

# Solvent Diffusion in Molten Polyethylene

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## Synopsis

Diffusivity data are presented for the *o*-xylene–polyethylene system in the temperature range 125–175°C. The diffusion coefficient increases slightly as the solvent concentration increases near the pure polymer limit. Although the concentration and temperature dependences of the diffusivity for this system are different from what are typically observed for polymer–solvent systems, they are consistent with the free-volume theory of diffusion.

## INTRODUCTION

A significant number of experimental diffusivity data has been collected for polymer–solvent systems at temperatures which are within about 100°C of the glass transition temperature of the pure polymer.<sup>1–3</sup> For such systems, the qualitative aspects of the temperature and concentration dependences of the mutual diffusion coefficient appear to be well established. At temperatures above the polymer glass transition temperature, there is a strong concentration dependence of the diffusivity at low solvent concentrations. This behavior is illustrated in Figure 1 where a large increase is observed in the diffusivity of the toluene–polystyrene system<sup>4</sup> as the solvent concentration is increased from the pure polymer limit. Furthermore, there can be a strong temperature dependence of the diffusion coefficient evaluated in the limit of zero solvent concentration. The activation energy for diffusion is high and decreases significantly with increasing temperature. An example of this type of behavior is presented in Figure 2 which shows that the diffusivity of the toluene–polystyrene system at the pure polymer limit increases substantially with increasing temperature, and this is accompanied by a large decrease in the activation energy.

These temperature and concentration variations of the mutual diffusion coefficient can be explained using the free-volume theory of diffusion.<sup>3,5–9</sup> The amount of free volume available for molecular transport is relatively small in polymers near their glass transition temperatures. Hence, the addition of solvent or an increase in temperature leads to a substantial fractional increase in the hole free volume and, thus, in the rate of molecular transfer in the polymer–solvent mixture. The free-volume model can be used to quantitatively predict the rapid increases in the diffusivity with increasing solvent concentration and increasing temperature.<sup>10,11</sup>

Relatively few studies have been concerned with both concentration and temperature effects in polymer–solvent systems at temperatures more than 200°C above the polymer glass transition temperature. Under such conditions, the free volume associated with the pure polymer may no longer be very low, and, from free-volume considerations, it would be expected that the effect of tem-

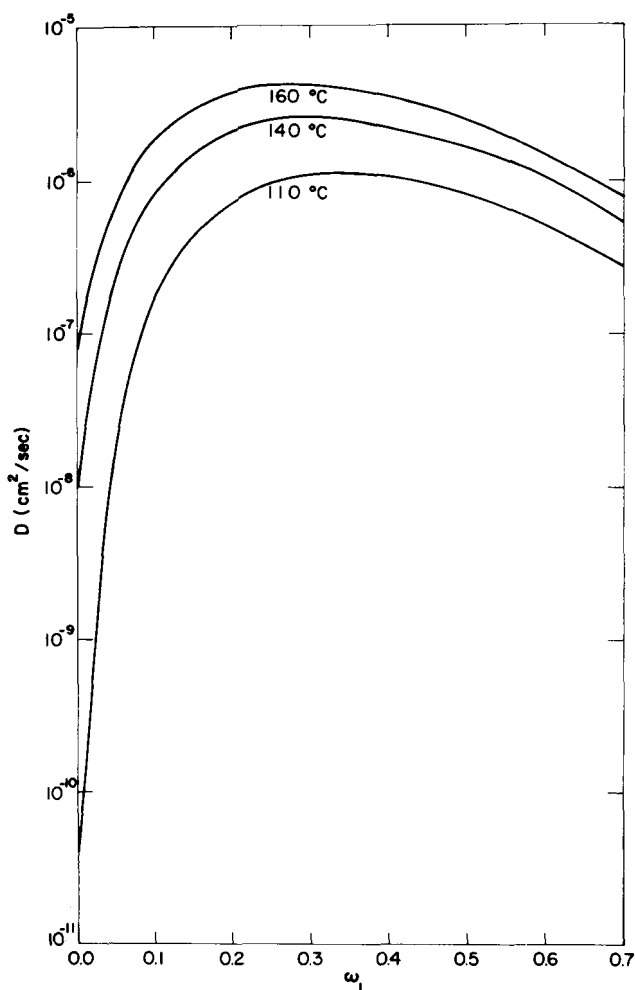


Fig. 1. Dependence of diffusivity on mass fraction for toluene-polystyrene system.

