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A New Equation Relating Self-Diffusion and Mutual Diffusion Coefficients in Polymer–Solvent Systems

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Introduction

The free-volume theory of transport provides a useful method for the determination of self-diffusion coefficients for polymer–solvent systems.[1-6] However, since mass transfer processes involving polymer–solvent mixtures are analyzed using the binary mutual diffusion coefficient, D, it is necessary to provide an equation relating D to the self-diffusion coefficients of the solvent and polymer, D_1 and D_2, respectively. In a previous investigation,[7] an equation was proposed which related D to D_1 and to the thermodynamic properties of the polymer–solvent system. It was expected that this equation would provide a valid relationship between D and D_1 in some concentration interval near $w_1 = 0$, where w_1 is the mass fraction of the solvent. Furthermore, it was argued that, for polymer–solvent systems, it might be expected that the proposed equation could be used to determine D over the major part of the concentration interval using only free-volume equations and thermodynamic data. However, it appears that the range of validity of the previously proposed equation is not always particularly large. Indeed, in some cases, this equation provides an adequate approximation for D only for concentrations close to the $w_1 = 0$ limit. This is illustrated below for the rubber–benzene system. Consequently, a new equation relating D to D_1 and D_2 and to thermodynamic data for the polymer–solvent system which can be used over the entire concentration interval is proposed here. In essence, the new form extends the validity of the previous result to higher solvent mass fractions. The new equation is developed in the second section of this paper, and comparisons of the predictions of this equation with experimental data are presented in the third section.

Theory

The usual equations relating diffusion and friction coefficients[1,7] can be combined to derive the following results:

$$D = \frac{Q\phi_2 D_1}{1 - D_1/D_1^*} \tag{1}$$

$$\phi_2 = \rho_2 \hat{V}_2 \tag{2}$$

$$Q = \rho_1 (\partial \mu_1 / \partial \rho_1)_{T,p} / RT \tag{3}$$

$$D_1^* = RTM_1 / \rho_1 \zeta_{11} N_A^2 \tag{4}$$

Here, ρ_I is the mass density of component I, ϕ_I is the volume fraction of component I, $\hat{V}_I$ is the partial specific volume of component I, μ_1 is the chemical potential of the solvent per mole, and M_I is the molecular weight of component I. Also, R is the gas constant per mole, ζ_{11} is a friction coefficient, T is temperature, and N_A is Avogadro's number. For reasonable behavior of the friction coefficients for the polymer–solvent system, it can be shown that $D/D_1^* = 0$ at $w_1 = 0$ and $D_1/D_1^* = 1$ at $w_1 = 1$. Consequently, there is a concentration interval near $w_1 = 0$ where D_1/D_1^* is small compared to unity, and, in this interval, eq 1 reduces to the result proposed in the previous study:

$$D = Q\phi_2 D_1 \tag{5}$$

This equation can be used to determine the concentration dependence of D at a particular temperature from thermodynamic information and from information on the concentration dependence of D_1. In particular, Q can be determined from experimental data or from an appropriate thermodynamic theory, like the Flory–Huggins theory.[8] The concentration dependence of D_1 can be obtained from self-diffusion data or from predictions based on the free-volume theory of transport.[1-6] However, as noted previously, the range of applicability of eq 5 is quite limited for some systems, and it seems necessary to derive a more general result from eq 1 by considering the concentration dependence of the denominator in this equation.

We postulate the following concentration dependence for the denominator of eq 1

$$1 - D_1/D_1^* = A + B\phi_2 + C\phi_2^2 + E\phi_2^3 \tag{6}$$

where A, B, C, and E are constants which can be determined from appropriate restrictions on D_1/D_1^* and on D. The following restrictions are used here:

$$D_1/D_1^* = 1 \qquad w_1 = 1 \tag{7}$$

$$D_1/D_1^* = 0 \qquad w_1 = 0 \tag{8}$$

$$D = D_2 \qquad w_1 = 1 \tag{9}$$

$$[\partial(D/QD_1)/\partial\phi_2]_{\phi_1=0} = 1 \tag{10}$$

The first two restrictions, eqs 7 and 8, are the required values of D_1/D_1^* at the end points of the concentration interval. Also, eq 9 is the well-known result that the mutual diffusion process and the polymer self-diffusion process are identical at $w_1 = 1$. Finally, eq 10 imposes the requirement that eq 5 is valid at least for some small concentration interval near $w_1 = 0$.

