Self-Diffusion of Toluene in Polystyrene Solutions

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ABSTRACT: The pulsed-gradient spin-echo (PGSE) NMR technique was used to acquire a broad range of solvent self-diffusion coefficients for the toluene/polystyrene (MW 270 000) system. Self-diffusion coefficients were determined for samples having polymer weight-fractions ranging from 0.04 to 0.90 over a temperature range of 25–115 °C. Several different approaches to interpretation of the diffusion data have been considered. The temperature dependence of the data exhibits Arrhenius behavior with energies of activation that increase with concentration from 2.6 to 16.2 kcal/mol. Several theories based on the assumption that the solvent diffusion is slowed by the polymer obstructing its diffusion path are also used to interpret these data. Our results support the hypothesis that the normalized diffusion coefficient is relatively independent of thermodynamic parameters. The data are in qualitative agreement with a "standard curve" for normalized diffusion coefficients. This approach shows potential as a tool for predicting diffusion rates over a wide concentration range for a variety of polymer solvent systems. The final approach used to interpret these data is that of the free volume theory proposed by Vrentas and Duda. The agreement between the free volume theory and experimental data is improved considerably if two of the needed parameters are adjusted to give optimum fits to the experimental diffusion data. This approach yielded a root mean squared of the fractional difference between experiment and theory of 14%.

Introduction

Small molecule transport in polymer solutions is of critical importance in many processes. It can determine polymerization, curing, and drug delivery rates;[1] plasticization, pigment stability, drying, and coloration of coatings;[2] and many other properties of polymeric systems. The role of diffusion in most of these processes has been reviewed elsewhere.[3-6] Although diffusion in gasses and small molecule liquids is better understood, there remains considerable uncertainty about such processes in polymer solutions. Much of this uncertainty is a result of the variety of different approaches for the determination of diffusion coefficients. Different approaches yield different diffusion coefficients whose interrelationship is unclear. The different diffusion coefficients and the various methods for determining them in polymer systems have also been reviewed.[7] Self-diffusion is a measure of transport due to Brownian motions of molecules in the absence of a chemical concentration gradient. One could argue that the presence of the nuclei, labeled by their precessional frequencies (as in the PGSE experiment), creates a thermodynamic concentration gradient. However, these gradients do not significantly affect the Brownian motion in the sample and the measurement is relatively nonperturbing. The lack of a chemical concentration gradient simplifies development of a theoretical understanding of this transport process. Thus self-diffusion can serve as a starting point for the analysis of the diffusion processes in polymeric systems. In the past, self-diffusion measurements were made with radioisotope tracers. Such procedures were long and tedious because of the synthetic pathways. As a result, the amount of self-diffusion data for polymer systems found in the literature is moderate at best. With the advent of the pulsed-gradient spin-echo (PGSE) NMR technique, self-diffusion coefficients can be routinely determined in favorable circumstances in about 30 min. It is therefore feasible to perform a complete study of solvent self-diffusion in an ideal system.

In the present report, we have chosen to study toluene diffusion in solutions of polystyrene because this system has been studied in great detail and many of the parameters needed in the analysis of the diffusion data have already been determined. Our analysis will begin with the more simple and empirical approaches to interpretation of self-diffusion data. Arrhenius plots of diffusion coefficients will be used to determine activation energies of the diffusion process as a function of concentration. We will then consider an analysis based on obstruction theories and modified Enskog theory, which corrects for momentum transfer between the solvent and polymer. Finally, the free volume theory of Vrentas and Duda (V&D) will be considered. The advantages and disadvantages of each approach will be discussed.

Experimental Section

The PGSE technique used was similar to the Stilbs modification[8] of the Stejskal–Tanner[9] method. The technique used a pulsed magnetic field gradient to create phase variations of nuclear spins, which are determined by the position of the nuclei in the field. Diffusion results in incomplete rephasing of the spins following the application of a refocusing pulse. The signal intensity is exponentially related to the diffusion coefficient and the length of the gradient pulse in an isotropic sample. By taking several spectra with different gradient pulse lengths, one can extract a diffusion coefficient from the rate of signal decay as a function of the gradient pulse length. Reviews of the technique[10-12] and its application to polymeric systems[13,14] have been published. One limitation of the technique is that the signal intensity is attenuated by spin–spin relaxation (T_2) as well as the diffusion coefficient. At ambient temperatures, samples with very high polymer concentration (above 80% w/w polymer) had T_2's that were prohibitively short. Thus it was not possible to determine self-diffusion coefficients in all samples at all of the temperatures of interest. Also, since the signal to noise ratio degrades as the relaxation time becomes shorter, the precision of the data for the high concentration samples was not as good as that of the other samples.

The diffusion coefficients were determined from the slope of a linear least-squares fit of the log of peak height vs $\beta = \delta^2(\Delta - \delta/3)$, where δ is the gradient pulse width and Δ is the time between the initial pulse and the refocusing pulse.[10] For each diffusion measurement, 11 spectra were typically obtained, using different gradient pulse widths. Often, a few of the spectra taken at long gradient widths were discarded because of insufficient signal to noise. At the value of Δ used in this study (typically 67 ms), the contributions of the polymer protons to the toluene methyl

