

Estimation of Diffusion Coefficients for Trace Amounts of Solvents in Glassy and Molten Polymers

J. S. VRENTAS, *Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616*, and H. T. LIU and J. L. DUDA, *Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

Two methods based on the free-volume theory of transport are developed for the estimation of diffusion coefficients for trace amounts of solvents in amorphous polymers. The first method uses diffusivity data for a polymer-solvent system above the glass transition temperature to estimate the temperature dependence of the mutual diffusion coefficient below this temperature. In the second method, mutual diffusion coefficients are estimated for a particular polymer-solvent system both above and below the glass transition temperature using no diffusivity data for the system. The predictions of the proposed theory are compared with diffusivity data for the *n*-pentane-polystyrene and ethylbenzene-polystyrene systems.

INTRODUCTION

Difficulties associated with the presence of trace amounts of low molecular weight impurities in plastic products have resulted in a considerable interest in determining the diffusion coefficients of such penetrants in molten and glassy polymers in the limit of zero solvent concentration. Diffusion coefficients for molten polymer-solvent systems are needed for the design of better devolatilizers that can reduce the impurity level in the polymer. Diffusivities for glassy polymer-penetrant systems are needed for determining the extent of the migration of impurities from a plastic product into the immediate surroundings. The determination of the amount of impurity migration from plastic containers into the container contents has especially been of great interest recently.¹

Unfortunately, only a relatively small number of mutual diffusion coefficients have been reported for polymer-solvent systems. Furthermore, the experimental determination of diffusivities for organic solvent-polymer pairs can be a difficult and time consuming process owing to the low diffusivity values characteristic of such systems. Finally, we know of no comprehensive predictive method for polymer-penetrant systems that can be used to provide reasonable estimates of mutual diffusion coefficients in mass transfer processes involving trace amounts of a solvent and an amorphous polymer. The purpose of this paper is to propose methods for estimating diffusivities for amorphous polymer-solvent systems in the limit of zero solvent mass fraction. A method is presented for estimating the temperature dependence of D , the mutual diffusion coefficient for a polymer-solvent system, below the polymer glass transition temperature if data for D vs. T are available for this polymer-penetrant pair

above the glass temperature of the pure polymer. In addition, a method is proposed for determining the temperature dependence of D for a polymer-solvent system both above and below T_{g2} , the polymer glass transition temperature, even if no diffusivity data are available for this particular polymer-penetrant pair. This can be done if diffusivity data are available for other solvents in the polymer above and below T_{g2} and if the temperature dependence of the viscosity of the pure solvent is known.

The predictive methods are formulated using the free-volume theory of transport as applied to polymer-solvent systems.²⁻⁶ These estimation techniques are based on the concept that a small amount of diffusivity data for a given polymer can be used as a basis for estimating the temperature dependence of D for the diffusion of various solvents in that polymer over wide temperature ranges. The equations that are used in the predictive schemes are presented below, and the auxiliary data needed for the implementation of these methods are listed in the next section of the paper. Procedures for analyzing the auxiliary data are summarized, and the diffusivity estimation methods are discussed. These predictive methods are illustrated by using diffusivity data for the *n*-pentane-polystyrene system above T_{g2} to predict the temperature dependence of D for this system below T_{g2} and by computing D vs. T for the ethylbenzene-polystyrene system above and below T_{g2} using diffusivity data for the carbon dioxide-polystyrene and ethyl bromide-polystyrene systems. The predictions of the theory are then compared with actual data for the *n*-pentane-polystyrene and ethylbenzene-polystyrene systems.

THEORY

We consider the isothermal diffusion of low molecular weight penetrants in amorphous polymers, and we introduce the following assumptions and restrictions into the development:

(1) The diffusion process both above and below T_{g2} is described by classical diffusion theory, and this Fickian diffusion process is completely characterized by the mutual diffusion coefficient D . Complications due to non-Fickian effects⁷ and the possibility that the dual-mode sorption mechanism⁸ may be present in glassy polymers are not considered here. A number of experiments⁹⁻¹² suggest that the diffusion of trace amounts of penetrants in glassy polymers can be described by the equations of the classical theory.

(2) Diffusive transport both above and below T_{g2} is described satisfactorily by free-volume theory so that D can be computed over a wide temperature range using the usual free-volume equations.²⁻⁶

(3) For one of the two methods, the size of the jumping unit of the solvent of interest is assumed to be known. A jumping unit is the part of a molecule which is capable of essentially independent movement over a short distance. Consequently, for this method, the analysis is restricted to solvents which have the entire solvent molecule as a jumping unit or to solvents in a homologous series of compounds. For the latter case, it is reasonable to expect that at least the larger members of the series have the same size jumping unit, and the jumping unit size can be determined by analyzing diffusivity data for one member of the series. In general, however, it will not be possible to use this predictive method to estimate D for solvents that have jumping units which constitute only a portion of the solvent molecule and which are of undetermined size.

(4) For one of the predictive schemes described below, it is necessary to utilize viscosity-temperature data for the pure solvent, and we assume that free-volume theory satisfactorily describes the self-diffusion process in the solvent at temperatures which can be significantly above the estimated glass transition temperature of the solvent.

