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Influence of Solvent Size on the Concentration Dependence of Polymer–Solvent Diffusion Coefficients

H. T. Liu and J. L. Duda*[1]

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

J. S. Vrentas

Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616.

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ABSTRACT: The effect of the size of the solvent on the concentration dependence of the diffusivity for polymer–solvent systems at low solvent concentrations is examined both theoretically and experimentally. From a new version of the free-volume theory of diffusion, it is shown that both the ratio of solvent to polymer specific hole free volumes and the solvent size strongly influence the variation of the diffusivity with concentration. The theory predicts that solvents which differ significantly in size will exhibit markedly different concentration dependences for the diffusivity even if they have comparable free-volume characteristics. Diffusivity data on six polymer–solvent systems provide direct experimental verification of the size effect, and the measured concentration dependences for the diffusivities of these systems are in reasonably good agreement with the predictions of the theory.

It has been observed experimentally that mutual diffusion coefficients for many polymer–solvent systems exhibit a strong dependence on concentration at low solvent concentrations.[2,3] The dramatic increase in the mutual diffusion coefficient can be explained by the fact that the mobilities of molecules in the mixture are sensitive to the average specific hole free volume of the system. The specific hole free volume of a solvent is usually much greater than that of a typical polymer, and the addition of solvent leads to an increase in the average specific hole free volume of the mixture and to a loosening of the polymeric structure. However, diffusivity data on water–polymer systems[2,4] exhibit a weak concentration dependence for the mutual diffusion coefficient even though it would appear that the increase in free volume is sufficient to lead to a substantial concentration dependence. Consequently, some other factor besides the change in free volume must play an important role in determining the concentration dependence of the diffusivity in polymer–solvent systems. In this paper, we further investigate[5,6] the influence of one such factor, the size of the solvent, on the variation of the diffusivity with concentration.

The concentration dependence of the mutual diffusion coefficient, D, for polymer–solvent systems in the limit of zero solvent concentration can be characterized by the quantity k_D which is defined as

$$k_D = [\{\partial(D/D_0)/\partial\rho_1\}_{T,p}]_{\rho_1=0} \qquad (1)$$

Here, D_0 is the mutual diffusion coefficient at zero solvent concentration and ρ_1 is the mass density of the solvent. From a new version of the free-volume theory of diffusion,[5-9] the following expression can be derived for k_D at a given temperature and pressure if the usually negligible thermodynamic, volumetric, and volume change on mixing contributions are omitted:

$$k_D = \frac{\gamma \hat{V}_1^\circ(0)}{f_2}\left[\frac{M_1}{M_j}\,\frac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1\right] \qquad (2)$$

In this equation, $\hat{V}_{FH}(0)$ is the specific hole free volume of the pure polymer at the temperature of interest, $\hat{V}_{FH}(1)$ is the specific hole free volume of the pure solvent, M_1 is the molecular weight of the solvent, M_j is the molecular weight of a polymeric jumping unit, and f_2 is the fractional hole free volume of the pure polymer. Also, $\hat{V}_1^\circ(0)$ is the specific volume of the equilibrium liquid solvent at 0 K, and γ is an overlap factor which is introduced because the same free volume is available to more than one molecule. For this study, we consider only solvents which jump as single units,[9] and, for the present, we ignore any possible differences in the overlap factor γ for different materials.

The experimental observation of a strong concentration dependence for $D(k_D \gg 1)$ at low solvent concentrations is consistent with the predictions of eq 2 when $M_1 \approx M_j$ since the specific hole free volume of the solvent is usually significantly greater than that of the polymer at the same temperature $[\hat{V}_{FH}(1) \gg \hat{V}_{FH}(0)]$. However, for small molecules of low molecular weight ($M_1 \ll M_j$), it is evident from eq 2 that relatively low values of k_D can be predicted even if the solvent contributes substantially more free volume than the polymer. Consequently, it is reasonable to expect significantly less concentration dependence for D for small solvents than is observed for solvents of higher molecular weight. This result is due to the fact that there

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Table I
Experimental Values of k_D for Polymer-Solvent Systems

system	T, °C	k_D, cm^3/g
PS-toluene	140	62.6
PS-ethylbenzene	140	64.3
PMMA-methanol	130	12.6
PMMA-toluene	130	48.6
PVAc-methanol	40	39.6
PVAc-acetone	40	90.0