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Table I
Toluene Self-Diffusion Coefficients[a] in Polystyrene Solutions as a Function of Concentration and Temperature

	temperature,[b] °C									
concn[c]	25	35	45	55	65	75	85	95	105	115
0	26.6	29.4[d]	32.2	34.5	45.4	48.3	55.3	58.7	61.6	72.7
0.036	24.1	26.9	29.7	30.5	41.1	43.4	46.8	53.3	59.3	66.9
0.150	19.0	21.2	23.2	25.7	30.3	35.4	38.7	44.4	46.8	53.1
0.201	16.9	18.8	20.1	23.0	28.1	33.4	34.8	41.9	44.2	49.8
0.267	13.6	15.2	17.4	19.6	23.9	27.8	31.1	34.9	37.7	41.2
0.369	9.5	11.2	12.6	14.2	18.4	20.4	23.5	26.9	31.4	33.0
0.444	7.26	8.27	9.46	10.3	14.3	16.6	19.1	22.1	24.9	27.0
0.486	5.97	6.85	8.15	8.78	12.9	13.7	16.1	19.8	21.7	24.2
0.580	3.15	3.89	4.65	5.54	7.57	9.41	11.0	13.0	15.0	17.7
0.603	2.57	3.15	4.08	4.66	6.58	8.18	9.55	11.4	13.9	15.6
0.661	1.51	1.85	2.30	2.94	4.50	5.70	6.84	8.18	10.2	11.7
0.714	0.79	0.95	1.37	1.61	2.80	3.43	4.49	5.66	7.04	8.54
0.791		0.51	0.59	0.60	1.06	1.28	1.77	2.55	3.31	3.97
0.830					0.43	0.64	0.87	1.17	1.89	2.49
0.852						0.27	0.44	0.78	1.21	2.08
0.886								0.27	0.46	0.85

[a] All diffusion coefficients are in units of 10^{-10} m^2/s. [b] Temperature was maintained with a precision of ±2 °C. [c] Polymer weight fraction. [d] Interpolated from pure toluene data.

resonance is negligible because of the short T_2 of the polymer protons. The standard deviation of the slope of the log-linear least-squares fit was taken as an indication of the precision of the diffusion measurement and ranged from 1 to 6% of the measured diffusion coefficient. However, the accuracy of the measurement in the PGSE experiment was estimated to be about 10% of the diffusion coefficient being measured in the range studied. The field gradient strength (0.047 T/m) was determined by using neat cyclohexane as a reference material. The value of the cyclohexane self-diffusion coefficient was taken to be 1.47 × 10^{-9} m^2/s at 25 °C.

All experiments were performed on a JEOL FX-90Q spectrometer operating at 89.5 MHz for protons. The spectra were taken with an external lithium lock so it was not necessary to incorporate deuterated solvent into the samples. All spectra were taken with a 1000-Hz window, 4000 points, and a pulse delay of 8 s. The number of scans required to attain reasonable signal to noise ranged from 8 to 128. A JEOL variable-temperature control unit was used in the elevated temperature studies and was capable of maintaining the temperature to ±2 °C. The temperature controller was calibrated with a blank sample prior to the diffusion measurements.

Samples were prepared by placing weighed amounts of the constituents in 5-mm NMR tubes. The tubes were then sealed and placed in a heating block at ca. 60 °C until homogeneous. Equilibration times were on the order of several weeks for the most concentrated samples. Toluene and polystyrene were purchased from Aldrich Chemical Co., Milwaukee, WI, and Scientific Polymer Products Inc., Ontario, NY, respectively. Both were used as received. The polymer molecular weight was characterized by gel permeation chromatography (GPC) and was found to have an average molecular weight of 270 000 g/mol and a polydispersity of 1.5. It has been demonstrated that the molecular weight distribution does not affect the solvent self-diffusion coefficient in polymer–solvent systems.[10] Therefore this broad molecular weight distribution is acceptable for the present study.

Polymer volume fractions were calculated from weight fractions by using the tabulated temperature dependencies of the densities of neat toluene[15] and polystyrene,[16] assuming ideal volumes of mixing. The densities vary from 0.862 to 0.773 g/mL and from 1.079 to 1.029 g/mL over the temperature range studied for toluene and polystyrene, respectively.

Results and Discussion

Toluene self-diffusion coefficients were determined over the temperature range 25–115 °C at 10-deg intervals for 15 samples having concentrations ranging from 3 to 89% w/w polymer. The results of these measurements are presented in Table I as a function of weight fraction polymer. The lack of data for the concentrated polymer samples at low temperature was due to the limitations imposed by short spin–spin relaxation times (T_2) due to the relatively slow molecular motion in those samples. A sudden decrease in T_2 at very high concentrations and low temperatures was observed and probably was due to the proximity of the glass transition (T_g) in these samples. The concentration dependence of T_g for the toluene/PS system has been previously studied for a system of MW = 18 000 g/mol.[17] Interpolation of these data indicates that the T_g of samples with polymer weight fractions of 0.791, 0.830, 0.852, and 0.886 should be -1, 7, 17, and 35 °C, respectively.[17] However, the molecular weight of the polymer used in that analysis was considerably below the value at which the limiting T_g is expected. Therefore, we can assume that in the samples used in the present study, the T_g will be somewhat higher than that predicted in the above analysis. For each of these samples, the lowest temperature at which the diffusion coefficient could be determined was approximately 50 °C above the reported T_g. This observation suggests a relationship between free volume, which determines the polymer molecular motions, and the solvent diffusion. Also, since a change in the dynamics of the system occurs at the glass transition temperature, diffusion measurements below this point would be indicative of different processes than those observed in solution. Thus the data set presented here is a complete representation of solvent self-diffusion in the liquidlike solution over the given temperature range.

Self-diffusion coefficients for neat toluene were also determined and listed in Table I. The diffusion coefficients and energies of activation (see Table II) for diffusion of neat toluene are consistent with data reported in the literature (E_a = 2.5 kcal/mol).[18,19] The overall trends in the data for the polymer solutions were consistent with one's expectations; diffusion coefficients increase as temperature increases and decrease as polymer concentration increases. The solution data were also quantitatively consistent with the limited self-diffusion data that have been previously reported[20–23] for this system. Several approaches to interpreting these data are available but only a few will be considered for simplicity, insight gained, and predictive ability.

