# Prediction of Differential Sorption Kinetics Near $T_g$ for Benzene in Polystyrene

A recent first principles theory for "anomalous" diffusion, which accounts for the effect of a protracted macromolecular response to a perturbation, is used to quantitatively predict the results from successive differential sorption experiments in the benzene/atactic polystyrene system. The physical constants in the theory are evaluated for the conditions of the experiment without reference to any non-Fickian diffusion data. The theoretical predictions are in reasonable agreement with the experimental observations.

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## Introduction

"Anomalous" or "non-Fickian" diffusion of organic solvents in concentrated polymer solutions occurs during many industrial processing operations such as the dry spinning of fibers, the etching of polymeric masks in the manufacture of integrated circuits, and the coating of substrates with polymers via deposition from solution. Clearly, a quantitative understanding of anomalous diffusion would benefit a wide variety of technological systems.

In simple, binary liquid mixtures interdiffusion follows Fick's law. A substantial body of research carried out in the past two decades on the interdiffusion of solvents and polymers has been devoted to detecting and analyzing violations of Fick's law. Roughly speaking, it appears that Fick's model provides a consistently accurate representation of interdiffusion for solutions well above the glass transition temperature. Near and often below the glass transition temperature, an "anomalous" interdiffusion occurs that does not lend itself to a description by Fick's law, with the usual interfacial boundary conditions, no matter how the diffusivity is assumed to depend on composition.

The theoretical and experimental investigations heretofore point to the main reason causing the anomalous phenomena. Under conditions where anomalous behavior occurs, there is a match between the time scale for macromolecular reconfiguration (the time scale $\tau$ for a single macromolecule to achieve steady state after experiencing a perturbation) and the time scale of the interdiffusion. To quantify this, Vrentas et al. (1975) introduced the diffusion Deborah number, $\theta = \tau/\tau_l$, where $\tau_l = l^2/D$ is the time scale for interdiffusion ($l$ is the membrane half thickness and $D$ is the mutual diffusion coefficient). In the few quantitative checks that have been done, anomalous behavior indeed appears to occur when $\theta$ is of order one (e.g., Vrentas et al., 1984; Billovits and Durning, 1988).

Mathematical models developed in the past for the anomalous interdiffusion inevitably rely on some kind of empiricism to include the effect of relatively slow macromolecular motions ("relaxations"). A recent theory (Durning 1985; Durning and Tabor, 1986) that incorporates this by the polymer's response to local, diffusion-induced deformations has given a qualitatively accurate description of interdiffusion in the linear limit, that is, when the initial disturbance from equilibrium is infinitesimal. In this limit, the change in composition during the interdiffusion is small enough to ignore the composition dependence of the transport properties, thus yielding a linear initial-value problem in analysis, hence the term linear limit. This paper analyzes published results from sorption experiments in the linear limit as a preliminary assessment of the predictive capability of the theory. In our view, a quantitatively accurate description of linear interdiffusion is a prerequisite for developing a more general nonlinear theory practical for engineering problems with large composition gradients.

## Experimental Data

Odani and his coworkers (Kishimoto et al., 1960; Odani et al., 1966) carried out a series of successive differential sorption experiments for benzene in thin films of atactic polystyrene (A-PS) at 35°C. Their results are shown in Figure 1, which is plotted as mass fraction of benzene (dry polymer basis) absorbed by the polymer film, $M(t)$, against square root of time. In each interval, the chemical potential of the solvent is incremented by a small amount by increasing the benzene pressure.

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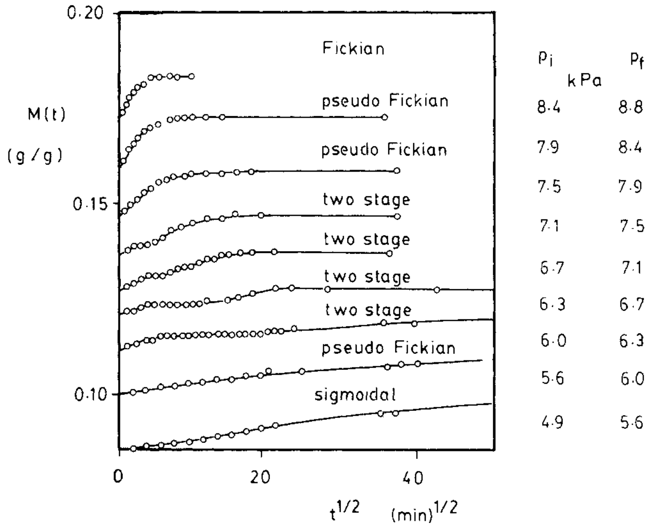

**Figure 1. Successive differential sorptions in the A-PS/benzene system at 35°C.**

Initial and final pressures, $p_i$ and $p_f$, of each step are given in the right column.
The figure shows the jargon invented by Odani to describe different non-Fickian sorption curves in a sequence of experiments with increasing average benzene content.
From Odani et al. (1966)

The weight-uptake curves follow a characteristic sequence of behaviors with increasing benzene content. Odani observed the following sequence: sigmoidal → pseudo-Fickian → two stage → pseudo-Fickian (see Figure 1). The most unusual of these is the two-stage sorption process, in which a distinct hesitation or "knee" appears in the weight-uptake data. It is the intent of this work to quantitatively predict these results without relying on the non-Fickian diffusion data to fix the physical constants in the theory.

