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# Dependence of the Solvent Diffusion Coefficient on Concentration in Polymer Solutions

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ABSTRACT: Self-diffusion coefficients of several different solvents in polystyrene as well as methyl methacrylate in poly(methyl methacrylate) have been determined at polymer concentrations from 0 to 50 wt % at 25 °C. The solvents used for the polystyrene solutions were toluene, ethylbenzene, cumene, *tert*-butyl acetate, chloroform, and methyl ethyl ketone. The diffusion data were used to evaluate several theories for the concentration dependence of the solvent diffusion coefficients, and in most cases the reduced diffusion coefficients, of solvents in polymer–solvent systems. In addition to the experimental data presented here, literature data for several systems were also used to test the models. The theories evaluated were based on widely different concepts including electrical conductivity, tortuosity, kinetic theory, and free volume. The results indicate that the kinetic theory and free-volume approaches fit the data most consistently, with the kinetic theory approach preferred at lower polymer concentrations and the free-volume approach favored at higher polymer concentrations.

## Introduction

Diffusion of small molecules in polymer solutions is often important in a variety of processes including polymer processing,[1,2] polymerization kinetics,[3–5] drug delivery,[6] and drying of coatings.[7] It would be useful in many of these areas if the diffusion coefficient of a particular molecule at a particular concentration and temperature could be determined easily without having to measure the value experimentally. We have found, to a first approximation, the concentration dependence in the 0–50% polymer range can be predicted from knowledge of the diffusion coefficient of the pure solvent[8–10] for single-solvent polymer systems. However, for more detailed knowledge of these dependencies, or use at higher concentrations, experimental measurements appear to be required.[10] To help describe solvent diffusion, models based on electric conductivity by Maxwell[11] and Fricke[12] and on tortuosity in a simple cubic lattice model by Mackie and Meares[13] have been used[10,12,14] because they offer a simple dependence of the reduced diffusion coefficient on the polymer volume fraction. While such a simple dependence is sought, these approaches do not account for subtle differences observed in experimental data. In this paper, we will explore two models which much more accurately describe the diffusion data.

The first model is based on the modified Enskog theory,[15] which uses kinetic theory and accounts for momentum transfer between rigid spheres. This theory gives a rather involved dependence of the solvent diffusion coefficient on concentration. The second theory can be used to predict the dependence of the reduced diffusion coefficient on polymer weight fraction from Vrentas–Duda free-volume theory.[16,17] This results in a simple expression with one fittable parameter for systems in which a variety of parameters are known. We will examine the effectiveness of these two theories for describing the concentration dependence of solvent diffusion coefficients by fitting the proposed equations to our own experimental data as well as experimental data taken from the literature.

## Experimental Section

**Pulsed-Gradient Spin-Echo NMR.** The diffusion measurements were performed using the PGSE-NMR technique.[9,18,19] In this technique, a spin-echo experiment is performed, and in between the radio-frequency (RF) pulses, magnetic field gradient (MFG) pulses are applied. The MFG pulses result in an attenuation of the echo amplitude. The resulting echo amplitude is given by the relationship

$$A = A_0 \exp(-\tau/T_2) \exp(-\gamma^2 G^2 D \beta) \qquad (1)$$

where $A$ is the echo amplitude, $\tau$ is the time between the RF pulses, $T_2$ is the spin–spin relaxation time, $\gamma$ is the magnetogyric ratio which is constant for a given type of nucleus, $G$ is the strength of the magnetic field gradient, $D$ is the self-diffusion coefficient, and $\beta = \delta^2(\Delta - \delta/3)$, with $\delta$ being the width of the gradient pulse and $\Delta$ the time from the start of the first gradient pulse to the second. If an array of experiments with varying values of $\delta$ are done, the self-diffusion coefficient of each component can be determined as long as a unique resonance, for that component, can be resolved. This is accomplished by plotting the natural logarithm of the amplitude of a resonance for the compound in question versus $\beta$. The slope of the resulting line is proportional to its diffusion coefficient. Since the slope of this line is also proportional to $\gamma$, the most convenient nuclei (largest $\gamma$) for diffusion studies are protons which were observed. Experiments were performed on a Varian VXR-200 which we have modified for diffusion studies.[20–22] Typical gradients used were 0.16 T/m, with pulse widths ($\delta$) up to 5 ms and echo times ($2\tau$) of 200 ms. Often the polymer and solvent resonances did not overlap, so that the solvent self-diffusion coefficients were easily obtained. In the case of overlap, echo times 200 ms were sufficient to remove the polymer signals from the spin-echo spectra due to the relatively short $T_2$ relaxation times of the polymers.

**Materials.** PS (Aldrich Chemical Co., Milwaukee, WI) with a molecular weight of 280 000 was used. The solvents used were *tert*-butyl acetate (Aldrich); chloroform, methyl ethyl ketone, and toluene (Fisher Scientific, Fair Lawn, NJ); and ethylbenzene and cumene (Eastman Kodak Co., Rochester, NY). Toluene, ethylbenzene, and cumene are similar chemically, while chloroform, methyl ethyl ketone (MEK), and *tert*-butyl acetate vary in size as well as polarity. To ensure that the observed behavior was not limited to PS systems, the diffusion of methyl methacrylate (MMA) in poly(methyl methacrylate) (PMMA) was also studied (both from Aldrich). The molecular weight of PMMA was 12 500, and polymer concentrations between 0 and 50% were studied for these systems. All materials were used as received. All of the experimental results reported for these systems are the average of multiple (two to five) runs.

