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Solvent Self-Diffusion in Rubbery Polymer-Solvent Systems

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ABSTRACT: The free-volume theory for solvent self-diffusion in polymer-solvent systems is applied to rubbery mixtures at temperatures both above and below the polymer glass transition temperature. A new parameter evaluation scheme is introduced, and it is shown that the theory provides good predictions for the solvent self-diffusion coefficient over wide temperature and concentration ranges.

Introduction

A free-volume theory of transport has been developed for predicting and correlating solvent self-diffusion coefficients for rubbery polymer-solvent systems.[1-8] There are two principal objectives of this theory: (1) to provide accurate predictions for solvent self-diffusion coefficients over wide temperature and concentration ranges and (2) to provide a method of evaluating the parameters of the theory which requires only a minimal amount of diffusion data. It has been shown recently[9] that the predictions of the free-volume theory for the solvent self-diffusion coefficient are good for temperatures above the glass transition temperature of the pure polymer. However, it has also been noted[7,10] that difficulties can be encountered for some systems at temperatures below the pure polymer glass transition temperature. These difficulties are caused by uncertainties in the nature of the temperature dependencies of the various expansion coefficients of the theory. The objective of this paper is to provide a reasonable framework for computing free volumes for the polymer in the equilibrium liquid state below its glass transition temperature. This framework should extend the temperature range over which the theory gives reasonable predictions and thus should produce good predictions for the solvent self-diffusion coefficient for rubbery polymer-solvent systems over all temperatures and concentrations of practical interest.

The modification of the free-volume theory is considered in the second section of the paper, and the parameter evaluation scheme is summarized in the third section. The predictions of the theory are compared with comprehensive sets of experimental data in the fourth section of the paper.

Theory

For a rubbery polymer-solvent system, the solvent self-diffusion coefficient, D_1, can be determined using the following equations:[1-8]

$$D_1 = \bar{D}_0 \exp\left[-\frac{E^*}{RT}\right] \exp\left[-\frac{\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*}{\hat{V}_{\mathrm{FH}}/\gamma}\right] \qquad (1)$$

$$E^* = E_{\mathrm{p}} - E_{\mathrm{S}} \qquad (2)$$

$$\frac{\hat{V}_{\mathrm{FH}}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} + T - T_{\mathrm{g}1}) + \omega_2 \frac{K_{12}}{\gamma_2}(K_{22} + T - T_{\mathrm{g}2}) \qquad (3)$$

In the above equations, the solvent is component 1 and the polymer is component 2. Also, $\bar{D}_0$ is an effectively constant preexponential factor, $\hat{V}_I^*$ is the specific hole free volume of component I required for a jump, ω_I is the mass fraction of component I, and $T_{\mathrm{g}I}$ is the glass transition temperature of pure component I. Also, T is the temperature, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, $\hat{V}_{\mathrm{FH}}$ is the average hole free volume per gram of mixture, and γ represents an average overlap factor for the mixture which is introduced because the same free volume is available to more than one jumping unit. The quantity γ_I represents the overlap factor for the free volume for pure component I. The quantities E_{p} and E_{S} represent energies per mole that a molecule needs to overcome attractive forces which hold it to its neighbors. The quantity E_{S} is the energy required at $\omega_1 = 1$ (pure solvent limit), and E_{p} is the energy required in the range $\omega_1 = 0$–0.9 (concentrated polymer solution for which the domains of polymer molecules overlap). Finally, K_{11} and K_{21} are free-volume parameters for the solvent, and K_{12} and K_{22} are free-volume parameters for the polymer. The polymer free-volume parameters can be defined as follows:[1,2,11]

$$K_{12} = \hat{V}_2^{\circ}(T_{\mathrm{g}2})[\alpha_2 - (1 - f_{\mathrm{H}2}^{\mathrm{G}})\alpha_{\mathrm{c}2}] \qquad (4)$$

$$K_{22} = \frac{f_{\mathrm{H}2}^{\mathrm{G}}}{\alpha_2 - (1 - f_{\mathrm{H}2}^{\mathrm{G}})\alpha_{\mathrm{c}2}} \qquad (5)$$

Here, $\hat{V}_2^{\circ}$ is the specific volume of the pure equilibrium liquid polymer, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer, $\alpha_{\mathrm{c}2}$ is the thermal expansion coefficient for the polymer for the sum of the specific occupied volume and the specific interstitial free volume, and $f_{\mathrm{H}2}^{\mathrm{G}}$ is the fractional hole free volume of the polymer at its glass transition temperature $T_{\mathrm{g}2}$. Similar equations can be used to define K_{11} and K_{21}.

It is important to note that the above free-volume formulation is based on the utilization of the following four assumptions:

(1) There is no volume change on mixing since it is assumed that the partial specific volumes of polymer and solvent are independent of composition.

(2) The thermal expansion coefficients α_2 and $\alpha_{\mathrm{c}2}$ are adequately represented by average values over the temperature interval of interest. Average values are also used for the corresponding solvent expansion coefficients.

(3) The overlap of free volume is adequately represented by eq 3. This equation is based on the assumption that the overlap of the free volume associated with component I in the mixture is the same as observed for the pure component I. Hence, the values of K_{11}/γ_1 and K_{12}/γ_2 determined from pure component data for solvent and

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polymer, respectively, can be used to compute the total hole free volume of the mixture.