## Theoretical Model

The development of the theory and its application to differential sorption have been presented in detail by Durning (1985) and Durning and Tabor (1986). The key physical notion is that the diffusion of solvent into the film drives a local dilation of the polymer component. Because of the relatively slow response of the polymer to this disturbance, the local chemical potential is not the thermostatic value consistent with the local composition but is elevated to some extent according to the exact local history of dilation. This affects the local driving force for diffusion (the gradient of the chemical potential) and therefore the macroscopically observed dynamics. A first principles development supplied a field equation governing the local composition in terms of the solution's thermostatic properties, its linear viscoelastic mechanical properties, and the binary mutual diffusion coefficient. We give below a summary of the key relationships using the notation of Durning (1985). For differential sorption, the system consists of a thin film of concentrated polymer solution of depth 2 ℓ in contact with a large reservoir of solvent vapor. The sorption experiment begins by incrementing the solvent chemical potential in the reservoir. Combining the continuity equation for the solvent in polymer-fixed coordinates with a flux law, which accounts for the coupling between molecular diffusion and polymer relaxation, results in the following linear integro-differential equation for the transient distribution of solvent in the film:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \xi^2} + \frac{D\overline{V}}{\mathbf{R}T}\frac{1}{w_2^2} \cdot \left(\frac{\partial f}{\partial w_1}\right)^{-1}\frac{\hat{V}_1}{\hat{V}_2}G_0\frac{\partial^2}{\partial \xi^2}\int_{-\infty}^{t}\phi(t-t')\frac{\partial C}{\partial t'}dt' \quad (1)$$

where $C = \rho_1/\rho_2\,\hat{V}_2$ is the solvent mass concentration per unit polymer volume; $\rho_i$ is the mass concentration of $i$ ($i = 1$ for solvent, $i = 2$ for polymer) while $\hat{V}_i$ is its partial specific volume. Also, $G_0\,\phi(t)$ is the shear relaxation modulus of the solution, as measured in linear viscoelastic experiments, with $G_0$ being the instantaneous shear modulus of the solution. Finally $f(C)$ is the (dimensionless) solvent chemical potential, $(\mu_1 - \mu_1^0)/\mathbf{R}T$, at equilibrium. In Eq. 1, the polymer-fixed coordinate, $\xi$, is employed and as a result the binary mutual diffusion coefficient, $D_{12}$, is replaced by $D = D_{12}\,\phi_2^2$, where $\phi_2 = \rho_2\,\hat{V}_2$ is the volume fraction of the polymer.

Introducing the following dimensionless variables:

$$\nu = \frac{C - C^-}{C^\infty a^+ - C^-}, \quad \tau = \frac{Dt}{l^2}, \quad \zeta = \frac{l-\xi}{l} \quad (2)$$

gives

$$\frac{\partial \nu}{\partial \tau} = \frac{\partial^2 \nu}{\partial \zeta^2} + \frac{\kappa\Lambda}{\theta}\frac{\partial^2}{\partial \zeta^2}\int_{-\infty}^{\tau}\phi(\tau-\tau')\frac{\partial \nu}{\partial \tau'}d\tau \quad (3)$$

with

$$\kappa = \frac{\frac{1}{w_2^2}\left(\frac{\partial f}{\partial w_1}\right)^{-1}}{\hat{V}_2 C^\infty a^+}, \quad \Lambda = \frac{D}{l^2}\frac{\overline{V}_1\eta_0\hat{V}_1}{\mathbf{R}T}C^\infty a^+, \quad \theta = \frac{D\tau_0}{l^2} \quad (4)$$

where the relationship, $G_0 = \eta_0/\tau_0$, has been used with $\eta_0$ and $\tau_0$ being the zero shear rate viscosity and dominant (longest) relaxation time of the polymer solution, respectively. It should be noted that the dimensionless relaxation function, $\phi(\tau)$, also contains the Deborah number, $\theta$. It is simple to show that, for $\theta \gg 1$ or $\ll 1$, Eq. 3 reduces to Fick's second law for any realistic relaxation function which shows that the theory is in qualitative agreement with Vrentas and Duda's Deborah number correlation.

The dimensionless initial and boundary conditions for sorption are:

at $\tau = 0^+$

$$\nu = \frac{\partial \nu}{\partial \tau} = 0 \quad (0 < \zeta < 1) \quad (5)$$

at $\zeta = 0$

$$\nu + \frac{\kappa\Lambda}{\theta}\frac{\partial^2}{\partial \zeta^2}\int_{-\infty}^{\tau}\phi(\tau-\tau')\frac{\partial \nu}{\partial \tau'}d\tau' = 1 \quad (6)$$

at $\zeta = 1$

$$\frac{\partial \nu}{\partial \zeta} + \frac{\kappa \Lambda}{\theta} \int_{-\infty}^{\tau} \phi(\tau - \tau') \frac{\partial \nu}{\partial \zeta \partial \tau'} d\tau' = 0 \tag{7}$$

Equation 5 implies that immediately after the perturbation in the environment (at $\tau = 0^+$), the benzene chemical potential inside the membrane is undisturbed. Equations 6 and 7 express that local equilibrium is maintained at the vapor/solution interface ($\zeta = 0$) and that the benzene flux is zero at the film centerline ($\zeta = 1$).