perature and solvent concentration on the diffusivity would be less pronounced. In this study, diffusivity data are obtained for the *o*-xylene-polyethylene system in the temperature range 125–175°C and for solvent mass fractions as high as 40 wt %. This temperature range is more than 200°C above the glass transition temperature of polyethylene.<sup>12</sup> Diffusivity data for such an important polymer as polyethylene are of interest in their own right, and, furthermore, it is of interest to see if the observed temperature and concentration dependences can be explained using the free-volume theory of diffusion. The data show a significantly different diffusivity-concentration relationship than has been observed for most polymer-solvent systems, but the data appear to be consistent with the equations of free-volume theory.

### THEORY

The mutual diffusion coefficient  $D$  for a polymer-solvent system can be described in terms of the self-diffusion coefficient of the solvent,  $D_1$ , and of a thermodynamic factor  $Q$  by the following set of free-volume equations<sup>10,11</sup>:

$$D = D_1 Q \quad (1)$$

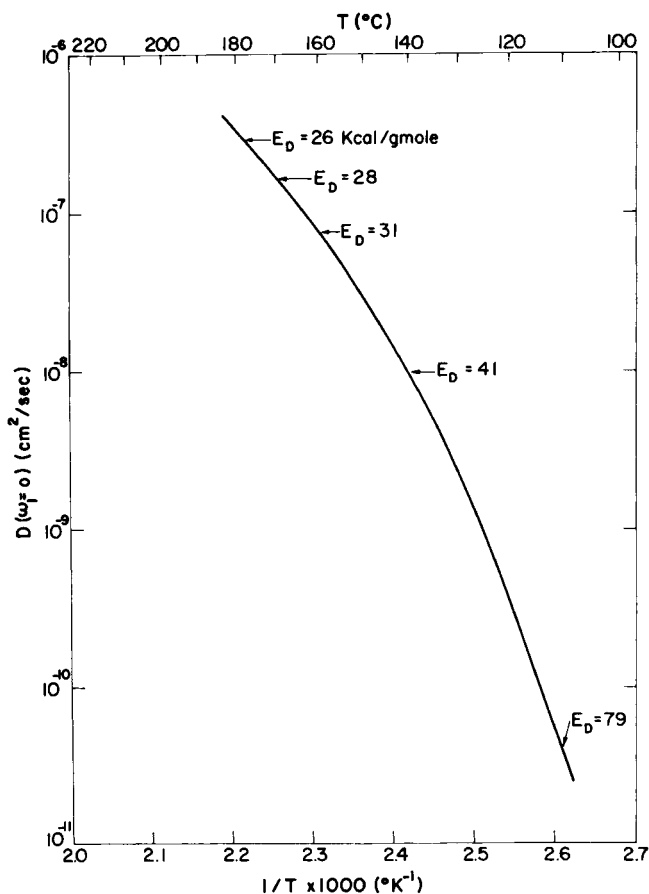


Fig. 2. Temperature dependence of diffusivity at zero solvent mass fraction for toluene-polystyrene system.

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp\left[-\frac{(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}/\gamma}\right] \quad (2)$$

$$Q = (1 - \phi_1)^2 (1 - 2\chi\phi_1) \quad (3)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{\hat{V}_{FH}(1)}{\gamma} + \omega_2 \frac{\hat{V}_{FH}(0)}{\gamma} \quad (4)$$

$$\frac{\hat{V}_{FH}(0)}{\gamma} = \frac{K_{12}}{\gamma} (K_{22} + T - T_{g2}) \quad (5)$$

$$\frac{\hat{V}_{FH}(1)}{\gamma} = \frac{K_{11}}{\gamma} (K_{21} + T - T_{g1}) \quad (6)$$

In this version of free-volume theory, we have assumed that the partial specific volumes of both polymer and solvent are independent of concentration and that the thermodynamics of the polymer-solvent system are described by the Flory-Huggins theory<sup>13</sup> with an interaction parameter  $\chi$  which is independent of concentration, but not necessarily of temperature. Furthermore, it is assumed

that all thermal expansion coefficients needed to calculate the various volumes required for the theory are approximated by average values in the temperature range under consideration.