(4) The energetics of the transport of solvent molecules is described by a concentration-dependent energy E, the energy per mole that a solvent molecule needs to overcome attractive forces which hold it to its neighbors. It is assumed that the concentration dependence of E can be described approximately by using an energy E_p in the concentration region where the domains of polymer molecules overlap (say, $\omega_1 = 0$ to $\omega_1 = 0.9$) and another energy E_S near the pure solvent limit. There should be a smooth transition from E_p to E_S as ω_1 approaches unity.

Assumption 1 is introduced because the required volumetric data for polymer–solvent systems are often not available. This assumption could easily be eliminated by using a generalized expression for $\hat{V}_{FH}$ whenever the appropriate volumetric data are available. Assumption 3 has usually been introduced implicitly since it provides a reasonable picture of free-volume overlap for the mixture. Similarly, assumption 4 appears to provide a reasonable description[12] of the concentration dependence of E. Although assumption 2 should be an adequate assumption for the solvent expansion coefficients and for α_2 and α_{c2} above T_{g2}, it is clear that changes in α_2 and α_{c2} must occur as the liquid polymer is cooled below T_{g2}. Consequently, the objective here is to provide a reasonable description of the temperature dependencies of α_2 and α_{c2} for amorphous polymers like polystyrene for a temperature range $T_{g2} - T_0 < T < T_{g2} + T_0$ where T_0 is of the order of 100 °C.

Volumetric data for polystyrene[13] indicate that α_2 changes less than 2% in the temperature range 100–200 °C. Hence, a reasonable assumption is to utilize a constant value of α_2 for $T > T_{g2}$. In addition, Rehage and Borchard[14] have described attempts to construct a curve for the equilibrium volume of the liquid polymer below T_{g2}. Estimates of the temperature dependence of α_2 below T_{g2} can be made using extrapolated volumetric data for polymer–solvent mixtures. For polystyrene, there is only a relatively small change in α_2 for temperatures as low as 70 °C below T_{g2}. Hence, a reasonable approximation is to assume that α_2 is approximately constant for $T_{g2} - T_0 < T < T_{g2}$, as long as T_0 is of the order of 100 °C. However, it is important to note that relatively small changes in α_2 can produce significant percentage changes in the polymer hole free volume because the hole free volume becomes very small for the pure polymer as the temperature is decreased below T_{g2}. Indeed, the extrapolated volumetric curve presented by Rehage and Borchard shows a slight upward curvature (and, hence, a decrease in α_2) as the temperature is decreased. Consequently, any reasonable estimates of a temperature dependence for α_2 below T_{g2} should be utilized whenever possible since even a relatively small decrease in α_2 can lead to a significantly greater polymer hole free volume than would be calculated using a constant value of α_2.

Some ideas of a possible temperature dependence for α_{c2} can be ascertained by noting that α_{c2} describes the addition to the system of interstitial free volume, the type of free volume which is uniformly distributed among the molecules of the system since the redistribution energy is large. The increase of interstitial free volume is realized by the homogeneous expansion of the material due to the increasing amplitude of the anharmonic vibrations with temperature. At the lowest temperatures, all of the thermal expansion arises from the anharmonicity of the vibrational part of the motion of a molecule. It is reasonable to suppose that α_{c2}, the expansion coefficient for this interstitial free volume, is effectively constant for sufficiently low temperatures. However, as the temperature of the amorphous polymer is increased, some of the increase in volume is realized by the formation of holes which are distributed discontinuously throughout the material at any instance. It is assumed that this hole free volume can be redistributed with no increase in energy. At high enough temperatures, the volumetric expansion will be great enough so that, for further increase in temperature, the thermal expansion is such that most of the additional volume added is free for redistribution and hence is hole free volume. Consequently, at low temperatures, α_{c2} is essentially constant, but, at a sufficiently high temperature, α_{c2} should effectively be zero since all of the added volume is essentially hole free volume. In addition, we adopt the point of view advanced by Turnbull and Cohen[15] that the glass transition temperature may be considered to be the approximate temperature at which most of the volume added in thermal expansion is free for redistribution and can thus be considered to be hole free volume.

In light of the above discussion, assumption 2 above is replaced by the following new set of assumptions which should be valid for $T_{g2} - T_0 < T < T_{g2} + T_0$ where T_0 is of the order of 100 °C:

(5) The expansion coefficient α_2 is effectively constant for $T > T_{g2}$.

(6) As a first approximation, α_2 can be considered to be independent of temperature for $T < T_{g2}$. However, if some estimate of a temperature dependence of α_2 is available, it should be used since any temperature dependence of α_2 can be important in calculating polymer hole free volumes for temperatures significantly below T_{g2}.

(7) The expansion coefficient α_{c2} is essentially constant below T_{g2} but drops rapidly in the vicinity of T_{g2}. The temperature dependence of α_{c2} is thus approximated as a step change at T_{g2}:

$$\alpha_{c2} = \text{constant} \qquad T < T_{g2} \tag{6}$$

$$\alpha_{c2} = 0 \qquad T > T_{g2} \tag{7}$$

This approximate temperature dependence will lead to a step change in the temperature dependence of the polymer free volume at T_{g2}. This step change is a mathematical idealization of the presumed rapid change in α_{c2} near T_{g2}.