In the limit of zero solvent mass fraction, the mutual diffusion coefficient for a polymer-solvent system for temperatures above T_{g2} can be described⁵ by the following expression:

$$\ln D = \ln D_{01} - \frac{\gamma \hat{V}_2^* \xi}{K_{12}(K_{22} + T - T_{g2})} \quad (1)$$

where D_{01} is a preexponential factor which is assumed to be independent of temperature and ξ is the ratio of the critical molar volume of a solvent jumping unit to the critical molar volume of the jumping unit of the polymer. The critical molar volume is the amount of local hole free volume per mole needed for the movement of a jumping unit. This should approximately be equal to the occupied volume per mole of the jumping unit, which is defined⁵ as the molar volume of the jumping unit at 0 K. The parameters K_{22} and $\gamma \hat{V}_2^*/K_{12}$ are simply related³ to the WLF constants of the polymer, C_1^ξ and C_2^ξ :

$$K_{22} = C_2^\xi \quad (2)$$

$$\gamma \hat{V}_2^*/K_{12} = 2.303 C_1^\xi C_2^\xi \quad (3)$$

A discussion of the parameters K_{12} , K_{22} , γ , and \hat{V}_2^* is given elsewhere.⁵

For temperatures below T_{g2} , the diffusivity in the limit of zero solvent mass fraction can be computed from the expression⁶

$$\ln \left[\frac{D(T)}{D(T_{g2})} \right] = \frac{\gamma \hat{V}_2^* \xi}{K_{12}} \frac{T - T_{g2}}{K_{22}[(K_{22}/\lambda) + T - T_{g2}]} \quad (4)$$

where the parameter λ describes the character of the change of the volume contraction which can be attributed to the glass transition.⁶ The temperature dependence of D at zero solvent concentration can be described by an apparent or effective activation energy for diffusion, E_D ,

$$E_D = RT^2 \left(\frac{\partial \ln D}{\partial T} \right)_p \quad (5)$$

and consequently for $T < T_{g2}$ we have the following equation relating E_D to the free-volume parameters:

$$E_D = \frac{RT^2(\gamma \hat{V}_2^* \xi / \lambda K_{12})}{[(K_{22}/\lambda) + T - T_{g2}]^2} \quad (6)$$

In addition, we note that the ξ values for two solvents can be related⁵ by the following expression:

$$\frac{\xi(\text{solvent 1})}{\xi(\text{solvent 2})} = \frac{\text{molar volume at 0 K (jumping unit of solvent 1)}}{\text{molar volume at 0 K (jumping unit of solvent 2)}} \quad (7)$$

This expression will of course be of use only if the jumping units for both solvents can be identified. Methods for estimating molar volumes at 0 K have been discussed by Sugden,¹³ Biltz,¹⁴ and Haward.¹⁵

If we assume that the temperature dependence of the self-diffusion process in the pure solvent can adequately be described by considering free-volume effects only, we can write the following result for the self-diffusion coefficient of the pure solvent, D_1 :

$$\ln D_1 = \ln D_{01} - \frac{\gamma \hat{V}_1^*}{K_{11}(K_{21} + T - T_{g1})} \quad (8)$$

where T_{g1} is the glass transition temperature of the solvent and K_{11} , K_{21} , and \hat{V}_1^* are free-volume parameters discussed elsewhere.³ From this equation it is easy to derive the result³

$$\frac{K_{21}}{K_{31}} + \frac{T - T_{g1}}{K_{31}} = \frac{T - T_1}{\ln[\eta_1(T_1)/\eta_1(T)]} \quad (9)$$

where $\eta_1(T)$ is the solvent viscosity at T , $\eta_1(T_1)$ is the solvent viscosity at a convenient reference temperature T_1 , and K_{31} is given by the following equation:

$$K_{31} = \frac{\gamma \hat{V}_1^*}{K_{11}(K_{21} + T_1 - T_{g1})} \quad (10)$$

Finally, we note that the self-diffusion coefficient of the solvent, D_1 , can be related to the solvent viscosity at the same temperature, η_1 , by a relationship proposed by Dullien¹⁶:

$$\eta_1 \tilde{V}_1 D_1 / RT = 0.124 \times 10^{-16} V_c^{2/3} \quad (11)$$

where \tilde{V}_1 is the molar volume of the solvent at the temperature of interest and V_c is the molar volume of the solvent at its critical temperature.

In the implementation of the predictive methods described below, some or all of the following data must be utilized:

(1) WLF constants and T_{g2} for the polymer. These quantities have been tabulated for many polymers by Ferry.¹⁷

(2) D -vs.- T data above T_{g2} at zero solvent mass fraction for at least one solvent in the polymer of interest. A summary of such data for polystyrene has been presented elsewhere,⁵ and data of this type are also available for other amorphous polymers.^{18,19}

(3) D -vs.- T data below T_{g2} at zero solvent mass fraction for at least one solvent in the polymer of interest. Data for the temperature dependence of D below T_{g2} for simple gas diffusion in a number of polymers have been tabulated by Stannett²⁰ in terms of an activation energy for diffusion, E_D . The size of the jumping unit for this solvent must be known.

