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Solvent Self-Diffusion in Glassy Polymer–Solvent Systems

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ABSTRACT: The free-volume theory for solvent self-diffusion in polymer–solvent systems is used to describe the self-diffusion process in glassy polymer–solvent mixtures. General predictions of the theory and comparisons of theoretical predictions with experimental data are considered.

Introduction

The solvent self-diffusion process for polymer–solvent systems can be analyzed by applying the free-volume theory of transport. Much effort has been expended in describing the self-diffusion of solvents in rubbery polymer–solvent systems,[1–10] and, recently, we have proposed a new theoretical framework which can be used to provide good predictions for the solvent self-diffusion coefficient in rubbery polymer–solvent mixtures over wide temperatures and concentration ranges.[11] In addition, a number of investigations have been concerned with the solvent self-diffusion process in glassy polymer–solvent systems.[10,12–17] The objective of this paper is to utilize the recently proposed framework as a basis for a revised version of free-volume theory for the solvent self-diffusion process in glassy polymers.

The modification of the free-volume theory of transport is considered in the second section of the paper, and the theory is used to describe general features of the concentration and temperature dependencies of solvent self-diffusion in the third section. Various aspects of antiplasticization and plasticization in glassy polymers are also discussed in this section. General predictions of the theory and a comparison of theoretical predictions with experimental data are presented in the fourth section of this paper.

Theory

The solvent self-diffusion coefficient, D_1, for diffusion in a polymer–solvent mixture can be determined using the following equations:[11]

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

$$E^* = E_p - E_S \tag{2}$$

In this paper, the solvent is component 1 and the polymer is component 2. In addition, $\bar{D}_0$ 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 is temperature. Also, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, 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, and ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. Furthermore, 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_p describes energy effects for concentrated polymer solutions for which the domains of polymer molecules overlap (say, $\omega_1 = 0$ to $\omega_1 = 0.9$), and E_S describes energy effects near the pure solvent limit. Hence, a single value of E^* is used in eq 1 over most of the concentration range, and E^* becomes zero at the pure solvent limit.

For rubbery polymer–solvent systems, it has been proposed that $\hat{V}_{FH}/\gamma$ can be calculated using the following equations:[11]

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} + T - T_{g1}) + \frac{\omega_2 \hat{V}_{FH2}}{\gamma_2} \tag{3}$$

$$\hat{V}_{FH2} = \hat{V}_2^{\circ}(T_{g2})[f_{H2}^{G} + \alpha_2(T - T_{g2})] \qquad T \geq T_{g2} \tag{4}$$

$$\hat{V}_{FH2} = \hat{V}_2^{\circ}(T_{g2})\left[f_{H2}^{G} - \int_T^{T_{g2}}(\alpha_2 - \alpha_{c2})\, dT'\right] \qquad T < T_{g2} \tag{5}$$

In these equations, T_{gI} is the glass transition temperature of component I, K_{11} and K_{21} are free-volume parameters for the solvent, γ_I represents the overlap factor for the free volume of pure component I, and $\hat{V}_{FH2}$ is the specific hole free volume of the equilibrium liquid polymer at any temperature. Also, $\hat{V}_2^{\circ}$ is the specific volume of the pure equilibrium liquid polymer, f_{H2}^{G} is the fractional hole free volume of the polymer at its glass transition temperature T_{g2}, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer, and α_{c2} is the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume for the equilibrium liquid polymer. In the above development, it is assumed that α_2 is constant above T_{g2} but possibly temperature dependent below T_{g2}. Also, it is assumed that α_{c2} is constant below T_{g2} but drops rapidly to 0 above T_{g2} (idealized as a step change at T_{g2}). The quantities f_{H2}^{G}, α_{c2}, γ_2, $\hat{V}_1^*$, and $\hat{V}_2^*$ can be computed using the equations[11]

$$f_{H2}^{G} = \alpha_2 K_{22} \tag{6}$$

$$\alpha_{c2} = \frac{\ln\left[\dfrac{\hat{V}_2^{\circ}(T_{g2})(1 - f_{H2}^{G})}{\hat{V}_2^{\circ}(0)}\right]}{T_{g2}} \tag{7}$$

$$\gamma_2 = \frac{\hat{V}_2^{\circ}(T_{g2})\alpha_2}{K_{12}/\gamma_2} \tag{8}$$

$$\hat{V}_1^* = \hat{V}_1^{\circ}(0) \tag{9}$$

$$\hat{V}_2^* = \hat{V}_2^{\circ}(0) \tag{10}$$

where $\hat{V}_I^{\circ}(0)$ is the specific volume of component I at 0 K and K_{12} and K_{22} are free-volume parameters for the polymer. Consequently, for rubbery polymer–solvent

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systems, the variation of D_1 with ω_1 and T can be determined using eqs 1, 3, 6–10, and either eq 4 (for $T \geq T_{g2}$) or eq 5 (for $T < T_{g2}$) if the following parameters are known: $\hat{D}_0$, 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 $\alpha_2(T)$. A parameter evaluation scheme has been presented elsewhere,[11] and it is noted that all of the above parameters can be determined in general with as few as two diffusivity data points.