Arrhenius Behavior. Diffusion coefficient data are often analyzed in terms of an Arrhenius energy of activation. In dilute solutions, where the diffusing species does not often encounter a polymer molecule, the diffusion rate is limited by the energy required for the diffusing species to escape its present surroundings and move into an ad-

Table II
Calculated Energies of Activation for Diffusion of Toluene in Polystyrene Solutions

wt fractn PS	E_a, kcal/mol	$D°$,[a] m^2/s
0.0	2.61 ± 0.15	−15.4 ± 0.2
0.036	2.66 ± 0.15	−15.4 ± 0.4
0.150	2.72 ± 0.10	−15.5 ± 0.1
0.201	2.89 ± 0.11	−15.4 ± 0.2
0.267	2.98 ± 0.07	−15.4 ± 0.1
0.369	3.33 ± 0.09	−15.2 ± 0.1
0.444	3.60 ± 0.15	−15.0 ± 0.2
0.486	3.77 ± 0.15	−14.9 ± 0.2
0.580	4.53 ± 0.10	−14.2 ± 0.1
0.603	4.77 ± 0.10	−14.1 ± 0.1
0.661	5.52 ± 0.16	−13.3 ± 0.2
0.714	6.40 ± 0.20	−12.5 ± 0.3
0.791	6.61 ± 0.42	−13.1 ± 0.6
0.830	9.17 ± 0.33	−10.2 ± 0.5
0.852	13.66 ± 0.30	−4.6 ± 0.4
0.886	16.26 ± 0.65	−2.1 ± 0.9
0.789	8.3[b]	
0.850	8.4[b]	
0.890	9.0[b]	
0.939	16.5[b]	

[a] D_0 is reported in units of 10^{-10} m^2/s. [b] From ref 22; see text for details.

jacent environment. Thus, in this regime one would expect the Arrhenius approach to be successful. However, in moderate to high concentration solutions, the diffusion process is limited by the polymer molecular motions. Such motions are highly cooperative, involving several monomer units within the chain as well as those polymer segments and solvent molecules adjacent to the chain undergoing the motion. One would not necessarily expect such a process to be characterized by a single energy of activation. However, there has been some experimental evidence that supports the validity of the Arrhenius type of approach. Mutual-diffusion coefficients of toluene in polystyrene were shown to exhibit Arrhenius behavior at weight fractions of 0.10 and 0.04 and over the temperature range 110–178 °C.[24] Although self- and mutual-diffusion are formally different processes,[25] they involve similar mechanisms. Self-diffusion data have also been presented that show Arrhenius behavior for this and similar systems over a limited temperature range at high polymer concentrations.[22]

The logarithm of the toluene self-diffusion coefficient vs inverse temperature is plotted in Figure 1. The weight fraction of polymer in each sample is listed in the legend. The deviations from linearity apparent in the data are attributed mainly to inaccuracies of the temperature controller. The larger amount of scatter in the low-concentration samples may have been due to the uncontrolled effects of convection. In the more concentrated samples, convection did not play a significant role because of the higher viscosity. The data in Figure 1 are linear within experimental error.

The energies of activation (E_a) and intercepts ($D° = D$ at infinite temperature) are listed in Table II and were determined from a log-linear least-squares fit of the plots in Figure 1. The standard deviations of the linear fits are also listed in the table. Activation energies increase gradually with concentration in the dilute regime and increase more rapidly at concentrations above 60% w/w polymer. The values of $D°$ show a similar trend. A plot of energy of activation as a function of concentration is shown in Figure 2. The error bars represent the standard deviations in the linear fits used to calculate the activation energies. Energies of activation for toluene diffusion in polystyrene have previously been determined for samples having concentrations in the range 80–95% polymer for the temperature range 60–105 °C.[22] These data have been included in Table II and Figure 2 for comparison and are similar to those in this work. A gradual increase in activation energy followed by a marked increase at high polymer concentration is apparent. However, the transition to rapidly changing activation energy occurs at

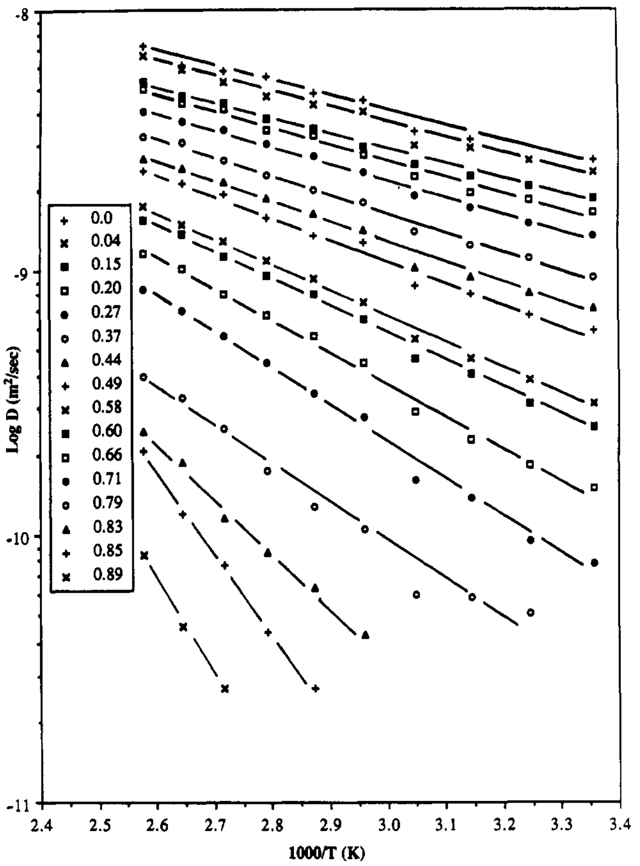

Figure 1. Plots of log D vs $1/T$ for toluene in polystyrene at several different weight fractions (listed in the legend). The lines drawn are best fits and are indicative of the energy of activation.

