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Effect of Solvent Size on Solvent Self-Diffusion in Polymer−Solvent Systems

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ABSTRACT: The free-volume theory for solvent self-diffusion coefficients in polymer−solvent systems is modified to include a more general analysis of the effects of solvent size. The predictions of the theory are compared with self-diffusion data for a diverse set of solvents and four polymers, polystyrene, poly(vinyl acetate), poly(methyl methacrylate), and poly(*p*-methylstyrene). The new prediction of size effects is based on the consideration of the asymmetry of solvent molecules.

Introduction

The free-volume theory of transport provides a useful framework for predicting and correlating solvent self-diffusion coefficients for polymer−solvent systems. Recently, it has been shown[1,2] that the equations of free-volume theory produce good predictions for the temperature and concentration variations of solvent self-diffusion coefficients for both rubbery and glassy polymer−solvent systems. The purpose of this paper is to examine the predictions of the theory for the effect of the size of the solvent on the self-diffusion process. The general equations of the theory are presented and discussed in the second section of the paper, and a more general analysis of size effects is developed in the third section. A comparison of the predictions of this more general version of free-volume theory with experimental data is presented in the fourth section of the paper.

Equations of Free-Volume Theory

For a rubbery polymer−solvent system, the solvent self-diffusion coefficient, D_1, can be determined using the following equations:

$$D_1 = \bar{D}_0 \exp\left[-\frac{E^*}{RT}\right] \exp\left[-\frac{\omega_1 \hat{V}_1{}^* + \omega_2 \xi \hat{V}_2{}^*}{\hat{V}_{\mathrm{FH}}/\gamma}\right] \qquad (1)$$

$$\frac{\hat{V}_{\mathrm{FH}}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} + T - T_{\mathrm{g1}}) + \frac{\omega_2 \hat{V}_{\mathrm{FH2}}}{\gamma_2} \qquad (2)$$

$$\hat{V}_{\mathrm{FH2}} = \hat{V}_2{}^0(T_{\mathrm{g2}})[f_{\mathrm{H2}}^{\mathrm{G}} + \alpha_2(T - T_{\mathrm{g2}})] \qquad T \geq T_{\mathrm{g2}} \qquad (3)$$

$$\hat{V}_{\mathrm{FH2}} = \hat{V}_2{}^0(T_{\mathrm{g2}})[f_{\mathrm{H2}}^{\mathrm{G}} - \int_T^{T_{\mathrm{g2}}} (\alpha_2 - \alpha_{\mathrm{c2}})\, \mathrm{d}T'] \qquad T < T_{\mathrm{g2}} \qquad (4)$$

$$\alpha_{\mathrm{c2}} = \frac{\ln\left[\dfrac{\hat{V}_2{}^0(T_{\mathrm{g2}})(1 - f_{\mathrm{H2}}^{\mathrm{G}})}{\hat{V}_2{}^0(0)}\right]}{T_{\mathrm{g2}}} \qquad (5)$$

$$f_{\mathrm{H2}}^{\mathrm{G}} = \alpha_2 K_{22} \qquad (6)$$

$$\gamma_2 = \frac{\hat{V}_2{}^0(T_{\mathrm{g2}})\alpha_2}{K_{12}/\gamma_2} \qquad (7)$$

$$\hat{V}_1{}^* = \hat{V}_1{}^0(0) \qquad (8)$$

$$\hat{V}_2{}^* = \hat{V}_2{}^0(0) \qquad (9)$$

In these equations, the solvent is component 1 and the polymer is component 2. Also, $\bar{D}_0$ is an effectively constant preexponential factor, $\hat{V}_I^*$ is the specific hole free volume of component I required for a jump, ω_I is the mass fraction of component I, T is the temperature, and $T_{\mathrm{g}I}$ is the glass transition temperature of pure component I. In addition, E^* is an energy parameter defined previously,[1] $\hat{V}_{\mathrm{FH}}$ is the average hole free volume per gram of mixture, $f_{\mathrm{H2}}^{\mathrm{G}}$ is the fractional hole free volume of the polymer at its glass transition temperature T_{g2}, γ represents an average overlap factor for the mixture, and γ_I represents the overlap factor for the free volume of pure component I. Also, $\hat{V}_I{}^0(0)$ is the specific volume of component I at 0 K, $\hat{V}_2{}^0(T_{\mathrm{g2}})$ is the specific volume of the liquid polymer at T_{g2}, K_{11} and K_{21} are free-volume parameters for the solvent, K_{12} and K_{22} are free-volume parameters for the polymer, and α_{c2} is the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume of the equilibrium liquid polymer. Furthermore, $\hat{V}_{\mathrm{FH2}}$ is the specific hole free volume of the equilibrium liquid polymer at any temperature, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, and α_2 is the thermal expansion coefficient for the equilibrium liquid polymer. An average value above T_{g2} is used in eqs 3 and 7, and a temperature-dependent $\alpha_2(T)$ should be used in eq 4 if the data are available.

