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A New Physical Model for the Diffusion of Solvents and Solute Probes in Polymer Solutions

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ABSTRACT: We propose a new physical model for the interpretation of the diffusion of solvent and other solute molecules in polymer solutions. In this model, the polymer solution is regarded as a network where the diffusing molecules have to overcome periodic energy barriers of equal magnitude, where the distance between the barriers corresponds to the correlation length in polymer solutions as defined in de Gennes' scaling theory. We demonstrate that this model applies to the diffusion of small molecules in polymer matrices, such as ternary aqueous systems of poly(vinyl alcohol) (PVA) and binary organic solutions of poly(methyl methacrylate) (PMMA). The model successfully interprets the diffusion of solute molecules and water in aqueous polymer solutions and that of solvent molecules in organic polymer solutions. In particular, the effects of polymer concentration and temperature on diffusion can be predicted. An energy barrier of 21 kJ/mol is calculated from the variable temperature studies of self-diffusion in the range 23−53 °C carried out on a PVA−water−*tert*-butyl alcohol ternary system.

Introduction

The diffusion of solvent and solute molecules in polymer solutions has attracted much recent interest because of its practical implications in applications of polymer materials. Small molecule diffusion is influenced by the polymer concentration, by temperature, by the detailed properties of the diffusing molecules, and by the dynamics of the polymer matrix. Various theoretical descriptions of solvent diffusion in polymers have been proposed. Free volume theory[1,2] has proved especially useful in describing the diffusion of organic solvents in polymer solutions but is less successful when the solvent is water. The obstruction theory set out by Mackie and Meares[3] includes aqueous systems but is strictly limited to small solvent molecules and does not account for all the properties of the solvent, particularly the size effects observed by Waggoner *et al.*[4] To explain such solvent size effects, a model based on kinetic theory has been proposed,[5] but proved to be less than satisfactory at higher polymer concentrations.

Understanding solute diffusion in polymer solutions presents even further challenges since one has to consider the size and shape of the solute molecules and the interactions between solute, polymer, and solvent, in addition to the effects of temperature and polymer concentration. Solute shape and size, in particular, will be a critical determinant of diffusion in semidilute polymer solutions. Diffusion of small solute molecules in polymer solutions is readily handled using free volume theories[1,2] or microscopic friction coefficients.[6] When the solute is an electrolyte, its diffusion can be described using an adaption of Fujita's free volume theory for pseudobinary systems, as shown by Yasuda.[7] Such a model can reproduce the polymer concentration dependence of the self-diffusion of small solute molecules in a poly(vinyl alcohol) (PVA)−water system[8] but fails to account for the temperature dependence. When the solute is a larger molecule such as poly(ethylene glycol), free volume theory proves especially limited as a means of predicting diffusion bahavior.[8] Although obstruction theories can be modified to describe the diffusion of larger spherical molecules in dilute media,[9,10] they still do not apply in concentrated solutions.

It is generally true that the polymer concentration dependence of the diffusion of larger solute molecules may be described using a stretched exponential of the form $D = D_0 \exp(-\alpha c^{\nu})$. Such an equation arises naturally in various hydrodynamic models of the interactions between solute and polymer.[11−16] Langevin and Rondelez derived a similar phenomenological law,[17] which is consistent with hydrodynamic theories[11−13] and predicts the sedimentation bahavior of larger solutes in semidilute polymer solutions. Unfortunately, in each different hydrodynamic model the physical significance of the quantities α and ν appearing in the stretched exponential is different.

It is evident that no one model of diffusion can as yet successfully treat solute diffusion in polymer solutions over a wide range of solute sizes and polymer concentrations. Any physical model capable of bridging the gap between the diffusion behavior of small versus large solute molecules needs first to distinguish small molecules from large. In semidilute polymer solutions a convenient discriminator of large versus small molecules is the mesh size ξ introduced by de Gennes[18] to describe the correlation length in his representation of the semidilute polymer solution as a statistical network. In this paper we propose a new physical model for the diffusion of solvent and solute molecules in polymer solutions. By treating the polymer solution as a statistical network through which the solute diffuses in a series of jumps over potential barriers determined by the correlation length, we find that we can predict the diffusion behavior of both small and large solutes,[8] in both dilute and more concentrated polymer solutions in water and organic solvents,[19,20] and over a range of temperatures.