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**Table I. Experimental Data for Diffusion of Ethylbenzene, Toluene, Cumene, *tert*-Butyl Acetate, Chloroform, and Methyl Ethyl Ketone in 280 000 MW Polystyrene at 25 °C**

| ethylbenzene | | toluene | | cumene | | *tert*-butyl acetate | | chloroform | | methyl ethyl ketone | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| wt % PS | $D^a$ | wt % PS | $D^a$ | wt % PS | $D^a$ | wt % PS | $D^a$ | wt % PS | $D^a$ | wt % PS | $D^a$ |
| 0.0 | 17.9 | 0.0 | 21.6 | 0.0 | 13.7 | 0.0 | 13.6 | 0.0 | 22.9 | 0.0 | 33.2 |
| 8.40 | 14.4 | 9.10 | 16.4 | 8.37 | 10.9 | 8.01 | 11.5 | 13.7 | 14.3 | 10.0 | 27.8 |
| 17.8 | 11.1 | 18.5 | 13.4 | 19.6 | 6.94 | 22.2 | 8.27 | 23.2 | 9.59 | 20.1 | 21.1 |
| 26.0 | 9.52 | 26.1 | 11.0 | 29.0 | 4.90 | 27.3 | 5.87 | 32.2 | 6.01 | 29.9 | 16.4 |
| 38.0 | 5.01 | 39.4 | 6.19 | 38.4 | 2.60 | 35.3 | 3.98 | 37.2 | 4.43 | 35.9 | 14.0 |
| 42.4 | 4.40 | 46.7 | 3.42 | 50.9 | 1.42 | 43.8 | 2.24 | 44.6 | 2.38 | 42.4 | 10.6 |
| | | | | | | 49.7 | 1.19 | | | 49.6 | 8.52 |

[a] $\times 10^{10}$ ($m^2/s$).

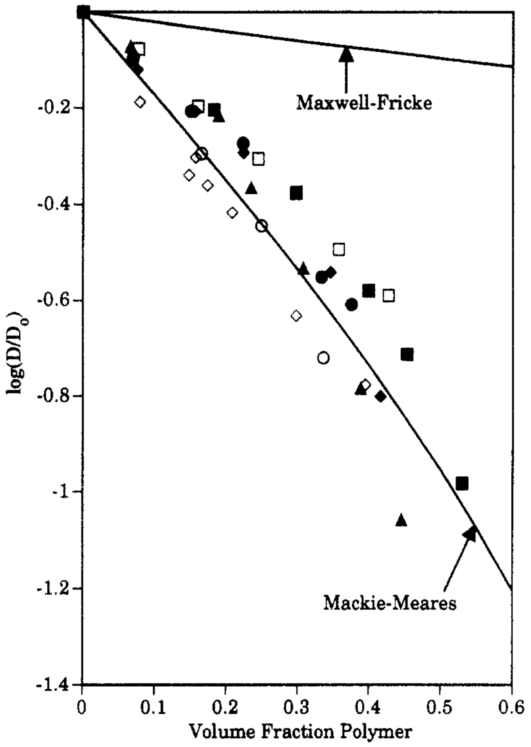

**Figure 1.** Solvent self-diffusion coefficient data and comparison with the predictions of the Maxwell–Fricke and Mackie–Meares models: (◆) toluene–PS, (●) ethylbenzene–PS, (○) cumene–PS, (▲) *tert*-butyl acetate–PS, (□) methyl ethyl ketone–PS, (■) chloroform–PS, (△) methyl methacrylate–PMMA.

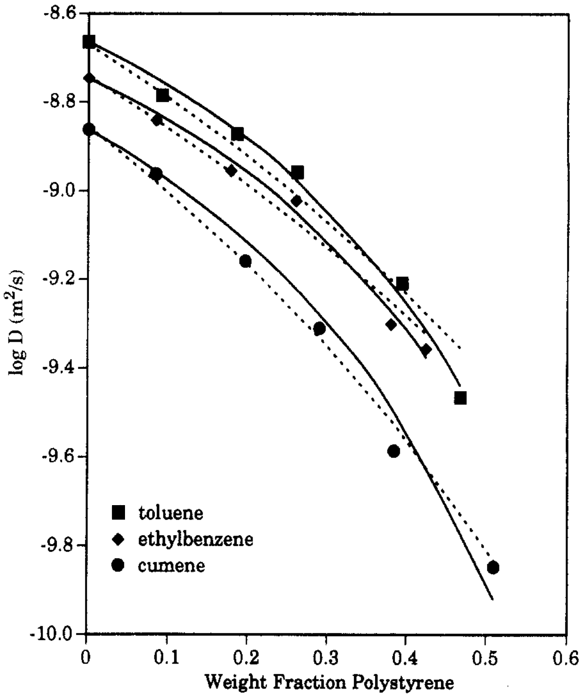

**Figure 2.** Logarithmic plot of solvent diffusion data along with best fits to free-volume (—) and kinetic theory (···) models.

**Literature Data.** To broaden the scope of this study, data were also taken from the literature and fit with the two theories. The literature data were for methyl ethyl ketone in PMMA (MW 960 000),[23] methyl ethyl ketone in poly(*n*-butyl methacrylate) (PBMA; MW 450 000),[24] toluene in poly(vinyl acetate) (PVA; MW 500 000),[25] tetrahydrofuran in PS (MW 540 000), and tetrahydrofuran in polyisoprene (PIP; MW 253 000).[26] The last three systems were studied by forced Rayleigh scattering (FRS) using methyl red as a tracer.

The least-squares fits for the free-volume approach were done using *Delta Graph Professional* (DeltaPoint Inc., Monterey, CA) which uses the Levenberg–Marquardt method to fit the data. For the kinetic theory approach, *Mathematica* (Wolfram Research, Champaign, IL) was used for data fitting.

## Results

Diffusion experiments were performed on the polymer–solvent systems at 25 °C and polymer weight fractions between 0 and 0.50. The results of these measurements are given in Table I. Figure 1 shows the reduced diffusion coefficients of these systems plotted as a function of polymer volume fraction. Also shown in Figure 1 are the predictions of the Maxwell–Fricke model and the Mackie–Meares model for the dependence of the diffusion coefficient on polymer volume fraction. We remind the reader that plotting $\log(D/D_0)$ has the effect of emphasizing the differences between the different systems, whereas plotting $D/D_0$ highlights the similarities in the different systems.[8,10]

In order to compare the predictive ability of the models, best fits to the data for the free-volume and kinetic theory models are shown in Figures 2–7 along with the experimental data. Figure 2 shows the data for toluene, ethylbenzene, and cumene in PS. These three solvents are very similar chemically. The solvent self-diffusion coefficient decreases with increasing molecular size at any given concentration. The data for toluene is somewhat lower than previously reported.[10,27] A similar trend is seen in Figure 3 for MMA and MEK in PMMA.