The dependence of D_1 on ω_1 and T can thus be determined[1] from the above equations for rubbery polymer−solvent systems if the following parameters are available: $\bar{D}_0$, E^*, $\hat{V}_1{}^0(0)$, $\hat{V}_2{}^0(0)$, ξ, K_{11}/γ_1, $K_{21} - T_{\mathrm{g1}}$, K_{12}/γ_2, K_{22}, T_{g2}, $\hat{V}_2{}^0(T_{\mathrm{g2}})$, and $\alpha_2(T)$. These parameters are also sufficient for the calculation of D_1 for glassy polymer−solvent systems.[2] From a parameter evaluation scheme presented previously,[1] it is evident that all of the above parameters, with the exception of ξ and E^*, can be determined using generally available data for the pure components. The parameters ξ and E^* can be determined using as few as two diffusivity data points, and either a temperature dependence method[1] or a concentration dependence method[3] can be used. For the temperature dependence method, ξ and E^* are determined using measured solvent self-diffusion coefficients at $\omega_1 = 0$ and at two or more temperatures. For the concentration dependence method, ξ and E^* are

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computed using at least two $D_1-\omega_1$ data points at a single temperature.

It of course would be preferable if ξ could be estimated without using any polymer−solvent diffusivity data. Also, it seems useful to generalize the present version of the theory for the prediction of solvent size effects. It is shown in the next section that a generalization of the size effect part of the theory leads to an equation for the direct estimation of ξ.

Theory for Effects of Solvent Size

In the original version of the free-volume theory of diffusion,[4] it was assumed that any difference in molecular types does not bias the random distribution of the hole free volume among all of the molecules of the mixture. This assumption leads to eq 1, where ξ is defined as follows:

$$\xi = \tilde{V}_1^*/\tilde{V}_2^* \tag{10}$$

Here, $\tilde{V}_1^*$ is the minimum or critical hole free volume per mole of solvent jumping units required for displacement of a solvent jumping unit, and $\tilde{V}_2^*$ is the critical hole free volume per mole of polymer jumping units required for displacement of a polymer jumping unit. It is primarily through the parameter ξ that solvent size influences the diffusion process. In the free-volume picture of the self-diffusion process, the polymer jumping unit is an intrinsic property of the polymer, and the size of the polymer jumping unit is not in any way influenced by solvent size and shape. For relatively small or symmetrically shaped penetrant molecules, it is reasonable to expect that the entire penetrant molecule will perform a jump so that[5]

$$\xi = \xi_L = \tilde{V}_1^0(0)/\tilde{V}_2^* \tag{11}$$

where $\tilde{V}_1^0(0)$ is the molar volume of the equilibrium liquid solvent at 0 K. This result is derived by assuming that the critical amount of hole free volume per mole necessary for a jump of a solvent molecule is equal to the occupied volume per mole, which is defined to be the molar volume of the equilibrium liquid solvent at 0 K. Hence, a plot of ξ versus the molar volume at 0 K of the entire solvent molecule will be a straight line through the origin for all solvents which jump as single units.[5,6]