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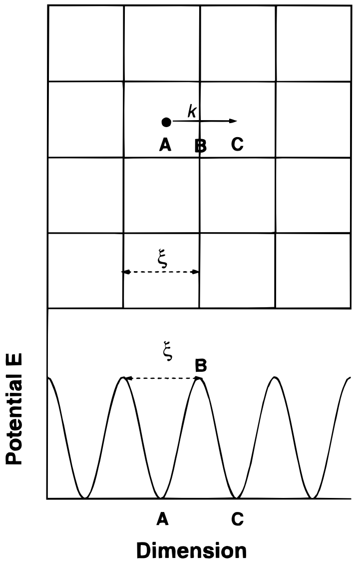

Figure 1. Representation of a polymer solution as a network of mesh size ξ (the correlation length) and potential E for the diffusion process of a molecule in a polymer solution.

The Physical Model

In the scaling theory of de Gennes,[18] a semidilute polymer solution is represented by a transient statistical network with mesh size ξ, known as the correlation length. We propose that the diffusion of a probe in such a polymer network can be regarded as a process involving a potential barrier. The diffusing molecules, either the solvents or the solutes, are regarded as particles residing temporally in a cavity. Diffusion occurs when the particles overcome a certain energy barrier and jump into the next cavity. For simplicity, we will consider one-dimensional diffusion through a periodic energy potential, as shown in Figure 1. The energy potentials are assumed to be of equal amplitude ΔE and spaced at intervals equal to ξ, which corresponds to the correlation length in semidilute polymer solutions as defined by de Gennes.

Applying Fick's first law of diffusion to a lattice model leads to the well-known relation for the diffusion coefficient:

$$D = \xi^2 k \tag{1}$$

where k is the jump frequency, which is expected to depend on temperature and size of the diffusant. For an ensemble of noninteracting particles moving in a matrix such as represented in Figure 1, this jump frequency over the periodic energy barriers, or escape rate as it is termed by Kramers,[21] can be written in an Arrhenius form:

$$k = F_{\mathrm{p}} \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \tag{2}$$

where F_{p} is a frequency prefactor, ΔE is the height of the potential barrier, k_{B} is the Boltzmann constant, and T is the temperature. The parameter k is the rate at which a particle originally residing in the potential hole at A jumps into C crossing the barrier at B as a consequence of Brownian motion, as shown in Figure 1. Although the potential barrier ΔE is a free energy arsing from both enthalpic and entropic contributions, we assume that it is more or less a constant within a certain temperature range. On the other hand, the dependence of ξ on the polymer concentration in the semidilute regime is given by[18]

$$\xi = R_{\mathrm{g}}\left(\frac{c^*}{c}\right)^{\nu} = \beta c^{-\nu} \tag{3}$$

where R_{g} is the radius of gyration of the polymer, c^* is the overlap concentration between the dilute and semidilute regime, and c is the polymer concentration. When the polymer chains are longer than the mesh size and in a solution where $c > c^*$, ξ depends only on the concentration and not on the molecular weight of the polymer.[18] Therefore, β should be a constant and does not vary as a function of polymer concentration or the molecular weight of the polymer. Substituting eq 3 into 1, we have

$$D = k\beta^2 c^{-2\nu} \tag{4}$$

This expression for D is valid when the polymer concentration is greater than zero but becomes inappropriate as the concentration approaches zero. To formulate a better expression, the friction coefficient of the diffusing molecules is considered. It is generally assumed that the total friction coefficient, f, experienced by a diffusing molecule results from an additive contribution from the liquid solvent background, f_0, and from the polymer network, f_{p}:[22,23]