It is of interest to utilize the basic framework proposed for rubbery polymer–solvent systems at temperatures below T_{g2} to analyze the solvent self-diffusion process for glassy polymer–solvent systems. This is done here by introducing one additional assumption so that no additional parameters are introduced into the equations for D_1. The specific hole free volume of the mixture is now calculated using the equation

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

where $\hat{V}_{FH2g}$ is the specific hole free volume of the glassy polymer at any temperature below T_{gm}, the glass transition temperature of the polymer–solvent mixture at a particular penetrant mass fraction. It is often useful to relate T_{gm} to T_{g2}, the glass transition temperature of the pure polymer, using the following linear approximation for the concentration dependence of T_{gm}:

$$T_{gm} = T_{g2} - A\omega_1 \qquad (12)$$

The coefficient A depends on the nature of the diluent used to depress the glass transition temperature for a particular polymer. An expression for $\hat{V}_{FH2g}$ can be derived by appropriate integration of the defining equations for α_{2g}, the thermal expansion coefficient for the glassy polymer, and α_{c2g}, the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume for the glassy polymer:

$$\frac{\partial \ln \hat{V}_{2g}{}^\circ}{\partial T} = \alpha_{2g} \qquad (13)$$

$$\frac{\partial \ln[\hat{V}_{FI2g} + \hat{V}_{2g0}]}{\partial T} = \alpha_{c2g} \qquad (14)$$

Here, $\hat{V}_{2g}{}^\circ$ is the specific volume of the glassy polymer, $\hat{V}_{FI2g}$ is the specific interstitial free volume of the glassy polymer, and $\hat{V}_{2g0}$ is the specific occupied volume of the glassy polymer. Integration of the above equations, utilization of the expression

$$\hat{V}_{FH2g} = \hat{V}_{2g}{}^\circ - [\hat{V}_{FI2g} + \hat{V}_{2g0}], \qquad (15)$$

introduction of eq 5, and elimination of higher order terms lead to the following expression for $\hat{V}_{FH2g}$:

$$\hat{V}_{FH2g} = \hat{V}_2{}^\circ(T_{g2})[f_{H2}^G - \int_{T_{gm}}^{T_{g2}}(\alpha_2 - \alpha_{c2})\, dT' - \int_T^{T_{gm}}(\alpha_{2g} - \alpha_{c2g})\, dT'] \qquad T < T_{gm} \quad (16)$$

It is important to note that the utilization of eq 11 and the derivation of eq 16 are based on the following assumptions:[15,18]

(1) The polymer–solvent system exists as a nonequilibrium liquid structure at a given concentration at temperatures below T_{gm}, and this structure remains effectively invariant during any experiments performed on the polymer–diluent mixture.

(2) All volumes associated with the diluent and the glassy polymer are additive at any concentration for temperatures below T_{gm}.

(3) It is assumed that the polymer–penetrant mixture is formed by first mixing the components above T_{gm} and then cooling the mixture to the desired temperature below T_{gm} using a conventional time scale. Furthermore, the value of α_{2g} used to compute volumetric properties below T_{gm} is the same as the value measured for the glassy state as the pure polymer is cooled below T_{g2}, its glass transition temperature. In general, α_{2g} is a function of temperature.

(4) The rapid change in the expansion coefficient of the pure polymer near T_{g2} is idealized as a step change from α_{2g} to α_2 at T_{g2}.

It is evident from the above results that D_1 can be determined as a function of ω_1 at any temperature less than T_{gm} by using eqs 1, 6–10, 11, and 16. The development, however, requires the introduction of an additional parameter, the expansion coefficient α_{c2g}. An estimate of this parameter can be derived by assuming that the process of cooling a glassy polymer below T_{g2} is simply a slower version of the process of cooling an equilibrium liquid polymer below T_{g2}. Hence, it seems reasonable to introduce the following additional assumption:

(5) The expansion coefficient α_{c2g} is constant below T_{g2}. Furthermore, it is assumed that

$$\frac{\alpha_{c2g}}{\alpha_{c2}} = \left(\frac{\alpha_{2g}}{\alpha_2}\right)_{T=T_{g2}} \qquad (17)$$

The introduction of assumption 5 thus permits immediate evaluation of α_{c2g}, once α_{c2} is calculated using eq 7. Consequently, calculation of D_1 for glassy polymer–solvent systems is no more difficult than computing D_1 for rubbery polymer–solvent systems. However, the predictions will be valid only for cases where the behavior of the polymer–solvent system is not overly sensitive to the exact nature of the sample preparation history. Various predictions for glassy polymer–solvent systems based on the proposed theoretical framework are considered in the next section of the paper.

Predictions of Theory

General features of the concentration and temperature dependencies of D_1 can best be examined by considering special forms of the above equations for D_1. If all expansion coefficients are assumed to be effectively constant, then eq 5 for rubbery polymer–solvent systems can be written as

$$\hat{V}_{FH2} = \hat{V}_2{}^\circ(T_{g2})[f_{H2}^G - (\alpha_2 - \alpha_{c2})(T_{g2} - T)] \qquad T < T_{g2} \quad (18)$$

and eq 16 for glassy polymer–solvent systems can be written in the form

$$\hat{V}_{FH2g} = \hat{V}_2{}^\circ(T_{g2})[f_{H2}^G - \omega_1 A(\alpha_2 - \alpha_{2g} + \alpha_{c2g} - \alpha_{c2}) + (\alpha_{2g} - \alpha_{c2g})(T - T_{g2})] \qquad T < T_{gm} \quad (19)$$

where it is assumed that T_{gm} can be adequately represented by eq 12. Also, for convenience, eq 11 can be rewritten in terms of $\hat{V}_{FH1}$, the specific hole free volume of the pure solvent at the temperature of interest:

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{\hat{V}_{FH1}}{\gamma_1} + \omega_2 \frac{\hat{V}_{FH2g}}{\gamma_2} \tag{20}$$

$$\hat{V}_{FH1} = K_{11}(K_{21} + T - T_{g1}) \tag{21}$$

Substitution of eq 19 into eq 20 and differentiation produce the following expression for the initial concentration dependence of $\hat{V}_{FH}$:

$$\left[\frac{\partial(\hat{V}_{FH}/\gamma)}{\partial\omega_1}\right]_{\omega_1=0} = \frac{\hat{V}_{FH1}}{\gamma_1} - \frac{\hat{V}_2{}^\circ(T_{g2})}{\gamma_2}[f_{H2}^{G} + (\alpha_{2g} - \alpha_{c2g}) \times (T - T_{g2})] - \frac{\hat{V}_2{}^\circ(T_{g2})}{\gamma_2}A[\alpha_2 - \alpha_{2g} + \alpha_{c2g} - \alpha_{c2}] \tag{22}$$