Laplace transformation of Eq. 3 and 5–7 and solution of resulting ordinary differential equation gives the following analytical solution for the Laplace transform of $\nu(\zeta, \tau)$, $\bar{\nu}(\zeta, s)$:

$$\bar{\nu}(\zeta, s) = \frac{\eta(s)}{e^{-2\vartheta(s)} + 1} \left(e^{\zeta\vartheta(s)} + e^{(2-\zeta)\vartheta(s)}\right) \tag{8}$$

with

$$\eta(s) = \frac{\theta}{s(\theta + \kappa\Lambda\overline{\phi}(s)s)}, \quad \vartheta(s) = \sqrt{\frac{s\theta}{\theta + \kappa\Lambda\overline{\phi}(s)s}} \tag{9}$$

where $\overline{\phi}(s)$ is Laplace transform of $\phi(t)$.

For the comparison of the data and theory, the simplest models were used for the relaxation function, $\phi(t)$, and the equilibrium chemical potential, $f$, to minimize computation but still capture the essential characteristics predicted by the theory. For $\phi(t)$, a simple Maxwell element was used:

$$\phi(t) = e^{-t/\tau_0} \tag{10}$$

where $\tau_0$ is a relaxation time. It is appropriate at this point to comment on the validity of this choice. Recall that $\phi(t)$ is the (dimensionless) shear relaxation modulus measured mechanically. Obviously, the Maxwell model is not a faithful representative of $\phi(t)$ over the whole range of time scales possible since it does not show the four regions of mechanical behavior typical of dense entangled systems (Aklonis, 1983). It does, however, supply a very good representation over a limited range of time scales.

For example, by setting $G_0$ equal to the plateau modulus, $G_e$, and $\tau_0$ equal to the terminal (reptation) time, the Maxwell model excellently describes linear mechanical behavior in the plateau and terminal regions (Ferry, 1980). Similarly, by setting $G_0$ equal to the glassy state modulus, $G_g$, and $\tau_0$ equal to the longest relaxation time in the transition zone [the "Rouse" time for a chain segment between entanglements (Ferry, 1980)], the model reasonably describes the linear viscoelastic response in the transition region. Therefore, if values for $G_0$ and $\tau_0$ (or equivalently for $G_0$ and $\eta_0$) were used with clear molecular-level interpretations, the use of the Maxwell model is not arbitrary nor empirical, but is a judicious simplification, motivated by the expectation that the macromolecular response to diffusion-induced deformations involves the same set of relatively slow macromolecular motions manifested in the viscoelastic mechanical response over time scales where the Maxwell model works well. This expectation seems justified since the Maxwell model was shown earlier (Durning, 1985) to provide qualitatively correct predictions of linear, anomalous sorption.

The equilibrium chemical potential of benzene in solution was calculated from the following simple equation:

$$f = \ln \frac{C}{C^{\infty}} \tag{11}$$

which accounts roughly for the translational entropy of mixing.

After introducing the appropriate $\phi(t)$ and $f$, Eq. 8 was inverted numerically using the method of Crump (1976) to compute the $\nu(\zeta, \tau)$ distribution at specified values of $\tau$. This was subsequently integrated by the trapezoidal rule to obtain the dimensionless weight gain, $\omega(\tau)$, related to the experimentally measured quantity, $M(t)$, by

$$\omega(\tau) = \frac{M(t)}{M(t = \infty)} = \int_0^1 \nu(\zeta, \tau)\, d\zeta \tag{12}$$

## Estimation of Physical Constants

There are three dimensionless groups in the model that need to be determined for each interval-sorption experiment: $\kappa$, $\theta$, and $\Lambda$. The following expression for $\kappa$ is derived from the substitution of Eq. 11 in Eq. 4:

$$\kappa = \frac{\dfrac{w_1}{w_2}}{\hat{V}_2 C^{\infty} a^+} = \frac{\dfrac{w_1}{w_2}}{\left(\dfrac{w_1}{w_2}\right)_{t\rightarrow\infty}} \tag{13}$$

Since the sorption experiments were performed under a very small perturbation of the benzene chemical potential, a value of $\kappa = 1$ was taken for all intervals. The values of $\Lambda$ and $\theta$, however, depend strongly on the concentration of benzene through their dependence on $\eta_0$ and $\tau_0$, respectively, and so vary from interval to interval. Their values for a given interval are based on the mean concentration of benzene.

Due to the simplification of a Maxwell model for $\phi(t)$, several different definitions were tried for the pair of constants, $\eta_0$ and $\tau_0$, each with a clear molecular level significance to decide the nature of the macromolecular motions which actually influence interdiffusion to produce non-Fickian effects. The calculations were based on the known mechanical properties of a monodisperse sample with a molecular weight equal to the average reported by Odani et al. (1966). Parameters that accurately describe the mechanical response in the plateau and terminal zones [i.e., $G_0 = \eta_0/\tau_0 = G_e$ and $\eta_0$ equal to the measured zero shear viscosity ($\propto M^{3.4}$)] overestimated the time scale for sorption, while parameters appropriate for the transition region [i.e., $G_0 = \eta_0/\tau_0 = G_g$ and $\eta_0$ equal to the calculated viscosity without the effect of entanglements ($\propto M$)] consistently underestimated the time scale for sorption. The best quantitative representation of the sorption data was based on taking $\eta_0$ as the measurable zero-shear viscosity ($\propto M^{3.4}$) and calculating $\tau_0$ using the glassy modulus, $G_g$, as described below. The value of $\eta_0$ was calculated from data on pure monodisperse A-PS melts measured by Akovali (1979) for $T = 129°C$. The viscosity-average molecular weight of $2.2 \times 10^5$ reported for the sorption experiments gives $\eta_0 \simeq 2.2 \times 10^9$ $P$ for pure monodisperse polystyrene at 129°C. This value was corrected to the conditions of the experiment ($T = 35°C$, mean concentration of benzene at each interval) using the Vrentas and Duda free volume theory (Vrentas and Duda, 1977; Vrentas et al., 1982) and the shifting rule discussed by Durning (1985).

