

# Prediction of Mutual Diffusion Coefficients for Polymer–Solvent Systems

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**ABSTRACT:** A new equation is proposed for relating solvent self-diffusion coefficients and mutual diffusion coefficients for polymer–solvent systems. The formulation of the new equation avoids a friction-coefficient formalism, and hence the new equation does not require the thermodynamic properties of the polymer–solvent system. A comparison has been made of the predictions of the proposed equation with experimental data for the benzene–rubber system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3195–3199, 2000

**Key words:** self-diffusion coefficient, mutual diffusion coefficient

## INTRODUCTION

An analysis of a mass transfer process involving a polymer–solvent system can be carried out only if the binary mutual diffusion coefficient,  $D$ , is known. Since the mutual diffusion coefficient for a polymer–solvent system is often a strong function of concentration and of temperature, the availability of a predictive method for  $D$  would of course be very helpful since a lengthy experimental program could be avoided. The free-volume theory of transport<sup>1</sup> provides a reasonable basis for predicting the solvent self-diffusion coefficient,  $D_1$ , for both linear and branched polymers over the complete concentration range and over a wide temperature range. This theory is valid for both rubbery and glassy polymer–solvent systems and also for monodisperse and polydisperse polymers. The predictive theory for  $D_1$  could serve as the basis for determining  $D$  if an equation relating solvent self-diffusion and mutual diffusion coefficients were available.

An equation that relates solvent self-diffusion and mutual diffusion coefficients for polymer–solvent systems has been developed<sup>2</sup> by using the generally much greater self-diffusion coefficients of solvents compared to polymers. Since this original expression is valid only over a limited concentration range, an improved version of this equation has recently been proposed.<sup>3</sup> Both these previous equations are based on a friction-coefficient formalism for the diffusion process, and hence both can be used to relate  $D$  to  $D_1$  only if thermodynamic data are available for the polymer–solvent system of interest. The objective of this study is to develop an equation for relating  $D$  to  $D_1$  that avoids the friction-coefficient approach and hence does not introduce the thermodynamic properties of the polymer–solvent system into the derived equation. The goal is therefore to derive an equation that can be used to determine  $D$  only from the concentration and temperature dependence of  $D_1$  and from the polymer self-diffusion coefficient at the infinitely dilute polymer limit (effectively pure solvent).

The pertinent theory is developed in the second section of this paper, and a comparison of the predictions of this theory with actual experimental data for  $D$  is presented in the third section.

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## THEORY

We consider isothermal diffusion in a binary system considered to be a mixture of three components: 1, 2, and 3. Components 1 and 2 are chemically identical versions of the solvent that are distinguishable through labeling, and component 3 is the polymer. The analysis of the diffusion process is carried out using  $j_1^\dagger$  and  $j_2^\dagger$ , the  $x$  components of the mass diffusion fluxes relative to the volume average velocity for components 1 and 2, respectively. The following constitutive equations relate these mass diffusion fluxes to concentration and pressure gradients:

$$j_1^\dagger = -D_{11} \frac{\partial \rho_1}{\partial x} - D_{12} \frac{\partial \rho_2}{\partial x} + k_1 \frac{\partial p}{\partial x} \quad (1)$$

$$j_2^\dagger = -D_{21} \frac{\partial \rho_1}{\partial x} - D_{22} \frac{\partial \rho_2}{\partial x} + k_2 \frac{\partial p}{\partial x} \quad (2)$$

Here,  $\rho_I$  is the mass density of component  $I$ ,  $p$  is pressure,  $k_1$  and  $k_2$  are constitutive coefficients for the pressure gradient, and the  $D_{IJ}$  are the four diffusion coefficients needed to describe the ternary diffusion process. In addition, the mass diffusion fluxes relative to the volume average velocity for a ternary system are related by the following equation

$$j_1^\dagger \hat{V}_1 + j_2^\dagger \hat{V}_2 + j_3^\dagger \hat{V}_3 = 0 \quad (3)$$

where  $\hat{V}_I$  is the partial specific volume of component  $I$ . Eqs. (1)–(3) can now be used to analyze both the self-diffusion process and the mutual process for the ternary version of our binary system.