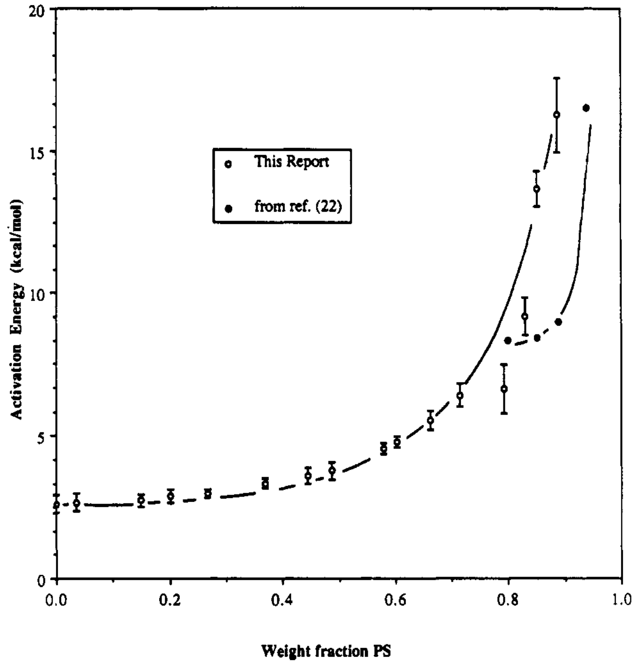

Figure 2. Energies of activation for toluene self-diffusion in polystyrene solutions plotted as a function of concentration. The curves are drawn to aid the eye only.

slightly lower polymer concentration in the present work. In addition, these data are also consistent with lower concentration diffusion data for benzene and cyclohexane in polystyrene solutions.[19]

The concentration dependence of the glass transition temperature (T_g) in polystyrene solutions of molecular weight similar to that used in the previous study[22] has been analyzed for a variety of solvents including toluene.[17] The T_g for a 95% PS/toluene system was reported to be 63 °C. This corresponds with the highest concentration and lowest temperature at which diffusion measurements were reported for the 18000 PS system. NMR diffusion measurements cannot be determined below the T_g on our system because of the very short spin–spin relaxation times in those samples. Our most concentrated samples were glasses at room temperature, as indicated by stress cracking of the samples on cooling to room temperature.

The differences in the behavior of the energies of activation in our two data sets are likely due to the lower molecular weight of the polymer used in the previous studies.[22] The relationship between glass transition temperature and molecular weight has been previously reported for polystyrene.[16] This study indicated that the lower molecular weight bulk polymer has a glass transition temperature that is significantly lower (87 °C) than the limiting value (100 °C) expected for the polymer used in the present study. The apparent relationship between activation energy for solvent diffusion and T_g suggests that the same free volume may determine both. The lower T_g of the low molecular weight polymer could be interpreted as an indication of a larger amount of free volume available in the bulk material. The activation energy is relatively independent of concentration until the available free volume reaches a critical level. At concentrations above this level, stronger temperature dependencies are observed. The transition in the low molecular weight polymer solutions occurs at a higher concentration because the low molecular weight polymer has more free volume than the higher molecular weight polymer.

These observations suggest that temperatures should be referenced to the T_g when performing calculations of activation energies. This approach has been applied with some success to mutual-diffusion data at zero solvent fraction by using free volume theories.[26] Extension of that analysis to self-diffusion is beyond the scope of this report. In the less concentrated solutions, which are well above T_g, the diffusion coefficient measurements were independent of the polystyrene molecular weight.[23]

Although the Arrhenius analysis shows limited predictive capability, it does offer some insight into the mechanism of diffusion. In solutions of low to moderate concentration (less than 50% polymer) the energy of activation is only slightly dependent on concentration. This implies that the transport process is limited by a single step with a measurable activation energy. In contrast, the rapidly changing activation energy observed in the concentrated samples implies a more complicated process. These observations are consistent with free volume theories, which predict that in dilute solution the diffusion coefficient is determined by the interactions of the solvent with its environment. However, in concentrated solutions the transport is determined by the availability of free volume. The movement of free volume is a cooperative process and is not expected to be characterized by a single activation energy.

Microscopic Approaches. There are several common approaches for treating the microscopic behavior of solvent transport in polymer solutions. Several of these have been reviewed for diffusion in gels by Muhr and Blanshard.[27] Formally, a loosely cross-linked gel and polymer solution are similar with respect to solvent transport because the local segmental motions of the polymer to which the solvent transport would be sensitive are similar. This has previously been shown for swollen polystyrene beads.[28] It is the microscopic solvent environment that controls solvent motion rather than the more macroscopic motion of entire polymer chains that determine the macroscopic viscosity. Muhr and Blanshard cite[27] (i) the obstruction effect, (ii) increased hydrodynamic drag, (iii) alteration of solvent properties (e.g., intermolecular spacings), and (iv) polymer involvement as major contributions for reduced solvent diffusion coefficients as compared to bulk solvent.

Since the polymer moves much slower than the solvent, it acts as an obstruction. The solvent must diffuse around the relatively stationary polymer, thereby increasing its diffusion path and decreasing its diffusion coefficient. The degree of obstruction is determined by the volume fraction of the polymer in the solution. Obstruction theories have been very popular because of their simplicity. For the present work, we are content to discuss only two of these, namely, the Maxwell–Fricke (or simply the Maxwell model) and Mackie–Meares models.