The specific hole free volume of the equilibrium liquid polymer at any temperature, $\hat{V}_{FH2}$, can be determined by appropriate integration of the defining equations for α_2 and α_{c2}:

$$\frac{\partial \ln \hat{V}_2^\circ}{\partial T} = \alpha_2 \tag{8}$$

$$\frac{\partial \ln[\hat{V}_{FI2} + \hat{V}_2^\circ(0)]}{\partial T} = \alpha_{c2} \tag{9}$$

Here, $\hat{V}_{FI2}$ is the specific interstitial free volume of the equilibrium liquid polymer, and $\hat{V}_2^\circ(0)$ is the specific equilibrium volume of the liquid polymer at 0 K. Integration of these equations, utilization of the expression

$$\hat{V}_{FH2} = \hat{V}_2^\circ - [\hat{V}_{FI2} + \hat{V}_2^\circ(0)] \tag{10}$$

and elimination of higher order terms produce the following equations for $\hat{V}_{FH2}$:

$$\hat{V}_{FH2} = \hat{V}_2^\circ(T_{g2})[f_{H2}^G + \alpha_2(T - T_{g2})] \qquad T \geq T_{g2} \tag{11}$$

$$\hat{V}_{FH2} = \hat{V}_2{}^\circ(T_{g2})[f_{H2}^G - \int_T^{T_{g2}} (\alpha_2 - \alpha_{c2})\, dT'] \qquad T < T_{g2} \tag{12}$$

A constant value of α_2 is used in eq 11 for $T \geq T_{g2}$ and a constant value of α_{c2} should be used in eq 12 for $T < T_{g2}$. However, the possibility of a temperature-dependent α_2 is included in eq 12 since any estimate of the temperature dependence of α_2 for $T < T_{g2}$ should be used if it is available. Also, from eqs 9 and 10, the following equation can be derived for the constant expansion coefficient α_{c2} below T_{g2}:

$$\alpha_{c2} = \frac{\ln\left[\dfrac{\hat{V}_2{}^\circ(T_{g2})(1 - f_{H2}^G)}{\hat{V}_2{}^\circ(0)}\right]}{T_{g2}} \tag{13}$$

In addition, eq 3 is replaced by the equation

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} + T - T_{g1}) + \frac{\omega_2 \hat{V}_{FH2}}{\gamma_2} \tag{14}$$

where $\hat{V}_{FH2}$ is calculated using eq 11 for $T \geq T_{g2}$ and eq 12 for $T < T_{g2}$. Furthermore, for $T \geq T_{g2}$, we can use eqs 3 and 11 to write

$$\frac{\hat{V}_{FH2}}{\gamma_2} = \frac{\alpha_2 \hat{V}_2{}^\circ(T_{g2})}{\gamma_2}\left[\frac{f_{H2}^G}{\alpha_2} + T - T_{g2}\right] = \frac{K_{12}}{\gamma_2}(K_{22} + T - T_{g2}) \tag{15}$$

Hence, the following expressions can be derived for f_{H2}^G and γ_2:

$$f_{H2}^G = \alpha_2 K_{22} \tag{16}$$

$$\gamma_2 = \frac{\hat{V}_2{}^\circ(T_{g2})\alpha_2}{K_{12}/\gamma_2} \tag{17}$$

Finally, it is reasonable to expect that the specific volume of component I required for a jump is equal to $\hat{V}_I{}^\circ(0)$, the specific volume of component I at 0 K (the so-called occupied volume):

$$\hat{V}_1{}^* = \hat{V}_1{}^\circ(0) \tag{18}$$

$$\hat{V}_2{}^* = \hat{V}_2{}^\circ(0) \tag{19}$$

From the above discussion, it is evident that the temperature and concentration dependencies of D_1 for a rubbery polymer–solvent system can be determined using eqs 1, 13, 14, 16–19, and either eq 11 (for $T \geq T_{g2}$) or eq 12 (for $T < T_{g2}$). This calculation of the dependence of D_1 on ω_1 and T depends on the availability of the following parameters: $\bar{D}_0$, E^*, $\hat{V}_1{}^\circ(0)$, $\hat{V}_2{}^\circ(0)$, ξ, K_{11}/γ_1, $K_{21} - T_{g1}$, K_{12}/γ_2, K_{22}, T_{g2}, $\hat{V}_2{}^\circ(T_{g2})$, and $\alpha_2(T)$. All but two of these parameters can be easily determined from data that are generally available, and the parameter estimation scheme is discussed in the next section.

Evaluation of Parameters

The parameters needed for the calculation of D_1 as a function of T and ω_1 can be evaluated using the following parameter estimation scheme:

(1) The volumes of the equilibrium liquids at 0 K, $\hat{V}_1{}^\circ(0)$ and $\hat{V}_2{}^\circ(0)$, can be determined using methods discussed by Haward.[16]

(2) WLF constants and glass transition temperatures, T_{g2}, are available for a large number of polymers.[17] Consequently, the parameters K_{12}/γ_2 and K_{22} can be evaluated using the equations

$$\frac{K_{12}}{\gamma_2} = \frac{\hat{V}_2{}^*}{2.303(C_1{}^g)_2(C_2{}^g)_2} \tag{20}$$

$$K_{22} = (C_2{}^g)_2 \tag{21}$$

where $(C_1{}^g)_2$ and $(C_2{}^g)_2$ are the WLF constants for the polymer.

