An Alternate Interpretation of Polymer/Solvent Jump Size Units for Free-Volume Diffusion Models

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ABSTRACT: Polystyrene/toluene mutual-diffusion coefficients have been measured as a function of temperature in the limit of infinite solvent dilution. The solvent to polymer jump size unit ratio (ξ) was determined from the Vrentas−Duda free-volume diffusion model for polymer self-diffusion and is in excellent agreement with values evaluated from solvent self- and binary mutual-diffusion coefficient data. Comparison of the free-volume model to a version of the Kirkwood−Riseman theory, modified for diffusion at infinite dilution under non-Θ conditions, suggests that ξ follows the temperature dependence of the root-mean-squared end-to-end distance of the polystyrene and can be estimated without the use of diffusion data. This result establishes an explicit theoretical coupling between thermodynamic interactions, Brownian dynamics, and free-volume theory.

Introduction

Studies of diffusion behavior in polymeric solutions are traditionally partitioned into concentration intervals based on the environment experienced by the polymer molecules. In infinitely dilute solutions, polymer molecules are widely dispersed and are essentially isolated in a sea of solvent. Molecular transport in this concentration limit is adequately represented by Kirkwood−Riseman theory[1] for Θ solutions and by a modified version of that theory[2] for non-Θ conditions. At somewhat higher polymer concentrations, the macromolecules begin to interact hydrodynamically even though the domains of individual polymer chains do not yet entangle. Statistical mechanical formalisms, such as the Pyun−Fixman model,[3] provide accurate representations of the diffusion coefficient concentration dependence when used in conjunction with two-parameter schemes[4] that reflect short- and long-range interactions through polymer conformations in solution. Finally, in concentrated polymer solutions, which constitute the majority of the concentration range, diffusional characteristics are generally modeled using free-volume (FV) theory. The Fujita[5] and Vrentas−Duda[6,7] formalisms, both of which stem from the older Cohen−Turnbull FV theory,[8] have dominated this discipline for several decades. Although the Fujita model correlates diffusion data very well, it is incapable of extrapolating results beyond the range of available data and thus has no predictive capabilities. Furthermore, it has been shown[7,9] that the Fujita theory is simply a subset of the more general Vrentas−Duda expression.

Analysis of polymer processing operations requires the ability to predict the temperature, concentration, and molecular weight dependence of mutual-diffusion coefficients, D. Although the most important processing procedures involve solvent devolatilization in concentration regimes for which free-volume formalisms are applicable, free-volume concepts inherently describe self-diffusion processes. Consequently, theories which enable mutual-diffusion coefficients to be calculated from self-diffusion coefficients are crucial.

An expression relating self- and mutual-diffusion coefficients in polymer−solvent systems has recently been proposed[10] which correctly forces D to equal (1) the solvent self-diffusion coefficient, D_1, when the solvent weight fraction, ω_1, approaches zero, and (2) the polymer self-diffusion coefficient, D_2, at infinite dilution, i.e., $\omega_1 \rightarrow 1$. Coupled with the free-volume model for solvent self-diffusion, it is conceivable that this single formalism may reasonably describe the mutual-diffusion process over the entire concentration interval.

A key parameter in FV models is the ratio of solvent to polymer jump size units, ξ. Although predictive methods of evaluating ξ have been proposed,[11−13] it is recognized that evaluating ξ directly from diffusion data yields inherently superior values. Accurate estimates of ξ are crucial to describe the dependence of diffusion coefficients on both temperature and concentration. This parameter is, however, one of the most difficult parameters to estimate *a priori*. Since solvent parameters critical to the FV model have been successfully estimated[14] by comparing the FV expression for D_1 to the Dullien model[15] for neat solvent diffusion, one might expect to have similar fortune by equating the FV model for polymer self-diffusion to existing dilute solution (or infinite dilution) models.

In this work, mutual-diffusion coefficients have been measured as a function of temperature for polystyrene in an infinitely dilute toluene mixture. Since these mutual-diffusion coefficients are numerically identical to polystyrene self-diffusion coefficients in this concentration regime, the results have been analyzed with the Vrentas−Duda FV model for polymer self-diffusion. The value of ξ obtained in the present work is in excellent agreement with that resolved from diffusion data in concentrated polymer solutions and melts. The success of this analysis implies that the FV polymer self-diffusion model may be equated to the modified Kirkwood−Riseman model when $\omega_1 \rightarrow 1$. This result leads to an alternate interpretation of polymer/solvent jump size units for free-volume diffusion models and consequently enables ξ to be determined without diffusion data.