Given $\eta_0$, $\tau_0$ was calculated from:

$$\tau_0 = \frac{\eta_0}{G_g - G_e} \approx \frac{\eta_0}{G_g} \tag{14}$$

We did not account for the composition or temperature dependence of $G_g$ but assumed this value was constant equal to $6.67 \times 10^9$ dyne/cm$^2$.

One should note that $\tau_0$ calculated in this way is numerically between the terminal (reptation) time and the dominant relaxation time in the transition region (Rouse time) for a monodisperse sample with the same molecular weight. This value successfully described the sorption data because of the broad molecular weight distribution of the samples used in the sorption experiments, which evidently makes it impossible to separate the effects on the diffusion of transition and terminal zone relaxation processes. [The reader should note an error in our earlier paper (Durning, 1985) identifying $\tau_0$ (denoted there as $\tau^3$) as the terminal relaxation time.]

The diffusion constant, $D$, in $\theta$ was determined from the Vrentas and Duda free volume theory and the Flory-Huggins solution theory. The relevant expressions are:

$$D_{12} = G D_{01}\, e\left[-\frac{\gamma(w_1 \hat{V}_1^* + w_2 \delta \hat{V}_2^*)}{\hat{V}_F}\right] \tag{15}$$

with

$$\frac{\hat{V}_F}{\gamma} = w_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + w_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T) \tag{16}$$

and

$$G = (1 - \hat{V}_1 \rho_1)^2 (1 - 2\chi \hat{V}_1 \rho_1) \tag{17}$$

A value $\chi = 0.14$ (reported by Kishimoto et al., 1960) was used in the last expression for the Flory-Huggins interaction parameter.

The free-volume parameters for pure A-PS, $K_{12}/\gamma$, $K_{22} - T_{g2}$, and $\hat{V}_2^*$, are taken from Vrentas et al. (1982). Two parameters related to the solvent (benzene), $K_{11}/\gamma$ and $K_{21} - T_{g1}$, are normally calculated from low-temperature (near glass transition temperature, $T_g$) viscosity data on the solvent (see Vrentas and Duda, 1977, for example). Benzene, however, freezes at a rather high temperature, far above $T_g$, and therefore the usual procedure could not be employed. Instead, the parameters were estimated from low-temperature viscosity data for toluene, ethyl benzene, and *n*-propylbenzene reported by Barlow et al. (1966). The group contribution method of Van Velzen (Reid et al., 1977) was used to correct the *n*-alkyl benzene viscosities to equivalents for supercooled benzene. The free-volume constants were then determined in the usual way as described by Vrentas and Duda (1977). The resulting three sets of free-volume constants were averaged. The remaining free-volume constant for benzene, $\hat{V}_1^*$, was calculated by the group contribution method of Sugden (1928).

The constant $D_{01}$ in Eq. 15 was obtained from a diffusion coefficient extracted from the sorption data in the top interval of Figure 1 by the procedure outlined by Vrentas et al. (1977). The remaining parameter, $\delta$, (denoted as $\xi$ by Vrentas and Duda, 1977) was determined from the diffusion data of Pawlisch et al. (1988), who reported the infinite-dilution diffusion constants for benzene in A-PS at various temperatures above the glass transition. Under these conditions ($w_1 = 0$), Eq. 15 reduces to:

$$D_{12} = D_{01}\, e^{-}\left[\frac{\hat{V}_2^* \delta}{\frac{K_{12}}{\gamma}(K_{22} - T_{g2} + T)}\right] \tag{18}$$

A plot of $\ln D_{12}$ vs. $1/(K_{22} - T_{g2} + T)$ was fit with a straight line, and its slope was used to calculate $\delta$. Table 1 lists the parameters used in the calculations.

## Results and Discussion

Figures 2a to 2g compare the experimental weight-gain curves of Figure 1, plotted in dimensionless form, with those computed *a priori* from the theory. Calculations for the top interval (Figure 2a), which was used in obtaining $D_{01}$ earlier, resulted in $\theta = 0.002$ which confirms the assumption that the diffusion is nearly Fickian. Note that the data fall below the prediction in Figure 2a at long times suggesting that the coupling between diffusion and relaxation is still present to some extent at very high benzene contents where the solution is rubber-like. At lower pressure intervals (Figures 2b and 2c), which Odani identified as pseudo-Fickian behavior, the deviation from the theoretical predictions become progressively larger suggesting more significant intrusions of the protracted macromolecular response on the process than predicted. These deviations could be accounted for by the use of a more realistic relaxation function with a relaxation spectrum peaked at $\tau_0$. The minor contribution of the longer relaxation times would delay the predicted approach to equilibrium at long times and produce a better fit. Although we did not pursue this calculation, it would be justified in the present case since the molecular weight distribution is broad.

