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

J. L. Duda,[1a] **Y. C. Ni,**[1a] **and J. S. Vrentas***[1b]

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616. Received January 4, 1979

ABSTRACT: An equation which relates the mutual diffusion coefficient in a polymer–solvent system to the self-diffusion coefficient of the solvent and to the thermodynamic properties of the mixture is proposed and tested. The validity of the equation is checked by collecting mutual diffusion, self-diffusion, and thermodynamic data for the polystyrene–toluene system at 110 °C. A new apparatus has been constructed for measuring self-diffusion coefficients for polymer–solvent systems at elevated temperatures. It is concluded that the equation is valid for at least 75% of the mass fraction interval for the toluene–polystyrene system and that similar behavior should be expected for other amorphous polymer–solvent systems.

Expressions for polymer and solvent self-diffusion coefficients have recently been derived[2-4] using a modified version of the free-volume theory of transport.[5,6] The self-diffusion coefficients for the solvent and polymer, D_1 and D_2, respectively, must be related to the binary mutual diffusion coefficient, D, if these free-volume results are to be of practical utility since mass transfer phenomena involving polymer–diluent systems are of course analyzed using D. From a phenomenological point of view, these three diffusion coefficients are independent quantities, and an equation relating them can be derived only if additional information is utilized. For example, an equation can be proposed relating the friction coefficients of the system, or a molecular model of the system can be developed. Considerable effort has been expended in attempting to obtain an expression relating D, D_1, and D_2 for binary mixtures of simple liquids. Bearman,[7] Mills,[8] McCall and Douglass,[9] Loflin and McLaughlin,[10] and Douglass and Frisch[11] have discussed and evaluated approximate theories for relating D to D_1 and D_2. These studies indicate that, in general, qualitative but not quantitative agreement is obtained between the predictions of any of the proposed theories and experiment.

The progress in successfully expressing D in terms of D_1 and D_2 for simple liquid mixtures has not been satisfactory, and it would appear that similar difficulties would be encountered for polymer–solvent systems. There appears to be no theory which can be easily evaluated to provide an equation connecting D to D_1 and D_2 for diffusion in solutions where one of the components is a macromolecule. In addition, there is an insufficient amount of data on self-diffusion and mutual diffusion coefficients for polymer–diluent systems which can be used as the basis for formulating an approximate expression relating these diffusion coefficients. However, it can easily be shown that $D_1 \gg D_2$ for a polymer–solvent mixture, and we now explore the possibility that this inequality will lead to a simple and useful result.

From the usual equations relating the diffusion and friction coefficients,[2] it can be shown that

$$D = \frac{\rho_2 \hat{V}_2 \rho_1}{RT}\left[\frac{D_1}{1 - (D_1/D_1{}^*)}\right]\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} \tag{1}$$

where ρ_I is the mass density of component I, $\hat{V}_2$ is the partial specific volume of component 2, μ_1 is the chemical potential of component 1 per mole, and $D_1{}^*$ is defined by the following equation:

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

Here, M_1 is the molecular weight of the solvent, ζ_{11} is a friction coefficient, and N_A is Avogadro's number. For reasonable behavior of the friction coefficients of the system, $D/D_1{}^*$ is 0 in the limit of zero solvent mass fraction and 1 for the pure solvent. Consequently, for solvent mass fractions less than 1, we can write

$$D_T = \frac{D_1}{1 - (D_1/D_1{}^*)} = D_1\left[1 + \frac{D_1}{D_1{}^*} + \left(\frac{D_1}{D_1{}^*}\right)^2 + \ldots\right] \tag{3}$$

and it is evident that eq 1 can be adequately approximated by the expression

$$D = \frac{\rho_2 \hat{V}_2 \rho_1 D_1}{RT}\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} = \frac{D_1 x_2}{RT}\left(\frac{\partial \mu_1}{\partial \ln x_1}\right)_{T,p} = \frac{D_1 \omega_2}{RT}\left(\frac{\partial \mu_1}{\partial \ln \omega_1}\right)_{T,p} \tag{4}$$

in some concentration interval near $\omega_1 = 0$ where the quantity $D_1/D_1{}^*$ is sufficiently small. Here, ω_I represents the mass fraction of component I and x_I represents the mole fraction of component I. Furthermore, if $D_1/D_1{}^*$ can be shown to be small over the major part of the concentration interval, then D can be computed from eq 4 over most of the concentration range where free-volume theory is applicable using only thermodynamic and free-volume information. From an approximate calculation,[3] it can be shown that free-volume theory typically describes the transport process for over 90% of the mass fraction interval for a polymer–penetrant system.

