

Prediction of Diffusion Coefficients for Polymer-Solvent Systems

A revised version of a recently proposed free-volume theory of polymer-solvent diffusion is introduced and evaluated using experimental diffusivity data collected over wide temperature and concentration ranges. The theory accurately predicts the large temperature and concentration variations typically observed for polymer-solvent diffusion coefficients.

J. L. DUDA, J. S. VRENTAS,
S. T. JU, and H. T. LIU

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

SCOPE

Mutual diffusion coefficients are needed for the analysis of many important mass transfer problems involving concentrated polymer solutions. Since the diffusivities for such systems are typically strong functions of temperature and concentration, the analysis of these problems is greatly facilitated if predictive methods are available for the determination of the required mutual diffusion coefficients. Fujita has proposed a free-volume theory of diffusion for concentrated polymer-solvent systems, and a new free-volume theory has been formulated which eliminates some of the shortcomings of the Fujita theory. Although this new theory describes the general behavior of mutual diffusion coefficients for polymer-solvent systems quite well over wide temperature and concentration ranges, satisfactory

quantitative agreement between theory and experiment has not been achieved. Furthermore, data needed for the evaluation of the parameters in the thermodynamic model used for the polymer-penetrant mixture are usually not available.

In this paper, we modify the new version of the free-volume theory by relaxing one of the assumptions and by utilizing a simpler thermodynamic model for the polymer-solvent system. The correlative and predictive capabilities of the proposed theory are evaluated using diffusivity data for three polymer-solvent systems. In addition, a comparison between the predictions of the proposed theory and the theory of Fujita is carried out.

CONCLUSIONS AND SIGNIFICANCE

A recently proposed free-volume theory of diffusion has been revised by introducing two modifications which serve to enhance its predictive capabilities and to facilitate its utilization. Evaluation of the parameters of the theory requires density and viscosity data plus a small amount of equilibrium and diffusivity data. Comparisons of the predictions of the proposed free-volume theory with experimental data collected over wide temperature and concentration ranges show that the theory can

accurately describe the diffusional behavior of polymer-solvent systems. The theory accounts for the very large variations of the diffusivity with temperature and concentration and removes the necessity of having to perform a large number of difficult mass transfer experiments. The predictions of the proposed theory are superior to those obtained using the free-volume theory of Fujita.

INTRODUCTION

One of the crucial problems of the polymer industry is the removal of small amounts of volatile residuals to meet environmental, health, and safety regulations. This concern with polymer purification has initiated a renewed interest in the area of molecular diffusion of solvents in molten polymers. Unfortunately, advances in this area have been slowed by experimental and theoretical limitations. It is quite difficult to measure diffusion coefficients at the elevated temperatures which are characteristic of most polymer purification processes. The experimental difficulties are aggravated by the fact that diffusion coefficients for polymer-solvent systems are strong functions of temperature and concentration. Theoretical progress has been hampered by the difficulty in applying molecular mechanics to transport processes in concentrated polymer solutions. For the past 15 years, the free-volume theory proposed by Fujita (1961) has served as the main basis for the description of the diffusion process for such systems. Recently, a new free-volume theory with predictive capabilities has been developed (Vrentas and Duda, 1977 a,b, 1979 a,b) for the deter-

mination of polymer-solvent diffusion coefficients for purely viscous diffusion.

In this version of free-volume theory, free-volume parameters are determined from pure polymer and pure solvent viscosity data, and these parameters are coupled with thermodynamic information and a limited amount of diffusivity data to predict diffusional behavior over wide ranges of temperature and concentration. Although this most recent free-volume theory appears to provide the best available description of purely viscous polymer-solvent diffusion in concentrated solutions at this time (Vrentas and Duda, 1976, 1977 a,b, 1979 a,b), it cannot be considered completely satisfactory from two points of view. First, although the theory describes the general behavior of mutual diffusion coefficients for polymer-solvent systems over wide temperature and concentration ranges quite well, the predicted values of the diffusivity are significantly higher than those obtained from experiments (Vrentas and Duda, 1977b, 1979a; Duda et al., 1978). Second, difficulty in determining the thermodynamic information needed for the computation of the binary mutual diffusion coefficient can severely limit the utilization of the new free-volume analysis. In the original development, the temperature and concentration dependences of the specific volume of the mixture and of the solvent chemical

potential were determined using the thermodynamic theory of Flory (1970). Although Flory's theory provides a satisfactory representation of the thermodynamic behavior of the liquid state, the data needed for the computation of the parameters required for the theory are not available for many polymer-solvent systems.

The purpose of this paper is to remove these two shortcomings from the new free-volume theory of diffusion. To obtain a theory with better predictive capabilities, one of the assumptions introduced into the original version is relaxed. Furthermore, to facilitate computation of the thermodynamic factor in the expression for the mutual diffusion coefficient, a simpler thermodynamic model of the polymer-solvent mixture is utilized. The correlative and predictive capabilities of this second version of the new free-volume theory of diffusion are examined using diffusivity data for three polymer-solvent systems collected over wide ranges of temperature and concentration. Finally, experimental data are also used to carry out a comparison between the predictive capabilities of this theory and the free-volume theory proposed by Fujita (1961).

THEORY

In the free-volume theory of Vrentas and Duda (1977a, 1979a), the expression for the binary mutual diffusion coefficient D can be written as

$$D = \frac{D_1 \rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,p} \quad (1)$$

$$D_1 = D_{01} \exp \left[- \frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}} \right] \quad (2)$$

where μ_1 and \hat{V}_{FH} can be computed using the thermodynamic theory of Flory (1970). In order to facilitate the determination of d , we simplify this theory by introducing the following assumptions:

1. All thermal expansion coefficients needed to calculate the various volumes required for the theory are approximated by average values in the temperature range under consideration.
2. The partial specific volumes of polymer and solvent are assumed to be independent of concentration so that the influence of volume change on mixing on the free volume of the system is considered negligible.
3. The solvent chemical potential in the mixture is given by the Flory-Huggins equation (Flory, 1953)

$$\mu_1 = \mu_1^0 + RT[\ln(1 - \phi_2) + \chi \phi_2^2 + \phi_2] \quad (3)$$

where the interaction parameter χ is assumed to be a constant, independent of temperature and concentration, for a given polymer-solvent system.