A self-diffusion process that involves both labeled and unlabeled solvent (components 1 and 2) and polymer (component 3) can be described by the following characteristics: (1) There are no pressure gradients; (2) There are no velocities or concentration gradients for component 3, the polymer; and (3) The total solvent concentration is the same everywhere in the diffusion field for all times:

$$\rho_1 + \rho_2 = \text{constant} \quad (4)$$

For the self-diffusion process, it is evident that

$$\frac{\partial \rho_1}{\partial x} = -\frac{\partial \rho_2}{\partial x} \quad (5)$$

$$\hat{V}_1 = \hat{V}_2 \quad (6)$$

$$j_3^\dagger = 0 \quad (7)$$

and consequently utilization of eq. (3) produces the following result:

$$j_1^\dagger = -j_2^\dagger \quad (8)$$

Also, the combination of eqs. (1), (2), and (5) yields the following equations:

$$j_1^\dagger = -(D_{11} - D_{12}) \frac{\partial \rho_1}{\partial x} \quad (9)$$

$$j_2^\dagger = -(D_{21} - D_{22}) \frac{\partial \rho_1}{\partial x} \quad (10)$$

The self-diffusion coefficient,  $D_1$ , can be defined by the following expression

$$j_1^\dagger = -D_1 \frac{\partial \rho_1}{\partial x} \quad (11)$$

and it is evident from eqs. (8)–(11) that the following equations relate  $D_1$  to the four  $D_{IJ}$ :

$$D_1 = D_{11} - D_{12} = D_{22} - D_{21} \quad (12)$$

It is reasonable to expect that

$$D_{11} = D_{22} \quad (13)$$

$$D_{12} = D_{21} \quad (14)$$

since components 1 and 2 are chemically identical. Equations (13) and (14) are consistent with eq. (12).

In a mutual diffusion process for labeled and unlabeled solvent components and polymer, there is no distinction made for any differences in the labeled and unlabeled solvent species. Hence, the mutual diffusion process is described by the following characteristic: The ratio of concentrations of the isotopic forms is constant everywhere in the diffusion field for all times:

$$\frac{\rho_1}{\rho_2} = \text{constant} \quad (15)$$

It follows from eq. (15) that the concentration derivatives in the diffusion field can be expressed as follows:

$$\frac{\partial \rho_1}{\partial x} = \frac{\rho_1}{\rho_1 + \rho_2} \frac{\partial(\rho_1 + \rho_2)}{\partial x} \quad (16)$$

$$\frac{\partial \rho_2}{\partial x} = \frac{\rho_2}{\rho_1 + \rho_2} \frac{\partial(\rho_1 + \rho_2)}{\partial x} \quad (17)$$

In addition, the total solvent diffusion flux can be obtained by simply adding eqs. (1) and (2):

$$j_1^\dagger + j_2^\dagger = -(D_{11} + D_{21}) \frac{\partial \rho_1}{\partial x} - (D_{12} + D_{22}) \frac{\partial \rho_2}{\partial x} + (k_1 + k_2) \frac{\partial p}{\partial x} \quad (18)$$

Combination of eqs. (16)–(18) produces the following expression for the total solvent flux:

$$j_1^\dagger + j_2^\dagger = - \left[ \frac{(D_{11} + D_{21})\rho_1}{\rho_1 + \rho_2} + \frac{(D_{22} + D_{12})\rho_2}{\rho_1 + \rho_2} \right] \times \frac{\partial(\rho_1 + \rho_2)}{\partial x} + (k_1 + k_2) \frac{\partial p}{\partial x} \quad (19)$$