In the above equations, the subscripts 1 and 2 refer to solvent and polymer, respectively. Also,  $D_0$  is a constant preexponential factor,  $\omega_I$  is the mass fraction of component  $I$ ,  $\hat{V}_I^*$  is the specific critical hole free volume of component  $I$  required for a jump, and  $\phi_I$  is the volume fraction of component  $I$ . Furthermore,  $T_{gI}$  is the glass transition temperature of component  $I$ ,  $K_{11}$  and  $K_{21}$  are free-volume parameters for the solvent,  $K_{12}$  and  $K_{22}$  are free-volume parameters for the polymer, and  $\gamma$  is an overlap factor for free volume. In addition,  $\hat{V}_{FH}$  is the average hole free volume per gram of mixture,  $\hat{V}_{FH}(0)$  is the specific hole free volume of the pure polymer at temperature  $T$ , and  $\hat{V}_{FH}(1)$  is the specific hole free volume of the pure solvent at  $T$ . Finally,  $\xi$  is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, and  $E$  is the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors. The definitions of the free-volume parameters  $K_{11}/\gamma$ ,  $K_{21}$ ,  $K_{12}/\gamma$ , and  $K_{22}$ , which are given elsewhere,<sup>7,8</sup> are not repeated here since they are not needed in the present context. However, we note that these four constants are directly related to the WLF constants<sup>7,9,14</sup> of the solvent and polymer. Solvent and polymer viscosity data can be used to determine  $K_{11}/\gamma$ ,  $K_{12}/\gamma$ ,  $K_{21} - T_{g1}$ , and  $K_{22} - T_{g2}$ .

We shall now use the above equations to derive results which show explicitly how increases in the temperature or the solvent concentration affect the diffusivity. We further derive an equation which can be used to confirm the applicability of free-volume theory to the type of diffusion data presented here. This equation can also be used to compute the ratio of the free volume of pure solvent to the free volume of pure polymer,  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ , at a given temperature.

An activation energy for diffusion in the limit of zero solvent mass fraction can be defined as

$$E_D = RT^2 \left( \frac{\partial \ln D}{\partial T} \right)_{P, \omega_1=0} \quad (7)$$

and, from eqs. (1)–(3), the free-volume result for  $E_D$  can be expressed as follows:

$$E_D = E + \frac{RT^2 \xi \hat{V}_2^* \gamma K_{12}}{[\hat{V}_{FH}(0)]^2} \quad (8)$$

In addition, the temperature dependence of  $E_D$  is given by the following equation:

$$\frac{\partial E_D}{\partial T} = \frac{2RT \xi \hat{V}_2^* \gamma K_{12}^2 (K_{22} - T_{g2})}{[\hat{V}_{FH}(0)]^3} \quad (9)$$

It is clear from eq. (8) that the activation energy for the diffusion of a trace of solvent in an amorphous polymer is very much dependent on the amount of hole free volume which is available to the polymer. At a given temperature, the activation energy is generally much greater for diffusion in a polymer which is relatively close to its glass transition temperature [low  $\hat{V}_{FH}(0)$ ] than for diffusion in a polymer which is significantly above its glass temperature [relatively high  $\hat{V}_{FH}(0)$ ]. Similarly, from eq. (9), it is evident that  $E_D$  is generally very temper-

ature-dependent for diffusion in a polymer near its glass temperature whereas  $E_D$  can be effectively constant for diffusion in a polymer at temperatures considerably above its glass transition temperature. Since  $K_{22} - T_{g2} < 0$  for all common polymers,  $E_D$  must decrease with increasing temperature.