(4) Viscosity-vs.- T data for the solvent of interest. Low temperature viscosity data are of particular interest, especially data taken on liquids supercooled below their freezing points. Barlow et al.²¹ have collected data of this type for a number of organic solvents. Low-temperature viscosity data are of course important in the determination of meaningful free-volume constants.

(5) Density-vs.- T data for the solvent of interest. Density data must be available for the same temperature range as the viscosity data, and the molar volume of the solvent at its critical temperature must also be known.

(6) An estimate of T_{g1} , the solvent glass transition temperature. Barlow et al.²¹ provide estimates of T_{g1} for a number of organic solvents and also discuss a method for estimating T_{g1} .

Since $\gamma \hat{V}_2^*/K_{12}$, K_{22} , and T_{g2} are known for most important polymers, it is evident from eqs. (1) and (4) that the diffusivity for a system consisting of a trace of solvent in an amorphous polymer can be computed both above and below T_{g2} if D_{01} , ξ , and λ can be determined from the auxiliary data. Procedures for determining these three parameters from these auxiliary data are discussed in the next section.

DATA ANALYSIS PROCEDURES

It is assumed in this study that values of C_1^f , C_2^f , and T_{g2} are available for a particular polymer so that values of K_{22} and $\gamma \hat{V}_2^*/K_{12}$ can be derived using eqs. (2) and (3). Diffusivity-temperature data above T_{g2} for a solvent diffusing in the polymer of interest can be used to evaluate D_{01} and ξ by the following method, which we denote as procedure I:

(1) Plot $\ln D$ vs. $1/(K_{22} + T - T_{g2})$ using the known properties of the polymer.

(2) From eq. (1), it is evident that the slope and intercept of the resulting straight line give D_{01} , $\gamma \hat{V}_2^*\xi/K_{12}$, and ξ for the polymer-solvent system.

Diffusivity-temperature data below T_{g2} (given as an activation energy at some temperature) for a solvent diffusing in the polymer of interest can be combined with a result derived from D -vs.- T data for polymer-solvent diffusion above T_{g2} (not necessarily the same solvent) to evaluate λ by the following method, which we denote as procedure II:

(1) It is assumed that a value of ξ has been derived for the solvent for which D -vs.- T data are available above T_{g2} .

(2) Use eq. (7) to evaluate ξ for the solvent for which E_D data are available below T_{g2} . The sizes of the jumping units of the two solvents must of course be known.

(3) Use the value of E_D at some temperature below T_{g2} , the known properties of the polymer, and the value of ξ determined in step 2 to calculate λ for the polymer of interest from eq. (6).

Data for the temperature dependence of the solvent viscosity can be used to evaluate D_{01} for a solvent using the following method, which we denote as procedure III:

(1) Choose a convenient reference temperature T_1 and construct a graph of $(T - T_1)/\ln [\eta_1(T_1)/\eta_1(T)]$ vs. $(T - T_{g1})$. From eq. (9), it is obvious that K_{21} is equal to the ratio of the intercept to the slope of the resulting straight line. The applicability of this plot is based on the assumption that free-volume theory adequately portrays the temperature dependence of η_1 at temperatures that are usually significantly above T_{g1} , the estimated glass transition temperature of the solvent.

(2) Convert $\eta_1(T)$ data to $D_1(T)$ data using eq. (11) and density-temperature data for the solvent.

(3) Plot $\ln D_1$ vs. $1/(K_{21} + T - T_{g1})$ using the known properties of the solvent. From eq. (8), the intercept of the straight line gives D_{01} for the solvent of interest.

PREDICTIVE METHODS FOR D

In the first predictive method, diffusivity data above T_{g2} for a polymer-solvent system are used to estimate the temperature dependence of D below T_{g2} for this polymer-penetrant pair. If the size of the jumping unit of the solvent of interest is known, this procedure can be carried out using the diffusivity data above T_{g2} , diffusivity data for another solvent in the same polymer below T_{g2} , and the properties of the polymer (C_1^0 , C_2^0 , and T_{g2}). If the size of the jumping unit of the solvent of interest is in question, then D -vs.- T data above T_{g2} for a solvent with a jumping unit of known size must also be available. This first estimation method, which is depicted in Figure 1, can be summarized as follows:

(1) Evaluate K_{22} and $\gamma \bar{V}_2^0/K_{12}$ for the polymer using WLF constants and eqs. (2) and (3).

(2) Obtain D_{01} and ξ for the solvent of interest by analyzing D -vs.- T data above T_{g2} for this solvent using procedure I.

(3) If the size of the jumping unit of the solvent of interest is known, use the value of ξ determined in step 2 and the diffusivity data for another solvent below T_{g2} to evaluate λ using procedure II.

(4) If the size of the jumping unit of the solvent of interest is in question, use D -vs.- T data above T_{g2} and procedure I to obtain ξ for a third solvent with a jumping unit of known size. Use this value of ξ and the diffusivity data for the solvent below T_{g2} (with a jumping unit of known size) to evaluate λ using procedure II.

(5) Determine D vs. T for $T < T_{g2}$ for the polymer-solvent system of interest using eq. (4).