For some solvents, however, $\xi < \xi_L$, and it has been assumed that such solvents move in a segmentwise manner with jumping units which constitute only a portion of the solvent molecule.[5,7,8] This may be true, for example, for flexible chain solvents of sufficient length. Consequently, the molecular shape and flexibility of a solvent, as well as the total molecular volume, may be of importance in the self-diffusion process. Segmentwise diffusion of penetrants in polymers implies that a single-size jumping unit of the solvent molecule has a significantly greater probability for jumping than a jumping unit of any other size and that such jumping units can exhibit reasonably independent movement over small distances. Furthermore, it has been shown[9] that it appears that the nature of the segmentwise movement for a particular solvent is strongly dependent on the characteristics of the polymer matrix through which the solvent is diffusing. It was argued previously that the large difference in $\tilde{V}_1^*$ values for a solvent which can move in a segmentwise manner in two different polymers is somehow related to differences in the attractive forces and structure of the two polymers. However, no explicit explanation was provided for this effect. Indeed, an analysis of a segmentwise diffusion process is quite difficult, and it appears unlikely that it will be possible to estimate ξ for cases when $\xi < \xi_L$ because of segmentwise motion.

Although there will of course be segmentwise movement in sufficiently long, flexible chain solvents (which begin to approximate polymer molecules), the possibility of segmentwise movement is not nearly as plausible for smaller solvents. The solvent size influences the diffusion process directly through the parameter ξ, and, hence, information on the effect of solvent size, shape, and flexibility on the diffusion process can be obtained by measuring ξ for a wide variety of solvents diffusing in several different polymers. A study of this type has been nicely carried out by Arnould[10] and Arnould and Laurence.[11] These investigators measured D_1 values for a wide variety of solvents in three polymers, and they reported a rather large set of ξ values. They showed that $\xi < \xi_L$ not only for *n*-alkane diffusion in polymers but also for solvents like toluene and ethylbenzene. The segmentwise movement of penetrants like toluene and ethylbenzene is somewhat debatable, and it seems preferable to seek an alternative explanation for the observation that $\xi < \xi_L$ for such penetrants.

As noted above, the present version of free-volume theory is based on the assumption that the nature of the molecular species in a binary mixture does not influence the random distribution of hole free volume. This convenient and apparently reasonable assumption can easily be relaxed; such a procedure leads to a more general analysis of solvent size effects in the solvent self-diffusion process. The total hole free volume in a binary system, V_{FH}, can be calculated using the following equation

$$V_{FH} = n_1\bar{V}_{FH1} + n_2\bar{V}_{FH2} \tag{12}$$

where n_I is the number of jumping units of component I and $\bar{V}_{FHI}$ is the average hole free volume associated with a jumping unit of component I. Previously, it was assumed that $\bar{V}_{FH1} = \bar{V}_{FH2}$, but here, in general, $\bar{V}_{FH1} \neq \bar{V}_{FH2}$. Hence, eq 12 can be written as follows

$$V_{FH} = \bar{V}_{FH1}[n_1 + n_2\psi] \tag{13}$$

$$\psi = \tilde{V}_{FH2}/\tilde{V}_{FH1} \tag{14}$$

where $\tilde{V}_{FHI}$ is the average hole free volume per mole of jumping units of component I. Previously, $\psi = 1$ and eq 1 was derived with ξ defined by eq 10. If we now assume more generally that $\psi \neq 1$, it is then possible to use exactly the same procedure to derive eq 1 again, but now ξ is defined by the new equation:

$$\xi = \frac{\tilde{V}_1^*}{\tilde{V}_2^*}\psi \tag{15}$$

This equation illustrates that there are two mechanisms by which ξ can be less than ξ_L. The first, as before, is the presence of segmentwise diffusion, with a solvent jumping unit smaller than the solvent molecule. The second method is the existence of values of $\psi < 1$, which means that the solvent jumping unit attracts more hole free volume than the polymer jumping unit. In this case, a large solvent molecule influences the distribution of hole free volume, presumably by providing a large site for the accumulation of this hole free volume. The additional hole free volume suggests the possibility that the large solvent molecule can move as a single unit.

The calculation of an appropriate value of ψ for a polymer–solvent system is certainly not straightforward. However, since the problem involves geometrical aspects of the system, it appears that estimating ψ is an easier problem than analyzing the segmentwise movement of a molecule. The following assumptions are introduced in the formulation of a model for the prediction of ψ and, hence, ξ:

(1) The average hole free volume associated with a polymer jumping unit is proportional to the size of the polymer jumping unit (which is the same as the critical volume):

$$\tilde{V}_{\mathrm{FH2}} = k\tilde{V}_2^* \qquad (16)$$

The parameter k is simply a proportionality constant.