Introduction of these assumptions into Eqs. 1 and 2 yields the following expression for D

$$D = D_{01} (1 - \phi_1)^2 (1 - 2\chi\phi_1) \exp \left[- \frac{(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}/\gamma} \right] \quad (4)$$

where

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} \omega_1 (K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma} \omega_2 (K_{22} + T - T_{g2}) \quad (5)$$

$$\phi_1 = \frac{\omega_1 \hat{V}_1^0}{\omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_2^0} \quad (6)$$

The definitions of the free-volume parameters K_{11}/γ , K_{21} , K_{12}/γ , and K_{22} , which are given elsewhere (Vrentas and Duda, 1977 b,c), are not essential in the present context. It should be emphasized that the above three assumptions are of course not necessary but are introduced solely to facilitate utilization of the free-volume theory proposed by Vrentas and Duda. The presumption is that these assumptions will lead only to a small loss in accuracy which will be more than compensated for by the increased applicability of the theory. Since the data needed to apply the more general

Flory theory are not available for many polymer-solvent systems, the simplified version is necessary if diffusivity predictions are to be made for such systems using the free-volume analysis. The Flory-Huggins theory was used here since it provides a simple but satisfactory representation of μ_1 for the polymer-penetrant systems considered in this study.

The second change in the recently proposed free-volume theory involves relaxation of an assumption concerning the preexponential factor D_{01} . In general, D_{01} should be expressed as (Vrentas and Duda, 1979a)

$$D_{01} = D_0 \exp(-E/RT) \quad (7)$$

and this result accounts for the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors. In the previous version of the theory, it was argued that the temperature variation of D_{01} is not important. Although a satisfactory representation of the temperature dependence of D at a single solvent mass fraction can be obtained by ignoring the temperature variation of D_{01} , it is shown below that unsatisfactory results are obtained for the temperature dependence of D at other values of the solvent mass fraction. Hence, we retain the temperature dependence of D_{01} in this version of the theory by utilizing Eq. 7.

The variation of D with temperature and mass fraction can be determined for a particular polymer-solvent system from Eqs. 4-7 once the following parameters are known: D_0 , E , χ , ξ , \hat{V}_1^* , \hat{V}_2^* , K_{11}/γ , K_{12}/γ , $K_{21} - T_{g1}$, $K_{22} - T_{g2}$, \hat{V}_1^0 , and \hat{V}_2^0 . Procedures for determining these parameters using polymer and solvent viscosity and density data and a small amount of thermodynamic and diffusivity data are considered in the next section.

In a comparison of the above free-volume theory with the free-volume theory proposed by Fujita (1961), it was concluded that the latter theory had two major shortcomings (Vrentas and Duda, 1977a, 1979a). First, the Fujita theory is restricted to the description of systems for which the molecular weight of a solvent jumping unit is approximately equal to the molecular weight of a polymeric jumping unit ($M_{j1} = M_{j2}$). Second, the Fujita theory has been set up as a correlative rather than a predictive theory in the sense that diffusivity vs. volume fraction data at each temperature are used to evaluate the parameters of the theory at that temperature. In this paper, we convert the Fujita theory to the same predictive basis as the free-volume theory proposed here and see whether a free-volume theory based on the assumption $M_{j1} = M_{j2}$ or $\xi = \hat{V}_1^*/\hat{V}_2^*$ can yield satisfactory predictions of the mutual diffusion coefficient.

DETERMINATION OF THEORY PARAMETERS

To evaluate the parameters of the theory, we assume that the following data are available.

1. Density data for the pure polymer and the pure solvent as a function of temperature.
2. Viscosity data for the pure polymer and the pure solvent as a function of temperature.
3. At least three values of the diffusivity for the polymer-solvent system at two or more temperatures.
4. Sorption equilibrium data for the polymer-solvent system at a single temperature or other thermodynamic data from which χ can be determined.

Density and viscosity data are usually available for common polymers and solvents, and equilibrium data are frequently collected during a diffusion experiment. Note that only a small amount of diffusivity data is required for the parameter determination. The procedures for determination of the theory parameters can be summarized as follows:

1. As discussed elsewhere (Vrentas and Duda, 1977a, 1979a), \hat{V}_1^* and \hat{V}_2^* are estimated by equating them to equilibrium liquid volumes at 0 K:

$$\hat{V}_1^* = \hat{V}_1^0(0) \quad (8)$$

$$\hat{V}_2^* = \hat{V}_2^0(0) \quad (9)$$

TABLE 1. SOLVENT FREE-VOLUME PARAMETERS

Solvent	$\gamma \hat{V}_1^*/K_{11}$ (K)	$T_{g1} - K_{21}$ (K)
Acetone	508	53.3
Carbon disulfide	704	10.4
Ethylbenzene	500	96.7
Methanol	824	47.9
Methyl acetate	682	38.5
Toluene	415	103

Haward (1970) has discussed procedures for estimating equilibrium liquid volumes at 0 K for both polymers and simple liquids. Hence, adequate estimates for $\hat{V}_1^0(0)$ and $\hat{V}_2^0(0)$ can usually be obtained with no further data collection, whereas values of \hat{V}_1^0 and \hat{V}_2^0 in the temperature range of interest are of course known if the appropriate density data are available.