In the second predictive method, the temperature dependence of D for a polymer-solvent system is determined both above and below T_{g2} using no dif-

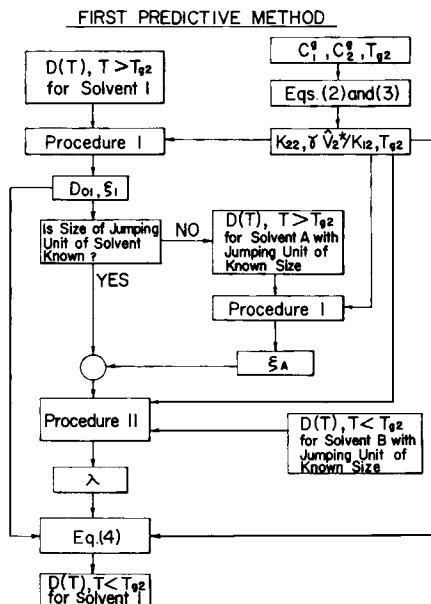


Fig. 1. Schematic diagram of method for predicting D below T_{g2} for a polymer-solvent system using diffusivity data for the system above T_{g2} .

fusivity data for this particular polymer-penetrant pair. The required auxiliary data are D -vs.- T data for another solvent in the same polymer above T_{g2} , D -vs.- T data for some solvent below T_{g2} , the polymer properties (C_1^g , C_2^g , and T_{g2}), T_{g1} , and viscosity and density data for the solvent over an appropriate temperature range. This second predictive method, which is depicted in Figure 2, can be summarized as follows:

- (1) Evaluate K_{22} and $\gamma \hat{V}_2^*/K_{12}$ for the polymer using WLF constants and eqs. (2) and (3).
- (2) Obtain D_{01} from procedure III using solvent viscosity and density data and an estimate of T_{g1} .
- (3) Use D -vs.- T data above T_{g2} for another solvent to obtain ξ value for this solvent using procedure I.
- (4) Determine ξ value for solvent of interest using eq. (7). The sizes of the jumping units of both solvents must be known.
- (5) Determine D vs. T for $T > T_{g2}$ for the polymer-solvent system of interest using eq. (1).
- (6) Use the value of ξ determined in step 3 and the diffusivity data for some solvent below T_{g2} to evaluate λ using procedure II.
- (7) Determine D vs. T for $T < T_{g2}$ for the polymer-solvent system of interest using eq. (4).

ILLUSTRATIONS OF PREDICTIVE METHODS

The first predictive method is illustrated by using n -pentane-polystyrene diffusivity data above T_{g2} and D -vs.- T data below T_{g2} for the carbon dioxide-polystyrene system to estimate the temperature dependence of D below T_{g2} for n -pentane diffusion in polystyrene. Since there is a possibility that the n -pentane molecule may not jump as a single unit, we also utilize diffusivity data for the ethylbenzene-polystyrene system in this analysis. The n -pentane-polystyrene and ethylbenzene-polystyrene data have been presented and ana-

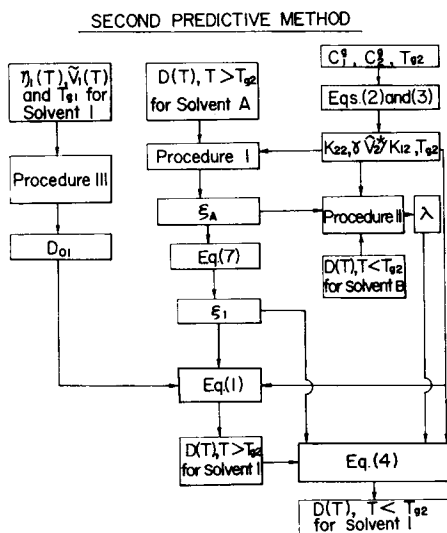


Fig. 2. Schematic diagram of method for predicting D both above and below T_{g2} for a polymer-solvent system using no diffusivity data for the system.

lyzed elsewhere.⁵ Using procedure I, the following parameter values have been derived for the *n*-pentane–polystyrene system: $\ln D_{01} (\text{cm}^2/\text{sec}) = -10.3$ and $\xi = 0.41$. An equivalent analysis using ethylbenzene–polystyrene diffusivity data above T_{g2} yielded a value of $\xi = 0.71$ for this system. From this result, a value of $\xi = 0.24$ was computed for the carbon dioxide system using eq. (7). This value of ξ , the activation energy of 8700 cal/g mol reported by Stannett²⁰ for the carbon dioxide–polystyrene system, and the appropriate polystyrene properties tabulated by Ferry¹⁷ were used in eq. (6) to compute a value of $\lambda = 0.16$ for polystyrene.