(2) For polymer–solvent systems, there is a considerable amount of polymer–polymer contact since the domains of polymer molecules begin to overlap at small polymer concentrations for polymers of reasonable molecular weight. Hence, the polymer segments dominate the volume of the system, and it seems reasonable to assume that the average hole free volume associated with a symmetrically shaped solvent jumping unit is the same as that for a polymer jumping unit. The polymer dominates the distribution of free volume because the symmetrically shaped jumping units do not promote the accumulation of additional hole free volume. For such solvents

$$\tilde{V}_{\mathrm{FH1}} = k\tilde{V}_2^* \qquad (17)$$

and, hence, $\psi = 1$.

(3) For an asymmetric solvent jumping unit, there is an enhancement of the accumulation of average hole free volume because of the asymmetry of the molecular shape. We thus assume that

$$\tilde{V}_{\mathrm{FH1}} = \text{average free volume for symmetric part of volume} + k\,[\text{total volume} - \text{symmetric part of volume}] \qquad (18)$$

As a very rough approximation, the jumping unit is approximated as a rectangular parallelepiped with a square cross section with side A and a height equal to B. Hence, eq 18 can be written as follows

$$\tilde{V}_{\mathrm{FH1}} = k\tilde{V}_2^* + k[BA^2 - A^3]N_{\mathrm{A}} \qquad (19)$$

where N_{A} is Avogadro's number. Consequently, since

$$\tilde{V}_1^* = A^2BN_{\mathrm{A}} \qquad (20)$$

it is easy to show that

$$\psi = \frac{1}{1 + \dfrac{\tilde{V}_1^*}{\tilde{V}_2^*}\left(1 - \dfrac{A}{B}\right)} \qquad (21)$$

Clearly, ψ depends on the sizes of the jumping units of polymer and solvent and on the aspect ratio B/A. As $B/A \to 1$, $\psi \to 1$.

(4) The aspect ratio B/A can be computed by putting the major plane of the jumping unit (or molecule) in the $X-Y$ plane and determining the size of the rectangle which encloses the molecule. Rohrbaugh and Jurs[12] arrived at the initial orientation by aligning the two principal moments of a molecule with the X and Y axes. They then calculated two aspect ratios. One aspect ratio was based on the rectangle with minimum area which could enclose the molecule. The second aspect ratio was based on the rectangle enclosing the molecule which maximized B/A. In most cases, the two B/A ratios were identical. For cases where they are not, it seems reasonable to utilize an average of the two. The aspect ratio B/A is a geometry-based descriptor of the molecular shape, and it can be computed for many penetrants using the ADAPT software package developed by Professor Jurs and his research group in the Chemistry Department at the Pennsylvania State University.

(5) It is assumed that most penetrants of interest jump as single units, the possible exceptions being very long, flexible chain solvents which begin to approach the characteristics of small polymer molecules. Large, asymmetric solvent molecules can jump as single units because their shape enhances the availability of hole free volume. Consequently, if we assume that most solvents will jump as single units, combination of eqs 11, 15, and 21 produces the following equation for estimating ξ for most solvents of interest:

$$\xi = \frac{\xi_{\mathrm{L}}}{1 + \xi_{\mathrm{L}}\left(1 - \dfrac{A}{B}\right)} \qquad (22)$$

For symmetric molecules, $B/A = 1$ and $\xi = \xi_{\mathrm{L}}$. For asymmetric molecules, $B/A > 1$ and $\xi < \xi_{\mathrm{L}}$. Also, for small solvent molecules (small $\tilde{V}_1^*$) or for polymers with large jumping units (large $\tilde{V}_2^*$), it is evident that ξ_{L} is significantly less than unity and $\xi \approx \xi_{\mathrm{L}}$. Finally, the present theory also allows for the possibility of segmentwise movement of the solvent with ξ defined as follows:

$$\xi = \frac{\dfrac{\tilde{V}_1^*}{\tilde{V}_2^*}}{1 + \dfrac{\tilde{V}_1^*}{\tilde{V}_2^*}\left(1 - \dfrac{A}{B}\right)} \qquad (23)$$

For this case, of course, ξ cannot be calculated since $\tilde{V}_1^*$ for the solvent is not known.