The diffusion results for MEK, chloroform, and *tert*-butyl acetate in PS are shown in Figure 4. Since both the solvent size and structure are varied for this group, results different from Figures 2 and 3 are seen. Chloroform is the smallest molecule of the three solvents (but the heaviest); its diffusion coefficient is much lower than MEK's at all concentrations. In addition, as the polymer concentration increases, the chloroform data show a markedly different concentration dependence. These effects are probably the result of chloroform's different structure and polarity compared to the other solvents.

The effect of varying the polymer for a given solvent, in this case MEK in PS, PMMA, or PBMA, is shown in Figure 5. The log $D$ values in this plot have been adjusted to spread the data out for ease of viewing. An explanation of the adjustment is given in the figure caption. This plot

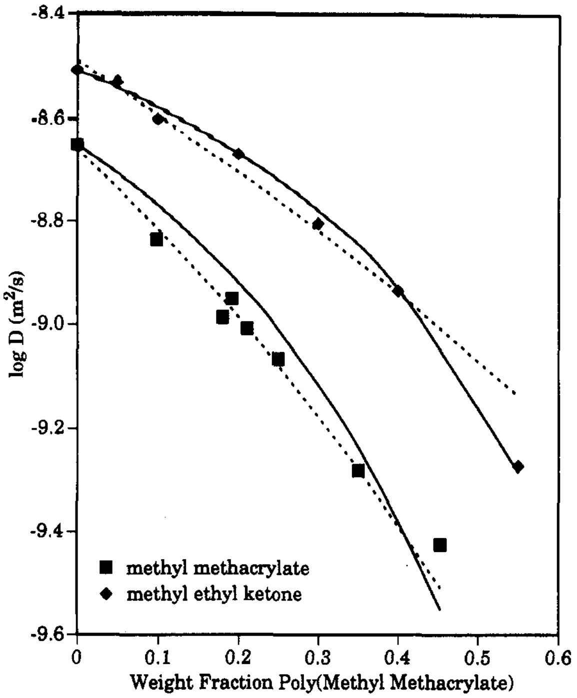

**Figure 3.** Fits to data for methyl methacrylate and methyl ethyl ketone in poly(methyl methacrylate). Solid lines represent free-volume fits; dashed lines represent kinetic theory fits.

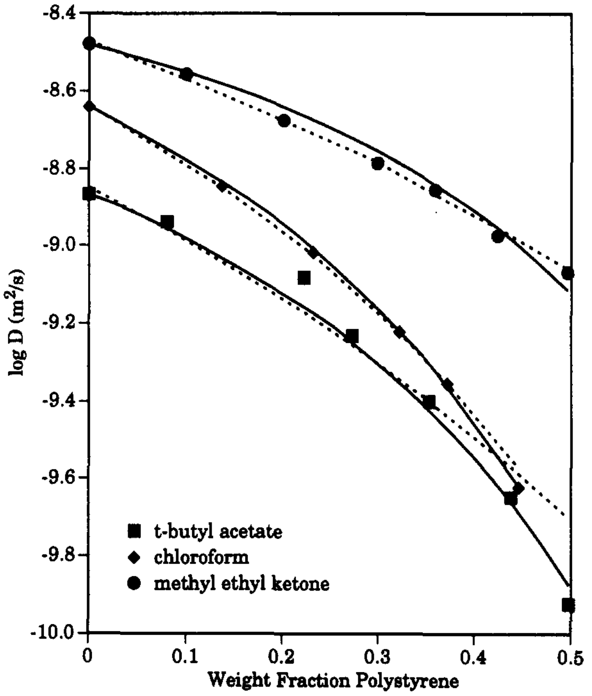

**Figure 4.** Fits to experimental data for nonaromatic solvents in polystyrene. Solid lines represent free-volume fits; dashed lines represent kinetic theory fits.

shows that the polymer has a significant effect on the concentration dependence of solvent diffusion. Figures 6 and 7 contain the FRS data showing that both the kinetic and free-volume theories are not limited in their application to data produced by NMR measurements. Figure 6 also shows a dependence on the polymer similar to that observed in Figure 5.

## Discussion

**Maxwell-Fricke Model.**[11,12] The Maxwell–Fricke model is based on electric conductivity and permeability. It assumes immobile, impenetrable species suspended in a mobile solvent continuum. The Maxwell–Fricke model predicts the maximum reasonable diffusion coefficient in the presence of obstructions when the obstructions are spheres.[10,14] Assuming this theory holds even for relatively small polymer segments which are immobile relative to the solvent, the Maxwell–Fricke equation is[10,14,28]

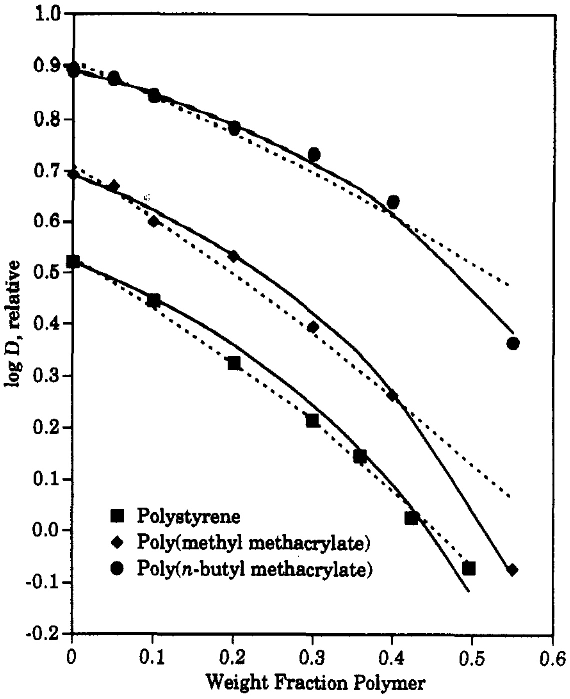

**Figure 5.** Fits for MEK in PS, PMMA, and PBMA. The log $D$ values have been adjusted to spread the data out for ease of viewing. In each case the closest tic marks to log $D_0$ (i.e., 0.9 for MEK/PBMA, 0.7 for MEK/PMMA, and 0.5 for MEK/PS) corresponds to a log $D$ value of −8.5. Solid lines represent free-volume fits; dashed lines represent kinetic theory fits.