(3) Volumetric data are available for $T \geq T_{g2}$ for most important polymers. Consequently, values of $\hat{V}_2{}^\circ(T_{g2})$ and an average value of α_2 for $T \geq T_{g2}$ are generally available. Furthermore, in some instances, a temperature dependence for α_2 below T_{g2} can be estimated using extrapolation techniques.[14]

(4) It is possible to determine the quantities $\bar{D}_0$, K_{11}/γ_1, and $K_{21} - T_{g1}$ using viscosity–temperature and density–temperature data for the solvent. The temperature dependence of the viscosity η_1 of the pure solvent can be described by the equation[8]

$$\ln \eta_1 = \ln\left(\frac{0.124 \times 10^{-16} \tilde{V}_c{}^{2/3} RT}{M_1 \hat{V}_1{}^\circ}\right) - \ln \bar{D}_0 + \frac{\hat{V}_1{}^*}{(K_{11}/\gamma_1)(K_{21} + T - T_{g1})} \tag{22}$$

where M_1 is the molecular weight of the solvent, $\tilde{V}_c$ is the molar volume of the solvent at its critical temperature, and $\hat{V}_1{}^\circ$ is the specific volume of the pure solvent at T. A nonlinear regression analysis based on the utilization of viscosity–temperature and density–temperature data for the solvent in eq 22 can be used to determine the parameters $\bar{D}_0$, K_{11}/γ_1, and $K_{21} - T_{g1}$.

(5) The parameters E^* and ξ can be determined using measured self-diffusion coefficients at $\omega_1 = 0$. The quantities X and Y can be calculated using $D_1(\omega_1 = 0)$ versus T data:

$$X = \frac{RT\left(\dfrac{\gamma_2 \hat{V}_2{}^*}{K_{12}}\right)}{T + K_{22} - T_{g2}} \tag{23}$$

$$Y = -RT[\ln D_1 - \ln \bar{D}_0] \tag{24}$$

Since X and Y are related linearly[8]

$$Y = E^* + \xi X \tag{25}$$

the slope and intercept of a Y versus X plot yield ξ and E^*. This procedure requires at least two diffusivity–temperature data points. If there is reason to expect that $E^* \approx 0$, then it is possible to determine ξ for solvents which jump as single units using the result

$$\frac{\gamma_2 \hat{V}_2{}^* \xi}{K_{12}} = \beta \tilde{V}_1{}^\circ(0) \tag{26}$$

where $\tilde{V}_1{}^\circ(0)$ is the solvent molar volume at 0 K and β is a constant. Values of β have been reported for a number of polymers.[18,19]

It is evident from the above discussion that all of the parameters of the theory can be determined in general with as few as two diffusivity data points. It may be possible to generate this type of data using a molecular simulation of the diffusion of a trace of solvent in the polymer. Furthermore, when $E^* \approx 0$, it is possible to

Table 1. Free-Volume Parameters

parameter	toluene–polystyrene system	ethylbenzene–polystyrene system
$\hat{V}_1^*$ (cm^3/g)	0.917	0.946
$\hat{V}_2^*$ (cm^3/g)	0.850	0.850
K_{11}/γ_1 (cm^3/(g K))	1.57×10^{-3}	1.49×10^{-3}
K_{12}/γ_2 (cm^3/(g K))	5.39×10^{-4}	5.39×10^{-4}
$K_{21} - T_{g1}$ (K)	−90.5	−84.4
K_{22} (K)	50	50
T_{g2} (K)	373	373
ξ	0.575	0.590
$\alpha_2(T \geq T_{g2})$ (K^{-1})	5.3×10^{-4}	5.3×10^{-4}
α_{c2} (K^{-1})	2.88×10^{-4}	2.88×10^{-4}
$\hat{V}_2^\circ(T_{g2})$ (cm^3/g)	0.972	0.972
f_{H2}^G	0.0265	0.0265
D_0 (cm^2/s)	4.17×10^{-4}	4.22×10^{-4}
E^* (kcal/(g mol))	0	0.61
γ_2	0.956	0.956

estimate ξ in some cases using no diffusion data for the polymer–solvent system of interest.

Results and Discussion

The proposed method for computing $D_1(\omega_1,T)$ can be regarded as a semipredictive method since only a small amount of diffusivity data is used in the parameter evaluation, and D_1 can subsequently be calculated over wide temperature and concentration ranges. In this investigation, the capabilities of this semipredictive procedure are examined using self-diffusion data for the polystyrene–toluene and polystyrene–ethylbenzene systems. Two sets of self-diffusion data for the polystyrene–toluene system[10,20] and a single set for the polystyrene–ethylbenzene system[21] are used in this data–theory comparison. Furthermore, mutual diffusion data for both solvents[4] for relatively small values of ω_1 ($0 \leq \omega_1 \leq 0.10$) have been converted to self-diffusion data by a procedure described elsewhere.[4] It is expected that the method used to convert the mutual diffusion data to solvent self-diffusion data is valid in this concentration interval.