Theory

Free-volume models are based on the premise that mass transfer rates are determined by the amount of empty space available for molecular transport. Furthermore, a molecule requires an adjacent vacancy to

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take a diffusive jump. For compact, rigid solvents, the minimum hole size needed can be assumed to be the volume occupied by the solvent at absolute zero temperature. A polymer molecule, on the other hand, diffuses segmentally and requires hole volumes on the order of the monomer size.[13] Application of these simple concepts has led to the development[6,7] of the following equations for solvent (1) and polymer (2) self-diffusion, respectively:

$$D_1 = D_{01} \exp\left(\frac{-\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{\mathrm{FH}}}\right) \qquad (1)$$

and

$$D_2 = D_{02}(\omega_1, T, M_2) \exp\left(\frac{-\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\xi \hat{V}_{\mathrm{FH}}}\right) \qquad (2)$$

The proportionality constant, D_{0i}, is approximately constant for solvent self-diffusion ($i = 1$) but introduces the effect of entanglements on polymer self-diffusion ($i = 2$) and is therefore dependent on concentration, temperature, and polymer molecular weight, M_2. The average hole free volume per gram of mixture is given by $\hat{V}_{\mathrm{FH}}$, $\hat{V}_i^*$ is the specific critical hole free volume of component i required for a jump, ω_i is the mass fraction, and γ is an overlap factor to account for shared free volume. Finally, the parameter ξ represents the ratio of the molar volume of solvent to polymer jump size units.

The shared specific hole free volume, $\hat{V}_{\mathrm{FH}}/\gamma$ can be approximated from the fractional free-volume contributions of each component within the system. The amount of hole free volume provided by component i is generally estimated from correlations of pure component viscosity data with the Vogel–Fulcher–Tamman (VFT) viscosity model[16–18]

$$\ln \eta_i = A_i + \frac{\gamma \hat{V}_i^*}{\hat{V}_{\mathrm{FH}_i}} \qquad (3)$$

where η_i is the viscosity of component i, and A_i is a constant preexponential factor.

Although FV theory provides an effective method for the determination of self-diffusion coefficients (D_i) for polymer–solvent systems, typical industrial mass transfer operations are analyzed using the binary mutual-diffusion coefficient (D). Two theoretical expressions coupling self-diffusion and mutual diffusion have been proposed, one which is limited to concentrations near the pure polymer limit[19] and another that shows promise in describing the mutual-diffusion process over the entire concentration range.[10] The problem of predicting mutual-diffusion coefficients, therefore, lies predominantly in the ability to accurately estimate the solvent self-diffusion coefficient (D_1). Since ξ is the most difficult parameter to ascertain in eq 1,[13] without the benefit of diffusion data for the polymer of interest, D estimates are largely governed by the accuracy with which ξ can be determined.

The relevance of ξ, however, is broader than simply a correlative parameter used in FV theory, since it signifies the extent to which the activation energy of shear viscosity and tracer diffusion are coupled, and whether an apparent activation energy ceiling value for penetrant diffusion in polymers exists.[20–24] Since both of these points have been controversially discussed in the literature without resolution, an alternate interpretation of the ratio of solvent to polymer jump size units may offer some new insights.

Although based upon an identical concept, the Vrentas–Duda free-volume model for solvent self-diffusion (eq 1) has received far more attention than their model for polymer self-diffusion (eq 2). The principal distinguishing feature between the two formalisms is the necessary inclusion of an additional factor to compensate for the effect of entanglements during polymer migration. Implementing the entanglement theory developed by Bueche[25] enables predictions of polymer self-diffusion coefficient dependence on ω_1, M_2, and T that are qualitatively reasonable.[26] Since the Bueche theory possesses deficiencies,[27] accurate quantitative predictions for D_2 are not generally expected.