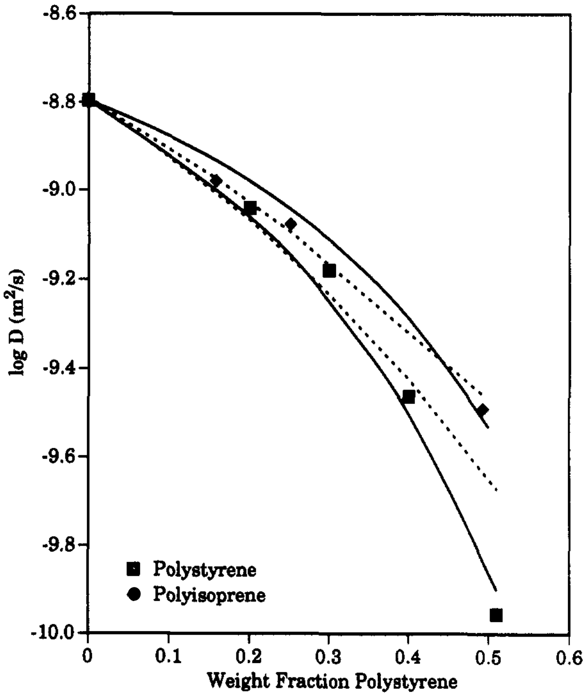

**Figure 6.** Fits to forced Rayleigh scattering data.[26] Solid lines represent free-volume fits; dashed lines represent kinetic theory fits.

$$\frac{D(1-\phi)}{D_0} = \frac{1-\phi'}{1+\phi'/\chi} \qquad (2)$$

where $D$ is the diffusion coefficient, $D_0$ is the diffusion coefficient of the pure solvent, $\phi$ is the polymer volume

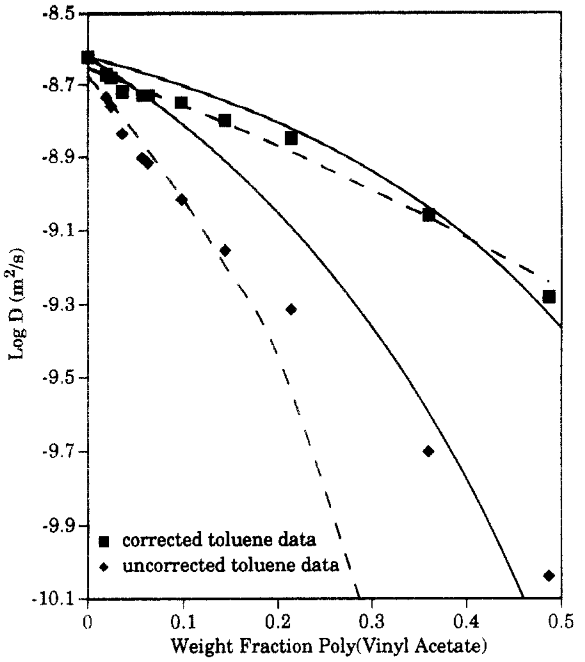

**Figure 7.** Fits to Lodge's[25,41] toluene–poly(vinyl acetate) FRS data: (◆) data displaying the hydrogen-bonding effect; (■) data with the hydrogen-bonding effect removed. Solid lines represent free-volume fits; dashed lines represent kinetic theory fits.

fraction, $\phi'$ is the volume fraction of polymer plus and "nondiffusing" solvent, and $\chi$ is the shape factor (ranging from 1.5 for rods to 2.0 for spheres). If we assume $\phi = \phi'$, eq 2 becomes[10]

$$\frac{D}{D_0} = \frac{1}{1 + \phi/\chi} \tag{3}$$

Equation 3 is the form of the Maxwell–Fricke model plotted in Figure 1. As can be seen, this model severely overestimates the diffusion coefficient and the fit is worse at higher concentrations. However, if one allows for some nondiffusing or bound solvent, eq 2 has been shown to effectively fit diffusion data as well as estimate the amount of nondiffusing solvent.[29] This approach differs from the other approaches presented in this work in that in order to fit the data the solvent needs to be partitioned into two fractions.

**Mackie–Meares Model.**[10,13,14] The Mackie–Meares model is based on tortuosity (the increased path length between two points due to obstructions) and the simple cubic lattice model and similar size sites for the solvent and polymer segments.[10,13,14]

$$\frac{D}{D_0} = \frac{(1 - \phi)^2}{(1 + \phi)^2} \tag{4}$$

The Mackie–Meares model does a reasonable job of fitting the experimental data in Figure 1. While to a first approximation the data are fairly well fit, there are subtle differences between the various systems that this model does not account for. Thus, even though this equation contains a simple dependence on polymer concentration, further models which allow for system-dependent variations are required for accurate modeling.

**Modified Enskog Model.**[10,15] As stated previously this is based on kinetic theory and takes into account momentum transfer between rigid spheres. It was developed to describe diffusion of liquids and gases in membranes, but the equations fit solution diffusion data quite well. The diffusion coefficient of a tracer molecule in a polymer solution is described by the equation[15]

$$D_t = \frac{1}{\dfrac{1}{D_{tM}} + \dfrac{1}{D_{ts}}\left[1 - x_t\left(1 - \dfrac{D_{sM}}{D_{tM}}\right)\right]} \tag{5}$$

where $D_t$ is the self-diffusion coefficient of the tracer molecule, $D_{tM}$ is the mutual diffusion coefficient of the tracer with respect to the polymer, $D_{ts}$ is the mutual diffusion coefficient of the tracer with respect to the solvent, $D_{sM}$ is the mutual diffusion coefficient of the solvent with respect to the polymer, and $x_t$ is the mole fraction of tracer in solution. For a system where $x_t$ is very small or where the tracer and the solvent are the same, eq 5 reduces to

$$\frac{1}{D_t} = \frac{1}{D_{tM}} + \frac{1}{D_{ts}} \tag{6}$$

This situation will hold true for all of our experimental data. For the FRS data, the tracer mole fraction was on the order of $10^{-4}$–$10^{-5}$.[25,26] For NMR diffusion measurements, the second condition holds where $D_{sM} = D_{tM}$. The respective mutual diffusion coefficients are expressed as[15]

$$D_{\alpha\beta} = \frac{3}{8n\sigma_{\alpha\beta}^2}\left[\frac{kT(m_\alpha + m_\beta)}{2\pi m_\alpha m_\beta}\right]^{1/2} \frac{1}{g_{\alpha\beta}(\sigma_{\alpha\beta})} \tag{7}$$

