

Concentration Dependence of Solvent Self-Diffusion Coefficients

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Synopsis

The concentration dependence of solvent self-diffusion coefficients is examined near the pure solvent limit. It is shown that it is possible to explain an apparently anomalous concentration dependence for the solvent self-diffusion coefficient at high penetrant mass fractions within the framework of the free-volume theory of transport.

INTRODUCTION

The free-volume theory of transport provides a rather satisfactory method of predicting and correlating solvent self-diffusion coefficients for polymer-solvent systems.^{1,2} It is reasonable to expect that this theory can be used to compute the solvent self-diffusion coefficient, D_1 , over the complete concentration range, and, indeed, in some cases, it is possible to do this. However, there have appeared data which show an apparently anomalous concentration dependence for D_1 near the pure solvent limit.³⁻⁵ The purpose of this note is to discuss the concentration dependence of D_1 and to examine the behavior of this quantity as the solvent mass fraction approaches unity. It is shown that it is possible to explain the concentration dependence of D_1 at high penetrant mass fractions within the framework of the free-volume theory of transport.

THEORY

The following expression has been proposed^{1,2} for the solvent self-diffusion coefficient in a polymer-penetrant mixture:

$$D_1 = D_0 \exp \left[-\frac{E}{RT} \right] \exp \left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}} \right] \quad (1)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma} (K_{21} + T - T_{g1}) + \omega_2 \frac{K_{12}}{\gamma} (K_{22} + T - T_{g2}) \quad (2)$$

Here, D_0 is a constant pre-exponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors, and T is temperature. Also, \hat{V}_I^* is the specific critical hole-free volume of component I required for a jump, ω_1 is the mass fraction of component I, T_{g1} is the glass transition temperature of component I, \hat{V}_{FH} is the average hole-free volume per gram of mixture, 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. Finally, 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 γ is an overlap factor which is introduced because the same free volume is available to more than one molecule.

There are nine parameters in this version of free-volume theory: K_{11}/γ , $K_{21} - T_{g1}$, K_{12}/γ , $K_{22} - T_{g2}$, \hat{V}_1^* , \hat{V}_2^* , D_0 , E , ξ . The first six parameters can be determined from pure component data which are generally readily available.² In addition, it is, in principle, possible to determine D_0 and E using viscosity-temperature data and density-temperature data for the solvent. In practice, however, it has been shown that it is not generally possible to determine meaningful values of D_0 and E from these data because of unacceptable parameter interaction effects.² Consequently, the parameters D_0 , E , and ξ are generally determined by utilizing a nonlinear regression analysis on $D_1(\omega_1, T)$ data collected at two or more temperatures. Unfortunately, the parameters D_0 and E appear to be sensitive to the temperature range over which data are available for utilization in the regression analysis.² Because of this sensitivity to temperature range, it is of course desirable to utilize D_1 data over as wide a temperature range as possible in the determination of D_0 and E . This sensitivity to temperature range is illustrated below using self-diffusion data for the ethylbenzene-polystyrene system.

Equation (1) can be used to predict D_1 for the entire concentration interval if a single value of E can be utilized for all solvent mass fractions.⁶ In this case, it can be shown from Eqs. (1) and (2) that the concentration dependence of D_1 at a particular temperature T obeys the following relationship:

$$\frac{\partial^2 \ln D_1}{\partial \omega_1^2} = - \frac{2[\hat{V}_{FH}(1) - \hat{V}_{FH}(0)]}{\hat{V}_{FH}} \frac{\partial \ln D_1}{\partial \omega_1} \quad (3)$$

Here, $\hat{V}_{FH}(0)$ is the specific hole-free volume of the pure polymer at T and $\hat{V}_{FH}(1)$ is the specific hole-free volume of the pure solvent at T . Typically, for polymer-solvent systems, $\hat{V}_{FH}(1) > \hat{V}_{FH}(0)$ and, furthermore,

$$\frac{\partial \ln D_1}{\partial \omega_1} > 0 \quad (4)$$

over the complete concentration range. Consequently, Eq. (3) predicts that

$$\frac{\partial^2 \ln D_1}{\partial \omega_1^2} < 0 \quad (5)$$

for all mass fractions.