$$f = f_0 + f_{\mathrm{P}} \tag{5}$$

where the term f_{p} represents the excess of friction due to the polymer. Using the Stokes−Einstein relation, $D = k_{\mathrm{B}}T/f$, and eq 1, we can rewrite eq 5 as the following:

$$\frac{1}{D} = \frac{1}{D_0} + \frac{1}{k\xi^2} \tag{6}$$

where D_0 is the diffusion coefficient of the diffusing molecule in the absence of the polymer. Combining eqs 3 and 6 followed by rearrangements gives

$$\frac{D}{D_0} = \frac{1}{1 + ac^{2\nu}} \tag{7}$$

where $a = D_0/k\beta^2$ and $k\beta^2$ and ν are the characteristic parameters of the model. According to the blob model of de Gennes,[18] ν values depend only on the quality of the solvent and should be a constant of the system. The parameter k, however, is not a constant. In fact, the parameters F_{p} and ΔE, upon which k depends, should both be functions of the polymer concentration, and over a large range of polymer concentrations this dependence will be evident. To simplify the treatment, we will assume that, to a first approximation, k remains constant within a certain concentration range; i.e., k does not change although the size of the cavity does with varying polymer concentrations. For a given polymer−solvent system, it is expected that β remains constant so that $k\beta^2$ depends only on the size of the diffusing molecule and on the temperature.

Experimental Section

The self-diffusion coefficients were measured using the pulsed-gradient spin-echo (PGSE) NMR technique described previously.[8,19,20] The experimental details and the preparation of the samples were also described in these reports. The results from the variable temperature experiments are new and were performed at 23, 33, 43, and 53 °C. All of the diffusion coefficients reported here have the unit of m²/s unless

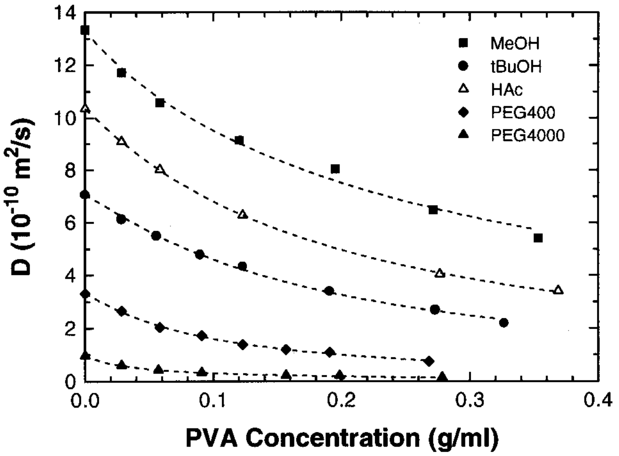

Figure 2. Solute probes diffusion coefficients in PVA1 solutions as a function of polymer concentration at 23 °C. Dashed lines are fittings to eq 7.

otherwise specified. The error of the measured self-diffusion coefficients was estimated as less than 5%. A nonlinear least-squares fitting method was used in all cases and the errors listed in the tables are expressed as the root-mean-square (RMS) fractional error.

The samples include binary PMMA–organic solvent[19,20] and ternary PVA–water–solute systems.[8] The ketone solvents include acetone (ACT), 2-butanone (methyl ethyl ketone, MEK), 2-pentanone (methyl propyl ketone, MPK), 3-methyl-2-butanone (methyl isopropyl ketone, MiPK), 2-hexanone (methyl butyl ketone, MBK), 3,3-dimethyl-2-butanone (methyl *tert*-butyl ketone, MtBK), and 4-methyl-2-pentanone (methyl isobutyl ketone, MiBK). The ester solvents include methyl acetate (MeAc), ethyl acetate (EtAc), propyl acetate (PrAc), isopropyl acetate (iPrAc), methyl propionate (MePr), methyl butyrate (MeBu), and methyl isobutyrate (MeiBu). PVA samples of different degrees of hydrolysis (DH) and molecular weights (M) were used as described previously.[8] These include the following samples: PVA1 (DH = 99% and M = 50 000), PVA2 (DH = 99% and M = 115 000), and PVA3 (DH = 87–89% and M = 115 000). The solute probes include methanol (MeOH), *tert*-butyl alcohol (tBuOH), acetic acid (HAc), tetramethylammonium chloride (TMACl), trimethylamine (TMA), formamide (FA), and poly(ethylene glycol) (PEG) of molecular weights 400 and 4000.