Table II
Properties of Polymers and Solvents

material	$\hat{V}_I°(0)$, cm^3/g	M_I or M_j, g/(g·mol)	$(C_1^g)_I$	$(C_2^g)_I$, K	T_{GI}, K
PS	0.85	163	13.6	46.6	373
PMMA	0.77	201	14.8	80.0	381
PVAc	0.75	118	15.6	46.8	305
ethylbenzene	0.95	106	13.3	15.1	112
toluene	0.92	92	15.8	11.4	114
acetone	0.95	58	16.0	13.2	70.5
methanol	0.96	32	6.64	45.3	108

Table III
Free-Volume and Size Properties for Polymer-Solvent Systems

system	$\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$	M_1/M_j
PS-toluene	13.6	0.56
PS-ethylbenzene	12.9	0.65
PMMA-methanol	16.4	0.16
PMMA-toluene	23.0	0.46
PVAc-methanol	14.2	0.27
PVAc-acetone	20.3	0.49

are less molecules of the higher molecular weight solvent in the mixture for the same solvent mass fraction, and the increase in D is determined by the change in the average hole free volume per molecule. Previous versions[2,3] of the free-volume theory of polymer–solvent diffusion do not account for this direct effect of solvent size on the concentration dependence of the diffusivity since it is implicitly assumed that $M_1 = M_j$. It has been shown elsewhere[5] that this assumption is needed if the parameter B_d which appears in previous free-volume formulations is to be independent of concentration as has been assumed.

The above interpretation was offered previously[5,6] as an explanation for the fact that D for the poly(methyl acrylate)–ethyl acetate system exhibits a strong dependence on concentration whereas there is little or no concentration dependence for D for the poly(methyl acrylate)–water and poly(vinyl acetate)–water systems. However, there may be some question as to whether the lack of concentration dependence for the diffusivity of a polymer–water system is somehow related to the special nature of the water molecule, as manifested by its strong local interactions with polar groups and by its tendency to cluster in nonpolar materials. Consequently, it is useful to critically examine the effect of solvent size on the concentration dependence of mutual diffusion coefficients in polymer–solvent systems by utilizing diffusivity data on small solvents other than water. The purpose of this paper is to present and analyze diffusion coefficient data for the diffusion of both small and large solvents in the same polymer and to determine whether the variation of k_D with solvent size can be predicted by eq 2. Diffusivity data are presented and analyzed for the diffusion of ethylbenzene and toluene in polystyrene (PS) and for the diffusion of methanol and toluene in poly(methyl methacrylate) (PMMA). Furthermore, data reported by Kokes and Long[10] for the diffusion of methanol and acetone in poly(vinyl acetate) (PVAc) are also considered.

Results and Discussion

Data for the diffusion of ethylbenzene and toluene in polystyrene were collected at 140 °C, and data for methanol and toluene diffusion in PMMA were obtained at 130 °C. These diffusivity data were collected as a function of concentration, using a high-temperature quartz spring balance. Details of the experiment and the data analysis are given elsewhere.[11-14] Kokes and Long[10] reported mutual diffusion data at 40 °C for methanol and acetone diffusion in PVAc, and we have utilized results from the reanalysis of these data which was carried out by Fujita and Kishimoto.[15] Values of k_D which were derived from the diffusivity data for these six polymer–solvent systems are presented in Table I.

It is convenient to work with the ratio of k_D values for two solvents diffusing in the same polymer. It is easy to show that the ratio of k_D values for two solvents A and B is given by

$$\frac{(k_D)_A}{(k_D)_B} = \frac{[\hat{V}_1°(0)]_A}{[\hat{V}_1°(0)]_B}\left[\frac{\psi_A - 1}{\psi_B - 1}\right] \tag{3}$$

where ψ for a given polymer–solvent system is defined as

$$\psi = \frac{M_1\hat{V}_1°(0)(C_2^g)_2(C_1^g)_2[(C_2^g)_1 + T - T_{G1}]}{M_j\hat{V}_2°(0)(C_2^g)_1(C_1^g)_1[(C_2^g)_2 + T - T_{G2}]} \tag{4}$$

In this equation, $\hat{V}_I°(0)$ is the specific volume of the equilibrium liquid at 0 K for component I, $(C_1^g)_I$ and $(C_2^g)_I$ are the WLF constants[16] of component I, T_{GI} is the glass transition temperature of component I, and T is the temperature of interest. The subscripts 1 and 2 denote the solvent and polymer, respectively.

