Predicting Polymer/Solvent Diffusion Coefficients Using Free-Volume Theory

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The Vrentas/Duda free-volume diffusion model accurately correlates polymer/solvent diffusion coefficients over wide ranges of concentration and temperature. Currently the model is semipredictive: limited diffusion data are required to estimate model parameters that can then be used to predict diffusion coefficient behavior over sundry conditions. In this work, we present methods for estimating all of the model parameters without any diffusion data and examine the accuracy of the resulting diffusion coefficient predictions. This is the only technique known that predicts polymer/solvent diffusion behavior without any use of any diffusion data.

Introduction

The diffusion of small molecules in polymers has been studied extensively and is of considerable practical concern. Knowledge of the diffusion rate is essential in designing equipment for devolatilization, since the molecular diffusion of the volatile component is normally the rate-limiting step of the process. The drying of coatings is also limited by the ability of a solvent to diffuse to the surface, and often physical properties of coatings are significantly influenced by the presence of even trace amounts of solvent. Despite the obvious importance of polymer-solvent diffusion coefficients, proportionately little data of this type are available in the literature, particularly at varying solvent concentrations. Furthermore, the theories developed to predict diffusion in low-molecular-weight liquid systems provide little insight when one of the species in a binary system is a polymer chain.

Diffusion theories accounting for system free volume (FV) for polymer melts and solutions (Fujita, 1961; Vrentas et al., 1977a) are known to correlate accurately self-diffusion and binary mutual-diffusion coefficient data at various temperatures and over most of the concentration range. At present, these theories seem most likely to achieve predictive status in the future, since most of the required parameters may already be obtained from pure-component properties. With the use of limited diffusion data, successful predictions of solvent self-diffusion and polymer/solvent binary, mutual-diffusion coefficients have already been achieved (Vrentas et al., 1977b, 1989). The purpose of the present work is to examine the possibility of rendering the Vrentas/Duda free-volume diffusion models (Duda et al., 1982) for self- and mutual-diffusion coefficients completely predictive, so that all model parameters can be estimated without knowledge of any diffusion data. Determination of the model parameters will be considered and limitations of the theory discussed. Predictions of polymer/solvent diffusion coefficients are attempted for systems where extensive diffusion data are available for comparison and pure-component physical properties are readily accessible.

Theory

The volume of a liquid is viewed to consist of two parts: the volume occupied by the molecules themselves and the empty space between the molecules. The empty space is commonly referred to as the free volume, of which only the portion which is continuously redistributed by thermal fluctuations is available for molecular transport. This part of the free volume is denoted the *hole* free volume, while the remainder is termed the *interstitial* free volume. Diffusion, therefore, as well as all transport processes, is recognized as being controlled by the hole free volume. Hole free volume differs from and should not be confused with the free volume referred to in earlier work by Cohen and Turnbull (1954). Molecular transport, as perceived by current free-volume theory, is consequently governed by the probable occurrence of two events: (1) a hole of sufficient

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size appears adjacent to a molecule and (2) the molecule possesses enough energy to jump into the void.

These simple notions lead directly to expressions for the solvent self-diffusion coefficient, D_1, and the polymer/solvent binary mutual-diffusion coefficient, D (Duda et al., 1982). These expressions are given in Eqs. 1 and 2:

$$D_1 = D_o \exp\left(\frac{-E}{RT}\right) \exp\left[\frac{-(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\omega_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + \omega_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T)}\right] \quad (1)$$

$$D = D_1(1-\phi_1)^2(1-2\chi\phi_1) \quad (2)$$

where $\hat{V}_I^*$ is the specific critical hole free volume of component I required for a jump, ω_I is the mass fraction of component I, T_{gI} is the glass transition temperature of component I, ϕ_1 is the solvent volume fraction, and χ is the polymer-solvent interaction parameter. D_o is a constant pre-exponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors, and γ is an overlap factor (between 1/2 and 1) which is introduced because the same free volume is available to more than one molecule. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are free-volume parameters for the polymer. Finally, ξ is the ratio of molar volumes for the solvent and polymer jumping units. For convenience in the forthcoming discussion, solvent parameters will be subscripted 1 and polymer parameters 2.

Equation 2 contains the following implicit assumptions:

- The mutual-diffusion coefficient is related theoretically to the solvent and polymer self-diffusion coefficients through an expression developed by Bearman (1961).
- The contribution of the polymer self-diffusion coefficient to the mutual-diffusion coefficient is negligible.
- The Flory-Huggins model (1953) accurately describes the penetrant activity.

The general validity of the relationship between self- and mutual-diffusion coefficients has not yet been established; however, incorporation of these assumptions provides a useful first approximation for this study. The basic FV model (Eq. 2) can be easily modified if a more suitable thermodynamic expression becomes available and the self/mutual-diffusion coefficient coupling is elucidated. In addition, the specific free volumes of the polymer and solvent are presumed to be additive (without a volume change on mixing), and thermal expansion coefficients are approximated by average values over the temperature intervals of interest, thereby limiting the range of applicability of the model (Lodge et al., 1990; Frick et al., 1990). These approximations, however, can be relaxed and more rigorous formalisms can be adopted (Vrentas et al., 1977b).

In Eqs. 1 and 2, both γ and E can be assumed to remain constant with the *proviso* that the domains of the polymer molecules overlap and the environment experienced by a solvent molecule does not change significantly. In the pure-solvent limit, however, as the polymer molecules become infinitely dilute, it is reasonable to expect that the energy required for a solvent molecule to break free from neighboring molecules, $E(\omega_1 \rightarrow 1)$, will differ from the activation energy in the pure-polymer limit, $E(\omega_1 \rightarrow 0)$, due to changes in molecular interactions with concentration (Vrentas et al., 1980b).

There are 13 independent parameters to be evaluated in Eq. 2. Grouping some of them together means that only ten need ultimately to be determined to estimate mutual-diffusion coefficients: K_{11}/γ, $K_{21}-T_{g1}$, K_{12}/γ, $K_{22}-T_{g2}$, $\hat{V}_1^*$, $\hat{V}_2^*$, χ, D_o, E, and ξ. χ is not required in estimating the solvent self-diffusion coefficient. All of these parameters have physical significance, are rooted in free-volume theory, and are not simply adjustable parameters that allow for good empirical fits to data. To substantiate this point unequivocally, one must be able to determine every parameter from sources other than diffusion studies and then successfully predict diffusion behavior. In the following section, methods for calculating each parameter are presented.

Determination of Free-Volume Parameters

$\hat{V}_1^*$ and $\hat{V}_2^*$

The two critical volumes, $\hat{V}_1^*$ and $\hat{V}_2^*$, represent the minimum specific hole free volume required to allow a solvent and polymer molecule to take a diffusive jump and are estimated as the specific volumes of the solvent and polymer, respectively, at absolute zero temperature. Molar volumes at 0 K can be estimated using group contribution methods developed by Sugden (1927) and Biltz (1934). These methods were summarized by Haward (1970) and are reproduced in Table 1.