The present version of the free-volume theory of transport retains the basic picture of the self-diffusion process and also yields exactly the same equation for D_1. The new result for this paper is a more general analysis of size effects which allows both segmentwise movement of solvent molecules and the possibility that the average hole free volumes associated with polymer and solvent jumping units are different. This new size effect analysis leads to a new definition for ξ which includes both the effects of a possible segmentwise movement and the possibility of a difference between the average hole free volumes of the solvent and polymer. Also, an equation is presented (eq 22) which allows for the direct estimation of ξ for cases where solvent molecules jump as single units. In this equation, $\tilde{V}_1^*$ can be set equal to $\tilde{V}_1^0(0)$, the molar volume of the equilibrium liquid solvent at 0 K; this quantity can be determined using methods discussed by Haward.[13] The parameter B/A can be calculated using the ADAPT software developed by Rohrbaugh and Jurs.[12] The quantity $\tilde{V}_2^*$ cannot be calculated directly. However, since it is independent of the nature of the solvent, it can be determined using diffusion data for a single solvent since it can be regarded as an intrinsic polymer property. Values of $\tilde{V}_2^*$ for four polymers are reported here, and these of course provide a basis of predicting ξ

Table 1. $\tilde{V}_2^*$ Values for Four Polymers

polymer	$\tilde{V}_2^*$ (cm^3/mol)
PVAC	88.8
PS	135
PMMA	135
PPMS	345

Table 2. ξ Values for PVAC−Solvent Systems

solvent	B/A	ξ_L	ξ(theory)	ξ(expt)
methanol	1.251	0.346	0.32	0.31
acetone	1.160	0.646	0.59	0.60
benzene	1.091	0.792	0.74	0.74
toluene	1.242	0.950	0.80	0.75
cyclohexane	1.089	0.954	0.89	0.88
ethylbenzene	1.409	1.11	0.84	0.78
p-xylene	1.387	1.11	0.85	0.79
m-xylene	1.168	1.11	0.96	0.80
o-xylene	1.037	1.11	1.07	0.82
methyl acetate	1.319	0.723	0.62	0.65
ethyl acetate	1.364	0.882	0.71	0.70
propyl acetate	1.681	1.04	0.73	0.74
butyl acetate	1.888	1.20	0.77	0.77
amyl acetate	2.284	1.36	0.77	0.78

for all other solvents in these polymers. Hence, once $\tilde{V}_2^*$ is determined, the theory for ξ can be regarded as a predictive theory. Predicted values of ξ are compared with experimental values of ξ in the next section of this paper.

Results and Discussion

The predictions of the new theory for ξ are compared with experimental ξ values for a diverse set of solvents in four polymers: polystyrene (PS), poly(vinyl acetate) (PVAC), poly(methyl methacrylate) (PMMA), and poly(*p*-methylstyrene) (PPMS). All of the ξ values for PVAC, PMMA, and PPMS were taken directly from the investigations of Arnould[10] and Arnould and Laurence.[11] These ξ values were derived using data on the temperature dependence of D_1 for trace amounts of the solvents. Some of these data were recently reanalyzed[14] using the temperature dependence method to include energy effects. It was found that there were generally small differences between the values calculated by the temperature dependence method and those reported previously. Consequently, the values presented in the tables of Arnould[10] were used as experimental ξ values for these three polymers. Values of ξ were reported by Arnould for 8 PMMA−solvent systems, 26 PVAC−solvent systems, and 8 PPMA−solvent systems. Only 41 of these 42 polymer−solvent pairs were used in the data−theory comparison. The ξ value for the PPMS−methanol system was not included because, as Arnould has noted, its ξ value is much too high compared to the other solvents. Diffusivity data from selected gas chromatography and sorption experiments[5,15,16] (those judged to be the most reliable) were used to determine ξ values for 8 PS−solvent systems.