The interval 7.1 → 7.5 kPa (Figure 2d) shows equivocal

**Table 1. Parameters for A-PS-Benzene**

| Symbol | Value |
|---|---|
| $\frac{K_{11}}{\gamma}$ | $1.83 \times$ m$^3$/kg |
| $\frac{K_{12}}{\gamma}$ | $5.82 \times 10$ m$^3$/kg |
| $K_{21} - T_{g1}$ | $-91.6$ K |
| $K_{22} - T_{g2}$ | $-327.0$ K |
| $\hat{V}_1^*$ | $0.9013 \times 10^{-3}$ m$^3$/kg |
| $\hat{V}_2^*$ | $0.850 \times 10^{-3}$ m$^3$/kg |
| $D_{01}$ | $7.8 \times 10$ m$^2$/s |
| $\delta$ | 0.379 |
| $\chi$ | 0.14 |

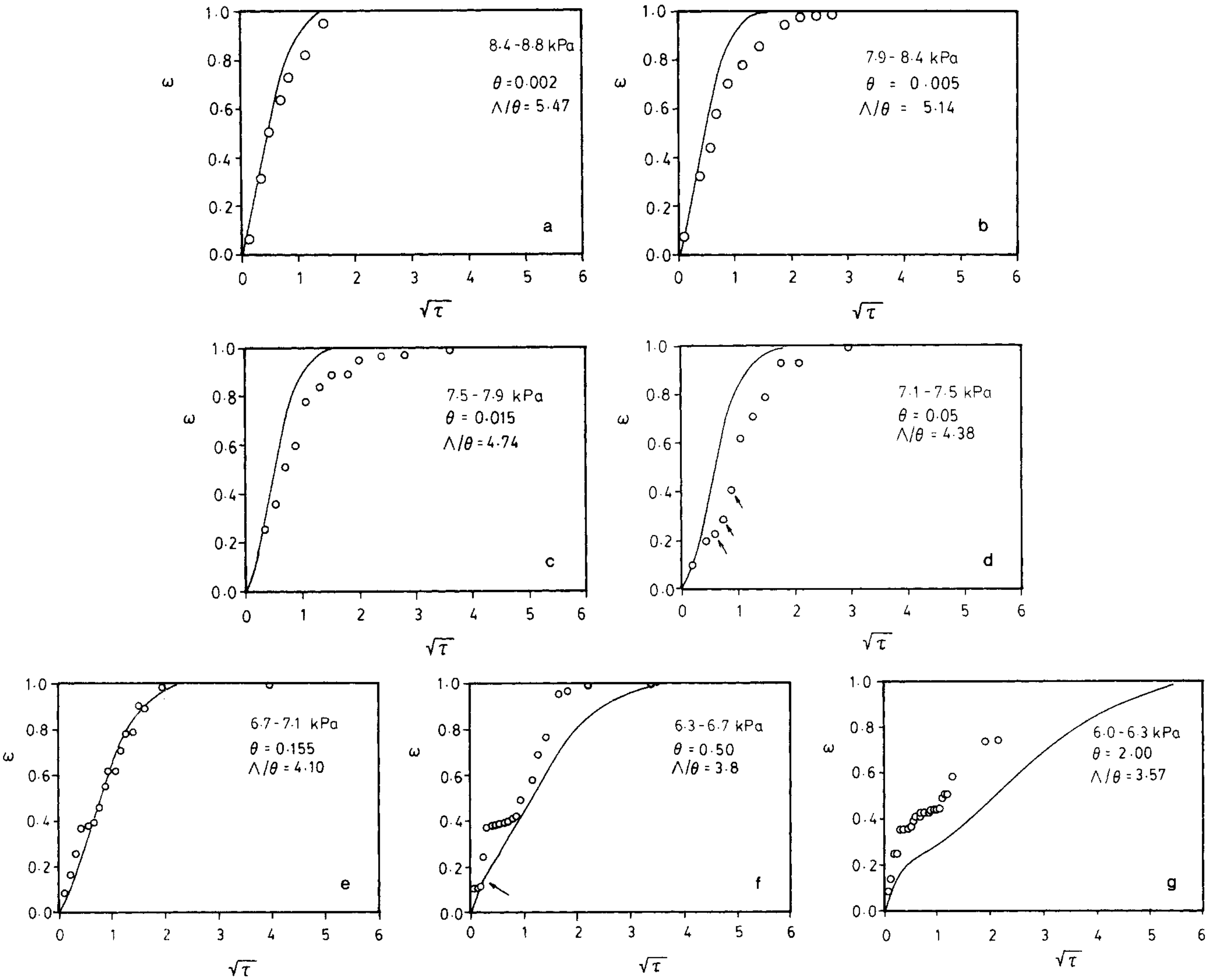

**Figure 2. Comparison of experimental and predicted relative weight gain, $\omega(\tau)$, as a function of $\sqrt{\tau}$ for benzene in A-PS at 35°C.**

Solid lines show the theoretical predictions.

The experimental pressure intervals and the dimensionless parameters for the predictions are indicated.

evidence of two-stage uptake even though it is identified as two-stage by Odani et al. The theory predicts only a mildly non-Fickian behavior (some upward curvature initially) since the Deborah number is still quite small, $\theta = 0.05$. It should, however, be noted that the data suggesting two-stage behavior are only three points (arrows in Figure 2d), so it is unclear whether truly two-stage or pseudo-Fickian behavior is appearing. If the data are accepted as pseudo-Fickian, the disagreement with theory could be largely corrected by the minor contribution of longer relaxation times as for Figures 2a-2c.