χ

Extensive tables for the polymer-solvent interaction parameter have been compiled by Sheehan (1966) and Orwoll (1977) for many common polymers and solvents. χ can also be determined from solubility data in which the equilibrium weight

Table 1. Group Contribution Methods for Estimating Molar Volumes at 0 K

Component	Sugden (cm^3/mol)	Biltz (cm^3/mol)
H	6.7	6.45
C (Aliphatic)	1.1	0.77
C (Aromatic)	1.1	5.1
N	3.6	—
N (in Ammonia)	0.9	—
O	5.9	—
O (in Alcohol)	3.0	—
F	10.3	—
Cl	19.3	16.3
Br	22.1	19.2
I	28.3	24.5
P	12.7	—
S	14.3	—
Triple Bond	13.9	16.0
Double Bond	8.0	8.6
3-Membered Ring	4.5	—
4-Membered Ring	3.2	—
5-Membered Ring	1.8	—
6-Membered Ring	0.6	—
OH (Alcoholic)	—	10.5
OOH (Carboxyl)	—	23.2

fraction of the solvent in the polymer is known as a function of solvent vapor pressure, P_1, using the Flory-Huggins equation (1953):

$$\frac{P_1}{P_1^o}=\phi_1\exp(\phi_2+\chi\phi_2^2) \tag{3}$$

where P_1^o is the solvent saturation vapor pressure. The solvent weight and volume fractions are related through:

$$\phi_1=\frac{\omega_1\hat{V}_1}{\omega_1\hat{V}_1+\omega_2\hat{V}_2} \tag{4}$$

where $\hat{V}_1$ and $\hat{V}_2$ are the specific volumes for the solvent and polymer, respectively. If the Flory-Huggins theory does not adequately describe the thermodynamics of the system, the basic free-volume model can be easily modified using a more suitable thermodynamic expression.

A final alternative for determining χ is the use of Bristow's (1958) semi-empirical equation given as:

$$\chi=0.35+\frac{\tilde{V}_1}{RT}(\delta_1-\delta_2)^2 \tag{5}$$

where $\tilde{V}_1$ is the solvent molar volume, and δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively. Equation 2 is relatively insensitive to the choice of χ (Ju, 1981c). Thus, either method for approximating the polymer/solvent solubility is deemed satisfactory.

(K_{12}/γ) and $(K_{22}-T_{g2})$

The Vogel (1921) equation has been used to correlate the viscosity-temperature relationship for glass forming liquids from the glass transition temperature (T_g) to approximately 100°C above T_g. Doolittle postulated that viscosity should be related to a system's free volume and subsequently derived the empirical Vogel viscosity model from free-volume concepts introduced by Doolittle (1951). Recasting Doolittle's expression using the nomenclature developed by Vrentas and Duda yields Eq. 6 for polymer viscosity.

$$\ln\eta_2=\ln A_2+\frac{\left(\dfrac{\gamma\hat{V}_2^*}{K_{12}}\right)}{(K_{22}-T_{g2})+T} \tag{6}$$

The free volume referred to in Eq. 6 is interpreted by Vrentas and Duda as the hole free volume, since viscosity is considered to be a transport property thereby governed by the hole free volume. When estimating the hole free volume, low-temperature viscosity data must be available to reflect accurately the inherent nonlinearity of the Eq. 6.

An alternate form of the Doolittle expression, developed by Williams, Landel and Ferry (WLF, 1955), has become the standard relation in correlating viscosity with temperature. The free-volume parameters used in this study for polymers and solvents are related to the WLF constants (C_{1i} and C_{2i}, where $i=1$ or 2 for solvent and polymer, respectively) through Eqs. 7-10. Thus, if the glass transition temperature is known, the Vrentas/Duda free-volume parameters can be calculated. An extensive list of polymer WLF parameters has previously been published by Ferry (1970).

$$\frac{\gamma\hat{V}_1^*}{K_{11}}=2.303(C_{11})(C_{21}) \tag{7}$$

$$K_{21}=C_{21} \tag{8}$$

$$\frac{\gamma\hat{V}_2^*}{K_{12}}=2.303(C_{12})(C_{22}) \tag{9}$$

$$K_{22}=C_{22} \tag{10}$$

Recent NMR studies have shown that variable temperature ^{13}C spin-lattice relaxation studies can be used successfully in calculating both polymer and solvent WLF coefficients (Schaefer et al., 1990; Dekmezian et al., 1985; Zielinski et al., 1992a), thereby offering a viable option to viscosity measurements.

D_o, E, (K_{11}/γ), and $(K_{21}-T_{g1})$

The assumption of negligible energy effects ($E=0$) is often acceptable in the predictive version of the theory (Vrentas et al., 1989) and continues to be the only available estimate of the activation energy without using any diffusion data. If the self-diffusion expressions for a pure solvent as given by Dullien (1972) and Vrentas/Duda (1977a) are equated, one obtains:

$$\ln\left(\frac{0.124\times10^{-16}\tilde{V}_c^{2/3}RT}{\eta_1 M_1\hat{V}_1}\right)=\ln D_o-\frac{E(\omega_1\rightarrow1)}{RT}-\frac{\dfrac{\gamma\hat{V}_1^*}{K_{11}}}{K_{21}-T_{g1}+T} \tag{11}$$

Here, $\tilde{V}_c$ (cm^3/mol) and M_1 (g/mol) are the solvent's critical molar volume and molecular weight, respectively, and 0.124×10^{-16} is a constant in Dullien's expression which has units of mol$^{2/3}$. η_1 (g/cm·s) and $\hat{V}_1$ (cm^3/g) are the viscosity and specific volume of the pure solvent, respectively, and are the only temperature-dependent parameters in the expression.

In principle, if viscosity and specific volume data are available for a pure solvent as a function of temperature, a four-parameter regression can be performed using Eq. 11 to determine K_{11}/γ, $K_{21}-T_{g1}$, D_o, and $E(\omega_1\rightarrow1)$. In practice, however, converging to a set of parameters that uniquely represents the viscosity and specific volume data is often impossible (Vrentas et al., 1989).

Incorporating the assumption of negligible energy effects, $E(\omega_1)=0$, is the only available estimate of the activation energy without use of any diffusion data. Introducing this assumption into Eq. 11 reduces the number of regression parameters to three and tremendously improves the likelihood of convergence. Parameters calculated by the method described are reported in Table 2 for various solvents.