Results and Discussion

(1) PVA–Water Systems. The polymer concentration dependences of the self-diffusion coefficients of a series of solvents and solutes, reported previously,[8,19,20] were fitted to eq 7 to obtain values of $k\beta^2$ and ν. Figure 2 shows the correspondence between the experimental data and the lines-of-best-fit for selected solutes in ternary PVA–water–solute mixtures at 23 °C. Table 1 lists the values of the fit parameters obtained for these and all other solute probes. The exponent ν appears to be a characteristic of a given polymer system, remaining more or less a constant for each group of the PVA samples. Mean values of ν are 0.52 for PVA1, 0.37 for PVA2, and 0.42 for PVA3. According to the scaling theory, the parameter ν depends largely on the quality of the particular solvent and should, therefore, be invariant over the range of PVA concentrations shown in Figure 1, as is found to be the case. For a good solvent it is predicted that ν equals about 0.75, for a Θ solvent ν equals 1.0, and for a marginal solvent ν equals about 0.5.[24] Water is not a Θ solvent for PVA at 23 °C (the value of the Flory–Huggins χ parameter for water in PVA at 30 °C is about 0.49[25]). Therefore, water can be regarded as a marginal solvent for PVA and the values of ν obtained from our fittings are in good agreement with de Gennes' prediction.

Table 1. Molecular Sizes, Self-Diffusion Coefficients, and Parameters $k\beta^2$ and ν Obtained from Solute Probe Diffusion in PVA–Water Systems at 23 °C by Curve Fitting to Eq 7[a]

PVA	solute	D_0 (10^{-10} m^2/s)	R_H (Å)	ν	$k\beta^2$ × 10^{10}	RMS error
M = 50 000	water	19.5	1.20	0.51	5.21	0.006
DH = 99%	MeOH	13.3	1.75	0.47	3.73	0.012
	tBuOH	7.07	3.30	0.56	0.98	0.010
	PEG 400	3.31	7.00	0.56	0.23	0.010
	PEG 4000	0.958	24.35	0.50	0.047	0.012
	$N(CH_3)_3$	7.96	2.93	0.50	1.68	0.007
	$^+N(CH_3)_4$	9.79	2.38	0.54	1.73	0.004
	HAc	10.35	2.25	0.53	1.73	0.010
	$HCONH_2$	7.37	3.16	0.52	1.27	0.007
M = 115 000	MeOH	13.3	1.75	0.35	5.8	0.011
DH = 99%	tBuOH	7.07	3.30	0.38	2.0	0.009
M = 115 000	MeOH	13.3	1.75	0.43	4.9	0.010
DH = 87–89%	tBuOH	7.07	3.30	0.42	1.7	0.007

[a] Data taken from ref 8.

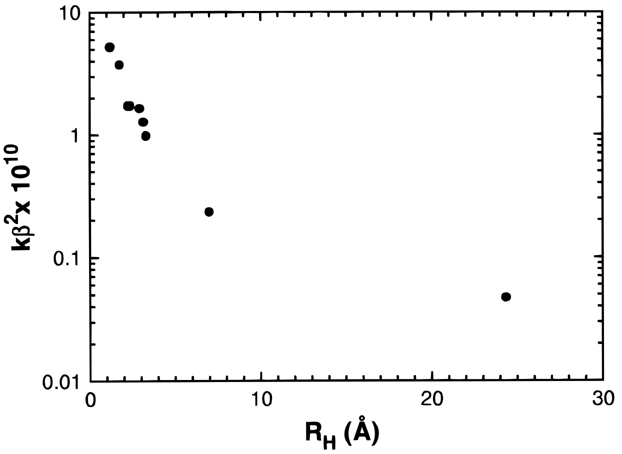

Figure 3. Semilogarithmic plot of the parameter $k\beta^2$ of the model as a function of the hydrodynamic radius of the solute probes for PVA1.