Since eq 4 permits the determination of D solely from free-volume equations and thermodynamic data, it is of interest to see whether this equation is indeed a satisfactory approximation for the mutual diffusion coefficient in polymer solutions (with $D_1 \gg D_2$) over the major part of the concentration interval. It does not appear possible at the present time to show theoretically that $D_1/D_1{}^*$ is generally small for most of the mass fraction interval whenever $D_1 \gg D_2$. However, for illustrative purposes, we can consider the special case where the three friction coefficients are related by a geometric mean expression[2,10] as a means of determining the possible effect of the inequality $D_1 \gg D_2$ on $D_1/D_1{}^*$. For this particular case, it can be shown[2] that $D_1/D_1{}^*$ is given by the following expression:

$$\frac{D_1}{D_1{}^*} = \frac{x_1 D_2}{x_1 D_2 + x_2 D_1} \tag{5}$$

0024-9297/79/2212-0459$01.00/0 © 1979 American Chemical Society

Table I
Diffusion Coefficients for the Ethylbenzene-Polystyrene System at 130 °C Based on Geometric Mean Approximation

ω_1, mass fraction of solvent	$D_1/D_1{}^*$	D(calcd using eq 4)/(actual value of D)
0	0	1.0
0.1	2.3×10^{-5}	1.0
0.2	1.8×10^{-4}	1.0
0.3	7.3×10^{-4}	1.0
0.4	2.3×10^{-3}	1.0
0.5	6.2×10^{-3}	0.99
0.6	1.6×10^{-2}	0.98
0.7	3.9×10^{-2}	0.96
0.8	9.3×10^{-2}	0.91
0.9	2.5×10^{-1}	0.75
1.0	1.0	0

It is evident from eq 5 that the quantity $D_1/D_1{}^*$ will be small over the major part of the mole fraction interval for a typical polymer–solvent system with $D_2/D_1 \ll 1$. In addition, calculations based on eq 5 and the free-volume properties of the ethylbenzene–polystyrene system[2,3] indicate that $D_1/D_1{}^*$ is less than 0.1 for over 80% of the mass fraction interval. Consequently, eq 4 estimates D with less than 10% error for this concentration range. These illustrative calculations are summarized in Table I.

In the above example, it is evident that the inequality $D_1 \gg D_2$ is responsible for $D_1/D_1{}^*$ being small and, hence, for the fact that eq 4 provides a satisfactory estimate for D over much of the concentration interval. Although this conclusion is based on results for a special case, it is possible that $D_1/D_1{}^*$ will be small and, hence, eq 4 generally valid over a significant part of the concentration range for most polymer–solvent systems owing to the large difference in D_1 and D_2. Since it appears that no general conclusion on the validity of eq 4 can be deduced from theoretical considerations at the present time, an experimental evaluation of this equation is necessary. Equation 4 can be tested if mutual diffusion, self-diffusion, and thermodynamic data are available for a binary system over a large fraction of the concentration range. The quantity D_T can be calculated from eq 1 using mutual diffusion and thermodynamic data, and this value of D_T can be compared with the corresponding experimental value of D_1 to see if $D_1 \approx D_T$, as required for the validity of eq 4.