The Maxwell[27,29,30] model for diffusion is formally similar to that for electric conductivity and permeability. It assumes immobile, impenetrable species suspended in a mobile solvent continuum. It has been shown that the Maxwell theory predicts the maximum reasonable diffusion coefficient in the presence of obstructions when the obstructions are assumed to be spheres.[27] This approach has been shown to accurately predict the diffusion coefficient of water in suspensions of latex and silica particles at low concentrations.[31,32] This is taken as an indication that the theory accounts for the effects of obstructions on the diffusion rate for large particles. If one assumes that this theory holds even for relatively small polymer segments that are stationary relative to the solvent, the Maxwell equation for diffusion simplifies to[27,31,32]

$$D(1-\phi)/D_0 = (1-\phi')/(1+\phi'/\chi) \qquad (1)$$

where D is the observed diffusion coefficient, D_0 is the diffusion coefficient of the neat solvent, ϕ is the volume fraction of polymer, ϕ' is the volume fraction of the polymer plus any "nondiffusing" solvent, and χ is the shape factor. Nondiffusing solvent is defined as that just next to a polymer segment with a very slow diffusion coefficient. The shape factor can take values ranging from 2 for spheres to 1.5 for rods. We will assume a value of 2 for χ. For the discussion below, the difference between 1.5 and 2 for χ is small compared to the differences between their predictions and the data. For this model the $(1-\phi)$ correction term has been applied to D/D_0 in order to account for the proper reference volume in the solution to Fick's law.[31-34] If as a first approximation we set $\phi = \phi'$, eq 1 reduces to

$$D/D_0 = 1/(1+\phi/\chi) \qquad (2)$$

This has the physical significance of assuming that there is no nondiffusing solvent that is appropriate for colloidal species with minimal surface effects.[31,32]

A second approach by Mackie and Meares[27,35] is based on tortuosity and a simple cubic lattice model with similar size sites for the solvent and polymer segments (repeat units). A more general theory based simply on the volume fraction of polymer, ϕ (rather than the fraction of repeat units), yields

$$D/D_0 = (1-\phi)^2/(1+\phi)^2 \qquad (3)$$

This model deals with the small size of the impenetrable polymer segment. Extensions of this model have been suggested which consider the redistribution of polymer segments. For rapid polymer segment redistribution, this results in[27]

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

Slower molecular motion should yield a result between these two extremes. This approach is interesting in light of studies which suggest, through a simple free volume treatment, that the segmental motion of the polymer and diffusion of the solvent are correlated. This has been shown in the poly(isopropyl acrylate)–chloroform system[36] but is believed to be generalizable to other polymer solutions.

The modified Enskog result is based on kinetic theory and accounts for momentum transfer between rigid spheres.[37] The polymer is modeled as a set of immobile beads. The details of this approach will be discussed elsewhere. With the modified Enskog theory, the solvent self-diffusion coefficient is given by[37]

$$1/D = 1/D_{1,\mathrm{P}} + 1/D_{1,\mathrm{S}} \tag{5}$$

where $D_{1,\mathrm{P}}$ and $D_{1,\mathrm{S}}$ are the pair (mutual) diffusion coefficients of the tracer relative to the polymer and other solvent molecules, respectively. The value of the D_1's are calculated from eq 6 in ref 37. The ratio of the molecular diameters of the solvent to that of the polymer (mer) segment is a fitted parameter.

Shown in Figure 3 are the self-diffusion coefficients, normalized by D_0, as a function of polymer volume fraction. Also shown in the figure are the predictions of the Maxwell, Mackie, and Meares and modified Enskog theories. At first glance the most striking feature of Figure 3 is that the normalized diffusion coefficients fall on very similar curves. In fact, solvent self-diffusion coefficients from a number of systems also fall within experimental error of these curves.[23,33,38,39] A standard plot of this type can be used to predict diffusion rates in a variety of systems with a knowledge of the densities of the constituents and the self-diffusion coefficient of the neat solvent. This type of behavior is anticipated when[38] the system is well above T_g ($T > T_g + 50$ °C); the polymer molecular weight is high; and in the case of multi-solvent systems, there are no strong specific polymer–small molecule interactions. Lee and Lodge have found that methyl red in the methyl red–toluene-poly(vinyl acetate) system does not follow this universal behavior because it preferentially binds to poly(vinyl acetate) and toluene does not.[38]

A definite temperature dependence is found in the normalized diffusion coefficients in Figure 3. In general, the normalized diffusion coefficient (D/D_0) increases with increasing temperature, although these effects are not much larger than the experimental errors. Similar effects are also found in this system at lower temperatures, even if volumes of mixing are accurately accounted for.[40] The magnitude of this effect is small, which is not surprising because the energies of activation are similar from 0–50 wt % polymer. Unfortunately, with this type of analysis all of the data depend on the accuracy of the D_0 measurement, which is difficult to make because of convection.

A comparison of the theories with the experimental values in Figure 3 suggest that the Maxwell theory gives a poor approximation to the experimental data, while the others seem more reasonable. The experimental data fall well below the prediction of the Maxwell theory. This could be due to setting $\phi = \phi'$. An alternative approach using the Maxwell theory would be to use eq 1 and solve for ϕ' for a given value of $D(1 - \phi)/D_0$. The difference between ϕ and ϕ' could then be used to estimate the amount of nondiffusing solvent.