The temperature dependence of D for the *n*-pentane–polystyrene system below T_{g2} , calculated using eq. (4), along with the measured temperature dependence of the mutual diffusion coefficient above T_{g2} , is presented in Figure 3. Also included in this figure are experimental data reported by Holley et al.²² for the *n*-pentane–polystyrene system. The points represent averages of diffusion coefficients determined for cast-annealed and biaxially oriented polystyrene. The agreement is reasonably good, although the experimental value of the apparent activation energy for diffusion is significantly lower than the theoretical estimate for E_D . It is not clear how much significance should be placed on this apparent discrepancy because of the relatively narrow temperature range covered by the *n*-pentane–polystyrene desorption experiments.²²

The second predictive method is illustrated by computing D vs. T both above and below T_{g2} for the ethylbenzene–polystyrene system without using any diffusivity data for this system. Estimates of the diffusivity for this polymer–penetrant pair are of particular interest since such a prediction provides a reasonable approximation of the mutual diffusion coefficient for the important styrene–polystyrene system. In addition to the usual polymer properties, the

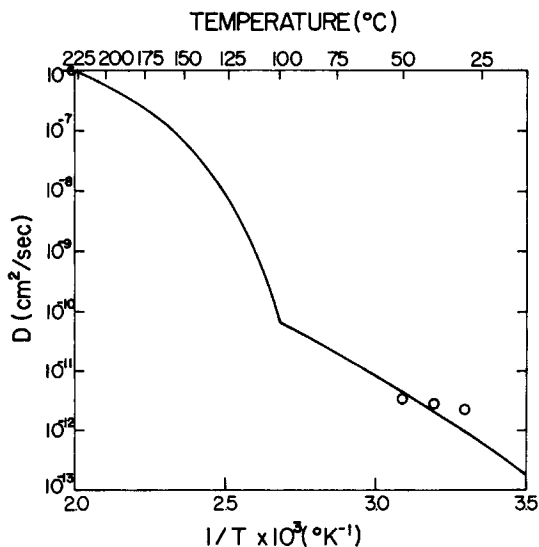


Fig. 3. Comparison of predictions with experiment for the *n*-pentane–polystyrene system. Circles represent the data of Holley et al.²²

following data were utilized in applying the predictive scheme:

- (1) Viscosity data for ethylbenzene from 160.2 to 404.6 K.^{21,23}
- (2) Density data for ethylbenzene from 160.2 to 363.2 K.^{21,24} The density data were extrapolated using the equation of Höcker and Flory²⁴ to provide values of the density for the complete temperature range for which viscosity data are available.
- (3) A critical molar volume $V_c = 374 \text{ cm}^3/\text{g mole}$ for ethylbenzene.²⁵
- (4) Diffusivity data above T_{g2} for the ethyl bromide–polystyrene system.¹¹
- (5) Diffusivity data below T_{g2} for the carbon dioxide–polystyrene system.²⁰
- (6) An estimate of $T_{g1} = 111.8 \text{ K}$ given by Barlow et al.²¹

A value of $K_{21} = 15.1 \text{ K}$ was determined³ from a plot of $(T - T_1)/\log [\eta_1(T_1)/\eta_1(T)]$ vs. $(T - T_{g1})$ with $T_1 = 160.2 \text{ K}$. As is evident from Figure 4, the data appear to be well represented by a straight-line fit even though the temperature range extends nearly 300°C above the estimated value of T_{g1} . The graph of $\log D_1$ vs. $1/(K_{21} + T - T_{g1})$ is presented in Figure 5, and a value of $D_{01} = 2.83 \times 10^{-4} \text{ cm}^2/\text{sec}$ was determined from this straight-line plot. A value of $D_{01} = 4.89 \times 10^{-4} \text{ cm}^2/\text{sec}$ was calculated previously²⁶ using viscosity data in the temperature range 273.4–404.6 K instead of the temperature range 160.2–404.6 K.

A previous analysis^{3,5,26} of diffusivity data for the ethylbenzene–polystyrene system above T_{g2} in the temperature range $140\text{--}178^\circ\text{C}$ yielded the values $D_{01} = 2.2 \times 10^{-3} \text{ cm}^2/\text{sec}$ and $\xi = 0.71$. The unsatisfactory agreement between this value of D_{01} and the one determined from solvent viscosity data can be attributed

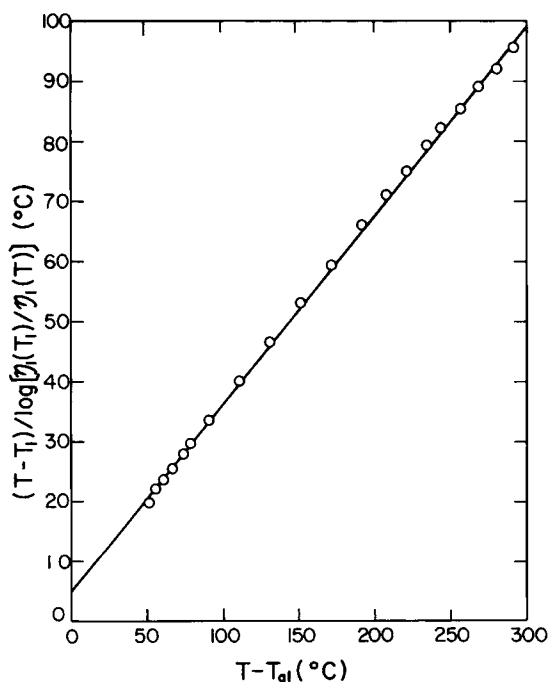


Fig. 4. Example of first plot used in procedure III for the ethylbenzene–polystyrene system.