According to Eq. 11, D_o is a solvent property and independent of the polymer matrix. This supposition may be verified by either (i) conducting different studies at high temperatures where transport is no longer free-volume limited or (ii) observing whether the D_o value for a solvent adequately

Table 2. Solvent Free-Volume Parameters*

Solvent	M_1	$\hat{V}_1^*$	$\tilde{V}_1^o(0)$	$(K_{11}/\gamma)\times 10^3$	$K_{21}-T_{g1}$	T_{g1}	$D_{o1}\times 10^4$
Acetone	58.08	0.943	54.77	0.983	−12.12	—	14.3
Benzene	78.11	0.901	70.38	1.07	−73.79	131.0	11.3
Carbon Tetrachloride	153.84	0.469	72.15	0.431	−38.00	129.0	9.77
Chloroform	119.39	0.510	60.89	0.652	−37.90	133.0	5.49
Ethylbenzene	106.16	0.946	100.43	1.40	−80.01	111.8	4.61
n-Hexane	86.17	1.133	97.66	1.41	−26.75	—	7.85
Methyl Acetate	74.08	0.855	63.34	0.934	−24.63	109.0	14.4
Methylene Chloride	84.94	0.585	49.69	1.05	−62.17	—	3.88
n-Octane	114.22	1.121	128.08	1.15	−37.36	—	9.33
n-Pentane	72.15	1.158	83.57	1.66	−23.62	—	6.86
Tetrahydrofuran	72.10	0.899	64.82	0.753	10.45	—	14.4
Toluene	92.13	0.917	84.48	1.45	−86.32	117.0	4.82
o-Xylene	106.16	1.049	111.36	0.899	−27.75	126.0	12.39

*Data collected from Angell et al. (1984), Boyer (1970), Dubochet et al. (1984), Ju (1981c), Liu (1980), and Zielinski (1992b). D_{o1} can be identified as D_o when E is set equal to zero in Eqs. 1 and 11.

describes transport in various polymers. The latter approach is taken in this work and will be further discussed.

ξ

The parameter that has been by far most evasive and controversial is ξ. This parameter is the ratio of the molar volume of a solvent jumping unit to the molar volume of a polymer jumping unit. If, for now, we restrict ourselves to small solvents, which are expected to move as units (such as benzene, carbon dioxide, and methane), ξ may be defined as:

$$\xi = \frac{\tilde{V}_1^o(0)}{\tilde{V}_{2j}} = \frac{M_1\,\hat{V}_1^*}{M_{2j}\,\hat{V}_2^*} \tag{12}$$

Here, M_1 is the molecular weight of the entire solvent, and M_{2j} is the molecular weight of the polymer jumping unit. Solvent molecules can be expected to move as single units in many cases. Polymer molecules, on the other hand, will unquestionably exhibit segmental motion. The question that must be addressed is whether there is any way of ascertaining the average size of a polymer jumping unit or, more precisely, the molar volume of a polymer jumping unit. Ehlich and Sillescu (1990) recently suggested that ξ must be less than 1 and has been somewhat successful at predicting ξ even when the solvent molecules are expected to move segmentally. Our experience has been that ξ is usually less than 1, although theoretically it need not be (Vrentas et al., 1980a).

Previous work by Ju et al. (1981a) has shown that a plot of $(\gamma\hat{V}_2^*\xi)/K_{12}$ is a linear function of the solvent molar volume (at 0 K) which passes through the origin, so that

$$\frac{\gamma\,\hat{V}_2^*\xi}{K_{12}} = \beta\,\tilde{V}_1^o(0) \tag{13}$$

This relationship suggests that the size of a polymer jumping unit is independent of the solvent and is polymer-specific. Consequently, once β is known for a particular polymer, the value of ξ for any solvent in that polymer can be determined fairly accurately, provided the solvent diffuses as a single unit. β values have previously been reported for various polymers (Ju et al., 1981a,b), and two additional data sets have been analyzed and are presented in Figure 1. Due to the scarcity of data available to create Figure 1, the β values obtained should be used with caution.

Recent publications suggest that geometric features of the solvent (Arnould et al., 1992; Mauritz et al., 1990) and the specific characteristics of a polymer matrix (Vrentas et al., 1990) will affect solvent mobility. In this work, we assume that the solvent molar volume at 0 K is sufficient to describe the jump size for solvents which diffuse as single units.

Larger molecules tend to act as more sensitive probes of the available free volume, and hence studies of their sorption characteristics are preferred to those of smaller solvents to determine free-volume parameters. Unfortunately, of the limited polymer/solvent diffusion data available in the literature, per-

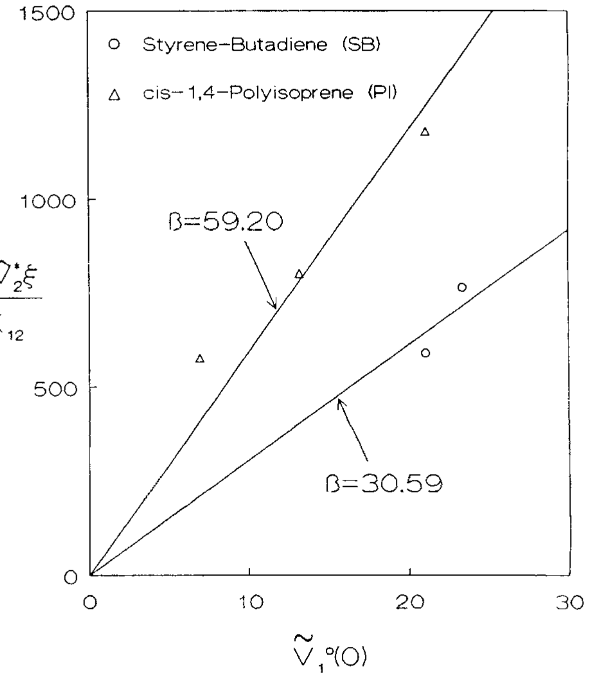

Figure 1. Variation of $(\gamma\hat{V}_2^*\xi)/K_{12}$ with solvent molar volume at 0 K for Poly(styrene-butadiene) (SB) and cis-1,4-Poly(isoprene) (PI).

Diffusion data used for analysis were extracted from Barrer (1939) and van Amerongen (1950).

Table 3. Polymer Free-Volume Parameters*

Polymer	$M_{2\text{mono}}$	M_{2j}	$\hat{V}_2^*$	$(K_{12}/\gamma)\times 10^4$	$K_{22}-T_{g2}$	C_{12}	C_{22}	β	T_{g2}
Butyl rubber	123.10		1.004	2.39	−96.4	16.76	108.60		205
Cis-1,4-poly(isoprene)	68.05	36.37	0.963	4.64	−146.4	16.79	53.60	59.20	200
Neoprene	88.53		0.708	3.91	−163.3	12.13	64.70		228
Poly(α-methylstyrene)	118.09		0.859	5.74	−395.7	13.17	49.30		445
Poly(carbonate)	254.29		0.732	15.20	−385.2	5.50	38.00		423
Poly(dimethyl siloxane)	74.15		0.905	9.32	−81.0	6.11	69.00		150
Poly(ethyl methacrylate)	113.86	140.00	0.915	3.40	−269.5	17.62	65.50	20.90	335
Poly(ethylene-propylene)	70.05		1.005	8.17	−175.3	13.11	40.70		216
Poly(ethylstyrene)	132.20		0.956	4.49	−286.9				355
Poly(isobutylene)	56.04		1.004	2.51	−100.6	16.63	104.40		205
Poly(methyl acrylate)	82.03	128.00	0.748	3.98	−231.0	18.13	45.00	19.50	276
Poly(methyl methacrylate)**	100.04	187.81	0.788	3.05	−301.0	14.02	80.00	17.46†	381
Poly(propylene)**	42.03		1.005	5.02	−205.4	18.24	47.60		253
Poly(*p*-methylstyrene)	118.17		0.860	5.18	−330.0	15.00	48.00		378
Poly(styrene)	104.08	163.60	0.850	5.82	−327.0	13.78	46.00	10.50	373
Poly(styrene-butadiene)	158.13	49.52	0.789	6.60	−184.4	25.60	20.27	30.59	205
Poly(vinyl acetate)	86.02	134.20	0.728	4.33	−258.2	15.59	46.80	17.20	305

* Data collected from Arnould (1989), Brandrup (1989), Ferry (1970), Haward (1970), Ju et al. (1981a,b).