2. The temperature dependence of the viscosity for pure polymers and pure solvents can often be adequately described by the free-volume theory of transport. For example, the viscosity of the pure polymer, η_2 , can be expressed as

$$\ln \eta_2 = \ln A_2 + \frac{(\gamma \hat{V}_2^*/K_{12})}{K_{22} + T - T_{g2}} \quad (10)$$

where A_2 is considered to be effectively constant. The quantities $\gamma \hat{V}_2^*/K_{12}$ (and hence K_{12}/γ) and $K_{22} - T_{g2}$ can thus be determined from viscosity-temperature data for the polymer using a non-linear regression analysis based on Eq. 10. If the glass transition temperature of the polymer is known, the actual value of K_{22} can be computed for the system. The parameters K_{22} and $\gamma \hat{V}_2^*/K_{12}$ are simply related (Vrentas and Duda, 1977b) to the WLF constants of the polymer, $(C_f)_2$ and $(C_g)_2$:

$$K_{22} = (C_g)_2 \quad (11)$$

$$\frac{\gamma \hat{V}_2^*}{K_{12}} = 2.303 (C_f)_2 (C_g)_2 \quad (12)$$

Values of $(C_f)_2$ and $(C_g)_2$, derived from viscosity-temperature data, have been tabulated for a large number of polymers (Ferry, 1970), and K_{22} and K_{12}/γ can be computed directly from these results using Eqs. 11 and 12. An alternative procedure is available for the determination of K_{22} and $\gamma \hat{V}_2^*/K_{12}$ from viscosity-temperature data (Vrentas and Duda, 1977b), but this method is more sensitive to scatter in the data and is not as satisfactory as a non-linear regression based on Eq. 10.

An identical procedure can be utilized for the determination of $\gamma \hat{V}_1^*/K_{11}$ (K_{11}/γ) and $K_{21} - T_{g1}$ from viscosity-temperature data for a pure solvent. However, there is some question as to the applicability of free-volume theory to viscous transport at temperatures which are usually significantly above the glass transition temperature of the solvent. Meaningful free-volume constants can often be determined if low temperature viscosity data are available for the solvent. In Table 1, we have listed a few solvents whose viscosity-temperature behavior can be satisfactorily described by free-volume theory. However, each solvent must of course be treated on an individual basis.

3. A sorption equilibrium experiment for a polymer-solvent system can be described by the expression

$$\frac{P_1}{P_1^0} = \phi_1 \exp[\phi_2 + \chi \phi_2^2] \quad (13)$$

if the thermodynamics of the liquid solution are adequately characterized by the Flory-Huggins equation. Consequently, if the temperature variation of χ is assumed to be negligible, this parameter can be determined from activity-mass fraction data at a single temperature. An example of the utilization of the Flory-Huggins theory in the correlation of sorption equilibrium data is presented in Figure 1 for the polystyrene-toluene system.

4. The density, viscosity, and sorption equilibrium data yield all of the theory parameters except D_0 , E , and ξ . These parameters can be evaluated using a limited amount of diffusivity data. At least three diffusivity data points are needed, and the data must be collected at two or more temperatures so that the parameters D_0 and E can be separated. If more than three diffusivity data points are utilized, the parameters D_0 , E , and ξ can be determined using a non-linear regression analysis based on Eqs. 4-7.

Since ξ represents the ratio of the critical molar volume of a solvent jumping unit to the critical molar volume of the jumping unit of the polymer, this parameter can also be determined directly from diffusivity data for another solvent in the same polymer. The ξ values for two solvents diffusing in the same polymer are related (Vrentas and Duda, 1977c) by the following expression:

$$\frac{\xi(\text{solvent 1})}{\xi(\text{solvent 2})} = \frac{\text{molar volume at 0 K (jumping unit of solvent 1)}}{\text{molar volume at 0 K (jumping unit of solvent 2)}} \quad (14)$$

The disadvantage of this method of determining ξ is of course the limited availability of reliable polymer-solvent diffusivity data.

RESULTS AND DISCUSSION

The correlative and predictive capabilities of the second version of the proposed free-volume theory are evaluated here using diffusivity data for the toluene-polystyrene (Duda et al., 1979a), ethylbenzene-polystyrene (Duda et al., 1978), and methyl acetate-polymethyl acrylate (Fujita, 1968) systems. The ability of the theory to correlate a given set of diffusivity data can be tested by using all of the data to determine D_0 , E , and ξ from a non-linear regression analysis based on Eqs. 4-7. The theory can then be evaluated by seeing how well the resulting theoretical curves agree with the experimental data. This approach was carried out for the toluene-polystyrene and ethylbenzene-polystyrene systems; the free volume theory parameters for these two systems are presented in Table 2. The theoretical calculations based on these parameters are compared against experimental data in Figures 2 and 3. It is evident that the proposed free-volume theory provides an excellent correlation of the toluene-polystyrene diffusivity data and a reasonably good correlation of the ethylbenzene-polystyrene data.

TABLE 2. PARAMETERS OF FREE-VOLUME THEORY FOR FIGURES 2 AND 3

Parameter	Ethylbenzene-Polystyrene System	Data Source	Toluene-Polystyrene System	Data Source
\hat{V}_1^* (cm ³ /g)	0.946	Haward (1970)	0.917	Haward (1970)
\hat{V}_2^* (cm ³ /g)	0.850	Haward (1970)	0.850	Haward (1970)
K_{11}/γ (cm ³ /g K)	2.05×10^{-3}	Barlow et al. (1966); Washburn (1930)	2.21×10^{-3}	Barlow et al. (1966)
K_{12}/γ (cm ³ /g K)	5.82×10^{-4}	Ferry (1970)	5.82×10^{-4}	Ferry (1970)
$K_{21} - T_{g1}$ (K)	-96.7	Barlow et al. (1966); Washburn (1930)	-103	Barlow et al. (1966)
$K_{22} - T_{g2}$ (K)	-327	Ferry (1970)	-327	Ferry (1970)
χ	0.45	This study	0.40	This study
ξ	0.56	Duda et al. (1978)	0.55	Duda et al. (1979a)
D_0 (cm ² /s)	6.92	Duda et al. (1978)	6.15×10^{-2}	Duda et al. (1979a)
E (kcal/g-mol)	9.18	Duda et al. (1978)	5.19	Duda et al. (1979a)
\hat{V}_1^0 vs. T	—	Höcker and Flory (1971)	—	Timmermans (1950)
\hat{V}_2^0 vs. T	—	Fox and Loshaek (1955)	—	Fox and Loshaek (1955)