The concentration dependence of the mutual diffusion coefficient can conveniently be assessed by computing the derivative of the diffusivity with respect to weight fraction at  $\omega_1 = 0$ . From eqs. (1)–(3), it is easy to derive the following result:

$$\left[ \frac{\partial \ln D}{\partial \omega_1} \right]_{\omega_1=0} = \frac{\gamma \hat{V}_1^*}{[\hat{V}_{FH}(0)]} \left[ \frac{M_{j1} \hat{V}_{FH}(1)}{M_{j2} \hat{V}_{FH}(0)} - 1 \right] - 2(1 + \chi) \frac{\hat{V}_1^0}{\hat{V}_2^0} \quad (10)$$

where we have used the definition

$$\xi = \frac{\hat{V}_1^* M_{j1}}{\hat{V}_2^* M_{j2}} \quad (11)$$

Here,  $M_{jI}$  is the molecular weight of the jumping unit of component  $I$  and  $\hat{V}_I^0$  is the specific volume of pure component  $I$ . The first term in eq. (10) describes how the addition of solvent molecules influences the solvent self-diffusion coefficient for low solvent mass fractions, and the second term characterizes the concentration dependence of the thermodynamic factor near the pure polymer limit. The ratio  $M_{j1}/M_{j2}$  is generally not too different from one except for the diffusion of very small solvents, like water, in amorphous polymers.<sup>5</sup>

It is evident from eq. (10) that a very substantial concentration dependence for  $D$  will be observed when  $\hat{V}_{FH}(0)$  is small and when the ratio  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  is large. This will generally happen when polymer–solvent diffusion is studied at temperatures close to the glass temperature of the pure polymer. Under these conditions, the positive first term overwhelms the negative thermodynamic term. On the other hand, when polymer–penetrant diffusion is investigated at temperatures substantially above the polymer glass transition temperature,  $\hat{V}_{FH}(0)$  is not particularly small and the ratio  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  may not be that large since both the solvent and polymer are far away from their respective glass temperatures. In this case, the positive self-diffusion term may no longer be large and a rapid change of  $D$  with  $\omega_1$  cannot be expected. Furthermore, the self-diffusion and thermodynamic terms in eq. (10) are much closer to each other in magnitude, and it is conceivable that the negative thermodynamic term will cause the diffusion coefficient to actually decrease with increasing solvent concentration. We know of no instance where this type of diffusivity–mass fraction behavior has been observed previously for polymer–solvent systems near the pure polymer limit.

Finally, from eq. (2), we can derive the following free-volume equation for the concentration dependence of  $D_1$ :

$$\frac{1}{\ln [D_1(\omega_1)/D_1(0)]} = \frac{[\hat{V}_{FH}(0)/\gamma][\hat{V}_{FH}(1) - \hat{V}_{FH}(0)]}{\xi \hat{V}_{FH}(1) \hat{V}_2^* - \hat{V}_{FH}(0) \hat{V}_1^*} + \frac{1}{\omega_1} \frac{[\hat{V}_{FH}(0)/\gamma] \hat{V}_{FH}(0)}{\xi \hat{V}_{FH}(1) \hat{V}_2^* - \hat{V}_{FH}(0) \hat{V}_1^*} \quad (12)$$

Here,  $D_1(\omega_1)$  is the self-diffusion coefficient of the solvent at  $\omega_1$  and  $D_1(0)$  is the solvent self-diffusion coefficient at  $\omega_1 = 0$ . If both equilibrium and diffusivity data are available for a polymer–solvent system, then  $D_1(\omega_1)$  can be computed

from eq. (1), and a plot of  $1/\ln [D_1(\omega_1)/D_1(0)]$  vs.  $1/\omega_1$  can be constructed. A linear relationship will be obtained if free-volume theory provides an adequate description of the diffusion process. Furthermore,  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  can be computed from the slope and intercept of the straight line represented by eq. (12), using the following expression:

$$\hat{V}_{FH}(1)/\hat{V}_{FH}(0) = 1 + \text{intercept/slope} \quad (13)$$

It should be noted that it is not possible to determine  $\hat{V}_{FH}(0)$  and  $\hat{V}_{FH}(1)$  individually from free-volume theory since it is  $K_{12}/\gamma$  and  $K_{11}/\gamma$  rather than  $K_{12}$  and  $K_{11}$  which are the calculated free-volume parameters. Hence, as is evident from eqs. (5) and (6), only  $\hat{V}_{FH}(0)/\gamma$  and  $\hat{V}_{FH}(1)/\gamma$  can be determined. However, eq. (13) provides a simple means of determining the ratio of hole free volumes of the individual species. Although  $\hat{V}_{FH}(0)$  cannot be determined directly from polymer viscosity data, we note that  $\hat{V}_{FH}(0)$  at  $T_{g2} + 200^\circ\text{C}$  is typically more than 5 times  $\hat{V}_{FH}(0)$  at  $T_{g2}$ .

## EXPERIMENTAL

The diffusivity and solubility data obtained in this study were collected using a step-change sorption experiment carried out on a high-temperature quartz spring sorption balance. The apparatus and experimental procedure are described in detail elsewhere.<sup>4,15,16</sup> The analysis of the variable diffusivity sorption experiment was carried out using a procedure based on the concept of an appropriate average diffusivity.<sup>17</sup>

The polymer used in this study was a commercial sample of linear low-density polyethylene with a weight-average molecular weight of 80,000 and a melting point range of 105–110°C.

## RESULTS AND DISCUSSION

Diffusivity and equilibrium data were obtained for the *o*-xylene–polyethylene system at 125°C, 150°C, and 175°C. The sorption equilibrium data are well represented at each temperature by the sorption isotherm from the Flory–Huggins theory for polymer solutions

$$\ln B = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \quad (14)$$

where

$$\ln B = \ln \left( \frac{P}{P_S} \right) + \int_{P_S}^P \frac{z-1}{P'} dP' + \frac{V_l^m}{RT} (P_S - P) \quad (15)$$

This form of the Flory–Huggins theory includes corrections for deviations from ideal gas behavior and for pressure effects in the liquid phase. In the above expression,  $P$  is the partial pressure of the solvent in the liquid mixture,  $P_S$  is the vapor pressure of the pure solvent,  $z$  is the compressibility factor for the gas phase, and  $V_l^m$  is the molar volume of the liquid solvent. Although the interaction parameter  $\chi$  is effectively constant over the entire concentration range considered at each temperature, there is a significant decrease of  $\chi$  with increasing temperature. Values of 0.35, 0.25, and 0.20 were estimated for  $\chi$  at 125°C, 150°C, and 175°C, respectively. The Flory–Huggins fit of the equilibrium

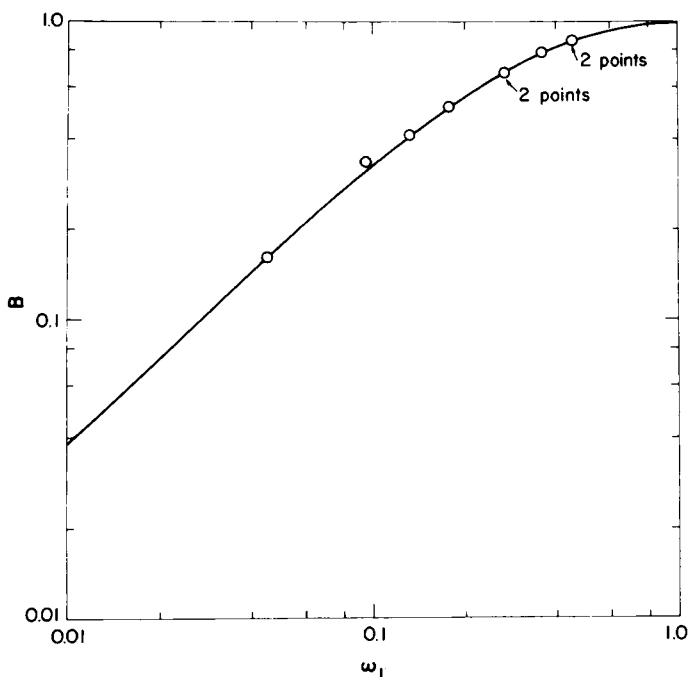


Fig. 3. Comparison of Flory-Huggins theory with thermodynamic data for *o*-xylene-polyethylene system at 125°C. Solid line represents theoretical prediction with  $\chi = 0.35$ .