The second fitting parameter $k\beta^2$ is inversely proportional to the molecular size of the diffusing solute molecules. This is evident in Figure 3, where the fitted values of $k\beta^2$ (Table 1) are plotted as a function of the hydrodynamic radius, R_H, of the particular solute molecules. The latter is calculated from the D_0 values in Table 1 by the use of the Stokes–Einstein equation. Since β is a constant for a given polymer system and does not depend on the size of the diffusing molecule, any change in $k\beta^2$ must be due to changes in k, the rate at which a molecule escapes from the potential hole. This will depend on the nature of the molecules, especially the molecular size. It is reasonable to expect that the larger molecules will have a lower jumping frequency k. Therefore, according to eq 2, the potential barrier ΔE associated with a lower jumping frequency is higher for the larger molecules.

The ability of our diffusion model to reproduce the temperature dependence of solute diffusion in PVA–water systems is demonstrated in Figure 4A, where we plot the logarithm of the diffusion coefficients of tBuOH in the aqueous solutions of PVA1 as a function of reciprocal temperature for different polymer concentrations. A certain curvature is observed for these lines, even within the relatively narrow temperature range studied here. Nevertheless, via linear regression analysis one may estimate an apparent activation energy for

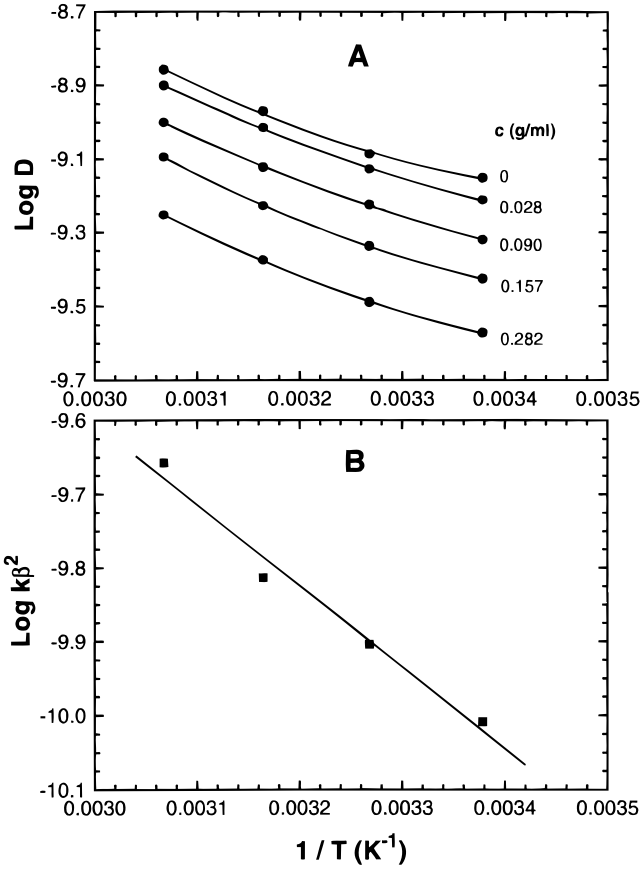

Figure 4. (A) Semilogarithmic plot of the diffusion coefficients of *tert*-butyl alcohol as a function of reciprocal temperature for each polymer concentration studied in PVA1. (B) Semilogarithmic plot of the parameter $k\beta^2$ of the model as a function of reciprocal temperature for *tert*-butyl alcohol in PVA1. A potential barrier ΔE of 21 kJ/mol can be calculated from the data.