Here the subscripts $\alpha$ and $\beta$ are generic subscripts for t, s, and M in eqs 5 and 6, $n$ is the number of molecules per milliliter, $\sigma_{\alpha\beta}$ is the hard-sphere collision radius of components $\alpha$ and $\beta$ which is the sum of the radii of the two components, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $m_i$ is the molecular mass of component $i$, and $g_{\alpha\beta}(\sigma_{\alpha\beta})$ is the rigid-sphere contact radial distribution function. This distribution function is obtained from scaled particle theory[15]

$$g_{\alpha\beta}(\sigma_{\alpha\beta}) = \frac{1}{1 - \xi_3} + \frac{6\xi_2}{(1 - \xi_3)^2}\left(\frac{R_\alpha R_\beta}{R_\alpha + R_\beta}\right) + \frac{12\xi_2^2}{(1 - \xi_3)^3}\left(\frac{R_\alpha R_\beta}{R_\alpha + R_\beta}\right)^2 \tag{8}$$

where

$$\xi_i = \frac{\pi}{6}\sum_{j=1}^{\nu} n_j (2R_j)^i \tag{9}$$

$\nu$ is the number of components in solution. The $j$'s are the components $\alpha$, $\beta$, or $\gamma$. Therefore, $n_j$ is the number of molecules per milliliter of component $j$, and $R_j$ is the molecular radius of component $j$.

The diffusion coefficient of component $\alpha$ with respect to the polymer molecule is $D_{\alpha M}$. However, the solvent and tracer molecules do not interact with an entire polymer chain at one time. Consequently, it is appropriate to scale the diffusion coefficient with respect to part of the chain, the example, an individual monomer unit, $D_{\alpha m}$[15]

$$D_{\alpha M} = nD_{\alpha m}/n_m \tag{10}$$

where $n_m$ is the number of monomer units per milliliter. Substitution of eqs 7–10 into either eq 5 or 6 gives a rather complicated dependence of the tracer diffusion coefficient on concentration. The resulting equation is a function of known constants (the molecular mass of each component, $m_j$), concentration terms (the number of molecules per millimeter, $n$; the number of molecules per millimeter of tracer, $n_t$; the number of molecules per millimeter of solvent, $n_s$; and the number of monomer units per

**Table II. Results of the Kinetic Theory Fit**

| system | diameter (nm) | |
|---|---|---|
| | solvent | monomer |
| toluene–PS | 0.572 | 0.666 |
| ethylbenzene–PS | 0.604 | 0.662 |
| cumene–PS | 0.641 | 0.680 |
| *tert*-butyl acetate–PS | 0.624 | 0.674 |
| chloroform–PS | 0.506 | 0.704 |
| MEK–PS | 0.520 | 0.650 |
| MEK–PBMA | 0.523 | 0.704 |
| MEK–PMMA | 0.522 | 0.538 |
| MMA–PMMA | 0.566 | 0.573 |
| THF–PS | 0.449 | 0.670 |
| THF–PIP | 0.393 | 0.573 |
| toluene–PVA (corrected) | 0.562 | 0.579 |
| toluene–PVA (raw data) | 0.478 | 0.742 |

millimeter, $n_m$), and the molecular radii of each component which are used as fitted parameters. To obtain the fits to the data shown in Figures 2–7, a nonlinear least-squares fit to eq 6 was performed, yielding values of the radii.

As can be seen from the plots, the Enskog theory does an excellent job of fitting the experimental data and accounting for the differences in solvents which the Mackie–Meares model did not. The plots show that the modified Enskog model fits the data best at the lower polymer concentrations; however, at higher concentrations in several systems, the fit diverges from the experimental data. In the toluene–PS, *tert*-butyl acetate–PS, MEK–PMMA, MEK–PBMA, and THF–PS systems, the modified Enskog fit deviates significantly from the experimental data at higher polymer concentrations. This is expected because it was assumed the solvent molecules and the polymer segments are rigid spheres that collide. At higher polymer concentrations, the polymer chains are closer and the solvent molecules may interact with more than one segment at a time. In addition, the polymer segments may not be able to move independently.

The solvent diameters and monomer segment diameters obtained from these fits are listed in Table II. These results are all reasonable sizes for the solvent molecules and monomer segments; however, the variation in size for PS, PMMA, and THF for different systems is higher than expected. In the cases of PS and PMMA these variations could indicate that solvent molecules are interacting with more than one monomer unit at a time.

The modified Enskog theory does not yield a simple dependence of diffusion coefficient on concentration. It does provide an experimental way to estimate solvent molecular size, or, alternatively, if this information is available elsewhere, this theory could be used as a predictive method for diffusion concentration dependence. Table III contains molecular volumes determined by group contribution methods which could be used as a source of molecular diameters. Diameters obtained from these volumes by assuming the molecules are spherical are significantly larger than the diameters determined from the fits, given in Table II. None of the molecules in question are nearly spherical in shape, and this approximation apparently overestimates the collision contact radius for these molecules. Zhu and Macdonald[30] have successfully treated the diffusion of nonspherical solvent molecules in polymer systems.