At infinite dilution, however, a single polymer chain has no interactions with neighboring polymer molecules and experiences no hindrance from entanglements. In this concentration limit, the preexponential factor in eq 2 adopts a meaning similar to D_{01} in eq 1 and can thus be approximated as a constant for a given molecular weight. In the pure solvent limit, $\omega_1 \rightarrow 1$, eq 2 reduces to

$$D = D_2(\omega_1 \rightarrow 1) = \bar{D}_{02} \exp\left(\frac{-\gamma \hat{V}_1^*}{\xi \hat{V}_{\mathrm{FH}_1}}\right) \qquad (4)$$

where $\bar{D}_{02}$ is a temperature-independent proportionality constant. Substitution of eq 3 into this expression yields the predicted scaling dependence with solvent viscosity, namely

$$D = D_2(\omega_1 \rightarrow 1) = K \eta_1^{-1/\xi} \qquad (5)$$

where K is a proportionality constant. It is interesting to note that $D_2(\omega_1 \rightarrow 1)$ is predicted to follow a scaling relationship differing from that suggested by the Stokes–Einstein model, i.e., $D_2(\omega_1 \rightarrow 1) \propto \eta^{-1}$.

The Kirkwood–Riseman theory[1] for translational diffusion at infinite dilution is appropriate in the non-free-draining hydrodynamic limit[28] and for Θ solutions. A modified version of this theory has been developed[2] for non-Θ conditions by assuming that excluded volume effects can be accounted for by introduction of an expansion parameter, α_f, which reflects the deviation from the unperturbed state. The modified Kirkwood–Riseman theory is given as

$$D = \frac{0.196 kT}{\eta_1 \alpha_f (\langle r_0^{\,2} \rangle / M_2)^{0.5} M_2^{\,0.5}} \qquad (6)$$

where η_1 is the solvent viscosity, $\langle r_0^2 \rangle$ is the mean-squared end-to-end distance for an unperturbed polymer chain, α_f is an expansion factor accounting for dimensional changes away from the unperturbed state, k is the Boltzmann constant, and T is the absolute temperature. The numerical constant in eq 6 is evaluated from an *approximate* solution of an integral equation. Exact solutions reveal[29] errors of less than 2% and are therefore neglected in this work. A comparison of $D(\omega_1 \rightarrow 1)$ predictions resulting from eq 6 with literature data for infinite dilution polystyrene/toluene mutual-diffusion coefficients has been previously performed,[30] revealing excellent agreement with experiment and theory. These results are reproduced, for convenience, in Table 1 along with recent data[31] acquired for this system. Since the polymer self-diffusion coefficient is

Table 1. Comparison of Measured and Predicted Values of $D(\omega_1 \rightarrow 1)$ for the Polystyrene/Toluene System

M_2 (g/mol)	T (°C)	measd $D(\omega_1 \rightarrow 1)$	pred $D(\omega_1 \rightarrow 1)$
6 100[b]	23	2.11×10^{-6}	2.42×10^{-6}
17 400[a]	25	1.44×10^{-6}	1.43×10^{-6}
48 800[b]	23	7.65×10^{-7}	7.83×10^{-7}
111 000[a]	25	4.42×10^{-7}	5.10×10^{-7}
299 000[c]	25	2.72×10^{-7}	3.06×10^{-7}
410 000[b]	23	2.10×10^{-7}	2.35×10^{-7}
900 000[a]	20	1.34×10^{-7}	1.40×10^{-7}

[a] From ref 30. [b] From ref 31. [c] This study.

identical to the polymer/solvent mutual-diffusion coefficient in the pure solvent limit, eqs 5 and 6 can be equated, yielding

$$\ln\left[\frac{\alpha_f}{T}\left(\frac{\langle r_0^{\,2}\rangle}{M_2}\right)^{0.5}\right] = \left(\frac{1-\xi}{\xi}\right)\ln \eta_1 + B \qquad (7)$$

where B is a collection of constants.

According to eq 7, the ratio of a solvent to polymer jump size unit reveals the difference in the temperature dependencies of the root-mean-squared (rms) end-to-end distance and the solvent viscosity. Since $\alpha_f\langle r_0^{\,2}\rangle^{0.5}$ is a direct measure of polymer/solvent compatibility and the VFT model for η_1 stems from free-volume theory, ξ reveals a coupling between thermodynamic interactions and Brownian dynamics.