** atactic.

† Ju et al. (1981b) have suggested $\beta = 11.9$, so that some ambiguity regarding this value exists.

manent gas studies (such as O_2 and N_2) represent the majority. The β values in Table 3 represent the best possible estimates with the currently available data. These values will be subject to further scrutiny as more diffusion data are collected. The values for poly(styrene), poly(methyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), and poly(vinyl acetate), in particular, are considered to be the most accurate due to extensive prior studies (Ju et al., 1981a,b).

To gain insight into the meaning of M_{2j}, Eq. 12 was multiplied and divided by the molecular weight of a monomer unit, $M_{2\text{mono}}$, and corresponding values of ξ, which were determined from the analysis of diffusion data, were plotted in Figure 2. The solid line of slope 2/3 indicates that the size of a polymer jumping unit is 3/2 times larger than the monomer segment. A preponderance of the data is represented well by this line. Notable exceptions to the "3/2 trend" are poly(methyl methacrylate) (PMMA) whose jumping unit is almost twice as large as its monomer segment and both rubbers whose jumping units are about half the size of a monomer. M_{2j} can be easily determined if one notes that:

$$M_{2j} = \frac{\gamma}{(\beta K_{12})} \tag{14}$$

Equation 14 is obtained by the substitution of Eq. 13 into Eq. 12.

The only drawback of estimating ξ using the β approach is the necessity of having diffusion data for various solvents in the polymer of interest to estimate β. An alternate method of estimating ξ is required if the free-volume diffusion model will ever be able to achieve a completely predictive capacity.

A closer examination of Figure 2 leads to the understanding that the size of the polymer segmental motion unit is larger for stiffer molecules than for more flexible ones. Since the polymer glass transition temperature, T_{g2}, has long been recognized as an indicator of chain stiffness (Lipatov et al., 1973; Privalko et al., 1974), a correlation of the molar volume of the polymer jump unit with the glass transition temperature was attempted. This correlation is given in Figure 3.

There appears to exist a linear relationship between $\tilde{V}_{2j}$ and T_{g2}. A linear least-squares analysis of the data yields:

$$\tilde{V}_{2j}\left(\frac{\text{cm}^3}{\text{mol}}\right) = 0.6224\,T_{g2}(\text{K}) - 86.95 \tag{15}$$

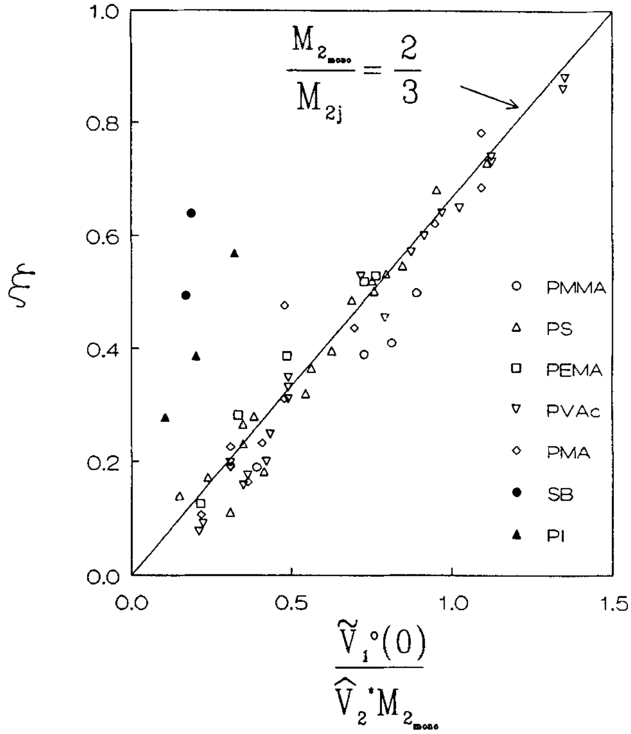

Figure 2. Comparison of M_{2j} and $M_{2\text{mono}}$ for various polymers.

Solid line indicates that the molecular weight of the segmental jump units is approximately 1.5 times that of a monomer unit. poly(methyl methacrylate), PMMA; poly(styrene), PS; poly(ethyl methacrylate), PEMA; poly(vinyl acetate), PVAc; poly(methyl acrylate), PMA; poly(styrene-butadiene), SB; and cis-1, 4-poly(isoprene), PI.
The data used for in this figure were taken from Barrer (1939), van Amerongen (1950), Liu (1980), and Ju (1981c).

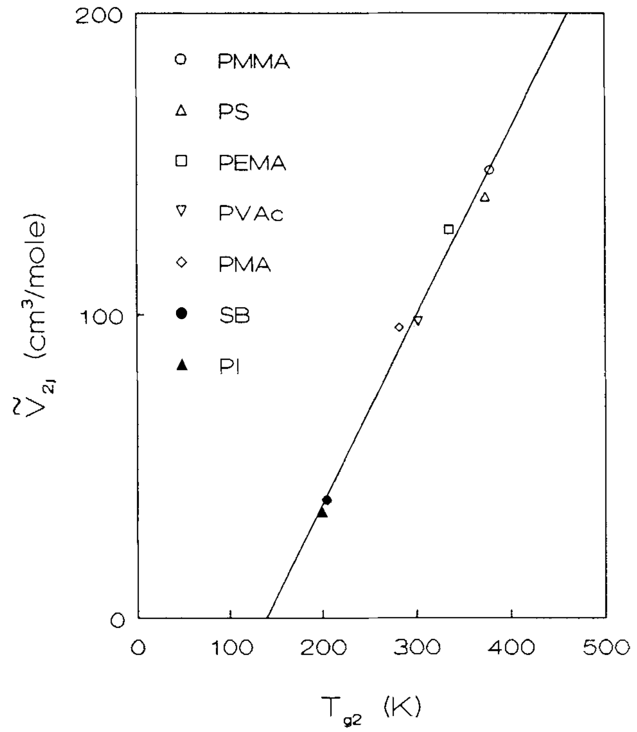

Figure 3. Correlation of the molar volume of a polymer jumping unit ($\tilde{V}_{2j}$) with the glass transition temperature (T_{g2}).

Values of $\tilde{V}_{2j}$ were extracted from Ju (1981a,b) and calculated from the diffusion data of Barrer (1939) and van Amerongen (1950).

Although T_{g2} values are readily available in the literature, $\tilde{V}_{2j}$ can be estimated only from diffusion data. One might anticipate that the correlation proposed in Eq. 15 will fail for polymers with low glass transition temperatures. ($\tilde{V}_{2j}$ is predicted to equal zero at a temperature of approximately 140 K.) Consequently, additional data are required to develop a more accurate relationship between $\tilde{V}_{2j}$ and polymer physical properties.