The importance of this type of equation in describing the effect of a penetrant on the transport properties of the glassy polymer has been noted previously.[16,18] It is evident that eq 22 illustrates the initial change in $\hat{V}_{FH}$ caused by the addition of a penetrant to a glassy polymer. The first term represents the hole free volume of the solvent at the temperature of interest, and the second term is the hole free volume of the pure glassy polymer. The difference of these two terms is generally positive since the penetrant usually possesses more free volume than the glassy polymer at a particular temperature T. The third term is negative and represents a loss of free volume due to structural changes in the polymer matrix with the addition of penetrant. This change in the molecular structure of the polymer as penetrant is added to the system leads to an eventual elimination of the extra hole free volume as the system moves toward an equilibrium liquid configuration. Clearly, since eq 22 contains terms with different signs, the magnitude and sign of the initial concentration derivative for the hole free volume depend on the relative magnitudes of the competing terms. The magnitudes of these competing terms are primarily governed by the quantities $\hat{V}_{FH1}/\gamma_1$ and A. Large values of $\hat{V}_{FH1}/\gamma_1$ will promote a rapid increase in the hole free volume of the system, whereas large values of A will promote rapid loss of the extra hole free volume trapped in the glassy polymer matrix. Equation 22 can be used to examine both the concentration dependence of D_1 for glassy polymer–penetrant systems and the nature of plasticization and antiplasticization for glassy polymers.

In studying the concentration dependence of D_1 for solvent self-diffusion in glassy polymers, it is convenient to define the dimensionless parameter

$$k_D{}^* = \left[\frac{\partial \ln(D_1/D_1{}^\circ)}{\partial\omega_1}\right]_{\omega_1=0} \tag{23}$$

where $D_1{}^\circ$ is the self-diffusion coefficient at zero solvent concentration. It can be easily shown using eqs 1 and 23 that $k_D{}^*$ can be expressed as

$$k_D{}^* = \frac{\hat{V}_2{}^*\xi}{\hat{V}_{FH}(0)/\gamma}\left[\frac{\left[\frac{\partial(\hat{V}_{FH}/\gamma)}{\partial\omega_1}\right]_{\omega_1=0}}{\hat{V}_{FH}(0)/\gamma} + 1 - \frac{M_{j2}}{M_{j1}}\right] \tag{24}$$

where $\hat{V}_{FH}(0)$ is the value of the specific hole free volume of the mixture at $\omega_1 = 0$. In the derivation of this equation, M_{j1} and M_{j2}, the molecular weights of the solvent and polymer jumping units, respectively, were introduced using the following definition for ξ:

$$\xi = \frac{\hat{V}_1{}^* M_{j1}}{\hat{V}_2{}^* M_{j2}} \tag{25}$$

Above T_{g2}, it follows from eqs 3, 21, 24, and 25 that $k_D{}^*$ can be expressed as

$$k_D{}^* = \frac{\hat{V}_1{}^*}{\hat{V}_{FH2}/\gamma_2}\left[\frac{M_{j1}}{M_{j2}}\frac{\hat{V}_{FH1}/\gamma_1}{\hat{V}_{FH2}/\gamma_2} - 1\right] \qquad T > T_{g2} \tag{26}$$

where $\hat{V}_{FH2}$ is given by eq 4. Similarly, below T_{g2}, combination of eqs 19, 20, 22, 24, and 25 produces the result

$$k_D{}^* = \frac{\hat{V}_1{}^*}{Q}\left[\left(\frac{\hat{V}_{FH1}/\gamma_1 - Q^*}{Q}\right)\frac{M_{j1}}{M_{j2}} - 1\right] \qquad T < T_{g2} \tag{27}$$

where

$$Q = \frac{\hat{V}_2{}^\circ(T_{g2})}{\gamma_2}[f_{H2}^{G} + (\alpha_{2g} - \alpha_{c2g})(T - T_{g2})] \tag{28}$$

$$Q^* = \frac{\hat{V}_2{}^\circ(T_{g2})A}{\gamma_2}(\alpha_2 - \alpha_{2g} + \alpha_{c2g} - \alpha_{c2}) \tag{29}$$

In the next section, the concentration dependence of D_1 will be illustrated in three different ways using the results of the above development. First, the dependence of $k_D{}^*$ on $\hat{V}_{FH1}/\gamma_1$ and A can be determined using eqs 27–29 at a particular temperature T below T_{g2}. This calculation illustrates how the concentration dependence of D_1 at the pure polymer limit depends on the characteristics of the solvent added to the glassy polymer. The critical solvent properties in eqs 27–29 are clearly $\hat{V}_{FH1}/\gamma_1$ and A. A second illustration of the concentration dependence can be carried out by using eq 1 to compute $\ln[D_1/D_1{}^\circ]$ as a function of solvent mass fraction at some temperature T below T_{g2}. In part of the concentration interval, $0 \le \omega_1 \le (T_{g2} - T)/A$, the polymer–solvent system will be in a glassy state, and $\hat{V}_{FH}/\gamma$ in eq 1 can be calculated using eqs 19 and 20. For $\omega_1 > (T_{g2} - T)/A$, the polymer–solvent system will exist in the rubbery state, and eqs 3, 18, and 21 can be used to compute $\hat{V}_{FH}/\gamma$ in eq 1. At a temperature T, the polymer–solvent mixture undergoes a glass transition at $\omega_1 = (T_{g2} - T)/A$, and this will lead to a step change in the concentration dependence of D_1. A third aspect of the concentration dependence of D_1 is the examination of how the concentration dependence at the pure polymer limit (as characterized by $k_D{}^*$) depends on temperature. Temperatures both above and below T_{g2} can be examined by using eqs 26 and 27. This investigation of the concentration dependence of D_1 for solvent self-diffusion in glassy polymers extends and modifies the analysis proposed in a previous study.[16]