It cannot be expected that eq 4 will generally provide an adequate estimate for D for simple liquid mixtures where D_1 and D_2 are of the same order of magnitude. As an illustration of this, we evaluate eq 4 using the acetone–water data presented by McCall and Douglass.[9] Values of D_T and D_1 for this system are presented in Table II, and it is evident that there exist significant differences between D_T and D_1, even at relatively low acetone mole fractions. This result is not surprising since there is no reason to expect that $D_1/D_1{}^*$ is close to zero over a significant part of the concentration interval for the acetone–water system. However, because of the above considerations, there exists a reasonable possibility that eq 4 will satisfactorily estimate D for the special case of polymer solutions. The purpose of this paper is to test eq 4 by collecting mutual diffusion, self-diffusion, and thermodynamic data over a large mass fraction interval for an amorphous polymer–solvent system. Measurements are made using the toluene–polystyrene system at 110 °C, and enough data are collected so that eq 4 can be tested over approximately 75% of the mass fraction range. The experimental techniques used to collect these data are discussed below, and an evaluation of the applicability of eq 4 is carried out.

Table II
Comparison of D_T and D_1 for the Acetone-Water System[9] at 25 °C

x_1, mol fraction of acetone	$10^5 D_1$, cm²/s	$10^5 D_T$, cm²/s
0	1.28	1.28
0.1	0.97	1.60
0.2	1.08	2.29
0.3	1.36	3.69
0.4	1.70	6.98
0.5	2.14	12.1
0.6	2.65	14.7
0.7	3.13	15.2
0.8	3.50	20.7
0.9	3.99	44.6
1.0	4.94	

Experimental Section

The binary mutual diffusion coefficient and the equilibrium solubility data for the toluene–polystyrene system were measured using a high-temperature quartz spring sorption apparatus. A thin pool of molten polymer in a quartz bucket was exposed to a step change in toluene vapor pressure, and the time dependence of the weight change was determined from measurements of the spring extension. Measurements of the weight pickup were obtained until equilibrium was effectively attained. Details of the apparatus, experimental procedure, and data analysis are discussed completely elsewhere.[12-16] One value of the binary mutual diffusion coefficient and an equilibrium solubility data point (mass fraction of toluene in the liquid phase at a given toluene vapor pressure) were determined from each step-change experiment. A sequence of 15 step-change sorption experiments was conducted, and binary mutual diffusion coefficients and equilibrium solubility data were obtained at 110 °C over the concentration range of approximately 0.02 to 0.77 weight fraction toluene. The polymer utilized in all of the measurements in this study was an additive-free commercial polystyrene with a weight-average molecular weight of 275 000.

Thermodynamic corrections for gas-phase nonideality and for pressure effects in the liquid phase were less than the estimated experimental error, and the weight fraction derivative of the chemical potential at 110 °C and a pressure of 1 atm can thus be approximated by the following expression

$$\frac{1}{RT}\left(\frac{\partial \mu_1}{\partial \ln \omega_1}\right)_{T,p} = \frac{1}{P_1}\left(\frac{\partial P_1}{\partial \ln \omega_1}\right)_{T,p} \tag{6}$$

where P_1 is the vapor pressure of the toluene over the binary polymer solution. Consequently, D_T can be calculated from the mutual diffusion and thermodynamic data using the following form of eq 1:

$$D_T = \frac{D}{\dfrac{\omega_2}{P_1}\left(\dfrac{\partial P_1}{\partial \ln \omega_1}\right)_{T,p}} \tag{7}$$

The major experimental contribution of the present investigation was the development of a radioactive tracer technique to measure the self-diffusion coefficient of the solvent, toluene, in polystyrene–toluene solutions over a wide range of concentration at an elevated temperature. Since little effort has been expended previously in measuring self-diffusion coefficients at high temperatures, a new technique and a new apparatus were developed for this purpose. In this method, a polymer sample was first brought into equilibrium with toluene vapor containing radioactive toluene ([methyl-^{14}C]toluene, from the Amersham/Searle Corp., Arlington Heights, Ill.). The pressure of the radioactive toluene was controlled by a liquid penetrant feed boiler. In the second phase of the experiment, nonradioactive toluene vapor at the same pressure, controlled by another feed boiler, was then introduced into the sample system to replace the radioactive toluene in the vapor phase. The nonradioactive toluene molecules diffuse into the polymer sample and replace the radioactive species. The sample surface was continually flushed with fresh nonradioactive toluene to eliminate the buildup of radioactive toluene in the vapor phase.