The calculations for the interval 6.7 → 7.1 kPa (Figure 2e) show an excellent agreement with the experimental results. The data show that this interval (as well as the previous one) is really showing pseudo-Fickian behavior even though it is identified as a two-stage by Odani et al. The relaxation time $\tau_0$ seems to properly capture the coupling at these conditions which has the effect of retarding the approach to equilibrium.

In the interval 6.3 → 6.7 kPa (Figure 2f), the data show a clear two-stage behavior. The theoretical result is only beginning to show a two-stage behavior (mild "knee" denoted by arrow); it still resembles more a pseudo-Fickian prediction. At the next lower interval, 6.3 → 6.7 kPa, (Figure 2g) both the data and theory are clearly two-stage. The theory predicts the correct shape, but the knee appears at $\omega = 0.2$ rather than the experimentally observed value of $\omega = 0.4$, and the time scale for the predicted behavior seems too long. There are two possible causes for the discrepancies. Calculations reveal that the value of $\omega$, where the knee appears, depends only on the value of $\Lambda/\theta$ and varies inversely with this ratio. Assuming that the modulus associated with $\tau_0$, $G_g$, is constant and that $f$ obeys Eq. 11, we predict that $\Lambda/\theta$ varies slowly with composition and has value around 4 at the conditions where two-stage weight uptake is encountered. These assumptions are very crude and it is likely that the real behavior of $\Lambda/\theta$ differs. Consequently, we treated $\Lambda/\theta$ as adjustable to see if a better representation of data in Figures 2f and 2g could be produced. Values of $\Lambda/\theta$ (with the values of $\theta$ fixed) were used that resulted in a knee around $\omega = 0.4$. Figures 3a and 3b show that the computed results with

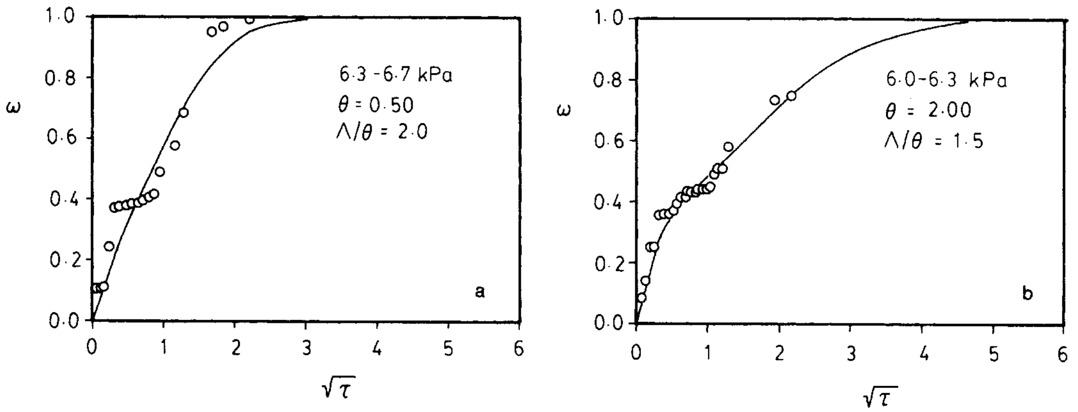

**Figure 3. Experimental vs. predicted relative weight gain, $\omega(\tau)$, as a function of $\sqrt{\tau}$ for benzene in A-PS at conditions where two-stage weight gain appears.**

The value of $\Lambda/\theta$ was treated as adjustable to improve the predictions in Figures 2f and 2g.

$\Lambda/\theta = 2.0$ for the interval 6.3→ 6.7 kPa, and with $\Lambda/\theta = 1.5$ for the interval 6.0 → 6.3 kPa give a better overall fit of the experimental results. Unfortunately, manipulating only $\Lambda/\theta$ still falls short of predicting a clear two-stage behavior for the 6.3 → 6.7 kPa interval.

A second approach to correcting the discrepancy between theory and experiment in Figures 2f and 2g is as follows. As demonstrated by Kishimoto et al. (1960), the non-Fickian behavior under study includes conditions where the solvent concentration falls below the value at which the polymer/solvent mixture glassifies. For the A-PS/benzene system, we calculated this value to be $M = 0.135$ of benzene per gram A-PS at $T = 35°\text{C}$ (Appendix); Kishimoto et al. (1960) estimate it to be 0.15 from their sorption data. Since the sorption data for the intervals for Figures 2f and 2g occur at compositions below this value, the effect of the glass transition on the physical constants should be considered. To do this, a modification of the free-volume theory to conditions below the glass transition was employed to calculate the mutual diffusion constant $D_{12}$ and $\tau_0$ (Vrentas et al., 1988). The modified version introduces an expression for the "excess" free volume in the glass state, $\hat{V}_F^E/\gamma$, which is added to Eq. 16. It takes into account the decrease in the thermal expansion coefficient of the polymer as the polymer/solvent mixture goes through the glass transition temperature:

$$\frac{\hat{V}_F^E}{\gamma} = w_2\left[\frac{\hat{V}_2^0(T_{g2})}{\gamma}\right] \cdot [1 - \alpha_2(T_{g2} - T_{gm})](T - T_{gm})(\alpha_{2g} - \alpha_2) \qquad (19)$$