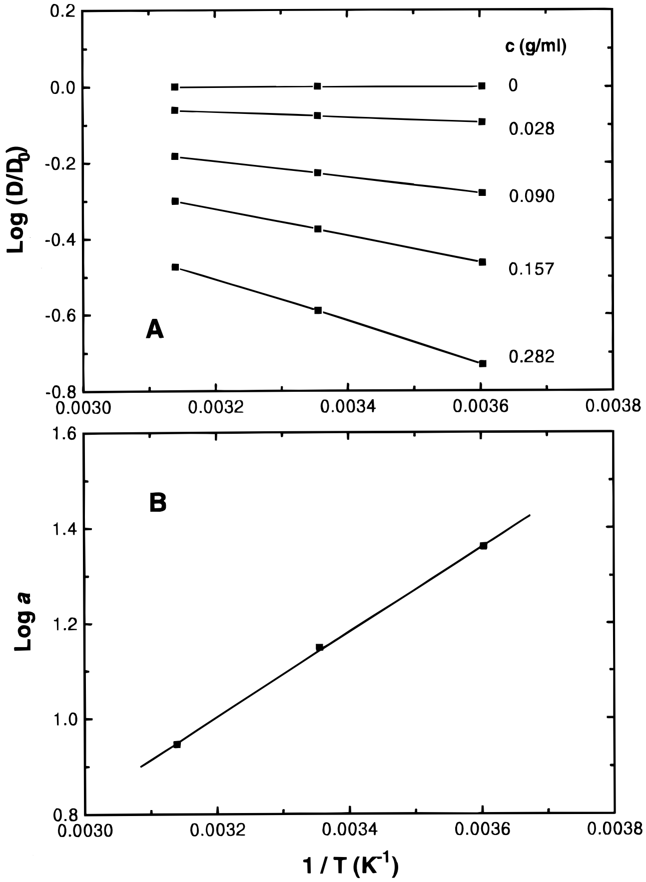

Figure 5. (A) Semilogarithmic plot of the reduced diffusion coefficients of 9,10-diphenylanthracene in THF solutions of polyisoprene[26] as a function of reciprocal temperature. (B) Semilogarithmic plot of the parameter a of the model as a function of reciprocal temperature for the probe in the polyisoprene solutions. Note that $a = D_0/k\beta^2$. A potential barrier ΔE of 30 kJ/mol can be calculated from the data.

Table 2. Parameters ν and $k\beta^2$ Obtained from the Diffusion Data of tBuOH in the PVA1−Water System at Different Temperatures by Fitting the Experimental Data to Eq 7

temp (°C)	D_0 (10^{-10} m^2/s)	ν	$k\beta^2 \times 10^{10}$	RMS error
23	7.07	0.56	0.98	0.010
33	8.18	0.57	1.25	0.006
43	10.7	0.58	1.54	0.004
53	13.9	0.58	2.21	0.003

the diffusion process. These range from 18.3 kJ/mol in the absence of PVA to an average of 19.7 kJ/mol for the polymer solutions. There is a discontinuity in the apparent activation energy between zero polymer concentration and the lowest polymer concentration measured, with a small, continuous increase in the apparent activation energy with increasing polymer concentration. It should be noted, however, that the dependence of the activation energy on polymer concentration is really quite small in this particular system. This may be attributed to the fact that the size of the diffusing solute tBuOH (3.3 Å) is small compared to the mesh size of the network (calculated to be on the order of 5−15 Å for PVA in the concentration range of interest[8]). Consequently, $2R_H < \xi$ and the polymer network does not create an effective barrier to the diffusion of small molecules. For larger diffusants ($2R_H \approx \xi$) there should be an obvious concentration dependence of the apparent activation energy. Johnson *et al.*[26] studied the diffusion of a much larger probe molecule, 9,10-diphenylanthracene, in tetrahydrofuran (THF) solutions of polyisoprene (PI) at three different temperatures. The reduced diffusion coefficients (D/D_0) reported by these researchers may be used to obtain a plot similar to that in Figure 4A, as shown in Figure 5A. It is clear that for this large solute there is a dependence of the apparent activation energy on the polymer concentration, as evidenced by the different slopes of the lines. We might speculate that when the size of the probe molecule is much greater than the mesh size of the polymer network ($2R_H \gg \xi$), if such a probe were available, the diffusion mechanism may be very different if diffusion takes place at all.