data is illustrated in Figure 3 for 125°C. The solubility data for the *o*-xylene-polyethylene system can be contrasted with the thermodynamic data collected by Newman and Prausnitz<sup>18</sup> for the absorption of *p*-xylene in low density polyethylene. These investigators reported  $\chi$  values of 0.28, 0.28, and 0.30 at 125, 150, and 175°C, respectively, using mixtures infinitely dilute in *p*-xylene.

The diffusivity data for the *o*-xylene-polyethylene system at 125, 150, and 175°C are presented in Figures 4 and 5. There is a slight increase of the diffusivity with increasing solvent mass fraction at all temperatures. For large sol-

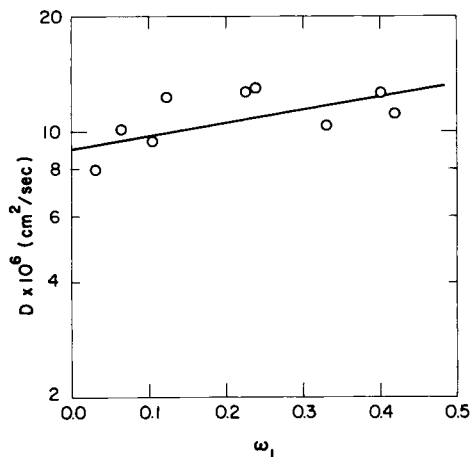


Fig. 4. Concentration dependence of mutual diffusion coefficient for *o*-xylene-polyethylene system at 125°C. The line represents a visual aid.

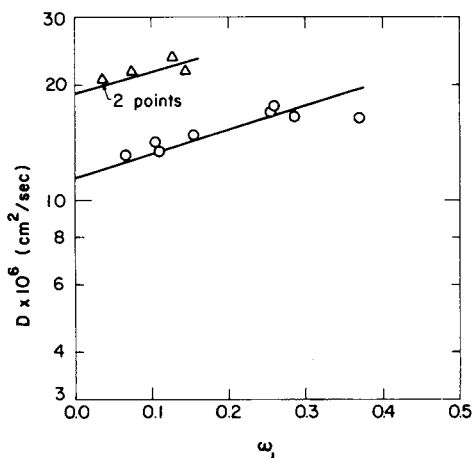


Fig. 5. Concentration dependence of mutual diffusion coefficient for *o*-xylene-polyethylene system at 150°C and 175°C; (O) 150°C; (Δ) 175°C. Lines represent visual aids.

vents, it is unusual to have a small increase in the diffusion coefficient as the solvent concentration increases for a polymer-solvent system near the pure polymer limit. The temperature dependence of the mutual diffusion coefficient evaluated in the limit of zero solvent mass fraction is illustrated in Figure 6. The activation energy for diffusion is much lower than activation energies reported for diffusion in typical polymer-solvent systems (for example, the toluene-polystyrene data presented in Fig. 2). Furthermore, the diffusion activation energy is essentially constant over the 50°C temperature range covered in the experiments. Again, this behavior is much different than that exhibited by the toluene-polystyrene system in Figure 2.

The differences between the diffusion behavior of the *o*-xylene-polyethylene system and that of a typical amorphous polymer-solvent system like toluene and polystyrene can be explained by considering the differences in the free-volume characteristics of the two systems. In the temperature range shown in Figure