By using Eq. 15, one can at least estimate diffusion coefficient behavior over ranges of both concentration and temperature from knowledge of pure polymer and solvent data alone. ξ values calculated with the correlation suggested in Figure 3 are certainly more questionable than those obtained from β. However, as more experiments are conducted, a better understanding of polymer segmental dynamics will result, and the likelihood of obtaining a more accurate correlation will undoubtedly improve.

For the sake of completeness, Tables 2 and 3 contain the available free-volume parameters for common solvents and polymers. In the next section, the accuracy of the proposed predictive technique is ascertained.

Results and Discussion

The Vrentas/Duda free-volume diffusion models for self-diffusion and mutual diffusion have been previously shown to correlate diffusion data over various temperature and concentration ranges. Both models are best suited for studies performed in a temperature range less than approximately 150°C above the glass transition temperature where transport is free-volume-limited. At high temperatures, where diffusion is no longer free-volume-limited and energy effects become dominant, the model is expected to deviate from experimental observations.

Diffusion of very small molecules, such as the noble gases, in polymers often is not significantly limited by the fractional free volume available for transport, since they require little space to take diffusive jumps. Consequently, larger molecules, such as benzene and toluene, are represented by the model over a much broader temperature range.

Predictions of self- and mutual-diffusion coefficients for various solvents in poly(styrene), poly(vinyl acetate), poly(methyl acrylate), and poly(methyl methacrylate) are compared to experimental data extracted from the literature (Liu, 1980; Ju, 1981c; Pickup, 1987; Sun, 1974; Zgadzai et al., 1985; Duda et al., 1978; Fujita et al., 1968; Kosfeld et al., 1979; Vrentas et al., 1989) in Figures 4–13. Diffusion coefficients were predicted using the parameters provided in Table 4 and are in fair qualitative agreement in all cases. All the parameters for Eqs. 1 and 2 were estimated without knowledge of any diffusion data.

There is no particular trend as to whether the predictions over- or underestimate the experimental data. Vrentas et al. (1989) estimate solvent self-diffusion coefficients (using the semipredictive β approach) with consistent accuracy over the entire concentration range as well as at various temperatures. Use of the same free-volume parameters along with an appropriate Flory-Huggins χ parameter yields predictions that deviate markedly from mutual diffusion coefficient data, particularly at high solvent concentrations ($\omega_1 > 0.7$). The deviation of the FV mutual-diffusion model at high solvent

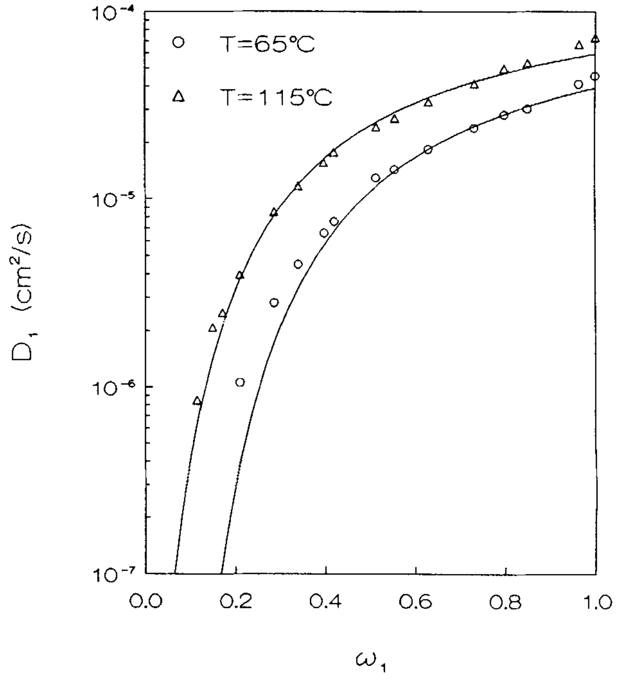

Figure 4. Experimental data (Pickup, 1987) and theoretical predictions for self-diffusion coefficients of toluene in poly(styrene).

Table 4. Parameters Used in Diffusion Coefficient Predictions*

Parameter	Tol/PS	Tol/PVAc	EB/PS	Clfrm/PVAc	MAc/PMA	Ben/PS	THF/PS	Tol/PMMA
$D_o \times 10^4$ (cm^2/s)	4.82	4.82	4.61	5.49	14.4	11.3	14.4	4.82
χ	0.354	0.393	0.363	0.351	0.630	—	—	0.9
$K_{11}/\gamma \times 10^3$ (cm^3/g·K)	1.45	1.45	1.40	0.652	0.934	1.07	0.75	1.45
$K_{12}/\gamma \times 10^4$ (cm^3/g·K)	5.82	4.33	5.82	4.33	3.98	5.82	5.82	3.05
$K_{21} - T_{g1}$ (K)	−86.32	−86.32	−80.01	−37.90	−24.63	−73.79	10.45	−86.32
$K_{22} - T_{g2}$ (K)	−327.0	−258.2	−327.0	−258.2	−231.0	−327.0	−327.0	−301.0
$\hat{V}_1^*$ (cm^3/g)	0.917	0.917	0.946	0.510	0.855	0.901	0.899	0.917
$\hat{V}_2^*$ (cm^3/g)	0.850	0.728	0.850	0.728	0.748	0.850	0.850	0.788
ξ	0.58	0.82	0.69	0.59	0.75	0.48	0.45	0.56
E (cal/mol)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Values for the temperature-dependent parameters, χ, $\hat{V}_1$, and $\hat{V}_2$, were obtained from Liu (1980), Ju (1981c), McGowan (1969), and Daubert et al. (1989). Since χ did not vary much, a single value is reported here for polymer/solvent systems where mutual-diffusion coefficients were predicted. ξ was estimated from Eq. 12, using Eq. 15 for the polymer jump unit and the solvent 0 K molar volumes in Table 2 for the solvent jump unit.

concentrations from experimental data are presumed to occur from a combination of three effects:

(1) No direct relationship exists between self-diffusion coefficients and the binary mutual-diffusion coefficient for mixtures of even simple molecules (Bearman, 1961); thus, the approximations implemented to couple self-diffusion coefficients to mutual-diffusion coefficients in polymer/solvent mixtures are even more questionable.

(2) The polymer self-diffusion coefficient, which is assumed negligible in the development of the Vrentas/Duda model, may be contributing to the mutual-diffusion coefficient at high solvent concentrations (Pattle et al., 1967; Sillescu, 1991).

(3) The Flory-Huggins thermodynamic model (1953), which is usually chosen to describe the change of the penetrant activity with concentration, may not be adequately describing polymer/solvent interactions (Mossner et al., 1988).

These difficulties do not exist in considering solvent self-diffusion and, consequently, one might expect that predictions of solvent self-diffusion would be correspondingly better. This belief is supported since the predictions in best quantitative agreement with experimental observations were for the self-diffusion of various solvents in poly(styrene).