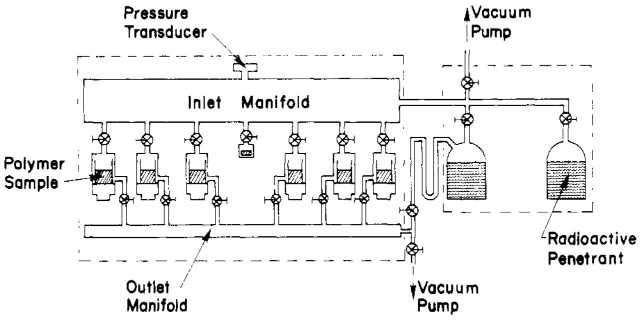

Figure 1. Schematic diagram for the self-diffusion apparatus.

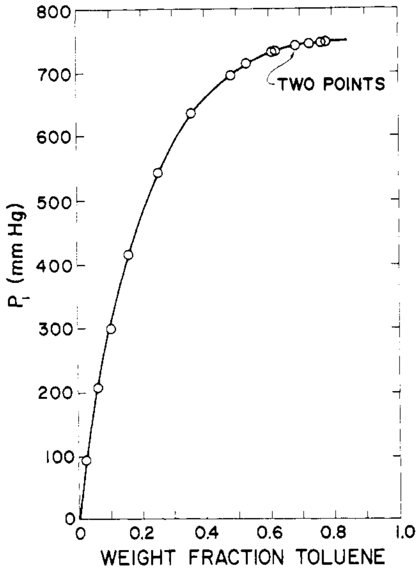

Figure 2. Solubility data for the toluene–polystyrene system at 110 °C.

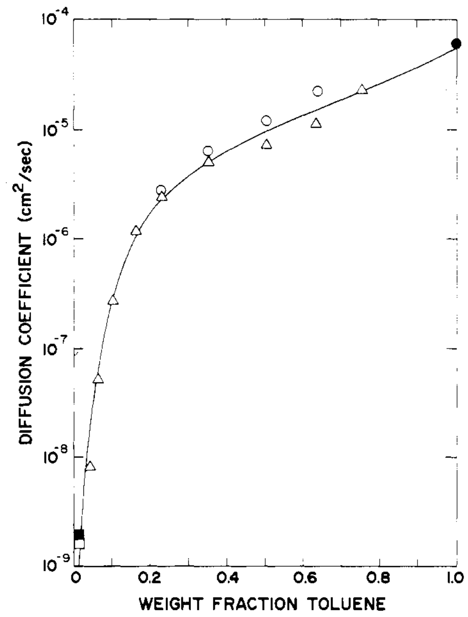

Figure 3. Various diffusion coefficients for the toluene–polystyrene system at 110 °C: (△) D_T; (○) D_1; (■) mutual diffusion coefficient determined using quartz spring balance; (□) mutual diffusion coefficient determined using self-diffusion apparatus; (●) self-diffusion coefficient for toluene computed from the equation of Dullien.[18] D_T is calculated using eq 7.

Since the toluene vapor pressure is the same during both of these steps, the total toluene concentration in the polymer will remain constant and the removal of radioactive toluene will be a self-diffusion process. After a specific exposure time to the nonradioactive toluene, this exchange was terminated, and the amount of radioactive toluene remaining in the polymer sample was determined using a liquid scintillation technique. By employing several polymer samples and utilizing different exposure times, it is possible to generate a standard fractional weight change versus square root of time sorption curve. The initial slope of this sorption curve can then be used[17] to determine the self-diffusion coefficient which controls the sorption process. The concentration dependence of the self-diffusion coefficient can be determined by conducting a series of runs with different toluene vapor pressures. Data were obtained at four toluene vapor pressures with toluene mass fractions ranging from 0.235 to 0.63.

A schematic diagram of the apparatus employed in the self-diffusion measurements is shown in Figure 1. The system consisted of seven stainless steel polymer sorption units, and each sorption chamber contained a thin layer of molten polymer in a sample bucket. The smaller, centrally located polymer sample vessel shown in Figure 1 was isolated after the first stage of the experiment. This sample was used to determine the equilibrium concentration of toluene in polystyrene at the vapor pressure and temperature of the experiment. This concentration could be used to convert the measured radioactive concentration in each of the six main sample vessels to a fractional weight change value which was then used in the determination of the self-diffusion coefficient of toluene in the polymer solution.