**Free-Volume Theory.**[10,16,17] Some of the problems noted with the kinetic theory approach, such as isolated free volume and interaction with more than one monomer unit, are taken into account in a free-volume approach. The Vrentas–Duda free-volume theory[16,17] gives the concentration dependence of the diffusion coefficient as

$$D = D_{01}\exp\left[\frac{-E}{RT}\right]\exp\left[\frac{-(\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*)}{\left(\frac{K_{11}}{\gamma}\right)\omega_1(K_{21} - T_{g1} + T) + \left(\frac{K_{12}}{\gamma}\right)\omega_2(K_{22} - T_{g2} + T)}\right] \tag{11}$$

where $D_{01}$ is the preexponential factor, $E$ is the energy of activation for a solvent jump, $R$ is the gas constant, $T$ is the absolute temperature, $\omega_i$ is the weight fraction of component $i$ (1 is for the solvent and 2 is for the polymer), $\hat{V}_i^*$ is the specific volume needed for one jumping unit of component $i$ to make a jump, $\xi$ is the ratio of the volume of the solvent jumping unit to the polymer jumping unit which is not necessarily the same as the volume of one monomer segment, $K_{11}/\gamma$ and $K_{21} - T_{g1}$ are solvent free-volume parameters, and $K_{21}/\gamma$ and $K_{22} - T_{g2}$ are polymer free-volume parameters.

For a pure solvent eq 11 reduces to

$$D_0 = D_{01}\exp\left[\frac{-E}{RT}\right]\exp\left[\frac{-\hat{V}_1^*}{\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T)}\right] \tag{12}$$

Combining eqs 11 and 12 gives

$$\frac{D}{D_0} = \exp\left\{\left[\frac{-(\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*)}{\left(\frac{K_{11}}{\gamma}\right)\omega_1(K_{21} - T_{g1} + T) + \left(\frac{K_{12}}{\gamma}\right)\omega_2(K_{22} - T_{g2} + T)}\right] - \left[\frac{-\hat{V}_1^*}{\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T)}\right]\right\} \tag{13}$$

Assuming that $(K_{11}/\gamma)\omega_1(K_{21} - T_{g1} + T) \gg (K_{12}/\gamma)\omega_2(K_{22} - T_{g2} + T)$, which should be true at low polymer concentrations, eq 13 can be rearranged to give

$$\frac{D}{D_0} = \exp\left[\frac{-\omega_2\xi\hat{V}_2^*}{\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T)(1 - \omega_2)}\right] \tag{14}$$

Since there is much more free-volume per unit volume in a solvent than in a polymer,[31] the assumption made to get eq 14 should hold up to approximately 50% polymer. By this point the total free volume provided by the solvent will have been reduced to the point that the polymer free volume must be considered. The exponent in eq 14 is the free volume needed for a polymer segment to jump divided by the free volume available in the solvent.

At lower polymer concentrations (<50%) it is useful to rewrite eq 14 as

$$\log\left(\frac{D}{D_0}\right) = \frac{A\omega_2}{(1 - \omega_2)} \tag{15}$$

where

$$A = \frac{-\xi\hat{V}_2^*}{2.303\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T)} \tag{16}$$

This is a different functional form than those previously proposed, with $A$ being the only system-dependent parameter. Values for $K_{11}/\gamma$ and $K_{21} - T_{g1}$ for many solvents

**Table III. Results of Free-Volume Fits**

| system | $A$ | $\xi$[a] | vol[b] (nm$^3$) solvent | vol[b] (nm$^3$) monomer unit | monomer units per jumping unit[a] |
|---|---|---|---|---|---|
| toluene–PS | −0.884 | 0.781 | 0.140 | 0.147 | 1.22 |
| ethylbenzene–PS | −0.855 | 0.738 | 0.167 | 0.147 | 1.54 |
| cumene–PS | −1.02 | 1.20 | 0.187 | 0.147 | 1.06 |
| *tert*-butyl acetate–PS | −1.02 | 0.647 | 0.171 | 0.147 | 1.80 |
| chloroform–PS | −1.22 | 0.507 | 0.101 | 0.147 | 1.35 |
| MEK–PS | −0.644 | 0.477 | 0.108 | 0.147 | 1.54 |
| MEK–PBMA | −0.416 | 0.308 | 0.108 | 0.201 | 1.75 |
| MEK–PMMA | −0.636 | 0.509 | 0.108 | 0.131 | 1.62 |
| MMA–PMMA | −1.09 | 1.583 | 0.145 | 0.131 | 0.700 |
| THF–PS | −1.06 | 2.23 | 0.108 | 0.147 | 0.330 |
| THF–PIP | −0.736 | 1.37 | 0.108 | 0.113 | 0.699 |
| toluene–PVA (corrected) | −0.746 | 0.746 | 0.140 | 0.107 | 1.75 |
| toluene–PVA (raw data) | −1.73 | 1.73 | 0.140 | 0.107 | 0.757 |

[a] $\xi$ and the number of monomer units per jumping unit were determined from $A$. [b] The solvent and monomer unit volumes were calculates from group contribution methods.[33]

are available from the literature. In cases where these parameters are not available from the literature, they can be calculated from temperature-dependent viscosity data for the solvent.[17] Such data are readily available for many systems.[32] $\hat{V}_2^*$ is the volume needed per gram of polymer for a polymer jumping unit to jump, and this is equivalent to the polymer specific volume at 0 K which can be calculated from group contribution methods.[33] With the values for these parameters, when $A$ is determined by fitting eq 15 to experimental data, $\xi$ can be determined. Molecular volumes can be calculated from $\hat{V}_1^*$ and $\hat{V}_2^*$; then using the experimentally determined $\xi$, the number of monomer segments in a polymer jumping unit can be determined.

In contrast, past applications of free-volume theory to the concentration dependence of the reduced diffusion coefficient[24,30,34-36] have started with the free-volume theory of Fujita[37] and Doolittle.[38] This approach has been shown to yield a linear relationship between $\log(D/D_0)$ and $1/\phi_1$[24,30] or $1/\log(D/D_0)$ and $1/\phi_1$.[34,36] In some cases, pure polymer rather than pure solvent was used as the reference state;[34,35] however, in these instances there was a significant difference between experimental data and theory at high solvent concentrations. This was attributed to deviations from free-volume theory at high solvent concentrations.[34,35] While this approach can lead to values for free-volume parameters for the system, it does not give information on the size of the polymer jumping unit which we can get from the Vrentas–Duda theory.