Table 3. ξ Values for PVAC−Solvent Systems

solvent	B/A	ξ_L	ξ(theory)	ξ(expt)
hexane	2.201	1.10	0.69	0.74
heptane	2.518	1.26	0.72	0.81
octane	2.617	1.42	0.76	0.83
nonane	3.040	1.58	0.77	0.83
2-methylpentane	1.369	1.10	0.85	0.75
2,3-dimethylbutane	1.103	1.10	1.00	0.88
2,2-dimethylbutane	1.125	1.10	0.98	0.98
1,3,5-hexatriene	1.899	0.94	0.65	0.75
1,4-hexadiene	1.874	0.99	0.68	0.72
1-hexene	2.028	1.05	0.68	0.75
trans-2-hexene	2.014	1.05	0.68	0.76
trans-3-hexene	2.035	1.05	0.68	0.76

Table 4. ξ Values for PMMA−Solvent Systems

solvent	B/A	ξ_L	ξ(theory)	ξ(expt)
methanol	1.251	0.229	0.22	0.19
acetone	1.160	0.426	0.40	0.39
methyl acetate	1.319	0.477	0.43	0.41
ethyl acetate	1.364	0.582	0.50	0.42
propyl acetate	1.681	0.686	0.54	0.49
benzene	1.091	0.523	0.50	0.50
toluene	1.242	0.627	0.56	0.54
ethylbenzene	1.409	0.732	0.60	0.54

Table 5. ξ Values for PPMS−Solvent Systems

solvent	B/A	ξ_L	ξ(theory)	ξ(expt)
acetone	1.160	0.166	0.16	0.15
methyl acetate	1.319	0.186	0.18	0.16
ethyl acetate	1.364	0.227	0.21	0.18
benzene	1.091	0.204	0.20	0.20
toluene	1.242	0.245	0.23	0.23
ethylbenzene	1.409	0.285	0.26	0.26
nonane	3.040	0.406	0.32	0.39

Table 6. ξ Values for PS−Solvent Systems

solvent	B/A	ξ_L	ξ(theory)	ξ(expt)
methanol	1.251	0.228	0.22	0.23
toluene	1.242	0.625	0.56	0.56
ethylbenzene	1.409	0.730	0.60	0.59
octane	2.617	0.932	0.59	0.57
nonane	3.040	1.04	0.61	0.62
decane	3.107	1.14	0.64	0.65
triisopropylbenzene	1.086	1.46	1.31	1.29
benzene	1.091	0.521	0.50	0.45

As noted above, eq 22 can be used to estimate ξ for solvents which jump as single units if $\tilde{V}_2^*$ is known for the polymer of interest. For PMMA, PVAC, and PPMS, this quantity was determined using ξ data for benzene. For PS, the ξ value for toluene was used to compute $\tilde{V}_2^*$. The $\tilde{V}_2^*$ values for these four polymers are presented in Table 1. Equation 22 was then used to predict ξ values for the 45 other polymer−solvent pairs. The predictions of eq 22 are compared with experimental data in Tables 2−6. These tables include the 45 actual data−theory comparisons and also, for completeness, 3 polymer−benzene results (Tables 2, 4, and 5) and 1 polymer−toluene result (Table 6), which, of course, are not predictions since these data were used to determine the $\tilde{V}_2^*$ values for the four polymers. The results in Tables 1−6 can be summarized as follows:

(1) The $\tilde{V}_2^*$ values reported in Table 1 can be regarded as intrinsic polymer properties which can thus be used to analyze the diffusion behavior of any solvent in the polymer of interest. There appears to be no reliable method of directly estimating $\tilde{V}_2^*$. Zielinski and Duda[17] proposed the following empirical relationship for $\tilde{V}_2^*$:

$$\tilde{V}_2^*\left(\frac{\text{cm}^3}{\text{mol}}\right) = 0.6224T_{g2}\ (\text{K}) - 86.95 \qquad (24)$$

This empirical expression was derived by correlating ξ data for a number of polymers, including PVAC, PS, and PMMA. Equation 24 predicts values of 103, 145, and 156 cm^3/mol for PVAC, PS, and PMMA, respectively. As expected, these values are reasonably close to those reported in Table 1. However, eq 24 also predicts that $\tilde{V}_2^*$ = 150 cm^3/mol for PPMS, the only one of the four polymers not used to derive this correlating equation. This value is clearly considerably different from the value reported in Table 1, and, consequently, it does not appear that eq 24 will generally provide valid estimates for $\tilde{V}_2^*$.