A check of the accuracy of this technique was obtained by conducting a mutual diffusion experiment using this apparatus. The procedure was the same as for the self-diffusion experiments with the exception that the polymer samples were isolated during the first stage of the experiment when they were only partially saturated with radioactive toluene vapor. More details of both the self-diffusion and mutual diffusion experiments are given by Ni.[15]

Results and Discussion

The solubility data for the toluene–polystyrene system at 110 °C are presented in Figure 2. Results from both graphical and numerical differentiation of these data were averaged to yield values of $(\partial P_1/\partial\omega_1)_{T,p}$ for utilization in eq 7. Mutual diffusion data for the 15 step change sorption experiments have been presented elsewhere[14] and are thus not included here. The diffusivity and equilibrium data for a given sorption run are determined at different mass fractions because of the method used to obtain the mutual diffusion coefficients.[16] Consequently, interpolation of the mutual diffusion and solubility data was used to calculate D_T from eq 7 at appropriately spaced values of ω_1, including the four mass fractions for which self-diffusion data were obtained.

Values of D_T at nine values of the mass fraction of toluene, ω_1, are presented in Figure 3 along with the four experimental values of the self-diffusion coefficient of toluene, D_1. The self-diffusion coefficient of pure toluene, calculated using the empirical equation of Dullien[18] and toluene viscosity data, is also included for comparison purposes. Finally, mutual diffusion data obtained at the same toluene mass fraction using both the conventional quartz spring apparatus and the self-diffusion apparatus are presented in Figure 3. It is evident from this figure that there is reasonably good agreement (about 16% difference) between mutual diffusion coefficients obtained by these two experiments, thus providing one check of the reliability of the apparatus and technique used to obtain the self-diffusion coefficients. The probable source of this discrepancy is discussed below.

A line has been drawn by eye in Figure 3 to provide a single representation of the D_T and D_1 data. There is scatter of the D_T and D_1 data about this line, particularly at the higher toluene mass fractions. The maximum deviation of the D_1 data about the line is nearly 35% with an average deviation of approximately 20%. The maximum deviation of the corresponding four D_T data points from the line is approximately 30% with an average deviation of approximately 15%. Furthermore, the self-diffusion data are consistently higher than the values of D_T, although, in two of the four cases, the difference is only approximately 15%. An average deviation of 15% for the D_T data appears reasonable since this includes the experimental error in the quartz spring sorption experiment as well as the error introduced by the differentiation procedure. The average deviation of 20% for the self-diffusion values is higher than expected, and, furthermore, the observation that all D_1 values are high needs to be investigated.

In the self-diffusion experiment, there exists the distinct possibility of evaporation and leakage from the polymer sample after the sample vessel has been isolated. We believe that the high values of D_1 are caused by a small, but not negligible, loss of radioactivity from the polymer samples, and we present the following three independent pieces of evidence to support this hypothesis. First, the equilibrium solubility values determined during the self-diffusion experiments were on the average 6% lower than the solubility values determined from the conventional quartz spring apparatus. This could be interpreted as a loss of radioactivity, and, consequently, the fractional weight change values were actually determined for the self-diffusion experiments using the solubility data obtained from the conventional sorption apparatus. If there were a comparable loss of radioactivity from the partially desorbed polymer samples, high values of the self-diffusion coefficient would be computed (roughly 25% too high). Second, the mutual diffusion coefficient obtained from the radioactive technique was about 16% lower than that determined from the conventional sorption technique. For this case, a 6% loss of radioactivity leads to a mutual diffusion coefficient which is roughly 12% low. Third, from the definition of D_T, it is evident that $D_T > D_1$, and the experimental data must reflect this inequality regardless of the model being tested. It seems reasonable to attribute the experimental observation that D_1 is greater than D_T to a relatively consistent error in the experiment which reverses the magnitudes of D_1 and D_T. As noted above, loss of radioactive toluene leads to high self-diffusion coefficients and thus appears to be a likely candidate for this type of error. All of the above observations imply that a small loss of radioactivity during the self-diffusion experiments is quite probable. Finally, we note that a duplicate self-diffusion experiment at $\omega_1 = 0.235$ showed a precision of approximately 12%.