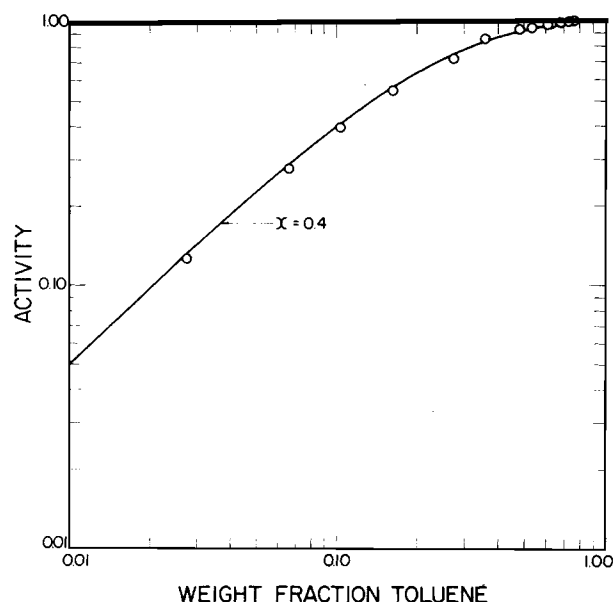


Figure 1. Activity (P_1/P_1^0) vs. weight fraction plot showing the correlation of sorption equilibrium data using the Flory-Huggins theory for toluene-polystyrene system at 110°C.

These figures give encouraging evidence that the proposed free-volume theory can accurately describe the temperature and concentration variations of D over wide temperature and concentration ranges provided appropriate values of the theory parameters are available.

Having examined the correlative capabilities of the proposed theory, we now consider the predictive capabilities. Specifically, we utilize a limited amount of diffusivity data to determine D_0 , E , and ξ and then compare the theoretical predictions based on these parameters with experimental data. This of course is the critical test of the theory since a useful theory of diffusion in polymer-solvent systems should have an established predictive capability. The predictive capability was tested using diffusivity data for the toluene-polystyrene and methyl acetate-polymethyl acrylate systems. The five data points represented by solid symbols in Figure 4 were used to determine D_0 , E , and ξ from the nonlinear regression analysis based on Eqs. 4-7. The calculated theory parameters for this case are presented in Table 3, and it is evident that there are no significant differences between these values and those computed using the entire diffusivity data set. The parameters in Table 3 were then used in Eqs. 4-7 to produce the lines in Figure 4. It is evident that the predictions are in good agreement with the available data, and this agreement is particularly impressive when one considers the wide temperature and concentration ranges which are covered. The same analysis was also carried out with $\xi = \hat{V}_1^*/\hat{V}_2^*$ as is assumed in the free-volume theory

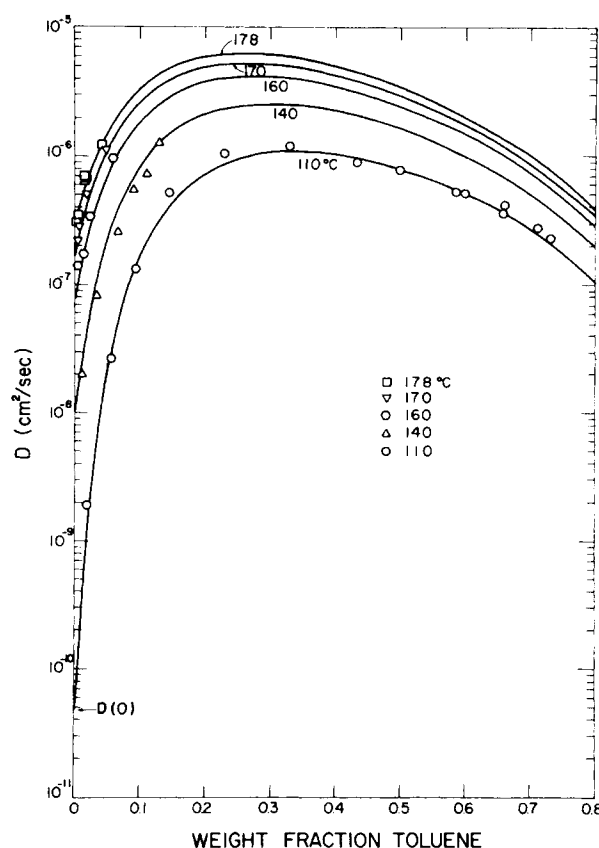


Figure 2. Correlation of diffusivity data for the toluene-polystyrene system using free-volume parameters contained in Table 2.

of Fujita (1961). It is evident from Figure 5 that there is now poor agreement between theory and experiment, and we conclude that removal of the restriction $\xi = \hat{V}_1^*/\hat{V}_2^*$ is essential for the establishment of a free-volume theory with satisfactory predictive capabilities.

Since ξ has a precise physical interpretation, it should not be considered as just an extra parameter which can be used to insure greater correlative and predictive capabilities of the theory. Indeed, the value of ξ determined using diffusivity data for the solvent of interest must be in accord with values determined from diffusivity data for other solvents using Eq. 14 if the proposed theory is to be of any value. If ξ values for the fluorobenzene-polystyrene and triisopropylbenzene-polystyrene systems which were determined previously (Vrentas et al., 1980) are used in Eq. 14, values of 0.62 and 0.56 are computed for the toluene-polystyrene system. These values are in good agreement with the value presented in Table 2 for this system.

