Prediction of the Molecular-Weight Dependence of Mutual Diffusion Coefficients in Polymer-Solvent Systems

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ABSTRACT: The ability of a proposed theory to describe the molecular weight dependence of mutual diffusion coefficients for polymer–solvent systems is examined by comparison with experimental measurements. Good agreement between experiment and theory was observed for two very different polymer molecular weights. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2778–2779, 2003

Key words: diffusion; solution properties; polystyrene

INTRODUCTION

A mass-transfer process involving a polymer-solvent system can be analyzed only if the binary mutual diffusion coefficient (D), for the system is known. Because mass-transfer experiments for polymer–solvent systems are often difficult to carry out, it would be very helpful if a predictive method for D were available. Such a method would prevent the lengthy experimental program needed for polymer–solvent systems because D for such systems is often a strong function of concentration, temperature, and polymer molecular weight. Although it does not appear that a comprehensive predictive method for D is available, the free-volume theory of transport[1] provides a reasonable basis for the prediction of the solvent self-diffusion coefficient (D_1), over the complete concentration range and for all temperatures of interest for polymer-solvent mass-transfer operations. Predictive theory for D_1 can be used for both linear and branched polymers, for both rubbery and glassy polymer-solvent systems, and for both monodisperse and polydisperse polymers. If an equation providing a simple relationship between D and D_1 were available, D could be determined directly with the predictive theory for D_1 as a basis.

Several methods[2–4] have been proposed for relating D to D_1 for polymer–solvent systems. The most recent formulation[4] does not use a friction-coefficient formalism and, hence, does not require the thermodynamic properties of the polymer–solvent system. The proposed relationship between D and D_1 can be described by the following expression:

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

where ϕ_1 is the solvent volume fraction. W is a constant for each temperature and polymer molecular weight and is defined as follows:

$$W = \frac{D}{D_1} (\phi_1 = 1) \qquad (2)$$

Consequently, the concentration dependence of D at a particular temperature and polymer molecular weight can be determined with only the concentration dependence of D_1 and an estimated value of W. As noted previously,[1] D_1 can be calculated with free-volume theory. In addition, W can be estimated with the theory[5,6] of diffusional behavior in infinitely dilute polymer solutions.

Two critical tests can be used to assess the predictive capabilities of eq. (1). The first test involves seeing how well the theory predicts the concentration dependence of D over the complete concentration range at a given temperature and polymer molecular weight. This type of test was carried out previously[4] with the benzene-rubber system at 25°C; the average absolute error in the predictions was less than 9%. A second critical test is to see how well the proposed equation predicts the strong molecular weight dependence for D that has been observed near the pure solvent limit. The objective of this study was to carry out this second type of critical test of eq. (1) with diffusion data for a toluene-polystyrene system at two very different polymer molecular weights (17,400 and 900,000).

RESULTS AND DISCUSSION

Mutual diffusion data were reported[7] for a toluene-polystyrene system at 25°C for the solvent mass fraction range 0.70–1 for a polymer molecular weight of 17,400. Mutual diffusion data were also presented[8] at 20°C for a toluene-polystyrene system for a polymer molecular weight of 900,000 and an approximate solvent mass fraction interval of 0.90–1. Finally, solvent self-diffusion data were reported[9] for a toluene-polystyrene system at 25°C and for solvent mass fractions
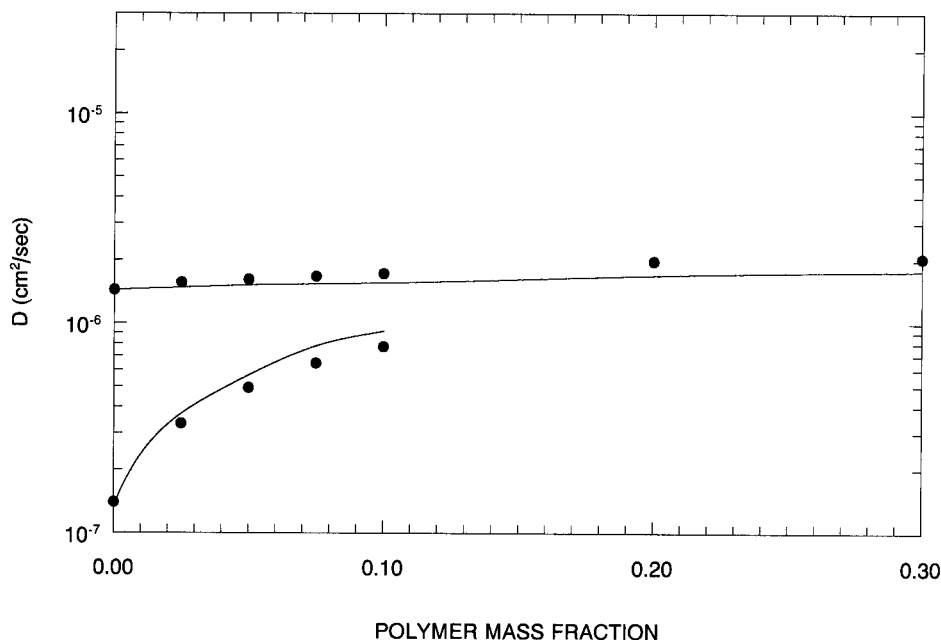
Figure 1 Comparison of theory and experimental data for the concentration dependence of D for a toluene–polystyrene system at 25°C. The continuous curves are the experimental data and the solid circles are theoretical data. Upper curve: polymer molecular weight = 17,400; lower curve: polymer molecular weight = 900,000.