Strictly speaking, comparing eqs 5 and 6 is unreasonable, since polymer diffusion in the pure solvent limit may not be free-volume limited. This comparison is prompted nonetheless due to the success of previous investigations[13,14] which have estimated solvent FV parameters by comparing the expression for D_1 (eq 1) when $\omega_1 \rightarrow 1$ to the Dullien model[15] for neat solvent diffusion.

In the next section, the validity of eq 7 is examined by determining ξ from knowledge of the T-dependence of polystyrene coil dimensions and comparing the value to that evaluated from solvent self- and mutual-diffusion data measured in concentration regimes strictly applicable to free-volume models. Since previous predictions of $D(\omega_1 \rightarrow 1)$ are in excellent agreement with experimental data (see Table 1), initial focus is placed on measuring the temperature dependence of $D(\omega_1 \rightarrow 1)$ and determining ξ directly from eq 5.

Results and Discussion

Infinite dilution mutual-diffusion coefficients for a binary solution consisting of polystyrene mixed with toluene have been measured by photon correlation spectroscopy and forced Rayleigh scattering as a function of temperature. The results are illustrated in Figure 1 in a form conducive for analysis using eq 5 and literature values[32] of toluene viscosity. The diffusion coefficient data are provided, for convenience, in Table 2.

The value for ξ, calculated from the slope of a linear least-squares regression fit through the data shown in Figure 1, is 0.66. This value is somewhat higher than that obtained from analysis of the concentration and temperature dependence of toluene self-diffusion in concentrated polystyrene solutions[33] ($\xi = 0.575$), although it agrees well with values previously reported from other predictive schemes[34] ($\xi = 0.62$). Two astonishing results are therefore noted: (1) the values of ξ determined in concentrated polymer solutions and in the infinite solvent dilution limit are comparable and (2) the scaling relationship followed by $D_2(\omega_1 \rightarrow 1)$ differs from that suggested by the Stokes–Einstein model.

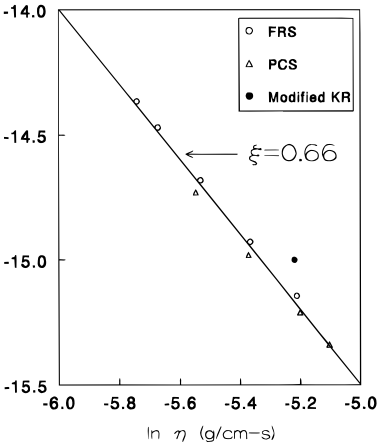

Figure 1. Experimental data and free-volume theory correlations of toluene/polystyrene mutual-diffusion coefficients in infinitely dilute polystyrene solutions. The ratio of toluene to polystyrene jump size units (ξ) is determined from the inverse slope of the correlation fit (see eq 5).

Table 2. Polystyrene/Toluene Infinite Dilution ($\omega_1 \rightarrow 1$) Binary Mutual-Diffusion Data Measured by Photon Correlation Spectroscopy and Forced Rayleigh Scattering

T (K)	D (cm²/s)	T (K)	D (cm²/s)
288.15	2.18×10^{-7}	331.22	4.21×10^{-7}
296.45	2.48×10^{-7}	333.15	4.01×10^{-7}
297.45	2.65×10^{-7}	350.15	5.20×10^{-7}
312.55	3.29×10^{-7}	360.65	5.77×10^{-7}
313.15	3.12×10^{-7}		

The fact that eq 5 can be employed successfully to correlate diffusion data and yields ξ values which are consistent with literature values implies that eq 2 is applicable in modeling polymer self-diffusion. Whether the concentration, temperature, and molecular weight dependence of D_{02} (see eq 2) can be accurately represented by a single theory, however, remains to be seen.

As a confirmation of the diffusion data, the modified Kirkwood–Riseman model (eq 6) is applied to predict D at infinite dilution at 25 °C for a polystyrene sample of weight- and number-average molecular weights 299 and 294 kDa, respectively. The values of η_1 and α_f used in the calculation[4,32] were 5.66×10^{-3} g/cm-s and 1.2716, respectively, while $(\langle r_0^{\,2}\rangle/M_2)^{0.5}$ was taken[35] as 0.67×10^{-8} cm. The $D(\omega_1 \rightarrow 1)$ prediction at 25 °C is included in Figure 1 and is in good agreement with the experimental data.