Rearrangement of eq. (12) gives the expression

$$D_{11} + D_{21} = D_{22} + D_{12} \quad (20)$$

and substitution of eq. (20) into eq. (19) produces the following result for the total solvent flux:

$$j_1^\dagger + j_2^\dagger = -(D_{11} + D_{21}) \frac{\partial(\rho_1 + \rho_2)}{\partial x} + (k_1 + k_2) \frac{\partial p}{\partial x} \quad (21)$$

In addition, the following constitutive equation can be used to define the binary mutual diffusion coefficient,  $D$ :

$$j_1^\dagger + j_2^\dagger = -D \frac{\partial(\rho_1 + \rho_2)}{\partial x} + (k_1 + k_2) \frac{\partial p}{\partial x} \quad (22)$$

Consequently, the following expressions relate  $D$  to the four  $D_{IJ}$ :

$$D = D_{11} + D_{21} = D_{22} + D_{12} \quad (23)$$

Equations (13) and (14) are consistent with this result.

A relationship between  $D$  and  $D_1$  can thus be formulated by combining eqs. (12), (14), and (23):

$$\frac{D}{D_1} = \frac{1 + \frac{D_{12}}{D_{11}}}{1 - \frac{D_{12}}{D_{11}}} \quad (24)$$

This equation can be used to determine the concentration dependence of  $D$  at a given temperature from the concentration dependence of  $D_1$ , if an expression can be developed for the concentration dependence of  $D_{12}/D_{11}$ . In the limit of zero solvent volume fraction ( $\phi_1 = 0$ ), there should be negligible interaction between components 1 and 2 so that

$$\frac{D_{12}}{D_{11}}(\phi_1 = 0) = 0 \quad (25)$$

It is evident from eq. (24) that this equation produces the expected result at the pure polymer limit:

$$D(\phi_1 = 0) = D_1(\phi_1 = 0) \quad (26)$$

If the above analysis is repeated for a ternary system consisting of solvent (component 1) and labeled and unlabeled polymer (components 3 and 4), an equation analogous to eq. (24) can be derived:

$$\frac{D}{D_3} = \frac{1 + \frac{D_{34}}{D_{33}}}{1 - \frac{D_{34}}{D_{33}}} \quad (27)$$

At the pure solvent limit ( $\phi_1 = 1$ ,  $\phi_3 = 0$ ), it is again reasonable to expect that

$$\frac{D_{34}}{D_{33}}(\phi_1 = 1) = 0 \quad (28)$$

so that we obtain the expected result at this limit:

$$D(\phi_1 = 1) = D_3(\phi_1 = 1) \quad (29)$$

Evaluation of eq. (24) at  $\phi_1 = 1$  and substitution of eq. (29) produces an expression for the value of  $D_{12}/D_{11}$  ( $\phi_1 = 1$ ):

$$\frac{D_{12}}{D_{11}}(\phi_1 = 1) = \frac{W - 1}{W + 1} \quad (30)$$

$$W = \frac{D_3}{D_1}(\phi_1 = 1) \quad (31)$$

Consequently, eqs. (25) and (30) provide values for the unknown function  $D_{12}/D_{11}$  at the two extremes of the volume fraction interval.

At this point in the development, the results should be applicable to a mixture of any two fluids because eqs. (13), (14), (25), and (28) constitute very reasonable assumptions. To proceed further, however, more has to be said about the dependence of  $D_{12}/D_{11}$  on the solvent volume fraction,  $\phi_1$ . For a general binary mixture, there appears to be no simple way to determine a reasonable dependence of  $D_{12}/D_{11}$  on  $\phi_1$ . However, for a polymer-solvent mixture, it is generally true that

$$D_1 \gg D_3 \quad (32)$$

so that for systems with polymers of sufficiently high molecular weight, the following relationship is valid:

$$\frac{d\left(\frac{D}{D_1}\right)}{d\phi_1} < 0 \quad (33)$$

Experimental data for polymer-solvent systems are generally described by eq. (33). Consequently, a linear dependence of  $D_{12}/D_{11}$  on  $\phi_1$  is proposed:

$$\frac{D_{12}}{D_{11}} = K_1\phi_1 + K_2 \quad (34)$$

The two constants in eq. (34) can be determined using eqs. (25) and (30), and, in addition, eq. (34) is consistent with eq. (33). Evaluation of  $K_1$  and  $K_2$  and substitution of eq. (34) into eq. (24) produces the following relationship between  $D$  and  $D_1$ :

$$\frac{D}{D_1} = \frac{1 + W + \phi_1(W - 1)}{1 + W - \phi_1(W - 1)} \quad (35)$$