For a typical polymer-solvent system, self-diffusion data follow Eqs. (4) and (5) over most of the concentration interval starting at $\omega_1 = 0$. In addition, for some systems, the diffusion data are consistent with Eqs. (4) and (5) all the way to the pure solvent limit. For example, it appears that Eqs. (4) and (5) are consistent with self-diffusion data for $C_{12}H_{26}$ and $C_{36}H_{74}$ in *cis*-4-polybutadiene^{7,8} for solvent mass fractions ranging from less than 0.1 to the pure solvent limit. Similarly, solvent self-diffusion data for the toluene-polystyrene and toluene-polyisobutylene systems⁹ appear to be consistent with Eqs. (4) and (5) for solvent volume fractions approaching unity. Finally, data for the self-diffusion of 5- α -cholestane in *cis*-polybutadiene¹⁰ are characterized by the

following inequalities over the complete concentration range:

$$\frac{\partial \ln D_1}{\partial \omega_1} < 0 \quad (6)$$

$$\frac{\partial^2 \ln D_1}{\partial \omega_1^2} < 0 \quad (7)$$

Since it is reasonable to expect that $\hat{V}_{FH}(0) > \hat{V}_{FH}(1)$ for this system, it is evident that these data are also consistent with the prediction from Eq. (3).

There are, however, instances^{3,5} where $\partial \ln D_1 / \partial \omega_1 > 0$ and $\partial^2 \ln D_1 / \partial \omega_1^2 > 0$ near the pure solvent limit even though $\partial^2 \ln D_1 / \partial \omega_1^2 < 0$ for smaller solvent mass fractions. It has been suggested¹⁰ that this behavior is caused by a diffusivity enhancement factor of up to 1.5 which results from the removal of laboratory-fixed polymer cages at very high diluent concentrations. We believe that another possibility is that the energy E can be a function of the solvent mass fraction. A concentration dependence for E in the determination of the viscosity of borate mixtures has been proposed by Macedo and Litovitz.¹¹ In addition, it has been noted previously¹² that E can change significantly for polymer-solvent systems near $\omega_1 = 1$ as the concentration is varied at fixed temperature. Since the domains of polymer molecules overlap for solvent mass fractions ranging from 0 to approximately 0.9, a solvent molecule sees the same type of surroundings over this mass fraction range. Consequently, E should not change appreciably in this mass fraction interval, and solvent self-diffusion coefficients can be calculated from Eq. (1) using an essentially constant value of E (which we denote as E_p). As the pure solvent limit is approached, however, the surroundings of the solvent molecule are altered as polymer molecules become scarce, and it is quite possible that there is a significant change in E near $\omega_1 = 1$. Consequently, the self-diffusion process in the pure solvent may involve a different value, E_s , for the energy needed to overcome attractive forces. Clearly, then, the actual value of D_1 at $\omega_1 = 1$ can be significantly different than the value of D_1 predicted from free-volume theory by assuming that $E = E_p$ over the complete concentration interval. This diffusivity difference can be characterized by a parameter q which is defined as follows:

$$q = \frac{D_1(\omega_1 = 1, E = E_s)}{D_1(\omega_1 = 1, E = E_p)} = \exp \left[\frac{E_p - E_s}{RT} \right] \quad (8)$$

The value of q of course depends on the size of the difference between E_p and E_s . The possibility that there is a diffusivity enhancement ($q > 1$) at $\omega_1 = 1$ when $E_p - E_s > 0$ is explored below. From data presented by Macedo and Litovitz,¹¹ it is reasonable to expect that $E_p - E_s > 0$ for a typical polymer-solvent system.

Equation (8) predicts that any diffusivity enhancement will decrease with increasing temperature. Furthermore, this equation implies that the diffusivity enhancement should be dependent on molecular constitution for a poly-

TABLE I
Free-Volume Parameters for Ethylbenzene-Polystyrene System

Temperature range of D_1 data used	115.5–178°C	20–178°C
ξ	0.59	0.58
D_0 (cm ² /s)	1.95	5.33×10^{-4}
E (kcal/g mol)	7.43	0.694

mer-solvent system since the magnitude of the difference between E_p and E_s should be dependent on molecular structure.