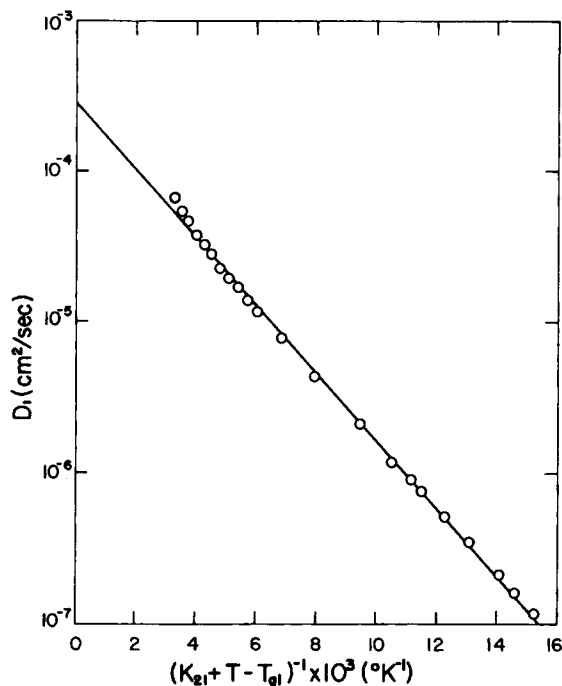


Fig. 5. Example of second plot used in procedure III for the ethylbenzene-polystyrene system.

to two factors. First, some error is introduced in the value of D_{01} derived from diffusivity data using procedure I because of the need to extrapolate the data to zero solvent mass fraction. This extrapolation procedure is especially difficult in the vicinity of T_{g2} owing to the strong concentration dependence of D . Second, the free-volume equation used to analyze the solvent self-diffusion data may be inadequate at high temperatures and at high solvent mass fractions. This is shown below.

From considerations discussed elsewhere,²⁶ it follows that a general free-volume equation for $D_1(\omega_1)$, the self-diffusion coefficient of the solvent in a polymer-solvent mixture, can be written as follows:

$$D_1(\omega_1) = \bar{D}_{01} \exp\left[-\frac{E}{RT}\right] \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \quad (12)$$

where \bar{D}_{01} is a constant preexponential factor, \hat{V}_{FH} is the specific hole-free volume of the mixture, E is the critical energy per mole that a molecule of the solvent must obtain to overcome attractive forces which hold it to its neighbors, and ω_1 and ω_2 are the mass fractions of solvent and polymer, respectively. For the major parts of the temperature and concentration ranges usually encountered in polymer-solvent diffusion, the solvent self-diffusion process is dominated by free-volume effects, and the variation of the solvent self-diffusion coefficient with temperature and concentration can be approximated satisfactorily by absorbing the energy term into an effectively constant preexponential factor D_{01} :

$$D_1(\omega_1) = D_{01} \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \quad (13)$$

This result, evaluated at $\omega_1 = 1$, is used above as the basis for analyzing the self-diffusion data for the pure solvent.

As discussed elsewhere,³ it is possible that the energy term can make a significant contribution to the temperature variation of the self-diffusion coefficient of the pure solvent at sufficiently high temperatures, although this does not appear to be the case for ethylbenzene. In addition, the contribution of the energy term to the concentration dependence of $D_1(\omega_1)$ near $\omega_1 = 1$ at a given temperature can be significant. This is partly due to the relatively high hole-free volume associated with the solvent and partly due to the possibility that E can change significantly near $\omega = 1$. For solvent mass fractions ranging from 0 to approximately 0.9, the domains of polymer molecules overlap, and a solvent molecule sees the same type of surroundings over this mass fraction range.

Hence, E should not change much in this mass fraction interval. However, as the pure solvent limit is approached, polymer molecules become scarce, and it is reasonable to expect that E can change significantly as the surroundings of the solvent molecule are altered. The variation of D_1 with ω_1 near $\omega_1 = 1$ can be described by the expression

$$\left(\frac{\partial \ln D_1}{\partial \omega_1}\right)_{\omega_1=1} = -\frac{1}{RT} \left(\frac{dE}{d\omega_1}\right)_{\omega_1=1} + \frac{\gamma \hat{V}_1^*}{f_1 \hat{V}_1^0} \left[\frac{M_1}{M_j} - \frac{f_2 \hat{V}_2^0}{f_1 \hat{V}_1^0} + \frac{\hat{V}_2^0 - \hat{V}_{20}}{f_1 \hat{V}_1^0} \right] \quad (14)$$

where M_1 is the molecular weight of the solvent, M_j is the molecular weight of a polymeric jumping unit, f_1 and f_2 are the fractional hole-free volumes of pure solvent and pure polymer, respectively, \hat{V}_1^0 and \hat{V}_2^0 are the specific volumes of solvent and polymer, respectively, at the temperature of interest, and \hat{V}_{20} is the partial specific volume of the polymer at $\omega_1 = 1$. The quantity $(dE/d\omega_1)_{\omega_1=1}$ approximates the energy change from $\omega_1 = 0.9$ to $\omega_1 = 1$. This result was used to construct Figure 6, from which it is evident that the concentration dependence of E can exert a significant influence on the variation of D_1 with concentration. Consequently, the concentration dependence of E cannot generally be ignored if $D_1(\omega_1)$ is to be calculated near $\omega_1 = 1$. In other words, if eq. (13) is used to