Both solvent self-diffusion and polymer/solvent mutual-diffusion data were available for only toluene and ethylbenzene in poly(styrene). Since the toluene self-diffusion coefficients are predicted accurately, the deviance of the predictions for toluene/poly(styrene) mutual-diffusion are presumed to arise from the difficulties alluded to above. For the ethylbenzene/poly(styrene) system, however, additional discrepancies must exist since even ethylbenzene self-diffusion is not well predicted.

A comparison of the parameters used in this study to predict mutual-diffusion coefficients with those obtained by correlat-

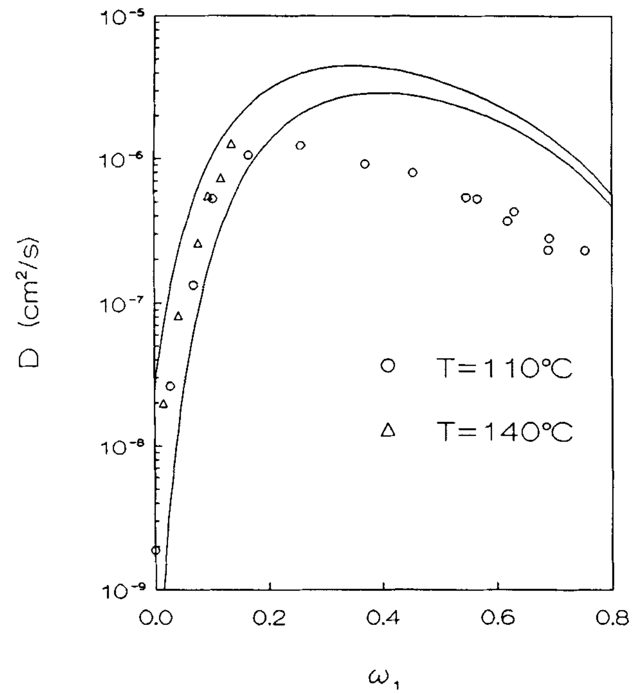

Figure 5. Experimental data (Sun, 1974) and theoretical predictions for toluene/poly(styrene) mutual-diffusion coefficients.

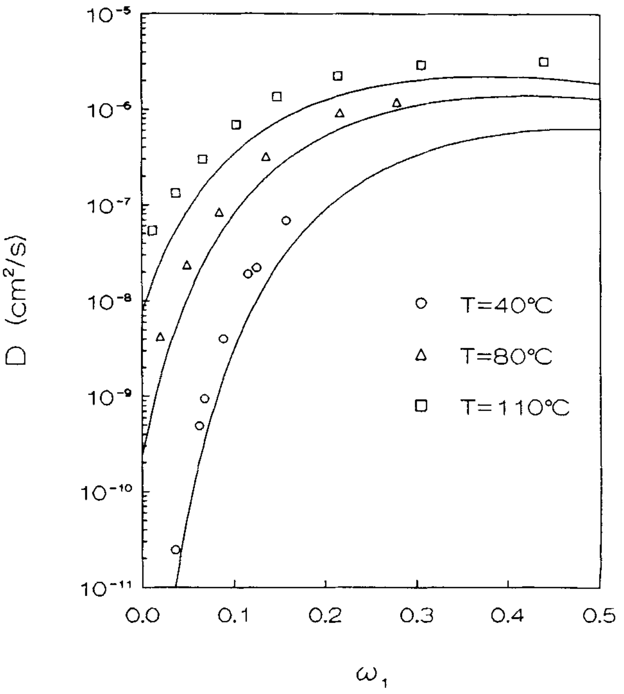

Figure 6. Experimental data (Ju, 1981c) and theoretical predictions for toluene/poly(vinyl acetate) mutual-diffusion coefficients.

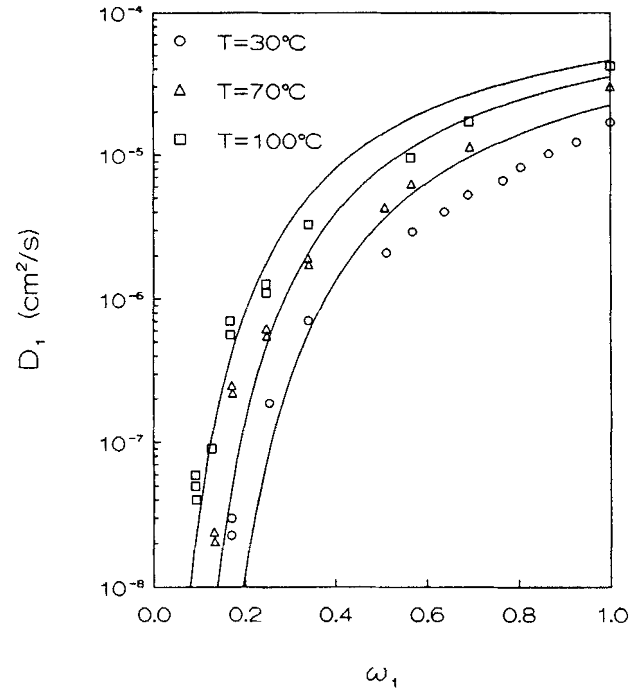

Figure 7. Experimental data and theoretical predictions for self-diffusion coefficients of ethylbenzene in poly(styrene).

The diffusion data source is Zgadzai et al. (1985).

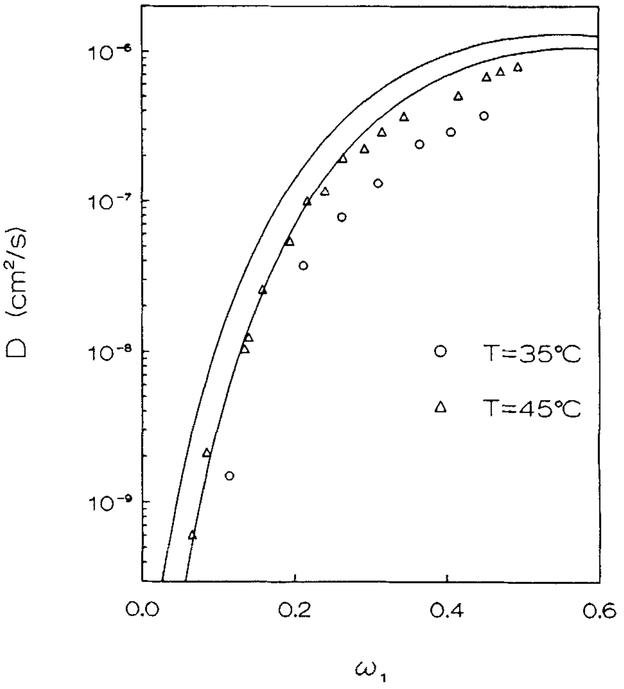

Figure 9. Experimental data (Ju, 1981c) and theoretical predictions for chloroform/poly(vinyl acetate) mutual-diffusion coefficients.

ing experimental data (Duda et al., 1982) reveals that D_o, E, and ξ are the parameters being estimated with least accuracy. All three of these parameters influence the magnitude of the resulting diffusion coefficient predictions; however, only ξ is considered to have an effect on the dependence of D_1 and D with concentration.

