

Effect of Glass Transition on the Concentration Dependence of Self-Diffusion Coefficients

J. S. Vrentas, C. M. Vrentas

Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: The free-volume theory of diffusion is used to predict the effect of the glass transition on the concentration dependence of the solvent self-diffusion coefficient at constant temperature. The theoretical prediction is in agree-

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Key words: glass transition; diffusion; solution properties

INTRODUCTION

It is well known that the glass transition has a significant effect on the solvent self-diffusion process in polymer–solvent systems.^{1,2} To develop a theoretical explanation of this effect, it is acceptable to use the following linear expression for the glass-transition temperature of the polymer–solvent mixture (T_{gm}) at a particular penetrant mass fraction:

$$T_{gm} = T_{g2} - A\omega_1 \quad (1)$$

where T_{g2} is the glass-transition temperature of the pure polymer, ω_1 is the solvent mass fraction, and A is a coefficient that depends on the nature of the penetrant used to depress the glass-transition temperature for a particular polymer. Over a limited range of concentration, this dependence should be approximately linear. The previous expression suggests two types of experimental procedures that can be used to ascertain the effect of the glass transition. In the first procedure, the temperature of the experiment is varied at a constant ω_1 . It has been found, both experimentally and theoretically,^{1,2} that the effective activation energy decreases as the temperature is lowered and the polymer–solvent system goes from the rubbery state to the glassy state at a constant solvent concentration. The effect of the glass transition on the solvent self-diffusion process as the temperature is varied at a constant ω_1 can be predicted with the free-volume theory of diffusion.^{1,2} The theory predicts that there is a difference in the temperature dependence of the solvent self-diffusion coefficient (D_1) between the glassy and rubbery states.

A second procedure that has been used experimentally^{3,4} is the variation of the solvent concentration in the polymer–solvent system at a constant temperature. As the solvent concentration is increased, the polymer–solvent system goes from the glassy to the rubbery state, and it is of interest to determine the nature of the difference between the concentration dependencies of D_1 in the glassy and rubbery states. The objective of this article is to use the free-volume theory of diffusion to predict the effect of the glass transition on the concentration dependence of D_1 at a constant temperature. This theoretical prediction is then compared with experimental data.

THEORY

D_1 can be determined with the following equation:

$$D_1 = \bar{D}_0 \exp\left[-\frac{E^*}{RT}\right] \exp\left[-\frac{\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*}{\hat{V}_{FH}/\gamma}\right] \quad (2)$$

where \bar{D}_0 is a constant preexponential factor, E^* is the effective energy per mole that a molecule needs to overcome attractive forces, T is 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, ω_I is the mass fraction of component I , \hat{V}_I^* is the specific hole-free volume of component I required for a jump, γ is the average overlap factor for the mixture, which is introduced because the same free volume is available to more than one jumping unit, and \hat{V}_{FH} is the average hole-free volume per gram of mixture.

For rubbery polymer–solvent systems for $T < T_{g2}$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1} (K_{21} + T - T_{g1}) + \omega_2 \frac{\hat{V}_2^0(T_{g2})}{\gamma_2} [f_{H2}^C - (\alpha_2 - \alpha_{c2})(T_{g2} - T)] \quad (3)$$

Correspondence to: J. S. Vrentas (jsv1@psu.edu).
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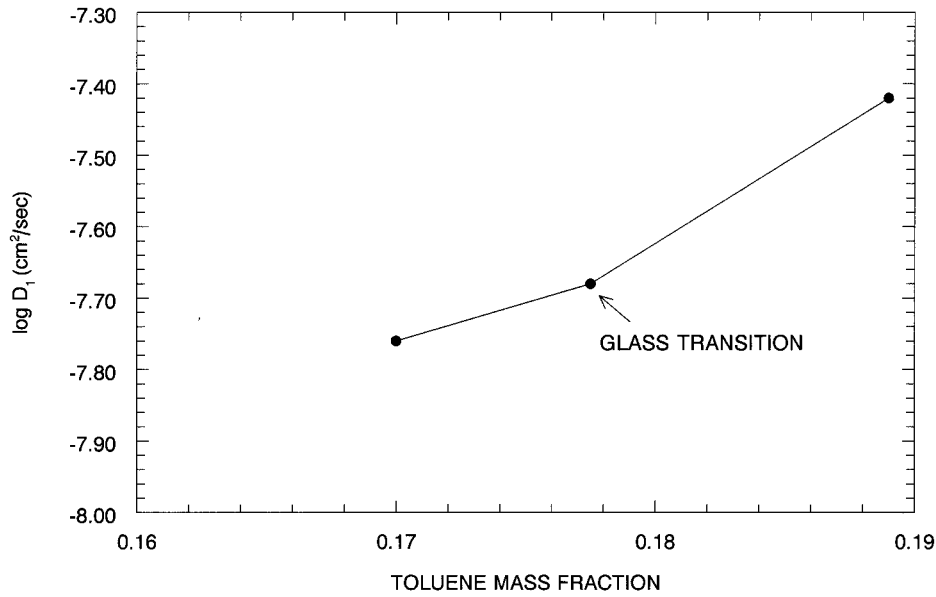


Figure 1 Concentration dependence of D_1 for toluene-polystyrene system at 5°C. The mass fraction consistent with a glass transition at 5°C is indicated in this figure.