The effect of the glass transition on the solvent self-diffusion process can be investigated by computing the temperature dependence of D_1 both above and below T_{gm} at a given solvent mass fraction. An effective activation energy E_D for the solvent self-diffusion process can be defined as follows:

$$E_D = RT^2\left(\frac{\partial \ln D_1}{\partial T}\right)_{p,\omega_1} \tag{30}$$

It is useful and convenient to use the following ratio r of activation energies to assess the effect of the glass transition on the self-diffusion process for a particular polymer–penetrant mixture:

$$r = \frac{E_D(T_{\mathrm{gm}}^-)}{E_D(T_{\mathrm{gm}}^+)} \tag{31}$$

Here, $E_D(T_{\mathrm{gm}}^+)$ is the activation energy in the liquid state of the mixture at the transition temperature T_{gm} and $E_D(T_{\mathrm{gm}}^-)$ is the activation energy in the glassy state at T_{gm}. It is convenient here to derive an expression for r for the special case when $E^* = 0$. Utilization of eqs 1, 3, 18–21, and 30 in eq 31 produces the following expression for r:

$$r = \frac{\dfrac{P\omega_1}{\omega_2} + \dfrac{\alpha_{2\mathrm{g}}}{\alpha_2}(\alpha_2 - \alpha_{\mathrm{c}2})}{\dfrac{P\omega_1}{\omega_2} + \alpha_2 - \alpha_{\mathrm{c}2}} \tag{32}$$

$$P = \frac{K_{11}/\gamma_1}{\hat{V}_2^\circ(T_{\mathrm{g}2})/\gamma_2} \tag{33}$$

As noted elsewhere,[15] it is expected that the glass transition will have the greatest effect on the temperature dependence of D_1 at fixed ω_1 at the pure polymer limit. Hence, eq 32 serves to indicate quantitatively the increase in r with increasing solvent mass fraction.

It is reasonable to expect that various aspects of transport behavior in polymer–diluent systems are governed by the amount of specific hole free volume in the polymeric system. Consequently, plasticization of a polymer should take place when the addition of a solvent leads to an increase in the free volume of the system, and antiplasticization should occur when the addition of a solvent leads to a loss in free volume. The specific hole free volume of a glassy polymer–solvent system can be computed using eqs 19 and 20, and it is clear that the concentration dependence of $\hat{V}_{\mathrm{FH}}/\gamma$ will be strongly dependent on the nature of the solvent, as characterized by the parameters A and $\hat{V}_{\mathrm{FH}1}/\gamma_1$. A diluent is a plasticizer for a particular polymer if it produces a positive initial concentration derivative in eq 22, and it is an antiplasticizer initially if the concentration derivative is negative.

Equation 22 can be rewritten in a slightly different form to facilitate explanation of the various possibilities for plasticization and antiplasticization:

$$\left[\frac{\partial(\hat{V}_{\mathrm{FH}}/\gamma)}{\partial\omega_1}\right]_{\omega_1=0} = \left[\frac{\hat{V}_{\mathrm{FH}1}}{\gamma_1} - \frac{\hat{V}_{\mathrm{FH}2\mathrm{g}}(\omega_1{=}0)}{\gamma_2}\right] - \frac{\hat{V}_2^\circ(T_{\mathrm{g}2})A}{\gamma_2}(\alpha_2 - \alpha_{2\mathrm{g}} + \alpha_{\mathrm{c}2\mathrm{g}} - \alpha_{\mathrm{c}2}) \tag{34}$$

As noted above, the term in the brackets in eq 34 is usually positive, since penetrants generally have more free volume than glassy polymers, and the other term is negative, reflecting a loss of free volume for the system. For diluents with relatively high glass transition temperatures, the difference in the diluent and polymer free volumes can be rather small since the glass transition temperatures of the two components will not be that far apart. In this case, the negative second term in eq 34 can lead to an initial decrease in specific hole free volume with increasing diluent concentration and the diluent causes antiplasticization. On the other hand, for penetrants with very low glass transition temperatures, the penetrant free volume is usually much greater than that of the glassy polymer, and the positive first term in eq 34 can be greater than the negative second term. In this case, there is an initial increase in specific hole free volume with increasing penetrant concentration, and the penetrant has a plasticizing effect. Consequently, the glass transition temperature of the diluent can serve as a rough measure of whether it is a plasticizer or an antiplasticizer. Also, it is clear that solvents with larger values of A have a greater possibility of acting as antiplasticizing agents.

Table 1. Free-Volume Parameters for Model Polymer–Solvent System

$\hat{V}_1^*$ (cm^3/g)	0.90
$\hat{V}_2^*$ (cm^3/g)	0.888
K_{11}/γ_1 (cm^3/g K)	1.5×10^{-3}
K_{12}/γ_2 (cm^3/g K)	5×10^{-4}
$K_{21} - T_{\mathrm{g}1}$ (K)	−100
K_{22} (K)	50
$T_{\mathrm{g}2}$ (K)	373
ξ	1.014
α_2 (K^{-1})	5×10^{-4}
$\alpha_{2\mathrm{g}}$ (K^{-1})	1.5×10^{-4}
$\alpha_{\mathrm{c}2}$ (K^{-1})	2.5×10^{-4}
$\alpha_{\mathrm{c}2\mathrm{g}}$ (K^{-1})	0.75×10^{-4}
$\hat{V}_2^\circ(T_{\mathrm{g}2})$ (cm^3/g)	1
$f_{\mathrm{H}2}^{\mathrm{G}}$	0.025
D_0 (cm^2/s)	arbitrary
E^* (kcal/g mol)	0
γ_2	1
A (K)	0–500
$\hat{V}_{\mathrm{FH}1}/\gamma_1$ (cm^3/g)	0.05–0.20 (used when a single temperature is considered)