The results presented in Figure 4 show that a few data points

TABLE 3. PARAMETERS OF FREE-VOLUME THEORY FOR FIGURES 4 AND 6

Parameter	Toluene-Polystyrene System	Data Source	Methyl Acetate-Polymethyl Acrylate System	Data Source
\hat{V}_1^* (cm ³ /g)	0.917	Haward (1970)	0.855	Haward (1970)
\hat{V}_2^* (cm ³ /g)	0.850	Haward (1970)	0.749	Haward (1970)
K_{11}/γ (cm ³ /g K)	2.21×10^{-3}	Barlow et al. (1966)	1.26×10^{-3}	Washburn (1930); Weast (1976); Liu (1980)
K_{12}/γ (cm ³ /g K)	5.82×10^{-4}	Ferry (1970)	3.99×10^{-4}	Ferry (1970)
$K_{21} - T_{g1}$ (K)	-103	Barlow et al. (1966)	-38.5	Washburn (1930); Weast (1976); Liu (1980)
$K_{22} - T_{g2}$ (K)	-327	Ferry (1970)	-231	Ferry (1970)
χ	0.40	This study	0.63	Fujita et al. (1960)
ξ	0.53	Duda et al. (1979a)	0.57	Fujita (1968)
D_0 (cm ² /s)	6.15×10^{-2}	Duda et al. (1979a)	8.71×10^{-2}	Fujita (1968)
E (kcal/g-mol)	5.26	Duda et al. (1979a)	3.68	Fujita (1968)
\hat{V}_1^0 vs. T	—	Timmermans (1950)	—	Timmermans (1950)
\hat{V}_2^0 vs. T	—	Fox and Loshaek (1955)	—	Van Krevelen (1972)

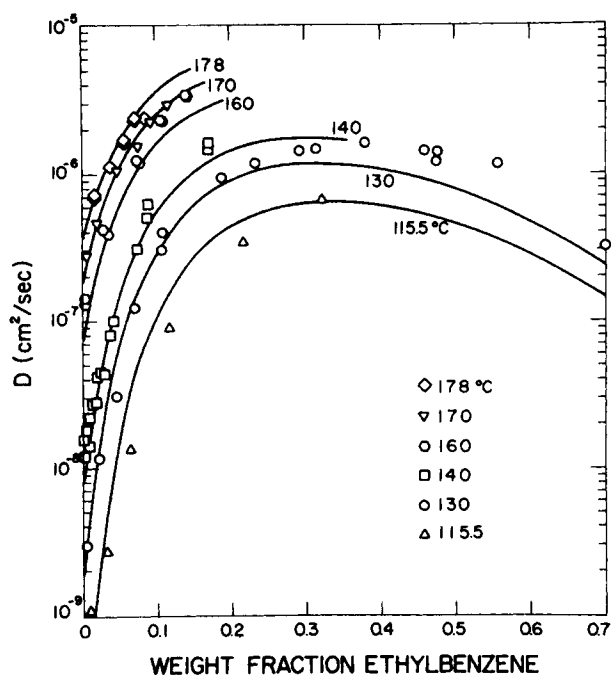


Figure 3. Correlation of diffusivity data for the ethylbenzene-polystyrene system using free-volume parameters contained in Table 2.

for the diffusivity as a function of temperature and concentration can be used to determine accurate parameters for the free-volume theory and hence to predict diffusional behavior over a wide range of conditions. The proposed free-volume theory can also be used to predict the influence of the concentration on the diffusivity with the only diffusivity data input being the temperature dependency of the diffusion coefficient. In Figure 6, data for the methyl acetate-polymethyl acrylate system are used to demonstrate this application of free-volume theory. The six data points at the zero concentration limit, which are represented by solid symbols in Figure 6, were used to determine D_0 , E , and ξ ; the theory parameters for this system are presented in Table 3. It is again evident from Figure 6 that there is good agreement between the theoretical predictions and the experimental data.

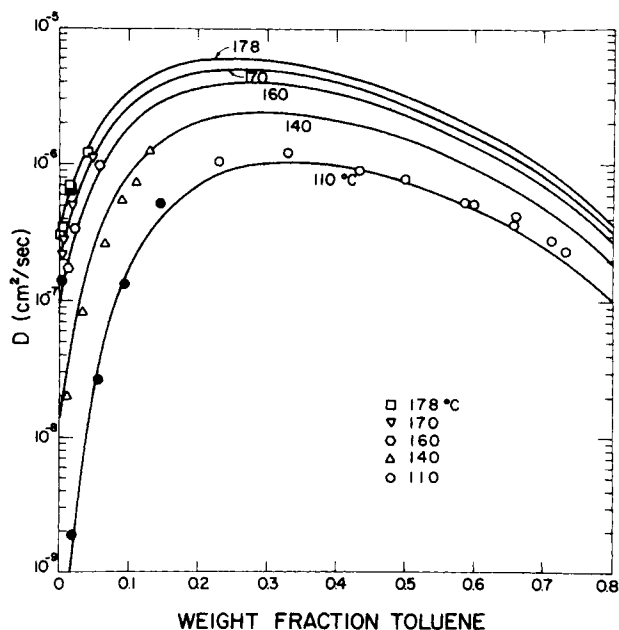


Figure 4. Test of predictive capabilities of proposed free-volume theory using data for the toluene-polystyrene system. Only data points represented by solid symbols were used to obtain free-volume parameters contained in Table 3.