The above evidence seems to indicate that an average deviation of approximately 20% for the D_1 data about the representative line in Figure 3 is quite reasonable since an error as high as 25% can be attributed to the loss of radioactive toluene without considering other sources of experimental error in the self-diffusion experiment. We therefore believe that the data of this study provide sufficient support for concluding that D_T and D_1 are effectively equal for at least 75% of the mass fraction interval for the toluene–polystyrene system. Consequently, we conclude that eq 4 is a valid equation for relating D to D_1 for the major portion of the concentration range for this system. In addition, since it appears that the above observations are a consequence of the inequality $D_1 \gg D_2$, it is reasonable to expect that similar behavior will be observed for other amorphous polymer–solvent systems. Indeed, it is reasonable to tentatively recommend the utilization of eq 4 for calculating D from D_1 and from thermodynamic data for at least 75% of the mass fraction range for polymer–solvent systems. It would of course be useful if this hypothesis could be further substantiated with additional mutual diffusion, self-diffusion, and thermodynamic data.

It is evident that eq 4 fails completely in the limit of pure solvent since it predicts a zero value of the diffusivity. Fortunately, this is of little consequence as far as the application of the free-volume theory is concerned since D cannot be calculated from free-volume results when ω_1 approaches 1. The range of applicability of eq 4 should thus be approximately coincident with the range of applicability of free-volume theory for the determination of D.

Finally, we note that Bearman[7] and McCall and Douglass[9] have noted that the following equation can be derived from absolute rate theory:

$$D = \frac{D_1}{RT}\left(\frac{\partial \mu_1}{\partial \ln \rho_1}\right)_{T,p} \tag{8}$$

This equation provides a simple relationship between D and D_1 and is similar in form to eq 4. It is evident that eq 8 will give a good estimate of D if

$$D_T \rho_2 \hat{V}_2 = D_1 \tag{9}$$

Equation 9 requires that D_1 be less than D_T; over the concentration range studied in this investigation, D_T would have to be as much as nearly four times D_1 in order for eq 8 to be valid. This is clearly not the case for the data of this study, and it should be expected that eq 4 will provide better estimates of D for polymer–solvent systems than eq 8. This is not surprising since none of the properties peculiar to polymer–solvent systems have been explicitly incorporated in the derivation of eq 8.

Acknowledgment. This work was supported by the National Science Foundation Grant ENG 74-23095.

References and Notes

(1) (a) The Pennsylvania State University; (b) Illinois Institute of Technology.
(2) J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 403 (1977).
(3) J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 417 (1977).
(4) J. S. Vrentas and J. L. Duda, *Macromolecules*, **9**, 785 (1976).
(5) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
(6) H. Fujita, *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
(7) R. J. Bearman, *J. Phys. Chem.*, **65**, 1961 (1961).
(8) R. Mills, *J. Phys. Chem.*, **67**, 600 (1963).
(9) D. W. McCall and D. C. Douglass, *J. Phys. Chem.*, **71**, 987 (1967).
(10) T. Loflin and E. McLaughlin, *J. Phys. Chem.*, **73**, 186 (1969).
(11) D. C. Douglass and H. L. Frisch, *J. Phys. Chem.*, **73**, 3039 (1969).
(12) J. L. Duda, G. K. Kimmerly, W. L. Sigelko, and J. S. Vrentas, *Ind. Eng. Chem., Fundam.*, **12**, 133 (1973).
(13) J. L. Duda, Y. C. Ni, and J. S. Vrentas, *J. Appl. Polym. Sci.*, **22**, 689 (1978).
(14) J. L. Duda, Y. C. Ni, and J. S. Vrentas, *J. Appl. Polym. Sci.*, **23**, 947 (1979).
(15) Y. C. Ni, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1978.
(16) J. S. Vrentas, J. L. Duda, and Y. C. Ni, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2039 (1977).
(17) J. Crank, "The Mathematics of Diffusion", Oxford University Press, Oxford, 1956.
(18) F. A. L. Dullien, *AIChE J.*, **18**, 62 (1972).