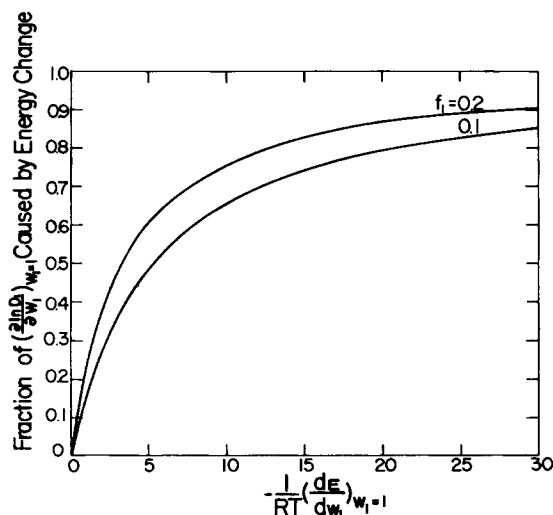


Fig. 6. Importance of energy effect in the concentration dependence of D_1 near $\omega_1 = 1$. Curves are based on $\gamma = 0.75$, $M_1/M_j = 1$, $f_2 = 0.03$, $\hat{V}_1^0 = \hat{V}_2^0 = \hat{V}_{20} = \hat{V}_1^* = 1 \text{ cm}^3/\text{g}$.

represent $D_1(\omega_1)$, it cannot generally be expected that a single value of D_{01} will represent the complete mass fraction interval satisfactorily.

Consequently, it is not surprising that the value of D_{01} calculated from data taken near $\omega_1 = 0$ differs from the value of D_{01} determined using data at $\omega_1 = 1$. There is no simple way to correct this shortcoming in the second predictive method, and the possible error in the value of D_{01} calculated using solvent viscosity data is the penalty that must be paid for not using any diffusivity data for the polymer-solvent system of interest. However, as will be evident below, reasonable estimates of D can be derived even though an approximate value of D_{01} is utilized. Furthermore, it is evident that the error introduced by an approximate value of D_{01} decreases as the temperature is lowered.

From ethyl bromide-polystyrene diffusivity data above T_{g2} , a value of $\xi = 0.38$ was determined previously⁵ for this solvent. From this result and eq. (7), a value of $\xi = 0.67$ was computed for the ethylbenzene-polystyrene system; this result is in reasonable agreement with the value $\xi = 0.71$ determined directly from the ethylbenzene-polystyrene diffusivity data above T_{g2} . The choice of ethyl bromide as the solvent for which diffusivity data are available above T_{g2} is of course arbitrary, since diffusivity data have been reported for a number of solvents diffusing in polystyrene. Values of ξ for ethylbenzene, computed using diffusivity data for 15 solvents, are presented in Table I. The ξ values from 12 of these solvents are within 13% of the value $\xi = 0.71$ determined directly from polystyrene-ethylbenzene diffusion data. The poor agreement of the hydrogen and ethylene values is to be expected because the quality of the data are not good, but the result for methane is surprising because these data appear to be of high quality. A value of $\xi = 0.23$ was determined for the carbon dioxide-polystyrene system using the ξ value for ethyl bromide and eq. (7). A value of $\xi = 0.24$ was calculated above in the *n*-pentane analysis, and a value of $\xi = 0.27$ was determined previously⁵ from D -vs.- T data for the carbon dioxide-polystyrene system. Finally, the ξ value for carbon dioxide and the reported activation energy of 8700 cal/g mol were used to compute a value of $\lambda = 0.16$ for polystyrene from eq. (6).

TABLE I
 ξ Values Computed for Ethylbenzene-Polystyrene Using Diffusivity Data for Other Solvents

Solvent	$\xi(\text{Solvent})$	$\xi(\text{Ethylbenzene})$
Hydrogen	0.13	1.0
Methane	0.11	0.40
Nitrogen	0.17	0.78
Methanol	0.25	0.74
Ethylene	0.18	0.48
Carbon dioxide	0.27	0.79
Ethanol	0.30	0.62
Methylene chloride	0.35	0.69
Ethyl bromide	0.38	0.67
Pyridine	0.48	0.70
Chloroform	0.46	0.75
<i>n</i> -Propyl chloride	0.50	0.73
Benzene	0.51	0.71
Fluorobenzene	0.52	0.69
Toluene	0.66	0.77

Diffusivity values for the ethylbenzene–polystyrene system above and below T_{g2} were computed using eqs. (1) and (4), respectively, and the results are presented in Figure 7. The predicted values of the mutual diffusion coefficient are compared with experimental data⁵ above T_{g2} , but no data are available for this solvent below T_{g2} . It is evident from Figure 7 that the estimated diffusivity values are from three to five times lower than the experimental values, which represent extrapolated estimates of the mutual diffusion coefficient at zero solvent concentration. The error decreases significantly as the temperature is decreased. Although the estimated diffusivities are not satisfactory for precise scientific work, they should be adequate for many mass transfer calculations. Furthermore, the predictive capabilities of the proposed scheme can be considered to be satisfactory when consideration is taken of the fact that no ethylbenzene–polystyrene diffusivity data were used in calculating the estimated values of D .