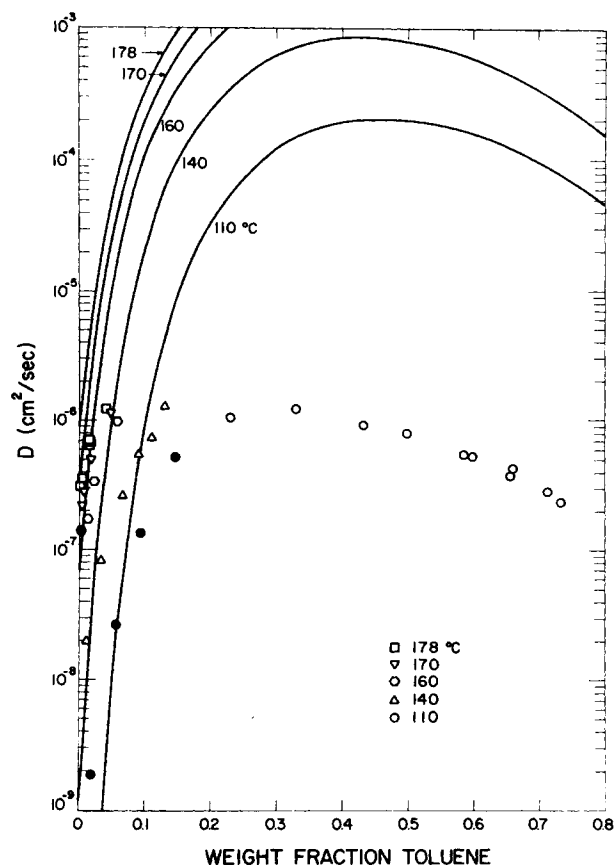


Figure 5. Test of predictive capabilities of free-volume theory of Fujita using data for toluene-polystyrene system. Only data points represented by solid symbols were used to obtain free-volume parameters of the theory.

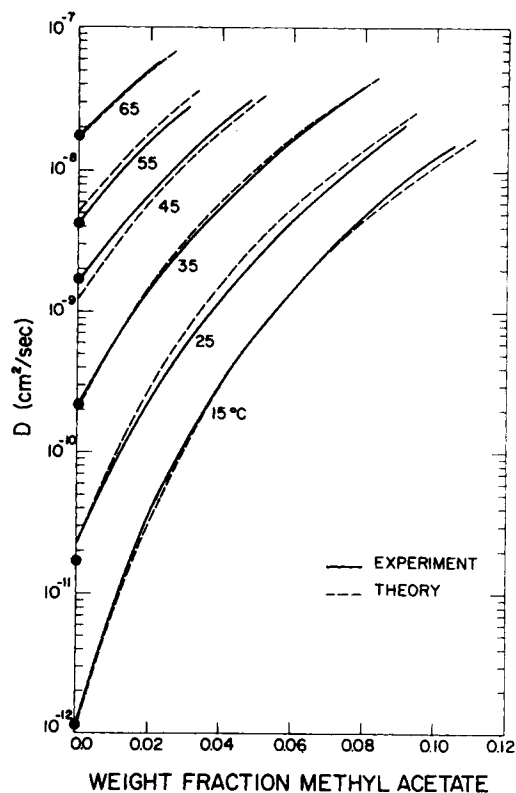


Figure 6. Test of predictive capabilities of proposed free-volume theory using data for the methyl acetate-polymethyl acrylate system. Data points represented by solid symbols were used to obtain free-volume parameters contained in Table 3.

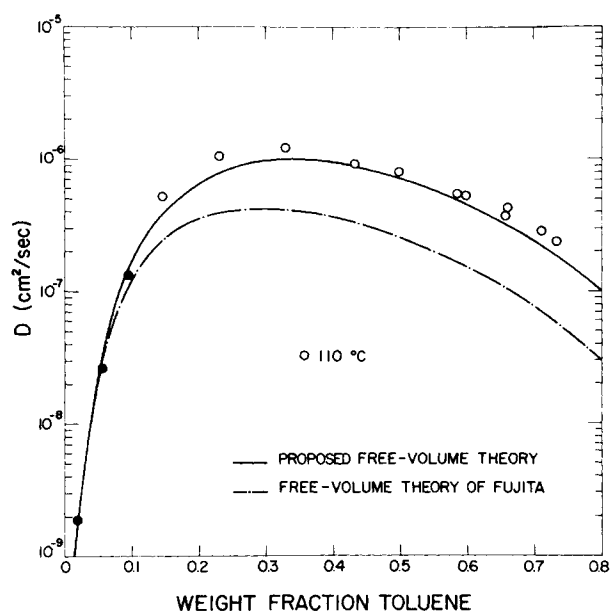


Figure 7. Test of predictive capabilities of proposed free-volume theory and free-volume theory of Fujita at a single temperature using toluene-polystyrene diffusivity data. Only data points represented by solid symbols were used to obtain free-volume parameters for the two theories.

The free-volume theory of Fujita was originally set up to correlate diffusivity-concentration data at a single temperature. We now ascertain whether this theory can also be used to predict diffusion coefficients at the same temperature by the following approach. The diffusivity data at low solvent concentrations are used to evaluate the free-volume parameters at the temperature of interest, and the theory is then used to predict the mutual diffusion coefficient at the same temperature at higher concentrations. For the free-volume theory proposed in this study, the three data points represented by solid circles in Figure 7 were used to determine D_{01} and ξ at 110°C, and these computed parameters were then used to predict D over the remainder of the concentration range. For the free-volume theory of Fujita, the same three data points were used to compute the two pertinent parameters of the Fujita theory, f_2/B_d and $f_2^0/B_d\beta$, by the method outlined by Fujita (1961, 1968). The free-volume equation of Fujita was then used to predict D at higher concentrations. From Figure 7, it is evident that both the proposed free-volume theory and the Fujita free-volume theory provide satisfactory representations of the data at low mass fractions. However, the former theory provides significantly better predictions for D at higher concentrations, and, again, the assumption $\xi = \hat{V}_1^*/\hat{V}_2^*$ leads to unsatisfactory results.