Introduction of these four restrictions into eqs 1 and 6 allows determination of the four constants in eq 6 and produces the following equation for D:

$$D = \frac{QD_1}{\alpha\phi_1^2 + (1 - \phi_1)(1 + 2\phi_1)} \tag{11}$$

$$\alpha = \frac{M_1 \hat{V}_1^0}{M_2 \hat{V}_{20}} \left(\frac{D_1}{D_2}\right)_{\phi_1=1} \tag{12}$$

Here, $\hat{V}_1^0$ is the specific volume of the pure solvent, and $\hat{V}_{20}$ is the partial specific volume of the polymer at $w_1 = 1$.

Equation 11 is the new expression which can be used to determine D from the thermodynamic and self-diffusion characteristics of the polymer–solvent system. As before, Q can be determined from experimental thermodynamic data or from an appropriate thermodynamic theory. If the Flory–Huggins theory[8] is used, Q is given by the following expression:

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$$Q = (1 - \phi_1)(1 - 2\chi\phi_1) + \phi_1/y \qquad (13)$$

$$y = M_2\hat{V}_{20}/M_1\hat{V}_1^0 \qquad (14)$$

where χ is the interaction parameter. Again, D_1 can be measured experimentally or computed using the free-volume theory of transport.[1-6] The new expression requires that the polymer self-diffusion coefficient at $w_1 = 1$ must be known. This value of $D_2(w_1{=}1)$ can be estimated using well-known results for diffusional behavior in infinitely dilute polymer solutions.[9,10] Near $w_1 = 0$, the new expression (eq 11) is identical to the previous form (eq 5), but, at higher solvent concentrations, the two equations give very different results. The predictions of eq 11 will now be compared with experimental data on two polymer–solvent systems.

Evaluation of the Proposed Equation

Values of D, D_1, and Q have been reported[11] over the complete concentration range for the rubber–benzene system at 25 °C, and these data provide a good test of the proposed equation. Comparisons of the predictions of eqs 5 and 11 with the experimental data are presented in Table I. The computations show that eq 5 provides reasonable predictions only for the range $\phi_1 = 0$–0.2, whereas eq 11 produces reasonably good predictions over the complete concentration range. The maximum error in using eq 11 is 30%, and the average absolute error (excluding the points at $\phi_1 = 0$ and 1) is less than 20%.

A second test of the proposed equation can be carried out using mutual diffusion, self-diffusion, and thermodynamic data for the polystyrene–toluene system at 25 °C. The thermodynamic properties for this system were estimated using the Flory–Huggins equation and reported data for the interaction parameter.[12] Vrentas and Chu[13] reported mutual diffusion data for this system for $w_1 = 0.70$–1 for a polymer molecular weight of 17 400. The value of D_2 at $w_1 = 1$ can be obtained using an extended version[10] of the Kirkwood–Riseman theory, and it was found[13] that it was effectively identical to the measured value of D at $w_1 = 1$. Finally, solvent self-diffusion coefficients for the polystyrene–toluene system at 25 °C have been measured by Pickup.[14] Comparisons of the predictions of eqs 5 and 11 with experimental data for the polystyrene–toluene system are presented in Table II.