RESULTS AND DISCUSSION

At least three cases of diffusivity enhancement have been reported for solvent self-diffusion coefficients near the pure solvent limit: self-diffusion of benzene³ in polyisobutylene at 70.4°C; self-diffusion of a light hydrocarbon oil⁴ in a polyisoprene polymer at 28, 59, and 90°C; and self-diffusion of ethylbenzene⁵ in polystyrene at 30, 70, and 100°C. In all three cases, there is an appreciable enhancement of the solvent self-diffusion coefficient for solvent volume or mass fractions greater than approximately 0.9. Since more is known² about the free-volume properties of the ethylbenzene-polystyrene system, we focus our discussion on this penetrant-polymer pair.

In a previous study,² mutual diffusion data for the ethylbenzene-polystyrene system in the temperature range 115.5–178°C were converted to self-diffusion data which were then used to estimate values of D_0 , E , and ξ . A satisfactory correlation of the ethylbenzene self-diffusion coefficients in this temperature range was obtained using the parameters presented in Table I. Additional solvent self-diffusion data for the ethylbenzene-polystyrene system have recently been reported by Zgadzai and Maklakov⁵ in the temperature range 20–130°C. The predictions of self-diffusion coefficients in this temperature range using Eq. (1) and values of D_0 , E , and ξ derived from the high temperature data are poor. This result is not surprising because, as noted above, the values of D_0 and E are sensitive to the temperature range over which data are available for the parameter estimation scheme. When data over the entire temperature range (20–178°C) are used to estimate D_0 , E , and ξ , a second set of values is derived for these parameters, and the new values of these constants are also presented in Table I. A reasonably good correlation is now achieved for the self-diffusion data over the entire temperature and concentration ranges studied with the exception, of course, of the concentration interval near $\omega_1 = 1$. The free-volume equation for D_1 with $E = E_p =$ constant is not capable of describing the concentration dependence of the solvent self-diffusion coefficient for this particular polymer-penetrant system near the pure penetrant limit.

The parameter q can be computed at each of the three temperatures studied by dividing the experimental value of D_1 at $\omega_1 = 1$ by the value of D_1 predicted using Eq. (1) with $E_p = 0.694$ kcal/g mol. From results presented in Table II, it is evident that there is a substantial diffusivity enhancement at each temperature and, furthermore, q decreases slightly with increasing temperature as predicted from Eq. (8). A value of $E_p - E_s = 0.490 \pm 0.040$ kcal/g mol describes the data.

TABLE II
Enhancement of Self-Diffusion Coefficients for
Ethylbenzene-Polystyrene System

Temperature (°C)	q	$E_p - E_s$ (kcal/g mol)
30	2.10	0.450
70	2.06	0.490
100	2.04	0.530

It is of interest to contrast the behavior of two similar polymer-penetrant pairs, the ethylbenzene-polystyrene and toluene-polystyrene systems. As noted above, there is appreciable diffusivity enhancement near the pure solvent limit for the ethylbenzene-polystyrene system. Furthermore, it has been shown elsewhere² that the energy term is needed in the expression for D_1 if acceptable predictions are to be achieved for the ethylbenzene-polystyrene system. For the toluene-polystyrene system, however, good predictions are realized² with $E = 0$. In addition, data² at 25°C indicate negligible diffusivity enhancement near the pure solvent limit. It is evident that the presence of diffusivity enhancement is strongly dependent on molecular structure.

The above discussion provides a plausible, if not definitive, explanation of diffusivity enhancement at very high diluent concentrations, and the proposed model is within the framework of the free-volume theory of diffusion. It is important to emphasize, however, that a definitive explanation for this apparently anomalous concentration dependence for D_1 is not crucial for the utilization of free-volume theory in the correlation and prediction of mutual and self-diffusion coefficients since this phenomenon is generally limited to solvent volume or mass fractions greater than 0.9. As discussed elsewhere,⁶ it is not expected that free-volume theory can be used to determine mutual diffusion coefficients for solvent mass fractions greater than 0.9, and, hence, a single value of E equal to E_p can be used to determine mutual diffusivities. In addition, values of D_1 up to $\omega_1 = 0.9$ can be computed using Eq. (1) with $E = E_p$, and D_1 at $\omega_1 = 1$ can be adequately estimated from solvent viscosity data using the relationship between solvent viscosity and D_1 proposed by Dullien.¹³ Values of D_1 in the region between $\omega_1 = 0.9$ and $\omega_1 = 1$ can then be estimated by appropriate interpolation.

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