In the original version of the new free-volume theory, the temperature dependence of D_{01} was ignored and diffusivity data in the limit of $\omega_1 = 0$ were used to evaluate D_{01} and ξ (Vrentas and Duda, 1977 b, c, 1979a). Although this method led to a very satisfactory representation of the temperature dependence of the diffusivity at $\omega_1 = 0$, the predictions of the temperature dependence of D at higher concentrations were not satisfactory. This is illustrated in Figure 8 where the predictions of the first version of the new free-volume theory ($E = 0$) are compared with those of the second version ($E > 0$). It is clear that the diffusivity-temperature behavior at $\omega_1 = 0$ is well represented by the first version of the theory (with parameters D_{01} and ξ), but substantial errors are observed when diffusivities at higher concentrations are computed.

We can conclude from the above results that the free-volume theory proposed in this paper can accurately predict diffusional behavior over wide ranges of temperature and concentration. Furthermore, evaluation of the parameters of the theory requires information that is usually available (density and viscosity data) plus a small amount of equilibrium and diffusivity data. The theory permits one to account for the very large variations of D with

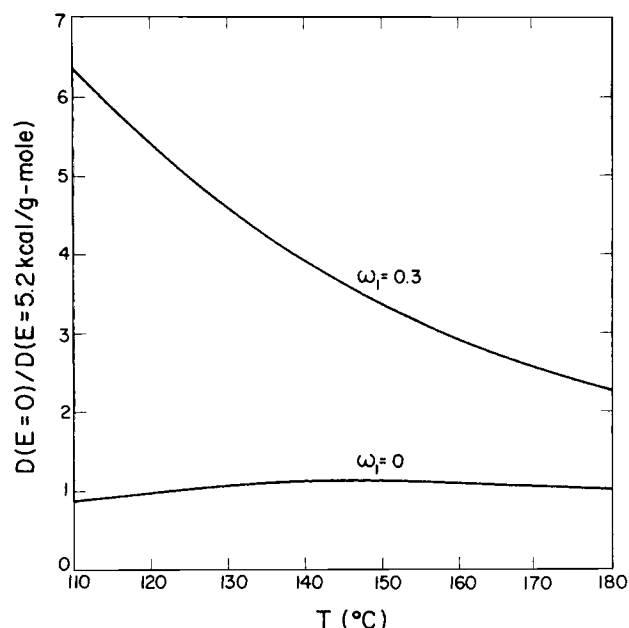


Figure 8. Errors in the diffusivity introduced at higher mass fractions when the assumption $E = 0$ is used. Calculations are carried out for the toluene-polystyrene system.

temperature and concentration that are typically observed in polymer-solvent systems without having to conduct a difficult series of experiments. In some instances, the value of the diffusivity is so low that experimental determination of D is highly impractical. In Figure 9, we have presented experimental diffusivity data and the theoretical predictions for the toluene-polyvinyl acetate system. The figure illustrates the low diffusivity values that are commonly observed in polymer-solvent systems and also the very strong concentration dependence. At 35°C, the diffusion coefficient changes approximately seven orders of magnitude when ten weight percent solvent is added to the polymer. Although the present evaluation of the proposed theory is very encouraging, more ex-

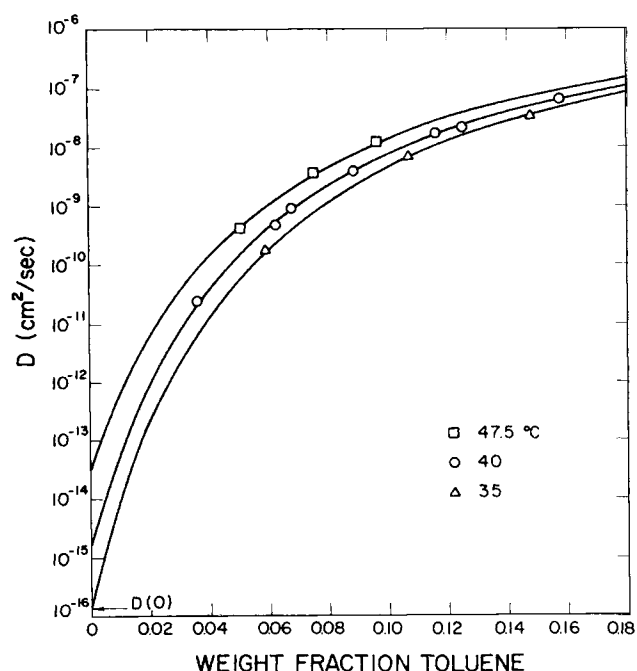


Figure 9. Example of the low diffusivity values and strong concentration dependence typically observed for polymer-solvent systems. Data and theoretical predictions are for the toluene-polyvinyl acetate system.

perimental diffusivity data are needed to further evaluate the accuracy and range of validity of this theory.

We conclude by noting that the theory holds both for solvents which jump as single units and for solvents for which the jumping unit is only a part of the solvent molecule. The size of the solvent jumping unit is incorporated in the parameter ξ (Vrentas and Duda, 1979b). Furthermore, the theory is based on the assumption that Eq. 1 is the appropriate relationship between the mutual diffusion coefficient and the solvent self-diffusion coefficient (Vrentas and Duda, 1977a, 1979a). This assumption is supported both by some theoretical considerations (Vrentas and Duda, 1979a) and by experimental data (Duda et al., 1979b). In addition, since the theory describes purely viscous polymer-solvent diffusion processes, solvent diffusion in glassy polymers, relaxing polymers, and cross-linked polymers cannot be analyzed using the proposed theory. Finally, we note that the Flory-Huggins theory with a constant interaction parameter will not always provide a satisfactory representation of the thermodynamic behavior of a particular polymer-solvent system, and a more general theory must then be utilized. For the systems included in Tables 2 and 3, it was possible to obtain a good representation of the thermodynamic properties over the complete concentration and temperature ranges studied using the Flory-Huggins equation with a constant χ .