The fits of eq 15 to the experimental data are shown as the solid curves in Figures 2–7. As stated above $\log D$ was plotted rather than $\log(D/D_0)$ for ease of viewing. Equation 15 appears to describe the experimental data well, in fact in several cases better than the modified Enskog theory. However, at lower polymer concentrations this free-volume approach does not fit the data as well as the kinetic theory approach. This is because at very low polymer concentrations excluded volume does not play as significant a role as collisions between the solvent molecules and the polymer chains.[34,35] Table III shows the $A$'s and $\xi$'s determined from the fits as well as the number of monomer units per polymer jumping unit.

The free-volume approach does give a relatively simple dependence of the diffusion coefficient on concentration and accounts for differences between systems. Although this method is unable to be completely predictive, the experimental results indicate that $A$ will be close to −1. Most of the experimental values for $A$ shown in Table III range from −1.2 to −0.4. Table III also gives the number of monomer units per polymer jumping unit determined from the experimental fits. For the most part, the values seem reasonable, indicating that between one and two monomer units are involved in a jumping unit and that this varies somewhat for a given polymer depending on the solvent. The variation of the polymer jumping unit for solvents in the same polymer might be consistent with chain motions occurring with a broad range of torsion angle jumps rather than the same set jump each time (say 120°). This type of chain motion has also been observed in the bulk atactic polypropylene[39] and polystyrene[40] near the glass transition temperature by deuterium 2D exchange NMR.

Some of the systems studied yielded jumping units of less than one monomer unit such as PMMA in MA (0.70), PS in THF (0.33), and PIP in THF (0.699). For longer mers such as those in polyisoprene (PIP), not all of the backbone atoms need to be involved in segmental motions. This could account for the lower value found for it. For PMMA, side-chain motions may account for the jumping unit, possibly explaining the PMMA in MMA jumping unit of 0.70. However, the jumping unit for PMMA in MEK is 1.62 monomers units. This difference in the size of the jumping unit for the same polymer may be due to the way the different solvents interact with the polymer. However, these explanations for jumping units of less than one monomer unit will not work for PS, with only two atoms in the backbone and an aromatic group for a side chain. In determining the monomer units per jumping unit from $\xi$, it was assumed that an entire solvent molecule was the solvent jumping unit. If this is not true, then the results will be distorted. This seems an improbable cause for the extremely small polymer jumping unit in the THF/PS system. The data for this system came from FRS measurements so the diffusion coefficient is actually that of methyl red not THF. However, since the methyl red is at such a low concentration, it should make little difference in the free volume available; it would seem that it would follow the same concentration dependence as the solvent[25,41] (which is responsible for nearly all the free volume). However, if the methyl red would preferentially associate with the polymer, it would show a greater concentration dependence and thus falsely indicate a smaller monomer unit per polymer jump unit.

The assumption that preferential association will result in increased concentration dependence is borne out in Figure 7. Lodge et al.[25,41] have shown that methyl red preferentially binds to poly(vinyl acetate) in a toluene–poly(vinyl acetate) solution via hydrogen bonding. The data shown in Figure 7 are experimentally determined data (squares) and the data with Lodge's correction to

**Table IV. Comparison of Free-Volume and Kinetic Theory Results**

| system | $\lvert\xi_{fv} - \xi_{kt}\rvert$ | $\chi_{kt}{}^{2\,a}$ | $\chi_{fv}{}^{2\,a}$ | best fit[b] |
|---|---|---|---|---|
| toluene–PS | 0.147 | 0.016 2 | 0.003 07 | fv |
| ethylbenzene–PS | 0.022 | 0.006 07 | 0.002 68 | fv |
| cumene–PS | 0.363 | 0.004 69 | 0.015 8 | kt |
| *tert*-butyl acetate–PS | 0.147 | 0.065 4 | 0.009 41 | fv |
| chloroform–PS | 0.136 | 0.002 40 | 0.000 296 | fv |
| MEK–PS | 0.035 | 0.000 918 | 0.004 77 | kt |
| MEK–PBMA | 0.102 | 0.013 9 | 0.001 44 | fv |
| MEk–PMMA | 0.404 | 0.020 2 | 0.001 39 | fv |
| MMA–PMMA | 0.619 | 0.009 56 | 0.042 8 | kt |
| THF–PS | 1.927 | 0.085 3 | 0.009 98 | fv |
| THF–PIP | 1.043 | 0.001 30 | 0.003 58 | kt |
| toluene–PVA (corrected) | 0.168 | 0.005 45 | 0.024 8 | kt |

[a] The $\chi^2$'s are the sums of the squares of the residuals for the kinetic theory (kt) and the free-volume theory (fv) for each fit. [b] The last column indicates which method fits the data best.

remove the hydrogen-bonding effect (diamonds), for the toluene–poly(vinyl acetate) system.[25] Kinetic and free-volume theory fits are shown for both sets of data, and it can be seen that neither theory fits the uncorrected data very well. Table II gives the solvent and monomer radii determined from kinetic theory for both the corrected and the uncorrected data. The uncorrected data give a substantially smaller solvent radius and larger monomer radius. It would be difficult to use this as a test for preferential binding. The free-volume fit results given in Table III are more helpful; here the noncorrected data give a polymer jumping unit of 0.757 monomers, while the data corrected to remove hydrogen-bonding effects yield 1.75 monomer units per jumping unit. The latter value seems much more reasonable and supports the conclusions given above regarding the effect of preferential binding of the tracer on the free-volume fit results. Therefore, preferential binding of the methyl red tracer is likely in the case of THF–PS and possibly in THF–PIP as well.

Diffusion of MEK in PS, PMMA, and PBMA (Figure 5) shows that the polymer has a significant effect on the concentration dependence of solvent diffusion. The free-volume results indicate that, as the polymer jumping unit per monomer unit increases, the decrease in the diffusion coefficient with increasing polymer concentration is reduced. This can be seen since $A$ decreases from PBMA to PS, as does the monomer units per jumping unit. However, the volume of the jumping unit does not follow this trend and neither does the volume of the monomer unit. This indicates that, as longer range chain motions are needed for a polymer jumping unit to jump, the probability that the jumping unit will jump decreases, leaving more free volume available to the solvent.