The parameters needed for the evaluation of D_1 were evaluated using the procedure described above and are presented in Table 1. Since the physical properties of polystyrene are readily available, the evaluation procedure, with two exceptions, is straightforward. The first exception involves a possible temperature dependence for α_2 below T_{g2}. The extrapolated volumetric curve presented by Rehage and Borchard[14] was used in eq 12 to evaluate $\hat{V}_{FH2}$ for $T < T_{g2}$. The temperature dependence of $\hat{V}_{FH2}$ calculated using $\alpha_2(T)$ and that calculated using a constant value of α_2 (extrapolated from $T > T_{g2}$) are compared in Figure 1. Clearly, there are significant differences below about 40 °C. Consequently, some extrapolated estimate of the temperature dependence is effectively a necessity for temperatures sufficiently far below T_{g2}. The second exception concerns the evaluation of ξ and E^* for the two polymer–solvent systems. The parameters ξ and E^* can be evaluated if $D_1(\omega_1{=}0)$ versus temperature data are available for $T > T_{g2}$. The inverse gas chromatography experiment[22-24] can be used to measure infinite dilution diffusion coefficients over significant temperature ranges, whereas it is generally difficult to obtain diffusivity data at very low solute concentrations using a vapor sorption experiment. Both the inverse gas chromatography experiment and the vapor sorption experiment have been used to measure mutual diffusion coefficients for the polystyrene–toluene and polystyrene–ethylbenzene systems. Unfortunately, the results from two independent chromatography experiments[22,25] are not consistent, and it seems necessary to rely on $D_1(\omega_1{=}0)$ values obtained from extrapolations of vapor sorption data.[4] For the polystyrene–toluene system, diffusivity data were used to obtain extrapolated estimates of $D_1(\omega_1{=}0)$ at temperatures of 160, 170, and 178 °C, since the weaker concentration dependence at the higher temperatures facilitates the extrapolation procedure. The Y versus X plot for this system is illustrated in Figure 2. A linear relationship represents the data quite well and produces a value of ξ = 0.575 and an energy E^* which is less than 5 cal/g mol (which is taken to be zero in Table 1). For the polystyrene–ethylbenzene system, there is considerable scatter in the higher temperature vapor sorption data, and it was necessary to obtain $D_1(\omega_1{=}0)$ by extrapolating data at 130 and 140 °C. The Y versus X plot for this system is also included (for completeness) in Figure 2, and values of ξ = 0.59 and E^* = 0.61 kcal/g mol are computed using the two diffusivity data points.

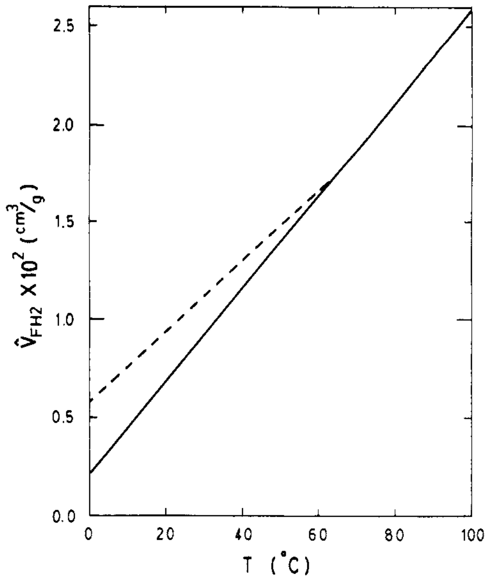

Figure 1. Temperature dependence of $\hat{V}_{FH2}$ for amorphous polystyrene. The solid line represents the volumetric behavior for constant α_2 and the dashed line for temperature-dependent α_2.

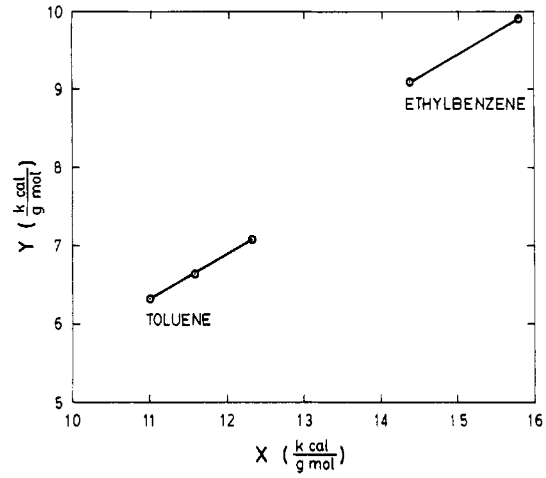

Figure 2. Y versus X plots for toluene and ethylbenzene diffusion in polystyrene.

For a typical polymer–solvent system, the D_1 versus ω_1 dependence at a given temperature is described by the inequality

$$\frac{\partial \ln D_1}{\partial \omega_1} > 0 \qquad (27)$$

over the complete concentration range. For such systems, it can easily be shown[12] that free-volume theory predicts that the inequality

$$\frac{\partial^2 \ln D_1}{\partial {\omega_1}^2} < 0 \qquad (28)$$

is valid for all mass fractions if the concentration dependence of E is ignored. Consequently, for the polystyrene–toluene system it is reasonable to expect that eq 28 will be obeyed over the complete concentration interval. On the other hand, a different possibility exists for the polystyrene–ethylbenzene system which has $E^* = 0.61$ kcal/g mol and hence a concentration-dependent energy term. Since $E_p > E_S$ for this system, there should be a diffusivity enhancement near $\omega_1 = 1$ and the possibility that

$$\frac{\partial^2 \ln D_1}{\partial {\omega_1}^2} > 0 \qquad (29)$$

near $\omega_1 = 1$ even though eq 27 is valid. The presence of a diffusivity enhancement in the vicinity of $\omega_1 = 1$ tends to give some creditability to the ability of the two-energy model to describe the concentration dependence of energy effects in the system.