In aqueous solutions it is common to assume that the nondiffusing solvent arises because of the association of water molecules with the polymer through hydrogen bonding. This approach has been used to measure hydration numbers in solutions of water-soluble polymers[33] and in biological systems.[34,41,42] In many cases the limiting form of the Maxwell theory is used at low concentrations. A comparison of solvent self-diffusion coefficients in a variety of polymer–solvent systems has shown that the apparent volume of the polymer-bound solvent is relatively independent of the presence of hydrogen bonding, solvent quality, polymer molecular weight, and temperature.[23,38] This implies that the chemical interaction between the solvent and polymer is not a critical factor in determining the diffusion coefficient. Others have noted that the normalization of the diffusion coefficient as is generally required by the obstruction theories removes many thermodynamic effects from the diffusion data.[20,43]

We believe that the interaction between the diffusing species and polymer that causes the disagreement between the Maxwell theories and experimental data is physical (not chemical) in nature. By this we mean that specific chemical interactions (e.g., hydrogen bonding) do not themselves cause the difference. We have previously called this the "surface drag" effect, which has been briefly discussed.[27] We envision that the solvent molecules next to the polymer molecule move at roughly the same rate as the polymer. Since the polymer segments move very slowly, the solvent next to them also moves very slowly compared to the bulk solvent. There may in fact be several layers of solvent molecules that are motionally restrained by the polymer. Dielectric dispersion data for solutions of polyethylene oxide in water at microwave frequencies show a broad range of water relaxation times, ranging from 1 to 10 times that of pure water.[44] This indicates that water is present in several different states in contrast to the two-state model assumed in the calculation of hydration numbers. The two-state model does, however, have the advantage of being computationally and conceptually simple. The chemical interaction between the solvent and polymer does determine the lifetime of the solvent next to a polymer segment; however, this time is very short relative to the diffusion time in the PGSE experiment even in strongly associated systems. The solvent exchanges rapidly between the different sites during the experiment and therefore one observes an average diffusion coefficient. The diffusion rate is determined only by the number of sites for the solvent interaction and the diffusion rate of the neat solvent. This behavior is not observed in suspensions of latex particles,[31,32] because the surface area of particles is very small relative to the number of sites in the polymer solution.

The prediction of the Mackie and Meares theory is much closer to the experimental data than the Maxwell theory but falls slightly below it. The limiting form of this model, assuming fast polymer motion, brackets the data on the other side (not shown). It seems reasonable that intermediate molecular motion would fit the data somewhere in between these two extremes. At present there is no simple extension of the theory to accommodate some limited polymer motion, but the effect of temperature could be explained by the decrease in the relative rates of solvent to polymer motion.

The modified Enskog theory fits the data quite well. This model properly accounts for the momentum transfer between the solvent and polymer.[45] The theory was fit to

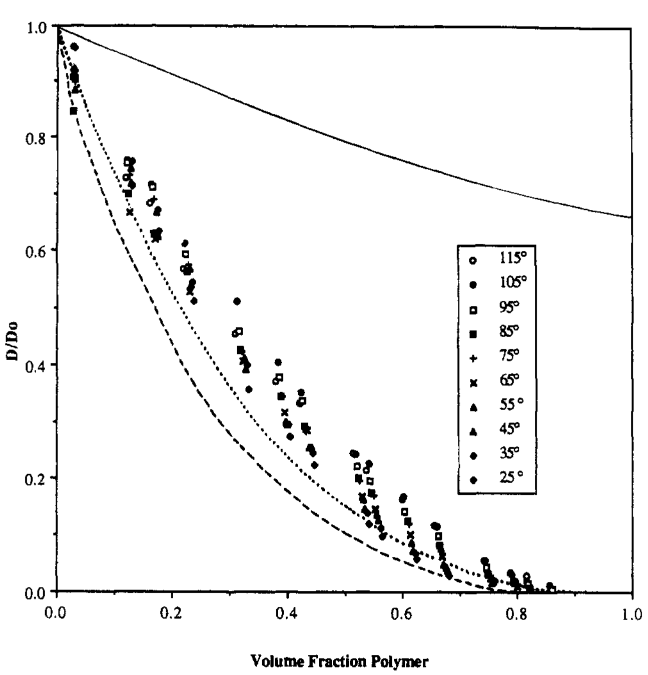

Figure 3. Normalized plots of toluene diffusion coefficients in polystyrene at several different temperatures (figure legend) as a function of composition. Also shown are the predictions of the Maxwell (—), Mackie and Meares (- - -), and modified Enskog (···) theories.

the data with one parameter, the radius of a polymer segment or, equivalently, the ratio of the solvent to polymer segment diameter. The curve shown is fit with this ratio equal to 0.9. We expect this treatment to not be valid at high polymer concentrations, i.e., >50%. This type of analysis can predict the temperature dependence as well and we are currently extending this treatment to other systems.[45]

These types of analyses are useful in the study of a wide variety of polymer solvent systems and over a wide range of temperatures and concentrations below ca. 60% polymer. However, at concentrations above approximately 60% w/w polymer, the magnitude of the experimental errors is larger than that of the normalized diffusion coefficient. Unfortunately, it is in this concentration regime that many polymer processes are diffusion limited. Thus an alternative approach to the analysis of this data is considered in the next section.

Free Volume. Free volume may be defined as the volume of a system that is not accounted for by the volume of the molecules as determined by the van der Waals radii of the atoms that make up the molecules. It is assumed that this additional volume is distributed randomly in the system and that it rearranges with little or no activation energy. When a portion of this free volume of sufficient size moves to a location adjacent to a diffusing molecule, the molecule may jump into that space. The diffusion process is assumed to be a series of these jumps.

Cohen and Turnbull[46] first proposed the dependence of diffusion coefficients on the available free volume for the case of hard spheres. This theory was adapted for polymer solutions by Fujita[47,48] and was shown to be reasonably successful at predicting self-diffusion coefficients over limited concentration and temperature ranges.[36,49,50] This theory was further modified by Vrentas and Duda (V&D) in order to account for the differences in the volumes required for diffusion by the solvent and polymer jumping units.[51] It has been shown that the Fujita theory is a special case of the more general V&D theory in which the solvent and polymer jumping units require the same free volume to jump.[52] Experimental evidence has been presented that correlates the molar volume of the jumping unit of a diffusing solvent with the diffusion coefficient.[23,53] The limited success of the Fujita theory is attributed to the fact that the systems studied meet the criterion of similar size for the solvent and polymer jumping units. In addition, the dependence of the Fujita theory on the reference diffusion values magnifies the importance of the accuracy of the chosen reference. When the extrapolated solvent-diffusion coefficient is used as the reference, this problem may be even worse.[54]

Another free volume theory proposed by Paul[55] is similar to that of V&D in its dependence on free volume; however, it includes a factor to account for the possibility of the solvent jumping back to the position from which it originated but ignores the effects of the relative size of solvent and polymer jumping units. The predictions of the Paul and V&D theories have been compared.[56] The results suggested that the Paul theory is reasonably accurate at low to moderate concentrations (where the jump-back factor is expected to play a significant role) but is ineffective at high polymer concentrations. Consequently we have chosen the free volume theory proposed by V&D for comparisons to our experimental results.