The concentration dependence of  $D$  at a particular temperature can be determined from the concentration dependence of  $D_1$  and from an estimated value of  $W$ . An estimate of  $W$  can be obtained by using well-known results<sup>4,5</sup> for diffusional behavior in infinitely dilute polymer solutions to estimate  $D_3(\phi_1 = 1)$ . The predictive capabilities of eq. (35) are evaluated in the next section.

## RESULTS AND DISCUSSION

Unfortunately, there are not many investigations involving the measurement of both  $D$  and  $D_1$  for polymer-solvent systems over the complete concentration range. One such study has been carried out for a benzene-rubber mixtures<sup>6</sup> at 25°C. The only missing piece of information is the value of  $D$  (and, hence,  $D_3$ ) at  $\phi_1 = 1$ . It seems reasonable to estimate  $D$  at  $\phi_1 = 1$  by extrapolating the mutual diffusion data at  $\phi_1 = 0.9, 0.925,$  and  $0.95$  to  $\phi_1 = 1$ . This procedure gives a value of  $D = 5.5 \times 10^{-7}$  cm<sup>2</sup>/s, and hence the following value of  $W$  can be calculated for this system:

$$W = 0.0245 \quad (36)$$

This value of  $W$  and the measured concentration dependence of  $D_1$  can then be used to predict the concentration dependence of  $D$  for the benzene-rubber system at 25°C.

Comparisons of the predictions of eq. (35) for the mutual diffusion coefficient  $D$  with experimental data for  $D$  are presented in Table I. The new equation provides reasonably good predictions over the complete concentration range for this particular system. The maximum error in the predictions of eq. (35) is about 15%, and the average absolute error (excluding the points at  $\phi_1 = 0$  and  $\phi_1 = 1$ ) is less than 9%. A previous equation relating  $D$  to  $D_1$ , based on a friction-coefficient formalism,<sup>3</sup> produced predictions for the same data set that had a maximum error of about 30% and an average absolute error of about 20%.

It is fair to conclude that the new proposed equation for relating  $D$  to  $D_1$  for polymer-solvent systems, eq. (35), is a promising possibility for providing good predictions for  $D$ . The proposed equation makes it possible to predict the concentration dependence of  $D$  directly from the concentration dependence of  $D_1$  using only one addi-

**Table I Comparison of Predicted and Experimental Values of  $D$** 

$\phi_1$	$D \times 10^7$ (Predicted) (cm <sup>2</sup> /s)	$D \times 10^7$ (Experiment) (cm <sup>2</sup> /s)
0	1.367	1.367
0.1	4.63	4.10
0.2	9.86	9.60
0.3	15.9	15.15
0.4	21.4	21.6
0.5	25.3	26.6
0.6	26.8	28.5
0.7	25.5	28.8
0.8	21.5	25.4
0.9	14.8	16.9
0.925	12.7	14.3
0.95	10.4	11.7
1.0	5.5	5.5

tional parameter—the polymer self-diffusion coefficient at  $\phi_1 = 1$ . The new equation provides better predictions for  $D$  for the benzene-rubber system than a previously proposed equation, and

no thermodynamic data are needed. Furthermore, the present method of relating  $D$  and  $D_1$  appears to be preferable to a friction-coefficient formalism. More comprehensive  $D$  and  $D_1$  data sets are of course needed to assess more completely the capabilities of the new equation.

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