(2) For the 45 predicted values of ξ in Tables 2−6, the average absolute error is 7.6%, which is 4 times better than the average absolute error (32%) in using the ξ_L values as estimates of ξ. Clearly, eq 22 provides a reasonable basis for estimating ξ, and the ξ estimates could presumably be improved if a more sophisticated method were used for estimating ψ from the geometry of the molecule. For the present method, 20 of the 45 predictions were within 5% of the experimental value, and only one of the predictions differed by more than 20%.

(3) The experimental data include ξ values for a series of *n*-alkanes in PVAC (Table 3) and in PS (Table 6) and a series of *n*-alkyl acetates in PVAC (Table 2), PMMA (Table 4), and PPMS (Table 5). For all these series, the data indicate that there is a gradual increase in ξ as the size of the molecule increases, so that there appears to be an effective leveling of ξ values for the larger members of the series. In all cases considered here, the theory correctly predicts the gradual increase in ξ with increasing solvent size, and the accuracy of the predicted values is at least reasonably good. In two of the five cases (*n*-alkyl acetate diffusion in PVAC and *n*-alkane diffusion in PS), excellent predictions are obtained.

(4) The importance of aspect ratio on ξ can be studied by collecting data on solvents which have the same volume (same ξ_L values) but not necessarily the same shape (possibly different B/A values). In Table 2, there are four solvents with $\xi_L = 1.11$, and in Table 3, there are four solvents with $\xi_L = 1.10$ and three solvents with $\xi_L = 1.05$. For the solvents with $\xi_L = 1.11$, the experiments show that ξ increases toward ξ_L as B/A decreases toward unity. The theory also predicts this pattern, but the predicted values of ξ approach ξ_L more quickly than the experimental ones. For the solvents with $\xi_L = 1.05$, all of the experimental ξ values are effectively the same, and this is what the theory predicts because the B/A ratios for the three solvents are very close to each other. For the solvents with $\xi_L = 1.10$, the theory predicts that ξ again increases toward ξ_L as B/A decreases, and the experimental data for the most asymmetrical solvents (hexane and 2-methylpentane) also show this trend. However, the ξ values for the other two solvents do not follow this trend, possibly because the B/A values for the two dimethylbutanes are very close. In general, however, the theory correctly portrays the basic nature of the dependence of ξ on molecular shape.

From the above discussion, it seems fair to conclude that the new generalized theory of size effects provides a plausible explanation for data which indicate that $\xi < \xi_L$. Also, it appears that eq 22 provides reasonably good predictions for ξ, especially when account is taken of the fact that careful experiments are needed if ξ values with an accuracy of less than 10% are to be determined. Also, as noted above, the present study provides a framework which can be used if more elaborate methods of evaluating ψ are developed. A viable method for estimating ξ leaves E^* as the only parameter which must be calculated using diffusivity data, and often E^* is small enough to be neglected. Finally, we note that eq 22 can be used to provide the following bounds for ξ for solvents which jump as single units:

$$\frac{\xi_L}{1+\xi_L} \le \xi \le \xi_L \tag{25}$$

Finally, we note that is reasonable to expect that eq 22 can be used to predict ξ for most solvents since segmentwise movement should be absent for the usual solvents of interest. As the solvent size increases, there will of course be an increased probability of segmentwise movement, but it is difficult to predict at what B/A value such movement will start. In the present study, it appears that there is no evidence for segmentwise movement for B/A values as high as 3. As noted above, the utilization of eq 22 requires estimates of B/A and $\tilde{V}_2^*$. In this study, the ADAPT software package was used to estimate B/A, but other molecular modeling software packages could of course be used. The parameter $\tilde{V}_2^*$ for a particular polymer should be determined using the most reliable solvent diffusivity data for that polymer. Also, solvents with B/A values close to unity should be used, if possible, to minimize the effect of any uncertainty in the B/A value. Hence, reliable diffusivity data on symmetric molecules are preferred. In this study, benzene data were thus used for three of the polymers because $B/A = 1.091$ for benzene and because the data were judged to be reliable. Toluene data were used for PS (even though $B/A = 1.242$ for toluene) because these data were thought to be more reliable than the benzene data for this polymer. Finally, we note that errors in estimated ξ values may be important in the prediction of solvent self-diffusion coefficients at low solvent concentrations but they have less of an effect with increasing solvent concentration.

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