Experimental data for the polystyrene–toluene system are compared with predicted values of D_1 in Figures 3–7. The theory is compared with self-diffusion data[10] collected using a forced Rayleigh scattering technique in Figures 3–5. The data were collected at fairly high polymer concentrations (ω_2 ranges from 0.790 to 0.903), but the data considered here are, in all cases, at temperatures above the glass transition temperatures of the polymer–solvent mixtures. The measured temperature variations of D_1 at nine polymer concentrations are compared with the predicted temperature variations in Figures 3 and 4. The agreement between theory and experiment is generally quite good. In Figure 5, experimental values of D_1 at the glass transition temperatures of six of the polymer–solvent mixtures are compared with the theoretical predictions. The data points in this figure are actually derived by extrapolations and interpolations of the actual data. Again, there is good agreement between the theoretical predictions and the experimental data. In Figure 6, the predictions of the theory are compared against the self-diffusion data of Pickup.[20] Good agreement is again observed, even though there seems to be a slight diffusivity enhancement in the experimental data near $\omega_1 = 1$. Finally, the predictions of the theory are compared in Figure 7 against self-diffusion data derived from mutual diffusion data[4] collected using a vapor sorption experiment. The predictions of the theory appear to be slightly high at 140 °C, but there is very good agreement at lower and higher temperatures.

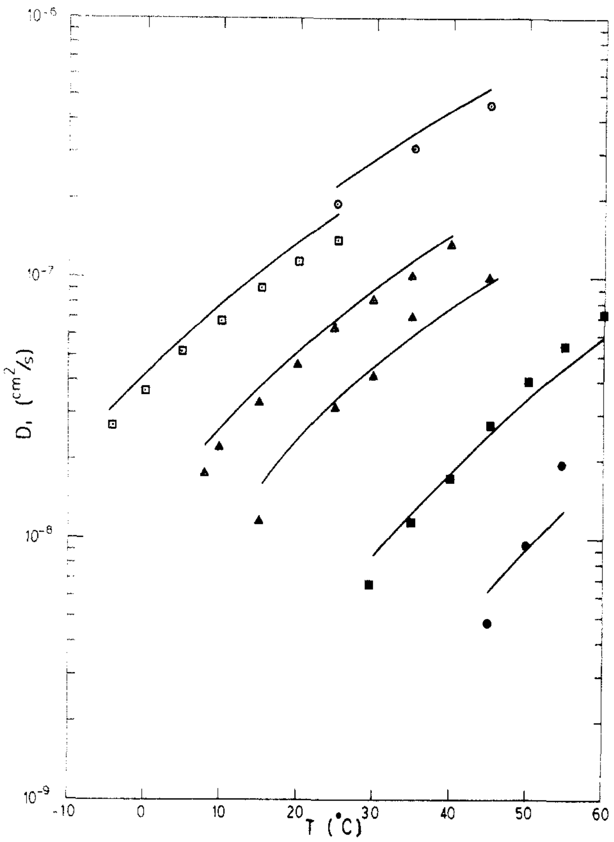

Figure 3. Temperature dependence of D_1 for the toluene–polystyrene system. Lines are theoretical predictions and points are experimental data for six polymer mass fractions: $\omega_2 = 0.790$ (○), 0.799 (□), 0.830 (△), 0.849 (▲), 0.881 (■), and 0.903 (●).

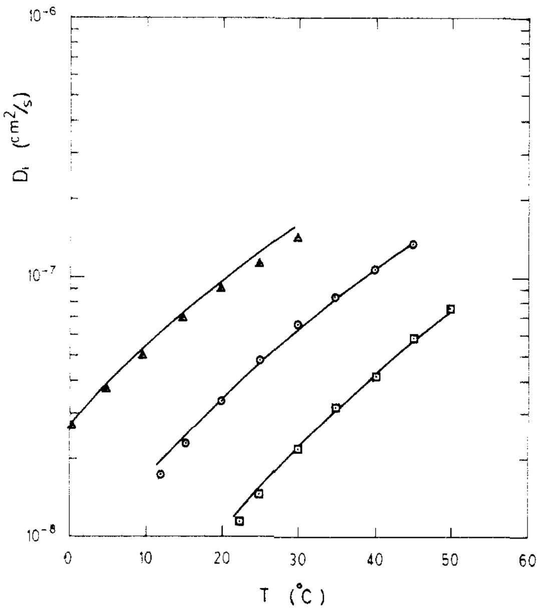

Figure 4. Temperature dependence of D_1 for the toluene–polystyrene system. Lines are theoretical predictions and points are experimental data for three polymer mass fractions: $\omega_2 =$ 0.811 (△), 0.840 (○), and 0.864 (□).