Listed in Table 2 are the parameters of the fit of our experimental data on the temperature dependence of tBuOH diffusion in the PVA1−water system to eq 7. The parameter ν does not depend on temperature and falls very close to the average value of 0.52 obtained for PVA1 with the various different solutes shown in Table 1. The energy barrier ΔE for the diffusion of tBuOH in PVA−water may be calculated when we assume that both β and F_p are independent of temperature. As shown in Figure 4B, plotting the logarithm of the parameter $k\beta^2$ as a function of $1/T$ yields a good linear relationship. From the slope of this relationship the energy barrier ΔE is calculated to equal 21 kJ/mol. This represents the height of the potential barrier that tBuOH has to overcome for the diffusion to take place. The value obtained in this fashion is very close to the average value of the apparent activation energy calculated above (19.7 kJ/mol). When the diffusion data of Johnson *et al.*[26] for 9,10-diphenylanthracene in PI−THF

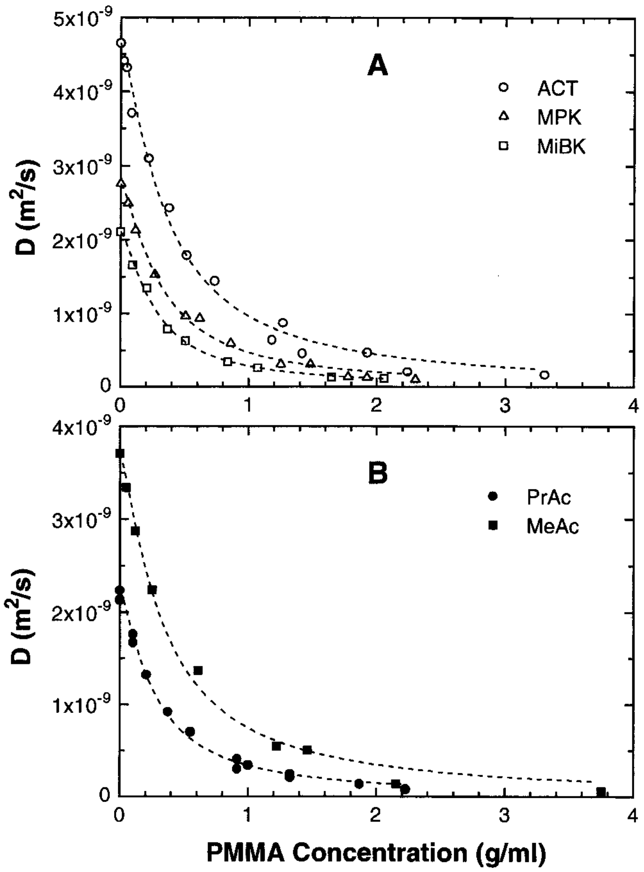

Figure 6. Solvent diffusion coefficients in PMMA solutions as a function of polymer concentration at 23 °C for ketones (A) and esters (B). Dashed lines are fittings to eq 7.

is plotted in a similar fashion (log *a* versus 1/*T*), as shown in Figure 5B, again a good linear relationship is found and one calculates a potential barrier of 30 kJ/mol. This is the correct trend expected for a solute molecule larger than any we have investigated here.

The proposed physical model in its present form does not predict any effect of the molecular weight of the polymer. We have measured the self-diffusion coefficients of two solute probes (MeOH and tBuOH) in PVA of different molecular weights, as shown in Table 1. Differences in the values of the fitting parameters $k\beta^2$ and ν are obtained for different molecular weights of PVA, and their origin is not yet clear.