Although the proposed two predictive schemes are, of course, not substitutes for actual experimental data, we believe that it is fair to conclude that useful estimates for mutual diffusion coefficients can be derived from these methods. These estimated diffusivities are particularly useful in instances where the time and expense of collecting the needed diffusivity data cannot be justified. Furthermore, in some instances, the mutual diffusion coefficients will be so low (particularly below T_{g2}) that experimental determination of these coefficients is highly impractical, and some predictive method is effectively necessary.

The diffusion coefficients predicted by the methods proposed in this article are valid at low penetrant concentrations and low pressures since concentration and pressure effects on the free volume of the system have, of course, not been considered. In addition, diffusion below the glass transition temperature has been described by free-volume theory rather than by dual-mode sorption and partial immobilization mechanisms.^{8,27} Although dual-mode sorption theory

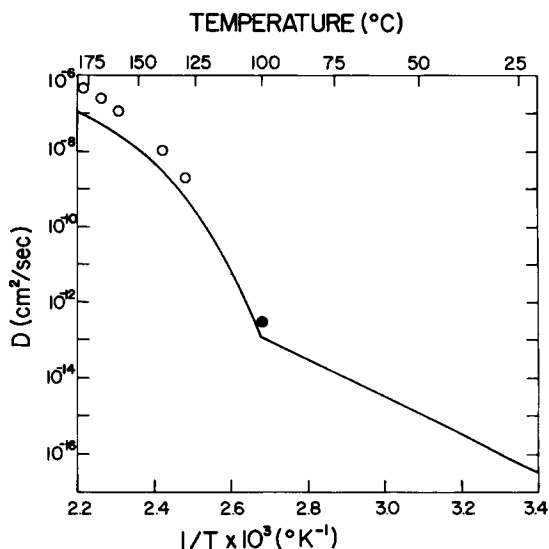


Fig. 7. Comparison of predictions with experiment for the ethylbenzene–polystyrene system. Open circles represent experimental data of Vrentas and Duda.⁵ The solid circle represents an extrapolation of these data based on the free-volume equation.

has been used to explain some aspects of sorption and transport behavior below the glass transition temperature, it is not clear at this time whether or not these phenomena can also be explained by using concepts that are compatible with the free-volume model utilized here. Although the agreement between the theory proposed here and the *n*-pentane-polystyrene diffusivity data is encouraging, more data and data analyses are needed before any definitive conclusions can be reached on the nature of sorption and transport in glassy polymers.

This work was supported by the National Science Foundation Grant ENG 78-26275.

References

1. G. A. Daniels and D. E. Proctor, *Modern Packaging*, 45 (April 1975).
2. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 403 (1977).
3. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 417 (1977).
4. J. S. Vrentas and J. L. Duda, *Macromolecules*, **9**, 785 (1976).
5. J. S. Vrentas and J. L. Duda, *J. Appl. Polym. Sci.*, **21**, 1715 (1977).
6. J. S. Vrentas and J. L. Duda, *J. Appl. Polym. Sci.*, **22**, 2325 (1978).
7. G. S. Park, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968, p. 141.
8. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 687 (1976).
9. P. Meares, *J. Am. Chem. Soc.*, **76**, 3415 (1954).
10. P. Meares, *Trans. Faraday Soc.*, **53**, 101 (1957).
11. S. N. Zhurkov and G. Ya. Ryskin, *J. Tech. Phys. (USSR)*, **24**, 797 (1954).
12. A. Kishimoto, E. Maekawa, and H. Fujita, *Bull. Chem. Soc. Jpn.*, **33**, 988 (1960).
13. S. Sugden, *J. Chem. Soc.*, 1786 (1927).
14. W. Biltz, *Rauchemie der festen Stoffe*, Voss, Leipzig, 1934.
15. R. N. Haward, *J. Macromol. Sci. Rev. Macromol. Chem.*, **4**, 191 (1970).
16. F. A. L. Dullien, *AIChE J.*, **18**, 62 (1972).
17. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.
18. H. Fujita, *Fortschr. Hochpolym. Forsch.*, **3**, 1 (1961).
19. H. Fujita, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968, p. 75.
20. V. Stannett, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968, p. 41.
21. A. J. Barlow, J. Lamb, and A. J. Matheson, *Proc. R. Soc. London Ser. A*, **292**, 322 (1966).
22. R. H. Holley, H. B. Hopfenberg, and V. Stannett, *Polym. Eng. Sci.*, **10**, 376 (1970).
23. E. W. Washburn, *International Critical Tables*, Vol. VII, McGraw-Hill, New York, 1930.
24. H. Höcker and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2270 (1971).
25. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.
26. J. S. Vrentas and J. L. Duda, *AIChE J.*, **25**, 1 (1979).
27. V. T. Stannett, W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, *Adv. Polym. Sci.*, **32**, 69 (1979).

Received June 29, 1979

Revised November 20, 1979