Experimental self-diffusion data for the polystyrene–ethylbenzene system[21] are compared against theoretical predictions in Figure 8. The solid theoretical curve is computed using a constant value of $E^* = 0.61$ kcal/g mol so it should yield low values near $\omega_1 = 1$ because of an expected diffusivity enhancement near the pure solvent limit caused by the fact that the magnitude of the energy term increases to unity there. From Figure 8, it is evident that there is good agreement between the solid theoretical curve and experiment up to about $\omega_1 = 0.70$ and a significant diffusivity enhancement with $\partial^2 \ln D_1/\partial {\omega_1}^2 > 0$ for higher solvent concentrations. The actual theoretical curve should involve a smooth transition between the solid curve and the predicted value of D_1 for the pure solvent. It is obvious from Figure 8 that it should be easy to construct such a composite curve which represents D_1 over the complete concentration range covered by the data.

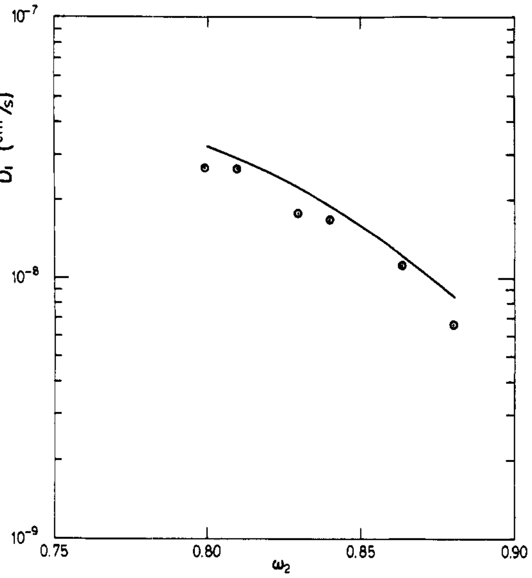

Figure 5. Composition dependence of D_1 at the solution glass transition temperature for the toluene–polystyrene system. Line is theoretical prediction and points are derived from experimental data.

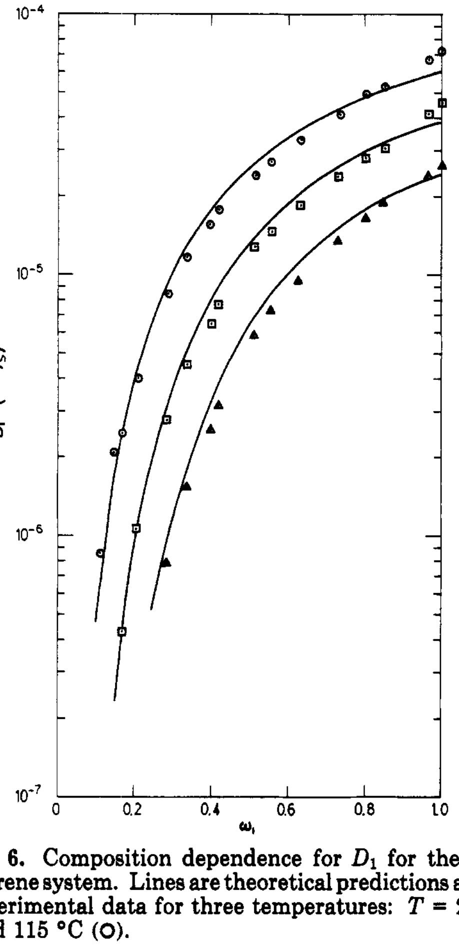

Figure 6. Composition dependence for D_1 for the toluene–polystyrene system. Lines are theoretical predictions and points are experimental data for three temperatures: T = 25 (△), 65 (□), and 115 °C (○).

The predictions of the theory are compared in Figure 9 against self-diffusion data which were derived from mutual diffusion coefficients measured using a vapor sorption apparatus.[4] Reasonably good predictions are obtained at 115, 130, and 140 °C. However, the predictions at 160 °C are too low. These are the only data for which the predictions of the theory are not in reasonably good agreement with the measured values.

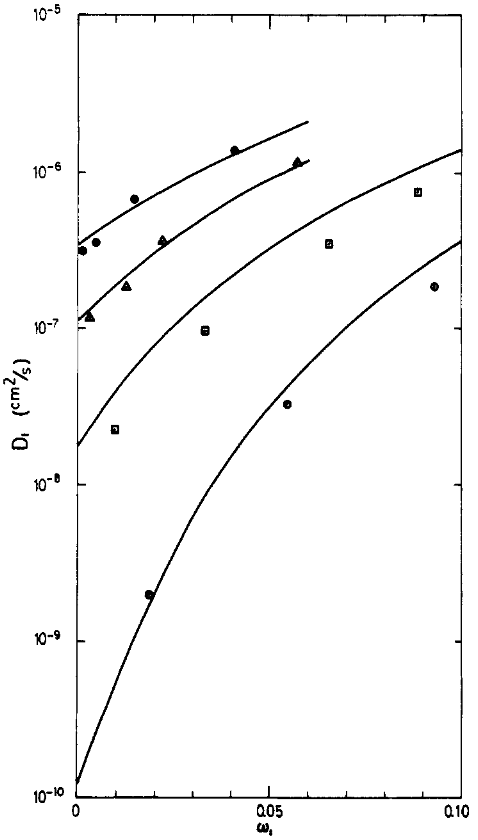

Figure 7. Composition dependence of D_1 for the toluene–polystyrene system. Lines are theoretical predictions and points are derived from experimental data at four temperatures: T = 110 (○), 140 (□), 160 (△), and 178 °C (●).