At zero weight-fraction solvent, Eqs. 1 and 2 both reduce

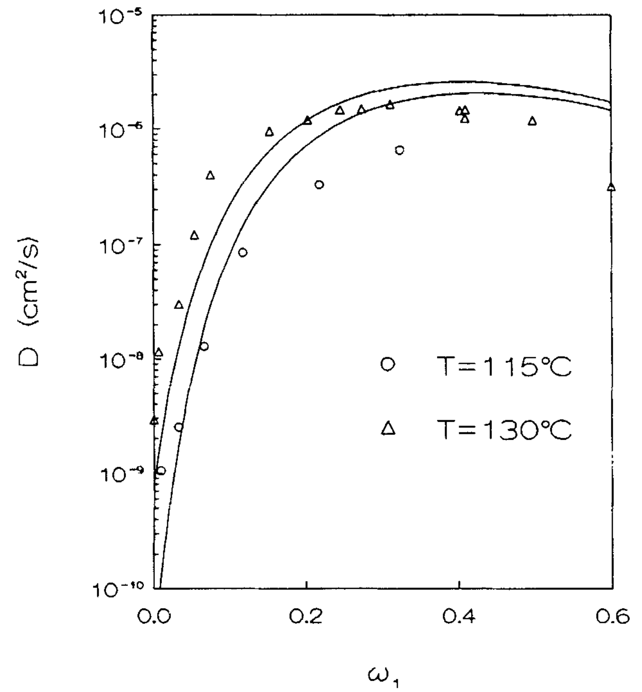

Figure 8. Experimental data and theoretical predictions for ethylbenzene/poly(styrene) mutual-diffusion coefficients.

Diffusion data were obtained from Duda et al. (1978).

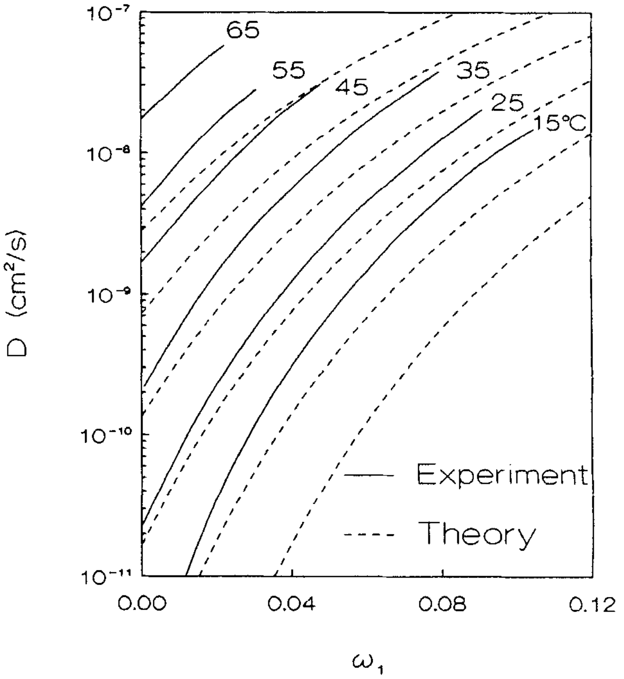

Figure 10. Experimental data (Fujita, 1968) and theoretical predictions for methyl acetate/poly(methyl acrylate) mutual-diffusion coefficients.

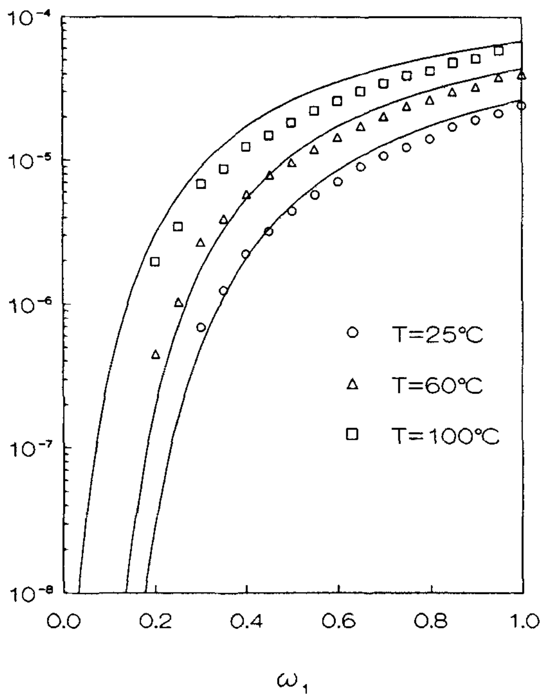

Figure 11. Experimental data and theoretical predictions for self-diffusion coefficients of benzene in poly(styrene).

The diffusion data source is Kosfeld et al. (1979).

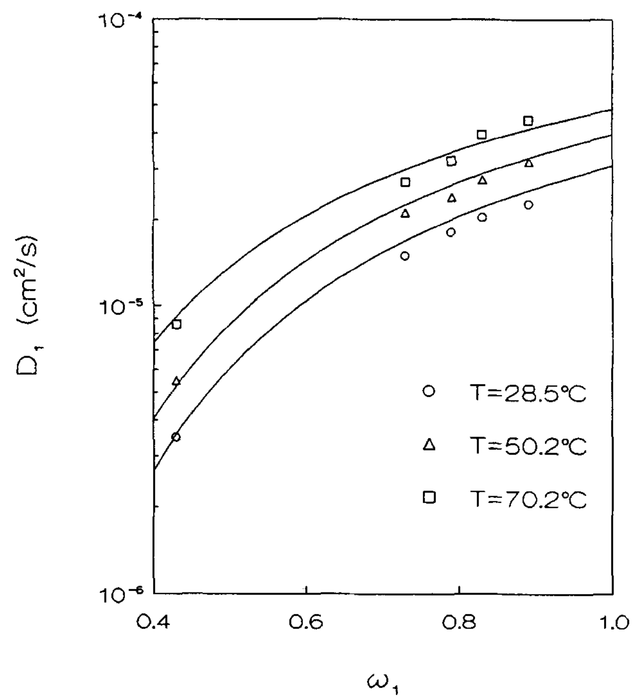

Figure 12. Experimental data (Vrentas et al., 1989) and theoretical predictions for self-diffusion coefficients of tetrahydrofuran in poly(styrene).

to the form shown below:

$$\ln D = \ln D_o - \frac{E(\omega_1 \to 0)}{RT} - \frac{\dfrac{\gamma \hat{V}_2^* \xi}{K_{12}}}{K_{22} - T_{g2} + T} \tag{16}$$

where D_o is the constant pre-exponential term, and $E(\omega_1 \to 0)$ is the activation energy required to break interactions with neighboring molecules in the pure-polymer limit. One expects that E could be concentration-dependent, since the environment a solvent molecule experiences when surrounded by identical solvent molecules dramatically differs from when it exists virtually alone in a polymer melt (Zielinski et al., 1992c). E is expected to reflect the molecular interaction between a polymer and a solvent penetrant. Consequently, assuming E equals zero at all concentrations, as was done in this study, may also be contributing to the deviance of predictions from experimental data.