The possibility of plasticization or antiplasticization effects for a particular solvent in a glassy polymer at some temperature T below $T_{\mathrm{g}2}$ can be ascertained by using eqs 19 and 20 to compute the concentration dependence of $\hat{V}_{\mathrm{FH}}/\gamma$ for the glassy polymer–solvent system. The influence of solvent properties on the concentration dependence can be examined by appropriate variation of $\hat{V}_{\mathrm{FH}1}/\gamma_1$ and A. In addition, the dividing line between initial antiplasticization (negative concentration derivative) and initial plasticization (positive concentration derivative) can be determined by setting the concentration derivative equal to zero in eq 34. This produces the result

$$\frac{\hat{V}_{\mathrm{FH}1}}{\gamma_1\hat{V}_2^\circ(T_{\mathrm{g}2})} = \frac{\hat{V}_{\mathrm{FH}2\mathrm{g}}(\omega_1{=}0)}{\gamma_2\hat{V}_2^\circ(T_{\mathrm{g}2})} + \frac{A}{\gamma_2}[\alpha_2 - \alpha_{2\mathrm{g}} + \alpha_{\mathrm{c}2\mathrm{g}} - \alpha_{\mathrm{c}2}] \tag{35}$$

which is a linear relationship between $\hat{V}_{\mathrm{FH}1}/\gamma_1$ and A. This expression can be used to construct a plot of plasticization and antiplasticization regions for solvents with different $\hat{V}_{\mathrm{FH}1}/\gamma_1$ and A values.

Results and Discussion

In this section, general predictions of free-volume theory for solvent self-diffusion in polymer–solvent systems are illustrated for a model polymer–solvent system with properties summarized in Table 1. In addition, a comparison is made between the predictions of the theory and experimental data[10] for the self-diffusion of toluene in polystyrene.

Transport behavior in glassy polymer–penetrant systems will be strongly dependent on $\hat{V}_{\mathrm{FH}}$, the specific hole free volume of the mixture, and on how $\hat{V}_{\mathrm{FH}}$ changes with concentration and temperature. The concentration and temperature variations of $\hat{V}_{\mathrm{FH}}$ will depend on the nature of the penetrant, as characterized by the parameters $\hat{V}_{\mathrm{FH}1}/\gamma_1$ and A. Widely different variations of $\hat{V}_{\mathrm{FH}}/\gamma$ with concentration are predicted for different combinations of $\hat{V}_{\mathrm{FH}1}/\gamma_1$ and A. This is illustrated in Figure 1 where the

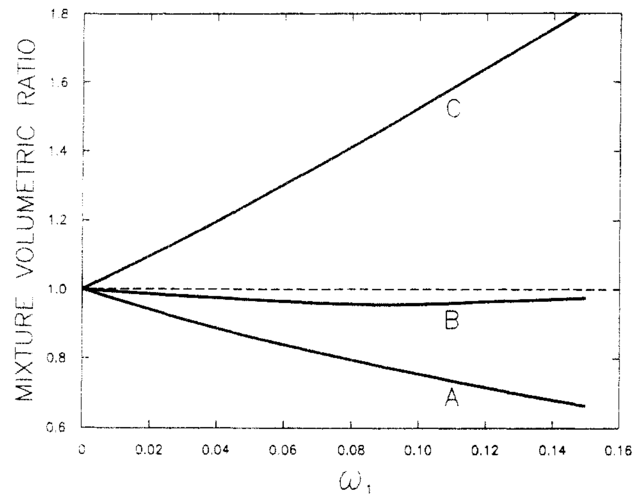

Figure 1. Dependence of volumetric ratio, $(\hat{V}_{FH}/\gamma)/(\hat{V}_{FH}(0)/\gamma)$, on solvent mass fraction for the model polymer–solvent system at 25 °C and A = 500 K. Curves A, B, and C represent values of $\hat{V}_{FH1}/\gamma_1$ = 0.05, 0.09, and 0.20 cm^3/g, respectively.

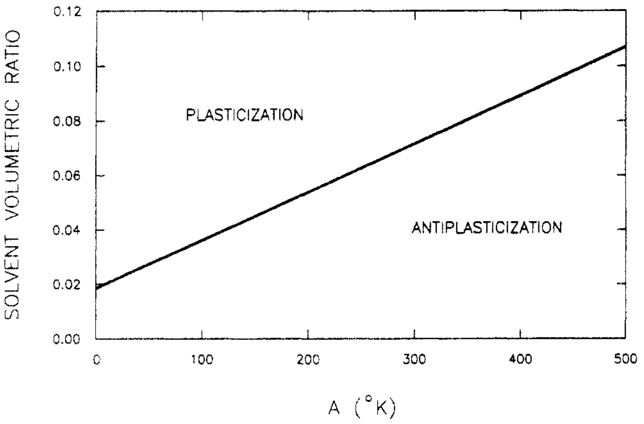

Figure 2. Regions of plasticization and antiplasticization for various solvents in the model polymer–solvent system at 25 °C. Solvents are characterized by A and the volumetric ratio $(\hat{V}_{FH1}/\gamma_1)/\hat{V}_2{}^{\circ}(T_{g2})$.