A comparison of the predicted $D(\omega_1 \rightarrow 1)$ molecular weight dependence with experimental values is provided in Table 1 for the toluene/polystyrene system. Molecular weight enters the calculation (eq 6) both explicitly, through M_2, and implicitly through α_f. The molecular weight dependence of α_f is accounted for within the Yamakawa–Tanaka formalism[4] and is employed here. The agreement between measured $D(\omega_1 \rightarrow 1)$ and theoretical predictions is excellent, confirming the conclusion reached in an earlier investigation.[30]

In order to employ eq 7 to estimate ξ, knowledge of the temperature dependence of the rms distance is required. Between the range of 34 and 70 °C, the temperature dependence of the unperturbed rms end-to-end distance is estimated to be[36]

$$\left(\frac{\langle r_0^{\,2}\rangle}{M_2}\right)^{0.5} = -2.039334 \times 10^{-11}T\,[\mathrm{K}] + 1.350950 \times 10^{-8} \qquad (8)$$

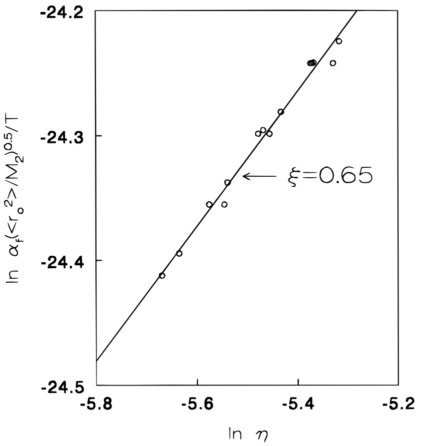

Figure 2. Estimation of ξ from the temperature dependence of the rms end-to-end distance (see eq 7). The value obtained here is nearly identical to that evaluated from diffusion coefficient data (see Figure 1).

while the temperature dependence of the expansion factor can be estimated from the Flory swelling equation[37]

$$\alpha_f^{\,5} - \alpha_f^{\,3} = 2\psi_1 C_m\left[1 - \frac{\Theta}{T}\right]M_2^{\,0.5} \tag{9}$$

For toluene/polystyrene solutions θ and ψC_m have been evaluated to be 160 K and 0.0030, respectively.[37] Employing eqs 8 and 9 in conjunction with eq 7 yields the result illustrated in Figure 2. The value of ξ can be determined from the slope of a line through the data (see eq 7) and is found to be 0.65, which is nearly identical to that evaluated previously from analysis of diffusion coefficient data.

The consistency with which ξ has been evaluated with both diffusion data and with knowledge of the temperature dependence of the rms end-to-end distance implies the validity of both eqs 5 and 7. Since the dimensions of a polymer in solution reflect its compatibility with the surrounding solvent matrix, eq 7 reflects an explicit means by which thermodynamic interactions are addressed within free-volume theory. Further investigations, however, are necessary to ascertain whether this result is generally true or simply fortuitous.

Conclusions

Forced Rayleigh scattering and photon correlation spectroscopy have been employed to measure infinite dilution binary mutual-diffusion coefficients for the polystyrene/toluene system. The ratio of solvent to polymer jump size units (ξ) could be determined from the Vrentas−Duda free-volume diffusion model for polymer self-diffusion, since mutual-diffusion and polymer self-diffusion coefficients are numerically identical in this concentration limit. The resulting ξ value is in good agreement with estimates determined from solvent self-diffusion and binary mutual-diffusion coefficient data available in the literature and with values assessed from predictive schemes. The effect of entanglements on the transport process could be neglected since diffusion coefficients were measured in the pure solvent limit.

Since $D(\omega_1 \rightarrow 1, T)$ is accurately represented by the free-volume formalism (eq 2), which predicts a scaling relationship contradicting that suggested by the Stokes−Einstein equation, the model (at $\omega_1 \rightarrow 1$) was equated to the Kirkwood−Riseman theory, modified for diffusion at infinite dilution under non-Θ conditions. This comparison reveals that ξ follows the temperature dependence of the root-mean-squared end-to-end distance and establishes a theoretical coupling between thermodynamic interactions, Brownian dynamics, and free-volume theory. The proposed relationship provides a means by which ξ can be evaluated without prior knowledge of any diffusion data, thereby extending predictive capabilities of the free-volume theory for diffusion in polymeric media. The accuracy with which D can be predicted using this approach, however, has yet to be examined.

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