All of the parameters in eq 3 and 4 can be determined by using only data for the pure components and diffusivity data for the polymer–solvent system in the limit of zero solvent concentration. The WLF constants for the solvent and polymer can be determined from viscosity data,[16] and $\hat{V}_1°(0)$ and $\hat{V}_2°(0)$ can be adequately estimated by methods discussed by Haward.[17] The temperature dependences of the viscosities of the four solvents considered here appear to be adequately described by free-volume theory at temperatures significantly above the glass transition temperatures of these solvents. The parameter M_j for a particular polymer can be determined from the temperature dependence of the diffusivity for a given solvent in that polymer in the limit of zero solvent concentration. As is shown elsewhere,[8,9] these data directly yield the quantity 2.303 × $(C_1^g)_2(C_2^g)_2\zeta$, where ξ is given by

$$\xi = \hat{V}_1°(0)M_1/\hat{V}_2°(0)M_j \tag{5}$$

Table IV
Comparison of Theory and Experiment for k_D

	k_D(PS-MePh)/ k_D(PS-EtPh)	k_D(PMMA-MeOH)/ k_D(PMMA-MePh)	k_D(PVAc-MeOH)/ k_D(PVAc-Me$_2$CO)
theory	0.88	0.18	0.33
theory with $M_1 = M_j$	1.03	0.64	0.64
experiment	0.97 ± 0.37	0.26 ± 0.08	0.44 ± 0.13

Hence, M_j can be calculated by using the WLF constants of the polymer and the estimated values of $\hat{V}_1°(0)$ and $\hat{V}_2°(0)$. Values of the parameters needed for the evaluation of the k_D ratio from eq 3 and 4 are presented in Table II for the seven materials utilized in this investigation.

From Table III, it can be inferred from the relatively large $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ values that the addition of solvent should lead to a considerably loosened polymeric structure and to a substantial increase in D with ρ_1 for all six of the systems studied. However, according to the theory, the actual values of k_D for the six polymer-solvent systems will not be as large as could be obtained for these substantial $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ values because M_1/M_j is less than 1 in all cases. This effect is particularly significant for the PMMA-methanol and PVAc-methanol systems, and the concentration dependence of D can be expected to be significantly less for methanol-polymer systems than for larger solvents like toluene and acetone with the same polymer.

A comparison of experimental and theoretical values of the k_D ratio for two solvents diffusing in the same polymer is presented in Table IV. In all cases, the ratio represents the k_D value of the smaller solvent divided by that for the larger solvent. Since toluene and ethylbenzene are of comparable size, little direct size effect can be expected for the polystyrene diffusion data. However, a significant size effect should be present in the diffusivity data for PMMA and PVAc since methanol is significantly smaller than both toluene and acetone. From Table IV, we first note from the theoretical calculation with $M_1 = M_j$ that, in two of the three cases, the smaller solvent has about a one-third smaller value of k_D than the larger solvent, owing to the fact that it does not provide as much specific hole free volume as the larger solvent. In addition, however, the theoretical calculations show that there is a considerable size effect when comparing the diffusion of methanol and toluene in PMMA and the diffusion of methanol and acetone in PVAc. For PMMA diffusion, the size effect is responsible for lowering the k_D ratio of the two solvents by a factor of 3.5 and, for PVAc diffusion, the size effect leads to a reduction by a factor of 2 in the k_D ratio. On the other hand, the size effect produces only a 15% difference in k_D between the polystyrene-toluene and polystyrene-ethylbenzene systems since toluene is only marginally smaller than ethylbenzene. Consequently, the theory predicts that solvents which differ significantly in size will exhibit markedly different concentration dependences for D, even if they have comparable $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ values.

The strong influence of the size effect on the k_D ratio for two solvents diffusing in the same polymer, which is anticipated theoretically above, is also evident in the experimental k_D ratios presented in Table IV. Furthermore, the theoretical and experimental k_D ratios are in reasonably good agreement when the estimated experimental uncertainty in the measured k_D ratio is taken into consideration. Thus, the diffusion data of this study and those reported by Kokes and Long[10] provide further experimental verification of a direct size effect on k_D for diffusion in polymer-solvent systems. We further conclude that the present version of the free-volume theory of diffusion[5-9] provides an adequate representation of the often competing roles which hole free volume and solvent size play in determining the concentration dependence of D for polymer-solvent systems.

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