Here, $\hat{V}_2^0(T_{g2})$ is the equilibrium-specific volume of the pure polymer at $T_{g2}$, $\alpha_2$ and $\alpha_{2g}$ are the thermal expansion coefficient of the polymer above and below $T_{g2}$, and $T_{gm}$ is the glass transition temperature of the mixture. Since the sorption experiments were performed at high concentrations of A-PS, we assumed that $T_{gm}$ decays linearly with benzene composition:

$$T_{gm} = T_{g2} - Aw_1 \qquad (20)$$

and used a value of 550 K for the constant $A$ (this value is consistent with the $w_1 \rightarrow 0$ limit of the equations in the Appendix). Lacking experimental data for $\alpha_{2g}$, we chose a value that would best represent the data. Other constants related to A-PS, $\hat{V}_2^0(T_{g2})$, and $\alpha_2$ are available in the literature (Hocker et al., 1971; Fox and Loshack, 1955). Table 2 lists the parameters used in obtaining the excess free volume.

Using the modified version of free volume theory resulted in $\theta = 0.33$, $\Lambda/\theta = 3.80$ for the interval 6.3 → 6.7 kPa, and $\theta = 0.85$, $\Lambda/\theta = 3.57$ for the interval 6.0 → 6.3 kPa. Figures 4a and 4b compare the computed weight-gain curves to those obtained experimentally. Although the agreement is improved, again the two-stage behavior observed in the interval 6.3 → 6.7 kPa is not predicted by the theory. Clearly, the theory is not completely satisfactory in reproducing two-stage uptake. It should, however, be remembered that the simple Maxwell model used for the relaxation function of A-PS was chosen for mathematical simplicity and one really needs to consider a distribution of relaxation times to fully describe the relaxation behavior of A-PS, particularly with a broad molecular weight distribution as the samples in this sorption work undoubtedly had.

We did not compare the theory and the data at benzene contents lower than that for Figure 2g. In these cases,

- The sorption experiments were not carried out with sufficient precision to make meaningful comparisons with the theory.
- The dependence of the transport properties on composition in this regime is not understood well enough yet to allow meaningful estimates from independent data. The latter is particularly true for the ratio $\Lambda/\theta$.

## Summary and Conclusions

A model accounting for the time-dependent response of polymer to diffusion-induced deformations has been used to

**Table 2. Excess Free Volume Parameters**

| Symbol | Value |
|---|---|
| $\frac{\hat{V}_2^0(T_{g2})}{\gamma}$ | $1.6403 \times 10^{-3}\,\text{m}^3/\text{kg}$ |
| $\alpha_2$ | $5.5 \times 10^{-4}\,\text{K}^{-1}$ |
| $\alpha_{2g}$ | $4.15 \times 10^{-4}\,\text{K}^{-1}$ |
| $T$ | 308 K |
| $T_{g2}$ | 373 K |

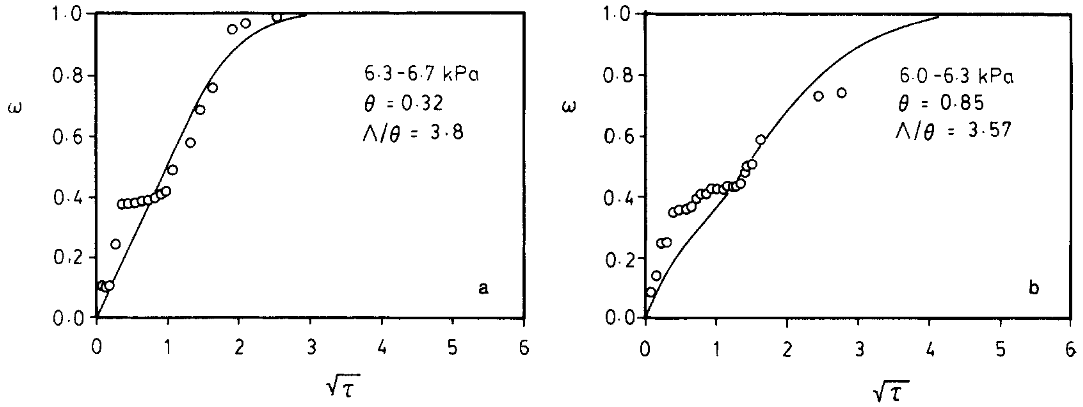

**Figure 4. Experimental vs. predicted relative weight gain, $\omega(\tau)$, as a function of $\sqrt{\tau}$ for benzene in A-PS at conditions where two-stage weight gain appears.**

Dimensionless numbers were computed from the free-volume theory including excess free volume to improve the predictions in Figures 2f and 2g.

quantitatively predict the experimental results of Odani and coworkers for successive differential sorptions of benzene in atactic polystyrene. For the range examined, the predicted trend with benzene content agrees with that seen experimentally: in order of decreasing benzene content, the uptake curves are in the sequence Fickian → pseudo-Fickian → two stage. The quantitative agreement is reasonable but not perfect. With a single Maxwell element for the relaxation function, the model overestimated the benzene uptake at long times for the Fickian and some of the pseudo-Fickian curves. Also, it predicts the appearance of two-stage behavior at too low a benzene content with a significantly slower second stage than observed . Accounting for the inaccuracy in estimating the ratio $\Lambda/\theta$ and the effect of the glass transition on the transport properties seems to reduce the latter discrepancy but does not fully correct the former. It is likely that the shortcomings of the theory are due, at least in part, to a distribution of relaxation times for the atatic polystyrene samples which had a broad molecular weight distribution.