The assertion that D_o is a solvent property is supported by Figures 4, 6 and 13 that illustrate the diffusion of toluene in three different polymers. The same values of D_o and E were used to predict diffusion coefficients in all three systems and seem to represent the data reasonably well. The curvature of $D(\omega_1)$ data in Figure 13, however, is not predicted well. Analysis of available data for solvent diffusion in PMMA (Liu, 1980; Arnould, 1989) yields uncertainty in the PMMA jump unit size. The position of $\tilde{V}_{2j}$ for PMMA in Figure 3, therefore, is still somewhat questionable. Variation of this point affects the predicted value of ξ and could account for the predicted curvature discrepancy in Figure 13.

The shape of the $D(\omega_1)$ curve for diffusion of methyl acetate in poly(methyl methacrylate), on the other hand, is predicted fairly well, although an offset exists between experimental data and theoretical predictions. This shortcoming is believed to arise from the scarcity of low-temperature viscosity and density data for pure methyl acetate to accurately estimate D_o, K_{11}/γ, and $K_{21} - T_{g1}$.

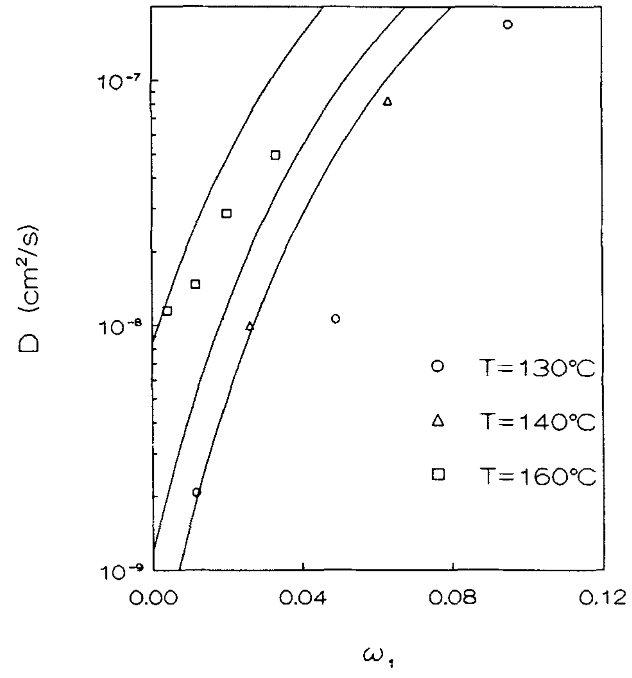

Figure 13. Experimental data and theoretical predictions for toluene/poly(methyl methacrylate) mutual-diffusion coefficients.

Diffusion data were obtained from Ju et al. (1981b).

Conclusions

All the parameters required for the Vrentas/Duda free-volume diffusion models for self-diffusion and mutual diffusion may be estimated without the knowledge of any diffusion data. Predictions of diffusion coefficients at various conditions of temperature and concentration have been shown to agree fairly well with experimental data in most cases.

In light of observed experimental data, treating D_o as a constant over all conditions of temperature and concentration appears to be a reasonable approximation. Future studies of the activation energy dependence on concentration are warranted to elucidate the molecular interaction between the polymer and the diffusing solvent.

The values of K_{11}/γ, $K_{21}-T_{g1}$, K_{12}/γ, and $K_{22}-T_{g2}$ reported in Tables 2 and 3 are fairly well-established, $\hat{V}_1^*$ and $\hat{V}_2^*$ can be estimated easily from group contribution techniques, and satisfactory χ values can be approximated. Thus, the only parameter remaining that influences the diffusivity is ξ. Comparisons for numerous systems indicates that calculating ξ from β (Eq. 13) is accurate to within approximately 10%. The correlation suggested in Eq. 15 is approximately as accurate for the systems where experimental data are available for comparison. Knowledge of some transport data in the polymer of interest will always facilitate predictions of diffusion coefficient behavior; however, through the use of Eq. 15, predictions can at least be attempted by knowledge of polymer and solvent physical properties alone.

The systems studied suggest that it may be possible to predict diffusion coefficients accurately from solely pure-component data. This development represents the only technique available for predicting diffusion coefficients in polymer/solvent systems. Additionally, if any transport data are available in the polymer of interest, better predictions will inherently result. Since diffusion data are already accurately correlated by the Vrentas/Duda diffusion model, one may expect that a more accurate predictive version of the model will evolve as better parameter estimates for the model become available.

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Notation

C_{11} = solvent WLF parameter
C_{12} = polymer WLF parameter
C_{21} = solvent WLF parameter, K
C_{22} = polymer WLF parameter, K
D = polymer/solvent binary mutual-diffusion coefficient, cm^2/s
D_o = constant pre-exponential factor, cm^2/s
D_{o1} = constant pre-exponential factor when E is presumed to be equal to 0, cm^2/s
D_1 = solvent self-diffusion coefficient, cm^2/s
D_2 = polymer self-diffusion coefficient, cm^2/s
E = energy required to overcome attractive forces from neighboring molecules, cal/mol
K_{11} = solvent free-volume parameter, cm^3/g·K
K_{21} = solvent free-volume parameter, K
K_{12} = polymer free-volume parameter, cm^3/g·K
K_{22} = polymer free-volume parameter, K
M_1 = solvent molecular weight, g/gmol
M_{2j} = molecular weight of polymer jumping unit, g/mol
$M_{2\text{mono}}$ = monomer molecular weight, g/mol
P_1 = solvent vapor pressure, mm Hg
P_1^o = solvent vapor pressure at saturation conditions, mm Hg
R = gas constant
T = absolute temperature, K
T_g = glass transition temperature, K
T_{g1} = solvent glass transition temperature, K
T_{g2} = polymer glass transition temperature, K
$\tilde{V}_c$ = solvent critical molar volume, cm^3/mol
$\hat{V}_1$ = solvent specific volume, cm^3/g
$\hat{V}_2$ = polymer specific volume, cm^3/g
$\tilde{V}_1$ = solvent molar volume, cm^3/mol
$\tilde{V}_{2j}$ = molar volume of polymer jumping unit, cm^3/mol
$\hat{V}_1^*$ = solvent specific critical hole free volume, cm^3/g
$\hat{V}_2^*$ = polymer specific critical hole free volume, cm^3/g
$\tilde{V}_1^o(0)$ = solvent molar volume at 0 K, cm^3/mol

Greek letters

β = polymer specific proportionality constant (Eq. 13)
γ = overlap factor which accounts for shared free volume
δ_1 = solvent solubility parameter, (cal/cm^3)$^{1/2}$
δ_2 = polymer solubility parameter, (cal/cm^3)$^{1/2}$
η_1 = solvent viscosity, g/cm·s
η_2 = polymer viscosity, g/cm·s
ξ = ratio of solvent and polymer jumping units
ϕ_1 = solvent volume fraction
ϕ_2 = polymer volume fraction
χ = Flory-Huggins polymer/solvent interaction parameter
ω_1 = solvent weight fraction
ω_2 = polymer weight fraction

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