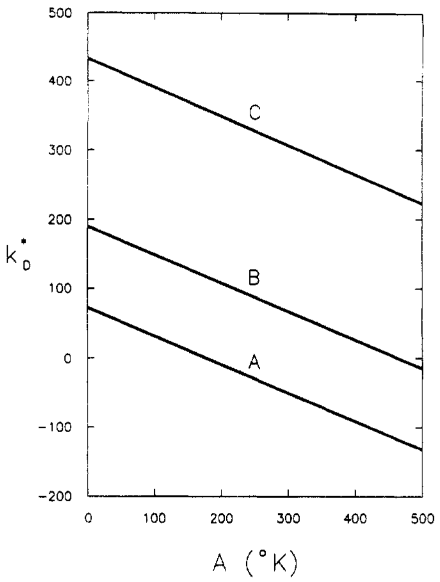

Figure 3. Dependence of $k_D{}^*$ on A and $\hat{V}_{FH1}/\gamma_1$ for the model polymer–solvent system at 25 °C. Curves A, B, and C represent values of $\hat{V}_{FH1}/\gamma_1$ = 0.05, 0.1, and 0.20 cm^3/g, respectively.

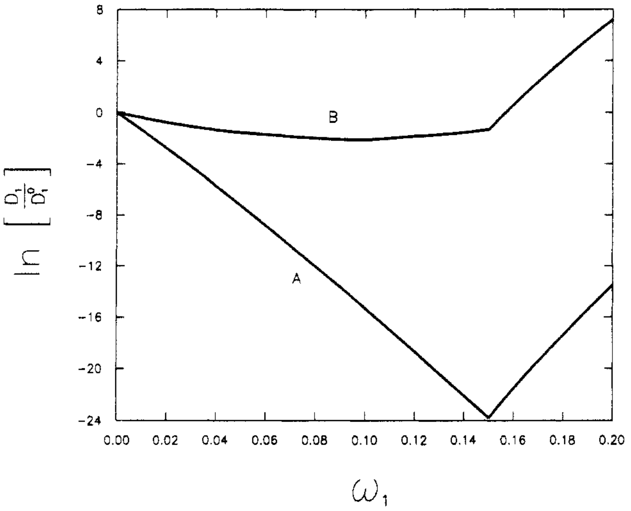

Figure 4. Concentration dependence of $\ln[D_1/D_1{}^{\circ}]$ for the model polymer–solvent system at 25 °C with A = 500 K. Curves A and B represent values of $\hat{V}_{FH1}/\gamma_1$ = 0.05 and 0.09 cm^3/g, respectively.

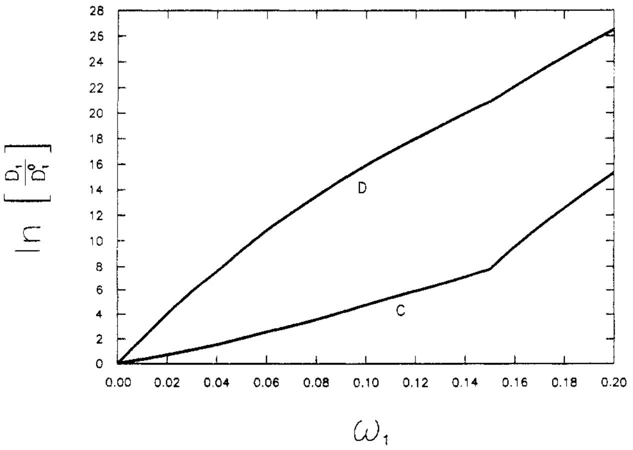

Figure 5. Concentration dependence of $\ln[D_1/D_1{}^{\circ}]$ for the model polymer–solvent system at 25 °C with A = 500 K. Curves C and D represent values of $\hat{V}_{FH1}/\gamma_1$ = 0.12 and 0.20 cm^3/g, respectively.

ratio of $\hat{V}_{FH}/\gamma$ to $\hat{V}_{FH}/\gamma$ at $\omega_1 = 0$ is plotted versus solvent mass fraction for the model polymer–solvent system at 25 °C with A = 500 K and with three different values for $\hat{V}_{FH1}/\gamma_1$. For the solvent with the highest free volume, there is an increase of the mixture free volume, and, for the solvent with the lowest free volume, there is a decrease. For an intermediate solvent free volume, there is an initial decrease and then an increase in the mixture free volume. As noted above, the dependence of $\hat{V}_{FH}/\gamma$ on concentration and temperature will affect the solvent self-diffusion coefficient and also any plasticization–antiplasticization behavior of the solvent. For example, the dependence of $\hat{V}_{FH}/\gamma$ on $\hat{V}_{FH1}/\gamma_1$ and A can be illustrated by using eq 35 to construct a plot of plasticization and antiplasticization regions for solvents with different values of $\hat{V}_{FH1}/\gamma_1$ and A. A plot of this type is presented in Figure 2 for the model polymer–solvent system at a temperature of 25 °C with different values of $\hat{V}_{FH1}/\gamma_1$ and A for the model solvent. This figure can be used to identify whether a particular solvent is a plasticizer or an antiplasticizer initially. Furthermore, the dependence of $k_D{}^*$ for the model polymer–solvent system at 25 °C on A for three values of $\hat{V}_{FH1}/\gamma_1$ is illustrated in Figure 3. The calculations for this figure are based on eqs 27–29. Large positive values of $k_D{}^*$ are obtained for low values of A and high values of $\hat{V}_{FH1}/\gamma_1$, whereas negative values of $k_D{}^*$ are observed when A is large and $\hat{V}_{FH1}/\gamma_1$ is sufficiently small. In the latter case, the collapse of free volume is not compensated for by the free volume added by the solvent. In addition, the dependence of $\ln[D_1/D_1{}^{\circ}]$ on solvent mass fraction is illustrated in Figures 4 and 5 for the model polymer–solvent system at 25 °C with A = 500 K and four