(2) PMMA–Solvents Systems. To verify the validity of the model in organic solvent–polymer solutions, we have used eq 7 to fit previously reported solvent diffusion data in PMMA solutions for a series of ketones and esters varying in size and shape.[19,20] As shown in Figure 6 for selected examples, eq 7 provides an excellent fit to the experimental diffusion coefficients as a function of PMMA concentration over a wide range of concentrations. The parameters from the fittings are listed in Table 3. The root mean square errors are somewhat higher than those listed in Tables 1 and 2 for the aqueous systems, possibly due to the fact that ketone and ester diffusion data cover a much larger concentration range, spanning both the dilute and semidilute regimes. Moreover, the experimental error involved in diffusion measurements of concentrated samples are usually higher than the dilute ones due to the limitations of the NMR technique.[19,20]

Table 3. Molecular Sizes, Self-Diffusion Coefficients, and Parameters ν and $k\beta^2$ Obtained from the Solvent Diffusion Data at 23 °C in PMMA Systems by Curve Fitting to Eq 7[a]

solvent	D_0 (10^{-9} m²/s)	R_H (Å)	ν	$k\beta^2 \times 10^{10}$	RMS error
MeAc	3.71	1.57	0.64	9.34	0.248
EtAc	3.04	1.63	0.57	6.77	0.204
PrAc	2.23	1.72	0.66	4.00	0.056
iPrAc	2.41	1.69	0.71	2.81	0.127
MePr	3.01	1.63	0.62	8.24	0.058
MeBu	2.36	1.65	0.68	5.54	0.024
MeiBu	2.42	1.77	0.78	3.81	0.064
ACT	4.65	1.45	0.65	12.2	0.084
MEK	3.58	1.49	0.72	7.52	0.055
MPK	2.76	1.62	0.68	5.70	0.110
MiPK	2.68	1.72	0.68	2.72	0.061
MBK	2.17	1.66	0.70	4.00	0.047
MtBK	1.58	2.01	0.67	2.19	0.019
MiBK	2.11	1.84	0.70	3.33	0.021

[a] Data taken from refs 19 and 20.

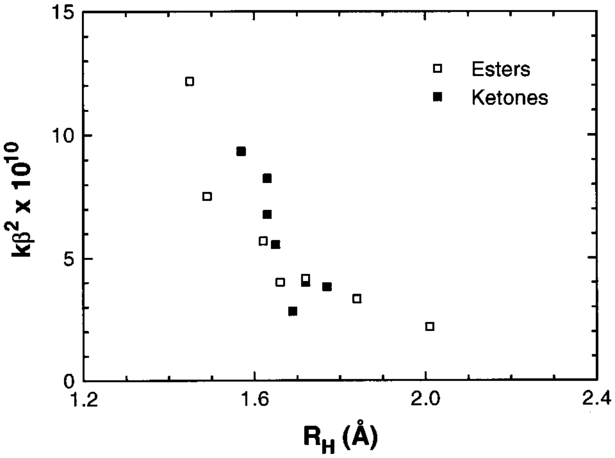

Figure 7. Semilogarithmic plot of the parameter of the model, $k\beta^2$, plotted as a function of the hydrodynamic radius of the solvent in PMMA–solvent systems.

In Table 3, the parameter ν is seen to be approximately the same for all the ester and ketone solvents investigated, with a mean value of 0.67 for the esters and 0.68 for the ketones. These values are in the vicinity of the value for a good solvent of the polymer. The value of $k\beta^2$ is inversely proportional to the hydrodynamic radius of each of the diffusing solvent molecules, as shown in Figure 7. The latter is calculated from the Stokes–Einstein equation.[19,20] Because of the similarity of these solvents, we assume that the value of β does not vary significantly so that its effect on $k\beta^2$ will be minor. Thus, for both ketone and ester solvents, *k* decreases as the size of the diffusing molecule increases.

Concluding Remarks

In the proposed physical model of diffusion, the polymer solution is regarded as a network where the diffusing molecules have to overcome certain periodical energy barriers of equal amplitude. The potential barrier is higher for the larger diffusants. We have shown here that such a model can reproduce the polymer concentration and temperature dependence of the diffusion of solute molecules in aqueous–polymer solutions and that of solvent molecules in organic solvent–polymer solutions.

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