It is interesting to note the best quantitative agreement between the theory with a Maxwell element and the sorption data by picking $\tau_0$ ***between*** the terminal (reptation) relaxation time and the longest relaxation time in the transition zone (Rouse time) for corresponding monodisperse polymer sample. This makes perfect sense since the relaxation spectrum for a concentrated system with a broad molecular weight distribution does not show sharp, well-separated peaks for the terminal and transition zones as for a monodisperse sample, but rather shows a broad featureless spectrum with the two peaked regions overlapping (Ferry, 1980). Consequently, distinct contributions from terminal and transition zone relaxations ***cannot*** be discerned in mechanical experiments; therefore, they probably cannot be discerned in the diffusion data discussed here. Consequently, the best overall agreement results from a relaxation time numerically between the dominant ones in the terminal and transition zones for a corresponding monodisperse sample.

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## Notation

$a$ = local activity of solvent
$a^-$ = initial solvent activity in the environment
$a^+$ = final solvent activity in the environment
$A$ = constant in Eq. 20
$C$ = local solvent concentration ($\rho_1/\hat{V}_2\rho_2$)
$C^-$ = value of $C$ at $t = 0^-$
$C^+$ = value of $C$ at $t = 0^+$
$C^\infty$ = solvent concentration in equilibrium with the environment at $a^+ = 1$
$D_{12}$ = binary mutual diffusion coefficient
$D$ = $(\rho_2\hat{V}_2)^2D_{12}$
$D_{01}$ = preexponential factor in Vrentas and Duda theory for $D_{12}$
$f$ = dimensionless chemical potential, $(\mu_1 - \mu_1^0)/RT$, at equilibrium
$G$ = thermodynamic factor in $D_{12}$ defined in Eq. 18
$G_e$ = shear modulus in the plateau region
$G_g$ = shear modulus in the glassy region
$K_{ij}$ = empirical constants in Vrentas and Duda theory related to WLF constants
$l$ = membrane thickness
$R$ = molar gas constant, 8.31441 J · mol$^{-1}$ · K$^{-1}$
$s$ = variable in Laplace space
$T$ = absolute temperature, K
$T_{gi}$ = glass transition temperature of pure $i$, K
$T_{gm}$ = glass transition temperature of polymer/solvent mixture, K
$t$ = lab time
$\bar{V}_i$ = molar volume of $i$
$\hat{V}_i$ = partial specific volume of $i$
$\hat{V}_F$ = specific hole free volume of the polymer/solvent mixture
$\hat{V}_i^*$ = critical occupied volume of $i$
$\hat{V}_i^0$ = equilibrium specific volume of $i$
$w_i$ = local mass fraction of $i$
$x$ = distance in the lab frame

### *Greek letters*

$\alpha_2$ = thermal expansion coefficient of polymer
$\alpha_{2g}$ = thermal expansion coefficient of polymer at $T_{g2}$
$\gamma$ = factor in the Vrentas and Duda theory indicating how the molecules share free volume
$\delta$ = ratio of critical occupied volume of solvent to critical volume of polymer jump unit
$\zeta$ = dimensionless distance in the polymer fixed fixed frame
$\eta_0$ = zero-shear viscosity
$\theta$ = diffusion Deborah number
$\kappa$ = dimensionless parameter defined in Eq. 4
$\chi$ = thermodynamic interaction parameter
$\Lambda$ = dimensionless parameter defined in Eq. 4
$\mu_1$ = local chemical potential of solvent
$\mu_1^0$ = chemical potential of solvent at reference conditions

$\nu$ = dimensionless concentration
$\xi$ = distance in the polymer fixed frame
$\rho$ = mass density of solution
$\rho_i$ = local mass density of $i$
$\tau$ = dimensionless time
$\tau_i$ = relaxation times of the polymer
$\omega(\tau)$ = relative weight gain

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## Appendix

We used the following equation, derived by Richards (1983) from the Vrentas-Duda free-volume theory, to obtain the benzene composition at which the glass transition of the atatic polystyrene/benzene mixture, $T_{gm}$, reaches the temperature at which the sorption experiments of Odani et al. were conducted (35°C):

$$T_{gm} - C_2 = \frac{w_1 \frac{K_{11}}{\gamma}(K_{21} - T_{g1}) + w_2 \frac{K_{12}}{\gamma}(K_{22} - T_{g2})}{w_1 \frac{K_{11}}{\gamma} + w_2 \frac{K_{12}}{\gamma}} \tag{A1}$$

where

$$C_2 = 51.6 \text{ K}$$

is a WLF constant for polystyrene. This relationship gives $M = 0.134$. Nearly the same value ($M = 0.136$) results from the expression of Chow (1980) based on the Gibbs-Dimarzio theory of the glass transition:

$$\ln\left(\frac{T_{gm}}{T_{g2}}\right) = \beta\left[\left(1 - \frac{\alpha\omega_1}{1 - \omega_1}\right)\ln\left(1 - \frac{\alpha\omega_1}{1 - \omega_1}\right) + \frac{\alpha\omega_1}{1 - \omega_1}\ln\left(\frac{\alpha\omega_1}{1 - \omega_1}\right)\right] \tag{A2}$$

where $\alpha = 0.684$ and $\beta = 0.616$ are constants of the polystyrene-benzene system.

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