ACKNOWLEDGMENT

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

NOTATION

B_d	= parameter in free-volume theory of Fujita
$(C_f)_2$	= WLF constant of polymer
$(C_g)_2$	= WLF constant of polymer
D	= binary mutual diffusion coefficient
D_1	= self-diffusion coefficient of solvent
D_0	= preexponential factor for Eq. 7
D_{01}	= preexponential factor defined by Eq. 7
E	= critical energy per mole needed to overcome attractive forces
f_2	= parameter in free-volume theory of Fujita
K_{11}, K_{21}	= free-volume parameters of solvent
K_{12}, K_{22}	= free-volume parameters of polymer
M_{ji}	= molecular weight of jumping unit of component i
p	= pressure
P_1	= partial pressure of solvent in liquid mixture
P_1^0	= vapor pressure of pure solvent
R	= gas constant per mole
T	= temperature
T_{gi}	= glass transition temperature of component i
\hat{V}_i	= partial specific volume of component i
\hat{V}_i^0	= specific volume of pure component i
$\hat{V}_i^0(0)$	= specific volume of pure component i at 0 K
\hat{V}_i^*	= specific critical hole free volume of component i required for a jump
\hat{V}_{FH}	= average hole free volume per gram of mixture

Greek Letters

β	= parameter in free-volume theory of Fujita
γ	= overlap factor for free volume
η_2	= viscosity of pure polymer
μ_1	= chemical potential of solvent in solution per mole
μ_1^0	= chemical potential of pure solvent per mole
ξ	= ratio of critical molar volume of solvent jumping unit to critical molar volume of jumping unit of polymer
ρ_1	= mass density of component i

ϕ_I	= volume fraction of component i
χ	= interaction parameter of Flory-Huggins theory
ω_I	= mass fraction of component i

Subscripts

1	= solvent
2	= polymer

LITERATURE CITED

- Barlow, A. J., J. Lamb, and A. J. Matheson, "Viscous Behavior of Supercooled Liquids," *Proc. Royal Soc.*, **A292**, 322 (1966).
- Duda, J. L., Y. C. Ni, and J. S. Vrentas, "Diffusion of Ethylbenzene in Molten Polystyrene," *J. Appl. Polymer Sci.*, **22**, 689 (1978).
- Duda, J. L., Y. C. Ni, and J. S. Vrentas, "Toluene Diffusion in Molten Polystyrene," *J. Appl. Polymer Sci.*, **23**, 947 (1979a).
- Duda, J. L., Y. C. Ni, and J. S. Vrentas, "An Equation Relating Self-Diffusion and Mutual Diffusion Coefficients in Polymer-Solvent Systems," *Macromolecules*, **12**, 459 (1979b).
- Ferry, J. D., *Viscoelastic Properties of Polymers*, 2 ed., Wiley, New York (1970).
- Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953).
- Flory, P. J., "Thermodynamics of Polymer Solutions," *Disc. Faraday Soc.*, **49**, 7 (1970).
- Fox, T. G., and S. Loshaek, "Influence of Molecular Weight and Degree of Crosslinking on the Specific Volume and Glass Temperature of Polymers," *J. Polymer Sci.*, **15**, 371 (1955).
- Fujita, H., "Diffusion in Polymer-Diluent Systems," *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
- Fujita, H., "Organic Vapors Above the Glass Transition Temperature," *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).
- Fujita, H., A. Kishimoto, and K. Matsumoto, "Concentration and Temperature Dependence of Diffusion Coefficients for Systems Polymethyl Acrylate and n-Alkyl Acetates," *Trans. Faraday Soc.*, **56**, 424 (1960).
- Haward, R. N., "Occupied Volume of Liquids and Polymers," *J. Macromol. Sci., Revs. Macromol. Chem.*, **C4**, 191 (1970).
- Höcker, H., and P. J. Flory, "Thermodynamics of Polystyrene Solutions," *Trans. Faraday Soc.*, **67**, 2270 (1971).
- Liu, H. T., "A Study of Thermodynamics and Molecular Diffusion in Polymer-Solvent Systems," Ph.D. dissertation, The Pennsylvania State University, University Park, PA (1980).
- Timmermans, J., *Physicochemical Constants of Pure and Organic Compounds*, I, Elsevier, Amsterdam (1950).
- Van Krevelen, D. W., *Properties of Polymers*, Elsevier, Amsterdam (1972).
- Vrentas, J. S., and J. L. Duda, "Diffusion of Small Molecules in Amorphous Polymers," *Macromolecules*, **9**, 785 (1976).
- Vrentas, J. S., and J. L. Duda, "Diffusion in Polymer-Solvent Systems. I. Reexamination of the Free-Volume Theory," *J. Polymer Sci., Polymer Phys. Ed.*, **15**, 403 (1977a).
- Vrentas, J. S., and J. L. Duda, "Diffusion in Polymer-Solvent Systems. II. A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration, and Molecular Weight," *ibid.*, **15**, 417 (1977b).
- Vrentas, J. S., and J. L. Duda, "Solvent and Temperature Effects on Diffusion in Polymer-Solvent Systems," *J. Appl. Polymer Sci.*, **21**, 1715 (1977c).
- Vrentas, J. S., and J. L. Duda, "Molecular Diffusion in Polymer Solutions," *AIChE J.*, **25**, 1 (1979a).
- Vrentas, J. S., and J. L. Duda, "Diffusion of Large Penetrant Molecules in Amorphous Polymers," *J. Polymer Sci., Polymer Phys. Ed.*, **17**, 1085 (1979b).
- Vrentas, J. S., H. T. Liu, and J. L. Duda, "Effect of Solvent Size on Diffusion in Polymer-Solvent Systems," *J. Appl. Polymer Sci.*, **25**, 1793 (1980).
- Washburn, E. W., *International Critical Tables*, VII, McGraw-Hill, New York (1930).
- Weast, R. C., *CRC Handbook of Chemistry and Physics*, 56 ed., CRC Press, Inc., Cleveland, (1976).

Manuscript received December 23, 1980; revision received May 18, and accepted June 22, 1981.