where γ_I represents the overlap factor for the free volume of pure component I , K_{11} , and K_{21} are free-volume parameters for the solvent, T_{g1} is the glass-transition temperature of component I , f_{H2}^G is the fractional hole-free volume of the polymer at T_{g2} , and $\hat{V}_2^0(T_{g2})$ is the specific volume of the polymer at its glass-transition temperature. In eq. (3), all of the thermal expansion coefficients are assumed to be effectively independent of temperature. Therefore, α_2 is the constant thermal expansion coefficient for the equilibrium liquid polymer, and α_{c2} is the constant thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume for the equilibrium liquid polymer. For glassy polymer-solvent systems for $T < T_{gm}$

$$\begin{aligned} \frac{\hat{V}_{FH}}{\gamma} = & \omega_1 \frac{K_{11}}{\gamma_1} (K_{21} + T - T_{g1}) \\ & + \omega_2 \frac{\hat{V}_2^0(T_{g2})}{\gamma_2} [f_{H2}^G - \omega_1 A(\alpha_2 - \alpha_{2g} + \alpha_{c2g} - \alpha_{c2}) \\ & + (\alpha_{2g} - \alpha_{c2g})(T - T_{g2})] \end{aligned} \quad (4)$$

where α_{2g} is the constant thermal expansion coefficient for the glassy polymer and α_{c2g} is the constant thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume for the glassy polymer.

The concentration derivative of eq. (2) can be expressed as follows:

$$\left(\frac{\partial \ln D_1}{\partial \omega_1} \right)_T = - \frac{\hat{V}_1^* - \xi \hat{V}_2^*}{\hat{V}_{FH}/\gamma} + \frac{\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*}{(\hat{V}_{FH}/\gamma)^2} \left[\frac{\partial(\hat{V}_{FH}/\gamma)}{\partial \omega_1} \right]_T \quad (5)$$

Differentiation of eqs. (3) and (4) produces the following result at the concentration consistent with the glass-transition point:

$$\begin{aligned} \left[\frac{\partial(\hat{V}_{FH}/\gamma)}{\partial \omega_1} \right]_G - \left[\frac{\partial(\hat{V}_{FH}/\gamma)}{\partial \omega_1} \right]_R = & - \frac{\hat{V}_2^0(T_{g2})}{\gamma_2} \\ & \times [\alpha_{2g} - \alpha_{c2g} - \alpha_2 + \alpha_{c2}] [T - T_{g2} - A(\omega_2 - \omega_1)] \end{aligned} \quad (6)$$

where the G and R subscripts refer to the glassy and rubbery states, respectively. The combination of eqs. (5) and (6) and the utilization of eq. (1) produce the following difference of mass fraction derivatives at the glass-transition point:

$$\begin{aligned} \left[\frac{\partial \ln D_1}{\partial \omega_1} \right]_R - \left[\frac{\partial \ln D_1}{\partial \omega_1} \right]_G = & \left[\frac{\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*}{(\hat{V}_{FH}/\gamma)^2} \right] \left[\frac{\hat{V}_2^0(T_{g2})}{\gamma_2} \right] \\ & \times [(\alpha_2 - \alpha_{c2}) - (\alpha_{2g} - \alpha_{c2g})] [A\omega_2] \end{aligned} \quad (7)$$

The difference of the concentration derivatives is equal to the product of the four factors on the right-hand side of eq. (7). The first, second, and fourth factors are obviously positive. A convenient way to determine the sign of the third factor is to introduce the following relationship, which was proposed previously:²

$$\frac{\alpha_{c2g}}{\alpha_{c2}} = \left(\frac{\alpha_{2g}}{\alpha_2} \right)_{T=T_{g2}} \quad (8)$$

If this expression is used to eliminate α_{c2g} , we have the following result:

$$(\alpha_2 - \alpha_{c2}) - (\alpha_{2g} - \alpha_{c2g}) = [\alpha_2 - \alpha_{2g}] \left[1 - \frac{\alpha_{c2}}{\alpha_2} \right] > 0 \quad (9)$$

Hence, all four factors in eq. (7) are positive, and consequently

$$\left[\frac{\partial \ln D_1}{\partial \omega_1} \right]_R > \left[\frac{\partial \ln D_1}{\partial \omega_1} \right]_G \quad (10)$$

These results may be useful if the concentration dependence of D_1 is needed for a constant-temperature process for which both glassy and rubbery regions exist in the system. The inequality of eq. (10) can, of course, be satisfied if both concentration derivatives at the transition point are positive or if the concentration derivative in the rubbery state is positive and that in the glassy state is negative. These possibilities were presented previously² in illustrative free-volume determinations of the concentration dependence of D_1 for a number of special cases.

DATA-THEORY COMPARISON

At least two investigations^{3,4} were concerned with the isothermal measurement of diffusion coefficients as a function of concentration through the glass-transition

point. Unfortunately, the scatter of the data in these two studies did not make it possible to test whether the theoretical result was consistent with the experimental concentration dependence. The error bars in these two investigations were too large to allow any definitive conclusions, although the most reasonable interpretation of the data in ref. 3 was consistent with eq. (10). However, the diffusion data of another study⁵ could be used to carry out a data-theory comparison if some appropriate data interpolation were utilized. The concentration dependence of D_1 for the toluene-polystyrene system at 5°C is presented in Figure 1. It is clear that the data at the transition point were consistent with eq. (10). Consequently, it is fair to conclude that the limited data available support the predictions of the theoretical results derived in this investigation [eqs. (7) and (10)].

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