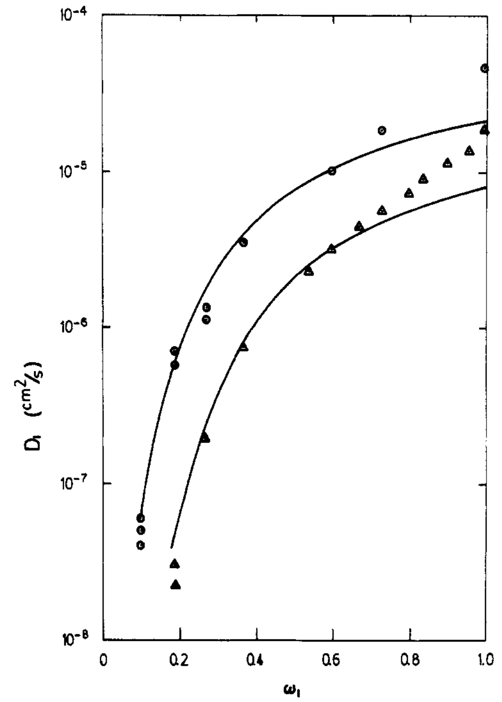

Figure 8. Composition dependence of D_1 for the ethylbenzene–polystyrene system. Lines are theoretical predictions and points are experimental data at two temperatures: T = 30 (△) and 100 °C (○).

It appears fair to conclude from the above results that the present version of the free-volume theory of diffusion provides good predictions for almost all of the self-diffusion data for two polymer–solvent systems over wide ranges of temperature and concentration. Furthermore, the theory is relatively easy to utilize since most of the information needed is available for most important polymer–solvent

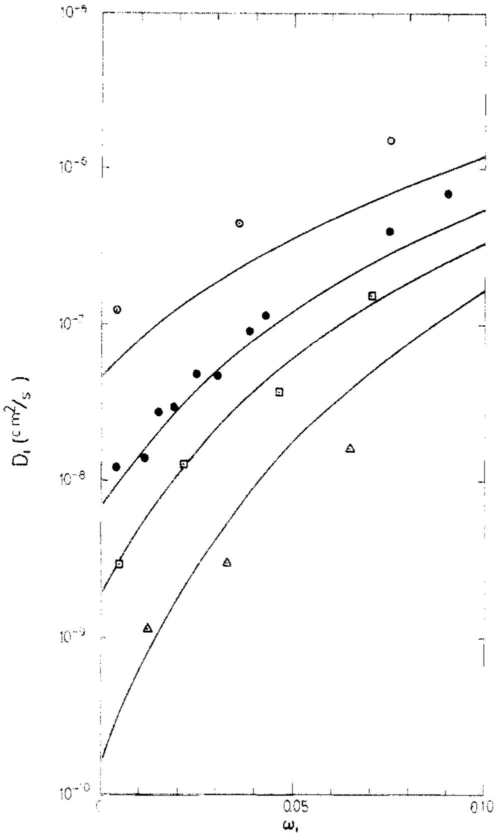

Figure 9. Composition dependence of D_1 for the ethylbenzene–polystyrene system. Lines are theoretical predictions and points are derived from experimental data at four temperatures: T = 115 (△), 130 (□), 140 (●), and 160 °C (○).

systems. There is, in general, of course the need for at least two diffusivity data points. However, as noted above, it is possible to obtain actual predictions for solvent diffusion in some polymers if it is assumed that $E^* \approx 0$ and that the entire solvent molecule performs a jump. Also, the accuracy of predictions at temperatures significantly below T_{g2} is improved if extrapolated estimates for the temperature dependence of α_2 below T_{g2} are utilized. Hence, we conclude that the present free-volume formulation provides an accurate and useful method for determining $D_1(\omega_1,T)$ for polymer–solvent systems. The utility of the theory would be further enhanced if molecular simulations were used to generate the diffusivity data needed for the evaluation of ξ and E^* and if simple methods were available for obtaining extrapolated estimates for α_2 for temperatures significantly below T_{g2}. It should be noted that molecular simulation calculations for large, nonspherical molecules like toluene and ethylbenzene may not be particularly easy to carry out. However, such calculations are of course preferable to using experimental data. Extrapolations of vapor sorption data, in particular, must be done carefully. Here, the extrapolation procedure for the polystyrene–toluene system is acceptable because three relatively high temperatures were utilized. For the polystyrene–ethylbenzene system, only two lower temperatures were utilized. However, the value of E^* = 0.61 kcal/(g mol) which was computed is consistent with a value of E^* = 0.49 ± 0.04 kcal/(g mol) deduced previously[12] from a diffusivity enhancement calculation.

The main purpose of the new version of the theory is to permit a consistent determination of self-diffusion coefficients for temperatures below the pure polymer glass transition temperature. The present version of the theory allows good predictions to be made for this temperature range. For the previous version, it was not possible to make definitive predictions under some conditions because calculation of the polymer contribution to the solution free volume was inadequate. Hence, an ad hoc calculation method had to be used to obtain an estimate for the self-diffusion coefficient. The present version avoids this by presenting a reasonable framework for computing the free volume of the equilibrium liquid polymer. In the proposed model, it is assumed that, at some temperature, the majority of interstitial fragments are large enough to be considered holes, and further increases in temperature simply increase the size of the holes.

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