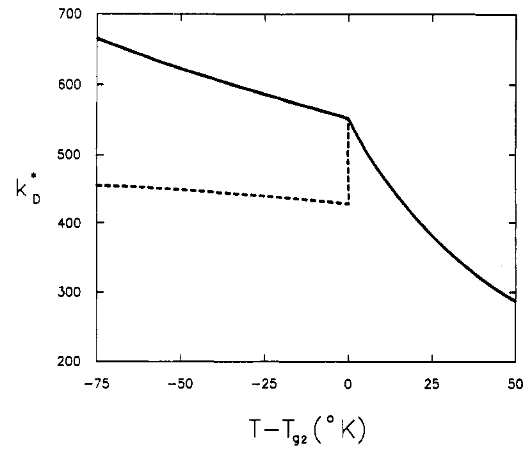

Figure 6. Temperature dependence of k_D^* for the model polymer–solvent system. For temperatures below T_{g2}, the solid line is for A = 0 K and the dashed line is for A = 500 K.

different values of $\hat{V}_{FH1}/\gamma_1$. The system is in a glassy state for $0 \leq \omega_1 \leq 0.15$ and in a rubbery state for $\omega_1 > 0.15$. Calculations were based on eqs 1, 19, and 20 for the glassy system and on eqs 1, 3, 18, and 21 for the rubbery mixture. A wide variety of behavior can be observed depending on the value of $\hat{V}_{FH1}/\gamma_1$. For the two highest values of $\hat{V}_{FH1}/\gamma_1$, D_1/D_1° increases with increasing ω_1 in the glassy region. For the lowest value of $\hat{V}_{FH1}/\gamma_1$ (0.05), there is a decrease in D_1/D_1° in the glassy region, whereas for $\hat{V}_{FH1}/\gamma_1 = 0.09$, there is an initial decrease and then an increase of D_1/D_1° in the glassy region. In all cases, there is an increase in D_1/D_1° for $\omega_1 > 0.15$ since the system is in a rubbery state, and there is no collapse of frozen-in hole free volume. It is evident from Figures 4 and 5 that there is a step change in the concentration dependence of D_1 at $\omega_1 = 0.15$. This step change simply reflects the fact that, at 25 °C, the system undergoes a glass to rubbery transition at $\omega_1 = 0.15$. The sharp change in concentration dependence is similar to step changes in temperature dependence commonly observed at the usual glass transition temperature. Such step changes are generally consequences of mathematical idealizations used to describe rapid property changes.

One way to illustrate temperature effects in the self-diffusion process is to evaluate the temperature dependence of k_D^* both above and below T_{g2} using eqs 26 and 27. This was done for the model polymer–solvent system with A = 0 and 500 K, with the temperature dependence of $\hat{V}_{FH1}/\gamma_1$ being calculated using eq 21. The temperature dependence of k_D^* is presented in Figure 6. At temperatures above T_{g2}, k_D^* increases significantly as T is decreased toward T_{g2}. The theory predicts that there will be a more pronounced concentration dependence as the temperature is decreased toward T_{g2}, and this is the usual behavior for polymer–solvent systems. Below T_{g2}, the temperature dependence of k_D^* is greatly influenced by the value of A. When A = 0 K (no collapse of free volume), k_D^* continues to increase as the temperature is decreased, but the rate of increase is significantly less below T_{g2} than it is above T_{g2}. When A = 500 K (significant collapse of free volume), there is a sharp drop in k_D^* near T_{g2} and then a gradual increase as T is further decreased. For this case, the concentration dependence of D_1 is more pronounced in the rubbery polymer above T_{g2} than it is for the glassy polymer. The effect of the glass transition on the solvent self-diffusion process for the model polymer–solvent system can be examined using eqs 32 and 33 to determine r, the ratio of activation energies at $T = T_{gm}$, as a function of concentration. The concentration dependence of r is presented in Figure 7, and it is evident that the ratio r more than doubles as the concentration is increased from $\omega_1 = 0$ to $\omega_1 = 0.15$. Hence, as noted in a previous study,[15] free-volume theory predicts that the effect of the glass transition on the diffusion process is reduced considerably as the solvent concentration increases. Indeed, it would probably be difficult to detect any effect at the transition temperature using solutions with mass fractions near ω_1 = 0.15.

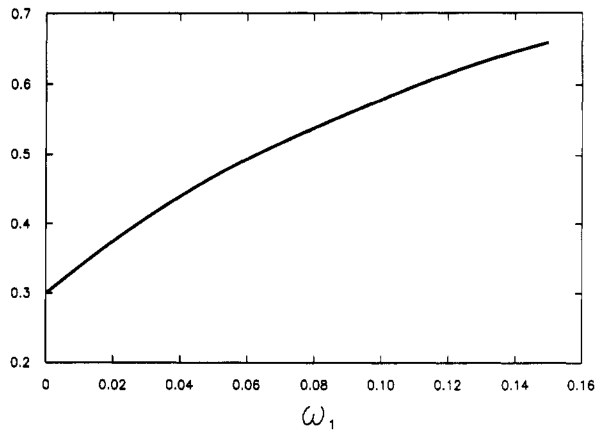

Figure 7. Dependence of r, ratio of activation energies at T_{gm}, on solvent mass fraction for the model polymer–solvent system.

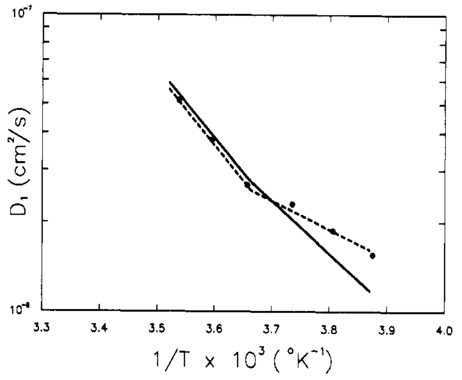

Figure 8. Comparison of theory and experiment for self-diffusion in the toluene–polystyrene system at $\omega_2 = 0.811$. T_{gm} = 0.3 °C. In Figures 8–10, the solid lines are the theoretical predictions, the solid circles are the experimental data, and the dashed lines are smoothed representations of the data.