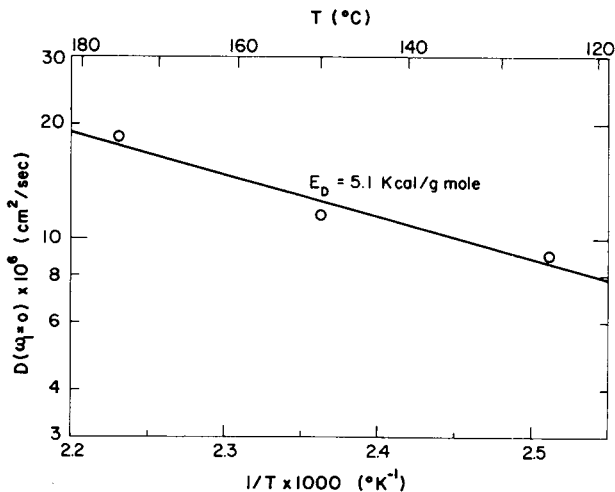


Fig. 6. Temperature dependence of diffusivity at zero solvent mass fraction for *o*-xylene-polyethylene system.



1 (110–160°C), polystyrene is within 100°C of its glass transition temperature (100°C). Thus, this system is a good example of diffusion under low free-volume conditions. Not only is the free volume of the polymer low, but, at 110°C, for example,  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  for the toluene–polystyrene system is approximately 19. Hence, the strong concentration dependence portrayed in Figure 1 can be anticipated from eq. (10), and the diffusivity–temperature behavior illustrated in Figure 2 can be predicted from eqs. (8) and (9). Furthermore, the first term of the right-hand side of eq. (10) should be a large positive number which completely dominates the negative thermodynamic factor. This is illustrated in Figure 7 which depicts the huge increase in  $D_1$  and the modest decrease in  $Q$  as  $\omega_1$  increases.

The free-volume characteristics of the *o*-xylene–polyethylene system appear to be entirely different than those for the toluene–polystyrene system. First, in the temperature range 125–175°C, polyethylene is more than 200°C above its glass transition temperature, and the free volume in the pure polymer which is available for molecular transport should be significantly greater than the available free volume in pure polystyrene. Second, we can use the diffusivity and solubility data for the *o*-xylene–polyethylene system to show that the free-volume ratio  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  for this system is not particularly large. The *o*-

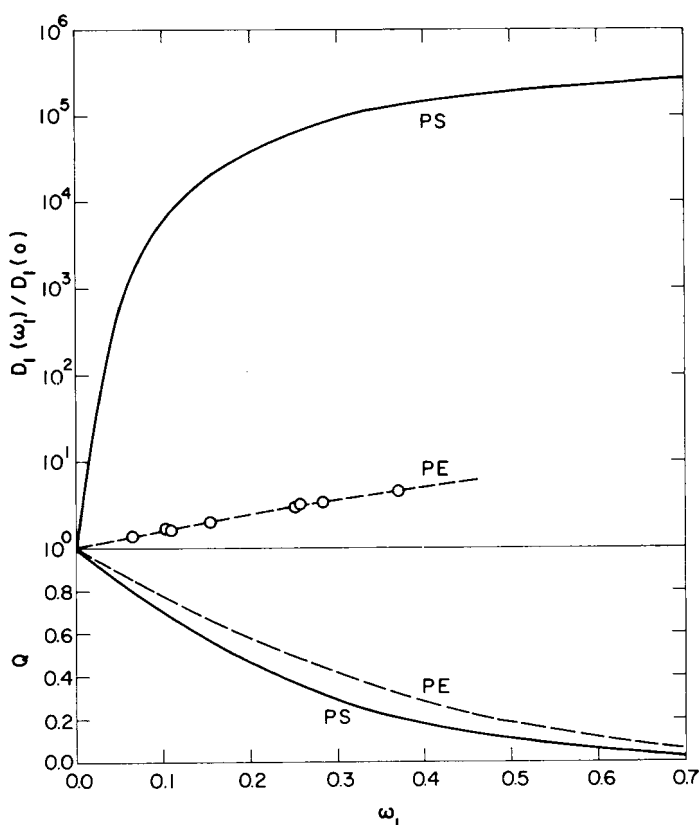


Fig. 7. Concentration dependence of the self-diffusion coefficient  $D_1$  and the thermodynamic factor  $Q$  for the toluene–polystyrene system at 110°C and for the *o*-xylene–polyethylene system at 150°C.

xylene self-diffusion coefficient  $D_1$  can be computed as a function of solvent mass fraction from eq. (1) using diffusivity and equilibrium data, and a plot of the form of eq. (12) can be constructed. A plot of this type is presented in Figure 8 for 150°C. The data are represented reasonably well by a straight line. Since plots of this form are very sensitive to scatter in the data, we feel that it is fair to conclude that a free-volume model adequately describes the concentration dependence of  $D_1$ . In addition, the slope and intercept of this straight line can be used in eq. (13) to give a value of  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0) = 1.4$  for the *o*-xylene-polyethylene system at 150°C.