The V&D theory states that the self-diffusion coefficient is given by[51]

$$D = D^* \exp\{-E_a/RT\} \exp\{-\gamma(\omega_1 V_1^* + \omega_2 \xi V_2^*)/V_{FH}\} \quad (6)$$

where D^* is a fitted parameter, E_a is the activation energy for moving the diffusing molecule from its initial environment to its destination (not the same energy of activation discussed in the Arrhenius Behavior), R is the gas constant, T is temperature, γ accounts for the fact that the same free volume is available to more than one molecule for diffusion and may take values ranging from $^1/_2$ to 1, V^* is critical volume (the volume of the diffusing species) of the solvent or polymer at 0 K, V_{FH} is the average free volume available for diffusion in the system, ξ is the ratio of the solvent critical free volume to that of the polymer jumping unit and accounts for the fact that the monomer is not the actual jumping unit, ω is the mass fraction, and the subscripts 1 and 2 refer to the solvent and polymer, respectively. The ratio γ/V_{FH} can be determined from available free volume parameters in the following manner:[56]

$$V_{FH}/\gamma = (K_{11}/\gamma)\omega_1(K_{21} + T - T_{g1}) + (K_{12}/\gamma)\omega_2(K_{22} + T - T_{g2}) \quad (7)$$

where T is temperature, T_g is the glass transition temperature, ω is the weight fraction, and the subscripts 1 and 2 refer to solvent and polymer, respectively. The K's are constants that are evaluated as

$$K_{11}/\gamma = 2V^\circ{}_1\alpha_1 \quad (8)$$

$$K_{12}/\gamma = V^*{}_2/(2.303C_1C_2) \quad (9)$$

$$K_{22} = C_2 \quad (10)$$

where $V^\circ{}_1$ is the molar volume of the solvent at the glass transition temperature, α_1 is the expansion coefficient for the solvent, and the C's are the Williams, Landel, and Ferry[47] (WLF) constants where the subscripts indicate which constant is used. Since the value of $(K_{22} - T_{g2})$ for this system is negative (Table III), eq 6 suggests that whenever the temperature falls below $(K_{22} - T_{g2})$, the polymer makes a negative contribution to the available free volume. However, it is unrealistic to expect that the addition of more material would remove free volume. In our analysis, this was compensated for by setting the polymer

Table III
Values for Free Volume Parameters Used To Fit the Diffusion Data

K_{11}/γ	1.57×10^{-3} cm^3/(g K)[a]
K_{12}/γ	5.82×10^{-4} cm^3/(g K)[a]
$K_{21} - T_{g1}$	−90.5 K[a]
$K_{22} - T_g^2$	−327 K[a]
V_1^*	0.917 cm^3/g
V_2^*	0.850 cm^3/g
E_a	0
ξ	0.536[b]
D^*	3.85×10^{-4} cm^2/s[b]

[a] From ref 56. [b] Determined by optimization of the data presented here.

contribution to free volume equal to zero whenever the temperature was below this critical value. This correction to the theory was found to have a moderate effect on the outcome of the analysis.

The theory does have a large number of parameters; however, many of them can be determined independently. The critical free volumes for diffusion are assumed to be equal to the molar volumes at 0 K and were calculated by the methods discussed by Haward.[57] Values of 0.917 and 0.850 cm^3/g were used for the critical free volumes of the solvent and polymer at 0 K, respectively. The WLF constants are determined from viscosity data and have been tabulated for a variety of polymer solvent systems.[47,50] A preliminary analysis of the data showed that the contribution of the E_a term to the quality of the fit was minimal.[58] Therefore E_a was set to zero and the remaining two parameters, ξ and D^*, were adjusted to minimize the root mean squared of the fractional difference between the theory and experimental data, which is given by the following equation:

$$\% \text{ deviation} = 100\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{D_{\text{ex}} - D_{\text{calcd}}}{D_{\text{ex}}}\right)^2\right]^{1/2} \quad (11)$$

where D_{ex} and D_{calcd} are the experimental and calculated self-diffusion coefficients and the summation is over n experimental data points. This type of analysis is preferable to standard least-squares fits because the data cover 2.5 orders of magnitude. The values of the optimized parameters as well as the remaining parameters used in this analysis are listed in Table III. Plots of the experimental data and the predictions of eq 6 are shown in Figure 4. The solid lines in the figure represent the theoretical predictions. Only a portion of the experimental data is shown in the figure in order to minimize overlap, although the entire data set was used in the analysis. The quality of the fit of the remaining data was similar to that shown in the figure. These values resulted in an average difference squared between theory and experiment of ca. 14%. We note that the present data are in better agreement (lower absolute error) than previously reported data from both self- and mutual-diffusion measurements.[56] In that study the mutual-diffusion coefficients were converted to self-diffusion coefficients. The best-fit values of ξ and D^* found in this study are similar to those reported previously.[56] The value of D^* is about 20% different and probably due to the different range of temperatures studied in this work.