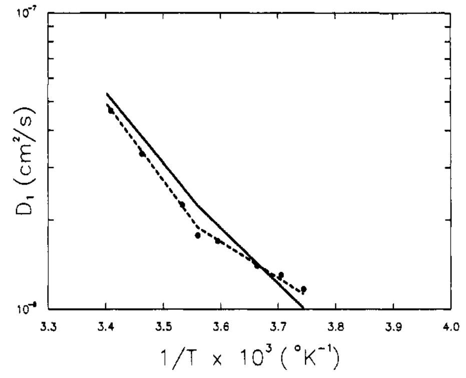

Figure 9. Comparison of theory and experiment for self-diffusion in the toluene–polystyrene system at $\omega_2 = 0.83$. T_{gm} = 7.9 °C.

A direct comparison of the predictions of the theory with experiment can be carried out using recently reported self-diffusion data for the polystyrene–toluene system.[10] The temperature dependence of D_1 both above and below T_{gm} was studied for polystyrene–toluene mixtures at three concentrations. The data–theory comparisons are presented in Figures 8–10. The theoretical predictions were carried out using the free-volume parameters listed in Table 2, and predictions both above and below T_{gm} are

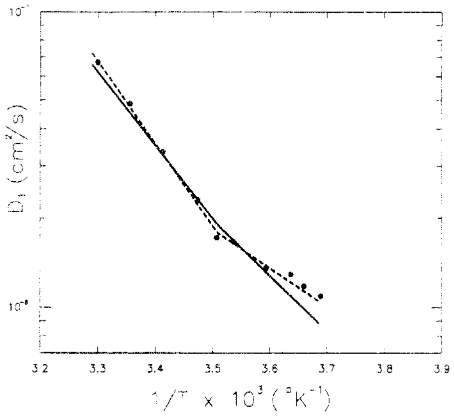

Figure 10. Comparison of theory and experiment for self-diffusion in the toluene–polystyrene system at $\omega_2 = 0.84$. $T_{gm} = 12$ °C.

Table 2. Free-Volume Parameters for Toluene–Polystyrene System

$\hat{V}_1^*$ (cm^3/g)	0.917
$\hat{V}_2^*$ (cm^3/g)	0.850
K_{11}/γ_1 (cm^3/g K)	1.57×10^{-3}
K_{12}/γ_2 (cm^3/g K)	5.39×10^{-4}
$K_{21} - T_{g1}$ (K)	−90.5
K_{22} (K)	50
T_{g2} (K)	373
ξ	0.575
$\alpha_2(T \geq T_{g2})$ (K^{-1})	5.3×10^{-4}
$\alpha_{2g}(T_{g2})$ (K^{-1})	1.6×10^{-4}
α_{c2} (K^{-1})	2.88×10^{-4}
α_{c2g} (K^{-1})	0.87×10^{-4}
$\hat{V}_2^\circ(T_{g2})$ (cm^3/g)	0.972
f_{H2}^G	0.0265
D_0 (cm^2/s)	4.17×10^{-4}
E^* (kcal/g mol)	0
γ_2	0.956

included in Figures 8–10. All of the parameters in Table 2 except α_{2g} and α_{c2g} were discussed previously.[11] A value of $\alpha_{2g} = 1.6 \times 10^{-4}$ K^{-1} was used at T_{g2}, and α_{c2g} was calculated using eq 17. A temperature dependence for α_2 below T_{g2} was estimated using the extrapolated volumetric curve presented by Rehage and Borchard.[19] Similarly, a temperature dependence for α_{2g} was estimated using data tabulated by Boyer.[20]

For all three concentrations studied, it is evident from Figures 8–10 that there is reasonably good agreement between theory and experiment for temperatures above T_{gm}. For temperatures below T_{gm}, there is fair agreement with a maximum error of about 30% and an average absolute error of about 10%. However, the theory does not do a good job of describing the experimental temperature dependence of D_1 below T_{gm}. It must be however noted that the experimental D_1 values for toluene are actually derived[10] from dye diffusion data using a correlation based on diffusion data collected above T_{gm}. In addition, the calculation of D_1 for toluene from the correlation is very sensitive to small changes in the slope of the correlation. For example, less than a 2% change in the slope leads to a 25% change in D_1 for toluene. In light of this uncertainty, the agreement between theory and experiment is reasonable, and it can be concluded that the proposed theory is a viable candidate for describing the solvent self-diffusion process below T_{gm}. However, much more data are needed to test all of the various theoretical predictions described above. As noted above, the theory predicts that it is typically difficult to detect the effect of the transition temperature on the diffusion process when ω_1 is near 0.15. Indeed, the theoretical predictions in Figures 8–10 indicate only a slight change in the temperature dependence at the transition temperature. The experimental data indicate a more pronounced effect of the glass transition, but, as noted above, the calculation of D_1 for toluene is sensitive to the form of the correlation used to derive D_1 from dye diffusion data.

Finally, it is important to emphasize that the behavior of glassy polymers can depend on the sample preparation history. Consequently, the present predictions are valid for sample preparation histories similar to the one used here or for cases where the exact nature of the sample preparation history is of secondary importance. In addition, it is assumed that once a polymer structure is formed at a given temperature and concentration, this structure is effectively invariant during any experiments carried out on the polymer–penetrant mixture until the concentration or temperature levels are changed. Consequently, aging effects are assumed to be negligible during the time scale of an experiment.

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