Again, the predictions of eq 11 are quite good, with the maximum error being less than 6%. On the other hand, the predictions of eq 5 are very poor. In a previous study,[7] it was concluded that eq 5 gave good predictions for the polystyrene–toluene system at 110 °C for $w_1 = 0$–0.75. However, it appears that the mutual diffusion data used in the previous data–theory comparisons are questionable. The mutual diffusion coefficients used in that previous data–theory comparison[7] at 110 °C are significantly lower than reported mutual diffusion coefficients[13] at 25 °C, and this result, of course, seems unlikely. Low values of D lead to low values of D/QD_1 and make it appear that eq 5 gives good predictions. The mutual diffusion data at 110 °C were obtained using a sorption experiment, and these apparently anomalous mutual diffusion measurements may reflect a basic difficulty in carrying out meaningful sorption experiments at high solvent concentrations. Although eq 5 should be adequate near $w_1 = 0$, it appears that the range of validity of this equation is much narrower than the previous indication. On the other hand, the new equation, eq 11, appears to provide good results even for high solvent concentrations.

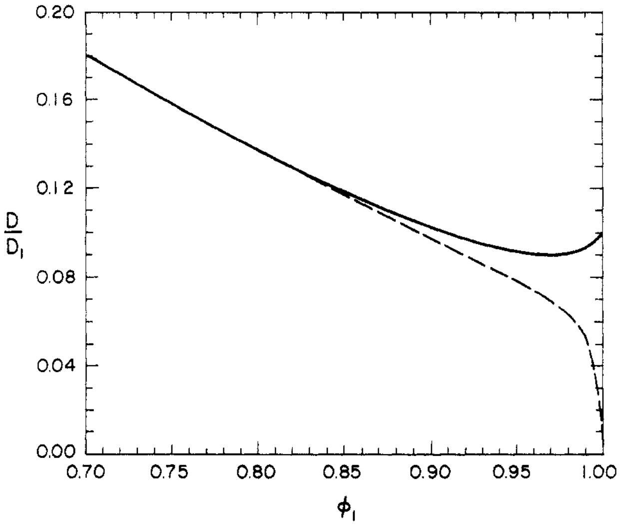

Figure 1. Concentration dependence of D/D_1 for a typical polymer–solvent system. The solid line represents $M_2 = 10^4$, and the dashed line represents $M_2 = 10^6$.

Table I. Comparison of Theory and Experiment for the Rubber–Benzene System

	D/QD_1		
ϕ_1	expt	eq 5	eq 11
0	1	1	1
0.1	0.88	0.9	0.92
0.2	0.98	0.8	0.89
0.3	1.02	0.7	0.89
0.4	1.19	0.6	0.92
0.5	1.33	0.5	0.99
0.6	1.45	0.4	1.11
0.7	1.61	0.3	1.34
0.8	1.90	0.2	1.81
0.9	2.4	0.1	3.12
0.925	3.0	0.075	3.89
0.95	4.2	0.05	5.26
1.0	20	0	20

Table II. Comparison of Theory and Experiment for the Polystyrene–Toluene System

	D/QD_1		
w_1	expt	eq 5	eq 11
0.70	1.44	0.25	1.44
0.80	1.87	0.16	1.91
0.90	3.08	0.079	3.02
0.95	4.59	0.039	4.34
1.0	7.93	0	7.93

Additionally, eq 11 indicates explicitly the dependence of D on polymer molecular weight, M_2. The quantity D/D_1 depends on molecular weight through the molecular weight dependence of Q (eq 13) and through the molecular weight dependence of α (eq 12). The molecular weight dependence of D/D_1 for a typical polymer–solvent system is illustrated in Figure 1. Clearly, D/D_1 is essentially independent of molecular weight up to $\phi_1 = 0.8$, and the biggest changes in D/D_1 with molecular weight occur in the interval $\phi_1 = 0.9$–1.

Finally, it is useful to note that the form of eq 6 is suggested by the presence of ϕ_2 in the numerator of eq 1 and by the need to provide higher order terms in the denominator. Also, a general form of Q based on dilute solution theory[9] has been used to evaluate the constants in eq 6.

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