The overall fit of the experimental data and theory is good; however, a systematic variation between the two is apparent. Specifically, in the low concentration regime an upward curvature is apparent in the experimental data. This curvature could not be accounted for by the theory as presented here. This behavior has been observed in other systems and has been addressed previously.[59] It has been suggested that this behavior is due to changes in the value of E_a as a function of temperature. In the low concentration region, the environment of the solvent molecules is changing rapidly. The environment is dominated by solvent molecules and not polymer chains. Thus the energy of interaction between the solvent and its environment is expected to change. At present the details of this interaction have not yet been determined and their relationship to system conditions is unclear. A further analysis of this interaction would offer greater utility to the free volume approach to solvent self-diffusion.

Finally, we should point out that similar types of measurements and comparisons have been made by using forced Rayleigh scattering[39,60] or photobleaching recovery experiments. In principle, these measurements may be applicable over a wider range than the data presented here but depend on the presence of a probe molecule. In polystyrene–tetrahydrofuran solutions, the self-diffusion of methyl red[60] was found to be adequately fit by either the Fujita or Vrentas–Duda theory. This is in agreement with the present work.

Conclusions

The usefulness of any theory for diffusion is determined by its ability to predict experimental phenomena and the amount of insight into the diffusion process that is gained by its application. Each of the three approaches presented here is somewhat successful in this regard. When treated in an Arrhenius format, the self-diffusion data yield energies of activation as a function of concentration. It is apparent from such data that the diffusion process changes dramatically as one approaches the glassy polymer. The behavior of activation energy at low polymer concentration suggests that the diffusion process can be defined by a single activation energy and perhaps a single step. At concentrations above 60% w/w polymer, the activation energy changes rapidly with concentration, which implies a multistep or cooperative process. Though such an analysis has little predictive capability, it does yield some insight into the diffusion process. With some modification, such that activation energies are referenced to glass transition temperatures, such an analysis could show improved predictive capability.

Three different approaches to the obstruction theory were considered. The simplified Maxwell theory is by far the least accurate for prediction of diffusion coefficients in polymer solutions. This is at least in part due to the assumption that there is no solvent associated with the polymer to cause an added obstruction volume. However, the Maxwell theory is useful in that it predicts a maximum possible diffusion coefficient in these systems and shows the obstruction effect alone cannot predict the experimental results. The second approach to obstruction theories to be considered was that of Mackie and Meares, which is based on a cubic lattice model. This approach gives reasonable agreement but falls slightly below the experimental data. Finally, the modified Enskog theory accounts for momentum transfer and fits the data within experimental error.

The obstruction theories have strong predictive abilities since plots of the normalized diffusion coefficient are relatively independent of all parameters, including the system being studied. Thus a standard curve could be used to predict diffusion rates with a knowledge of the densities of the components and the diffusion coefficient of the neat solvent. These data are generally available, but the approach is limited to polymer concentrations below about 60%. The discrepancy between theory and experiment is accounted for by a surface-drag effect. Though there

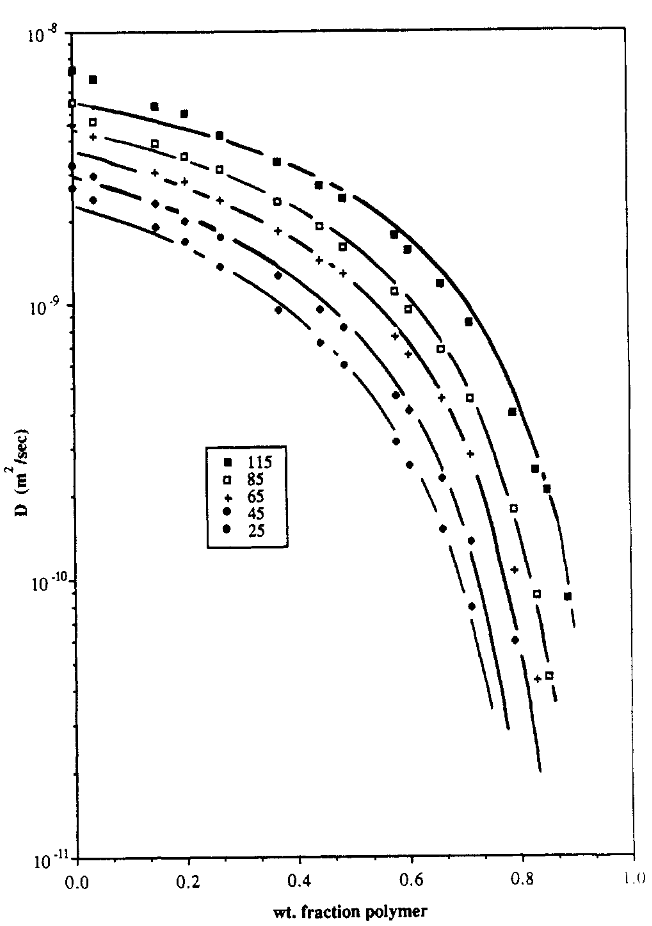

Figure 4. Plots of log D vs concentration at temperatures of 25, 45, 65, 85, and 115 °C. The solid lines represent the predictions of eq 6 using optimum free volume parameters. For clarity, not all of the data are shown.

is some evidence to support the surface drag concept, it has yet to be directly confirmed.

Free volume theories describe diffusion on a microscopic level and give some details about this process. Though a large number of parameters are needed to fit the theory, these parameters are available for a variety of polymer-solvent systems. In our analysis, two parameters were adjusted to give best fits of the experimental data. It is possible to approximate the adjustable parameters from limited diffusion data in order to give the theory predictive capability. This interpretation has strengths in both prediction and understanding the diffusion process. Systematic differences between the theory and experiment suggest that further modification of the theory is in order. Development of a specific relationship between the interaction energy and concentration would significantly improve the agreement between theory and experiment.

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