, $kL/D \gg 10$. Consequently, for these two cases, the Fickian limit has been essentially achieved. Therefore, it appears that the proposed model can correctly predict when anomalous sorption curves can be expected for differential sorption experiments in glassy polymers and when the Fickian limit has effectively been achieved. The proposed model is thus a viable alternative to a viscoelastic explanation for the presence of anomalous effects in differential sorption experiments in glassy polymers at the lowest penetrant concentrations.

Finally, it is useful to summarize the comparison between the predictions of the proposed theory and experimental data. As noted above, the two lowest sorption experiments reported by Billovits and Durning⁵ are somewhat suspect, and are thus ignored here. Billovits and Durning⁸ also did not analyze these experiments because they said that the data were not of the best quality. In Figure 6, the sorption curves proceed from sigmoidal shapes toward a Fickian shape in the elastic diffusion region. For the data of Billovits and Durning,⁵ there also is a progression from sigmoidal shapes toward a Fickian shape in the elastic region. In addition, as expected, viscous Fickian diffusion is observed at higher concentrations. The data presented by Billovits and Durning were collected on a polystyrene sample with a molecular weight of 305,000. Huang and Durning¹⁹ presented sorption data for ethylbenzene using polystyrene samples with molecular weights of 100,000 and 160,000. For the polystyrene sample with a molecular weight of 160,000, the sorption curves can be characterized as being slightly sigmoidal at the lower penetrant mass fractions. Non-Fickian behavior is reported at the higher mass fractions. Anomalous behavior occurs at lower concentrations for the 160,000 sample than for the 305,000 sample because of the effect of molecular weight on polymer relaxation times. The data reported by Huang and Durning for ethylbenzene sorption into a polystyrene sample with a molecular weight of 100,000 are non-Fickian because only relatively high penetrant levels were used. Hence, it appears that the data of Huang and Durning are also consistent with the proposed theory.

Tang et al.²⁰ presented data for ethylbenzene sorption into polystyrene samples with molecular weights of 100,000 and 350,000. Roughly speaking, there is two-stage sorption at the higher penetrant concentrations and a rough approximation to sigmoidal behavior at low penetrant concentrations if, again, the first few data points are ignored. It would, of course, be very helpful if the very early time behavior observed in these experiments could be characterized either as an experimental artifact or a valid sorption characteristic. Unfortunately, a definitive assessment is probably not possible for these data because it is difficult to carry out very accurate differential sorption experiments for glassy polymers. For example, ethylbenzene-polystyrene sorption data were collected by Billovits and Durning⁵ and by Tang et al.²⁰ for the same temperature and for approximately the same sample thickness and polymer molecular weight. However, the sorption levels and experimental time scales for these two investigations are very different.

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