Since we are studying polyethylene diffusion at temperatures more than 200°C above  $T_{g2}$ ,  $\hat{V}_{FH}(0)$  is relatively high. Also, we have computed a relatively low value of  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$  for the *o*-xylene-polyethylene system. Hence, it is possible to offer the following free-volume interpretation of the observed diffusivity behavior for this system. With relatively high values of  $\hat{V}_{FH}(0)$  for polyethylene in the temperature range 125–175°C, we anticipate from eqs. (8) and (9) that  $E_D$  for the *o*-xylene-polyethylene system is not large and not very temperature-dependent. These predictions are consistent with the diffusivity-temperature data presented in Figure 6. Also, from eq. (10), we would anticipate a rather weak concentration dependence for  $D$  since the first term is not large owing to the high values for  $\hat{V}_{FH}(0)$  and the low values for  $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ . This prediction is consistent with the diffusivity-weight fraction data presented in Figures 4 and 5. In addition, the negative thermodynamic term in eq. (10) is responsible for the small change in the diffusion coefficient with increasing  $\omega_1$ . This is evident from Figure 7, where the increase in  $D_1$  with increasing  $\omega_1$  for the *o*-xylene-polyethylene system at 150°C is not much greater than the decrease in the thermodynamic factor  $Q$ . It should also be noted from Figure 7 that the thermodynamic factor for the *o*-xylene-polyethylene system has a

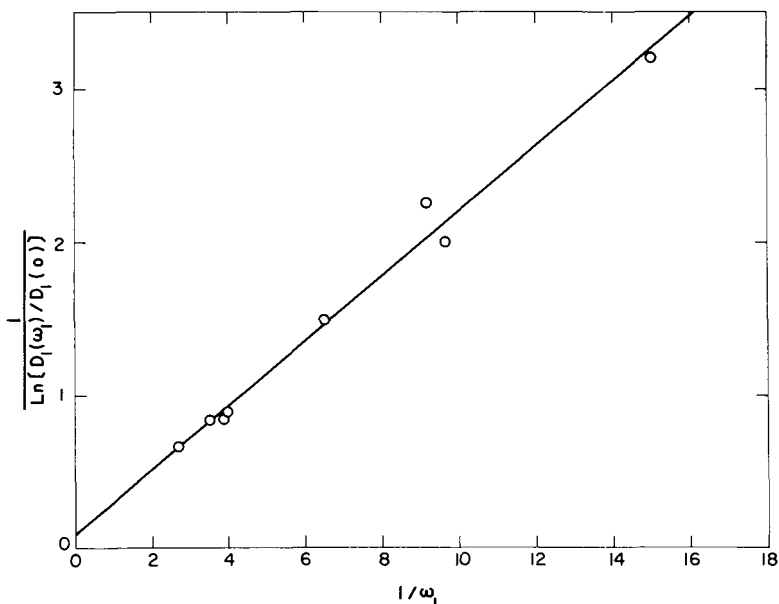


Fig. 8. Plot of eq. (12) for the *o*-xylene-polyethylene system at 150°C. The straight line represents a least-squares fit of the data.

concentration behavior similar to the thermodynamic factor for the toluene-polystyrene system. It is the substantial difference in the concentration dependences of  $D_1$  for these two systems which leads to the completely different diffusivity-weight fraction relationships which are observed.

Although the concentration and temperature dependences of  $D$  for the *o*-xylene-polyethylene system are different from what are usually observed for polymer-solvent systems, it appears that they are consistent with the equations of the free-volume theory of diffusion.

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