**Comparisons.** Table IV shows a comparison of the kinetic and free-volume theories. The ratio of the solvent jumping unit volume to polymer jumping unit volume, $\xi$, was determined for the kinetic theory results by calculating volumes from the diameters given in Table II. The absolute value of the difference between this value and $\xi$ determined from the free-volume approach (Table III) is shown in Table IV. The wide range in these values is indicative of a monomer unit and a polymer jumping unit not being equivalent. Table III also shows $\chi^2$, for both fits, for each system. The free-volume approach gave the best fit in 7 of the 12 systems.

## Conclusions

We have shown that a theory must take into account specific system effects in order to describe the diffusion of a solvent in a polymer–solvent mixture in detail. The two theories that take specific system effects into account, the kinetic theory approach and the free-volume approach, can fit the data adequately. Both the kinetic and free-volume theories can follow trends in solvent size and chemical nature as well as the effects of different polymers on the diffusion of one solvent.

Each approach has its advantages and disadvantages. However, both theories fit the data quite well, accounting for differences in solvents and polymers, and each provides unique information about the system. The kinetic theory comes the closest to predicting diffusion coefficients, needing only the radii of the solvent and monomer unit. The free-volume approach, however, gives a relatively simple dependence of the reduced diffusion coefficient on concentration. While it cannot predict the diffusion coefficient at a given concentration, without fitting to experimental results, it can be used to indicate a likely range for a given diffusion coefficient based on knowledge of $D_0$.

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## References and Notes

(1) Duda, J. L. *Pure Appl. Chem.* **1983**, *55*, 861.
(2) Duda, J. L. *Pure Appl. Chem.* **1985**, *57*, 1681.
(3) Mahabadi, H. K.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 283.
(4) Mahabadi, H. K.; O'Driscoll, K. F. *Macromolecules* **1977**, *10*, 55.
(5) North, A. M. The Influence of Chain Structure on the Free Radical Termination Reaction. In *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley-Interscience: New York, 1974; Chapter 5.
(6) Korsmeyer, R. W.; von Meerwall, E. D.; Peppas, N. A. *J. Polym. Sci. Polym. Phys. Ed.* **1986**, *24*, 409.
(7) Waggoner, R. A.; Blum, F. D. *J. Coatings Technol.* **1989**, *61* (768), 51.
(8) Blum, F. D.; Pickup, S.; Foster, K. R. *J. Colloid Interface Sci.* **1986**, *113*, 336.
(9) Blum, F. D.; *Spectroscopy* **1986**, *1* (5), 32.
(10) Pickup, S.; Blum, F. D. *Macromolecules* **1989**, *22*, 3961.
(11) Maxwell, J. C. *A Treatise on Electricity and Magnetism*, 2nd ed.; Clarendon Press: Oxford, U.K., 1881; Vol. 1, p 435.
(12) Fricke, H. *Phys. Rev.* **1924**, *24*, 575.
(13) Mackie, J. S.; Meares, P. *Proc. R. Soc. London*, A **1955**, *232*, 498.
(14) Muhr, A. H.; Blanshard, J. M. V. *Polymer* **1982**, *23*, 1012.
(15) MacElroy, J. M. D.; Kelly, J. J. *AIChE J.* **1985**, *31*, 35.
(16) Vrentas, J. S.; Duda, J. L.; Ling, H.-C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 275.
(17) Vrentas, J. S.; Duda, J. L.; Ling, H.-C.; Hou, A.-C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 289.
(18) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1964**, *42*, 288.
(19) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 1.
(20) Mehta, S. M. S. Thesis, University of Missouri—Rolla, Rolla, MO, 1989.
(21) Chang, C.-W. M.S. Thesis, University of Missouri–Columbia, Columbia, MO, 1991.
(22) Waggoner, R. A.; Pickup, S.; Chang, C.-W.; Mehta, S.; Counsil, J.; Blum, F. D., to be submitted for publication.
(23) Hwang, D.-H.; Cohen, C. *Macromolecules* **1984**, *17*, 2890.
(24) Hwang, D.-H.; Cohen, C. *Macromolecules* **1984**, *17*, 1679.
(25) Lodge, T. P.; Lee, J. A.; Frick, T. S. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 2607.
(26) Landry, M. R.; Gu, Q.-J.; Yu, H. *Macromolecules* **1988**, *21*, 1158.
(27) The diffusion data reported in ref 10 for toluene in polystyrene appear to have a systematic error in the absolute value of $D$ of about 30% too large. This did not affect the fitting of that data to the previous models as they were fit at $D/D_0$.
(28) Cheever, E.; Blum, F. D.; Foster, K. R.; Mackay, R. A. *J. Colloid Interface Sci.* **1985**, *104*, 121.
(29) naNagara, B.; O'Connor, R. D.; Blum, F. D. *J. Phys. Chem.* **1992**, *96*, 6417.
(30) Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1992**, *25*, 4345.
(31) Vrentas, J. S.; Chu, C.-H. *J. Colloid Interface Sci.* **1989**, *130*, 293.

(32) Gallant, R. W. *Physical Properties of Hydrocarbons*; Gulf Publishing Co.: Houston, TX, 1968.
(33) Haward, R. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*, 191.
(34) Boss, B. D.; Stejskal, E. O.; Ferry, J. D. *J. Phys. Chem.* **1967**, *71*, 1501.
(35) von Meerwall, E.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 877.
(36) Blum, F. D.; Durairaj, B.; Padmanabhan, A. S. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 493.
(37) Fujita, H. *Fortschr. Hochpolym.-Forsch.* **1961**, *3*, 1.
(38) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.
(39) Schaefer, D.; Spiess, H. W.; Suter, U. W.; Fleming, W. W. *Macromolecules* **1990**, *23*, 3439.
(40) Pschorn, U.; Rössler, E.; Sillescu, H.; Kaufmann, S.; Schaefer, D.; Spiess, H. W. *Macromolecules* **1991**, *24*, 398.
(41) Lee, J. A.; Lodge, T. P. *J. Phys. Chem.* **1987**, *91*, 5546.