greater than 0.50. The self-diffusion data were used in eq. (1) with estimated values of W to predict the dependence of D on the polymer mass fraction at each of the two polymer molecular weights. A value of D (ϕ_1 = 1) (and, hence, W) was obtained for the toluene-polystyrene system at a given temperature and polymer molecular weight with an extended version of the Kirkwood-Riseman theory[6] which is valid for non-theta conditions. The parameter W is the ratio of D to D_1 at the pure solvent limit where D is equal to the polymer self-diffusion coefficient. The proposed method for calculating W is based on the two-parameter theory of polymer solutions. Comparison of the predicted values of D, calculated with the previous procedure, with the experimental values of D provides a direct evaluation of the validity of eq. (1), the proposed expression that relates D and D_1.

A comparison between the theoretical and experimental results is presented in Figure 1. The experimental data are represented as continuous curves for each polymer molecular weight. There was an increase in D with increasing polymer concentration for both polymer molecular weights, but the concentration dependence for a molecular weight of 17,400 was much weaker than that for a molecular weight of 900,000. In the later case, D increased by a factor of about seven. The experimental curves suggest that at high enough polymer concentrations, the molecular weight dependence of D would become effectively negligible. The predicted values of D are presented as solid circles in Figure 1. Seven predictions were made for a molecular weight of 17,400 and five for 900,000. The theoretical curves were similar in shape to the experimental curves, and it appeared that

the theory provided adequate representations of the very different concentration dependencies for the two polymer molecular weights. The average absolute errors for polymer molecular weights of 17,400 and 900,000 were about 9 and 14%, respectively. Because there are not many investigations involving the measurement of both D and D_1 for polymer–solvent systems, it was not possible to carry out a comprehensive evaluation of eq. (1) at this time. However, the results of this evaluation and that carried out previously appear to indicate that eq. (1) provides a reasonable expression for relating D and D_1. Finally, eq. (1) could be evaluated with experimental data for D and theoretical free-volume predictions for D_1. However, such a procedure does not separate the accuracy of eq. (1) from the accuracy of free-volume theory in the prediction of D_1. The utilization of experimental values of both D and D_1 in the data–theory comparison allowed us to determine how accurately eq. (1) relates D and D_1 for polymer–solvent systems.

REFERENCES

1. Vrentas, J. S.; Vrentas, C. M. Eur Polym J 1998, 34, 797.
2. Duda, J. L.; Ni, Y. C.; Vrentas, J. S. Macromolecules 1979, 12, 459.
3. Vrentas, J. S.; Vrentas, C. M. Macromolecules 1993, 26, 6129.
4. Vrentas, J. S.; Vrentas, C. M. J Appl Polym Sci 2000, 77, 3195.
5. Yamakawa, H. Modern Theory of Polymer Solutions; Harper and Row: New York, 1971.
6. Vrentas, J. S.; Duda, J. L. J. Appl Polym Sci 1976, 20, 1125.
7. Vrentas, J. S.; Chu, C.-H. J Polym Sci Part B: Polym Phys 1989, 27, 465.
8. Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. Macromolecules 1986, 19, 2737.
9. Waggoner, R. A.; Blum, F. D.; MacElroy, J. M. D. Macromolecules 1993, 26, 6841.