R & D NOTES

Estimation of Limiting Diffusion Coefficients of High Molecular Weight Solutes

R. F. FEDORS

Jet Propulsion Laboratory
Pasadena, California 91103

In a recent report, it was shown that the diffusion coefficient of solutes at infinite dilution could be estimated using the relationship

$$D^0_{21}(V_2^* - \bar{v}_2^0)^{1/2} = D_{11}(V_1^* - v_1)^{1/2} \qquad (1)$$

where D^0_{21} and D_{11} are the limiting diffusion coefficients of the solute at infinite dilution and the self-diffusion coefficient of the solvent, respectively; V_2^* and V_1^* are the volumes at the critical temperature for the solute and solvent, respectively; $\bar{v}_2^0$ is the partial molar volume of the solute in solution; and v_1 is the molar volume of the solvent. Equation (1) was shown to be applicable to a diverse series of thirteen solvents and 126 solutes.

Furthermore, in a previous report, Fedors (1978) showed that the self-diffusion coefficient D_{11} itself could

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be estimated using

$$D_{11} = \frac{4.5 \times 10^{-9}\, T(V_1^* - v_1)}{\eta_1\, V_1^{*4/3}} \tag{2}$$

where T is the temperature in degrees Kelvin, η_1 is the viscosity expressed in poise, and D_{11} has the units square centimeters per second. Combining Equations (1) and (2), we get an equation from which $D^0{}_{21}$ can be estimated directly; namely

$$D^0{}_{21} = \frac{4.5 \times 10^{-9}\, T(V_1^* - v_1)^{3/2}}{\eta_1\, V_1^{*4/3}\, (V_2^* - \bar{v}_2{}^0)^{1/2}} \tag{3}$$

In the previous reports, comparisons of the predictions of Equations (1) and (2) were carried out using data mainly for low molecular weight liquids.

We would now like to show that these equations can be used to estimate the limiting diffusion coefficients for high molecular weight liquid solutes as well. If we use the extensive data for the diffusion of polymeric solutes in low molecular weight liquids compiled by Klarner and Ende (1975), the product of the diffusion coefficient $D^0{}_{21}$ and the factor $(V_2^* - \bar{v}_2{}^0)^{1/2}$ is essentially constant and independent of the molecular weight and temperature as required by Equation (1). For these calculations, V^* for the polymer was estimated using additive atomic and structural contributions developed for low molecular weight liquids (Fedors, 1978). Use of alternative estimation schemes for V^*, such as that of Lydersen (1955), lead to essentially similar values. $\bar{v}_2{}^0$ was taken equal to the volume of the polymer at the same temperature at which the diffusion coefficients were measured.

In most cases, however, the product $D^0{}_{21}(V_2^* - \bar{v}_2{}^0)^{1/2}$, while constant as required, was found to be less than the product $D_{11}\ (V_1^* - v_1)^{1/2}$ as predicted by Equation (1). This is most simply explained by the assumption that the polymeric solute is associated in solution. Similar assumptions have been applied to diffusion data for low molecular solutes in low molecular weight solvents (Reid et al., 1977). For example, the diffusion coefficient of 2-methyl propene in CCl_4 has been explained on the basis of the diffusion of the trimer (Biblack et al., 1969). For the polymeric solutes, the associated species involve one to about four molecules, depending on the polymer and the solvent.

Figure 1 shows as the ordinate the limiting diffusion coefficient for polystyrene (standard samples of the Polymer Society of Japan) in trans decalin as a function of both molecular weight and temperature ranging from a low temperature of 18.2°C to a high temperature of 110°C (Kotena et al., 1968). On abscissa are plotted the coefficients calculated from Equation (3), using the assumption that polystyrene in trans decalin diffuses as a tetramer. As may be seen, the agreement is satisfactory.

As a further point of interest, examination of Equation (3) indicates that the only factor which depends on the solute is $(V_2^* - \bar{v}_2{}^0)^{1/2}$ which occurs in the denominator. Since volumes are proportional to molecular weight, the equation predicts in general that $D^0{}_{21}$ varies as $1/M^{1/2}$ for a homologous series, and this is indeed the dependence usually obtained for polymeric solutes.

Bresler et al. (1962) measured the diffusion coefficient of sodium polymerized isoprene into natural rubber. These data correspond to the case of diffusion of a high molecular weight solute in a high molecular weight solvent. The data are shown plotted as the filled circles in Figure 2; the line also shown in the figure is the prediction of Equation (3). The agreement is considered satisfactory in view of the well-known difficulty of measuring very small diffusion coefficients of the order of 10^{-13} cm²/s. The greatest deviation involves only a factor of 3 between the measured and calculated coefficients. Data which would have served to characterize the natural rubber used were not reported, so it was assumed that the rubber had a molecular weight of 250 000 g/mole, which is a typical value for this polymer, and a viscosity of 4×10^5 poise, obtained from Holden (1965). This viscosity is an extrapolated value which corresponds to the viscosity of the polymer in the absence of chain entanglements. Chain entanglements constitute a mechanical contribution to viscosity which is not applicable to diffusion.

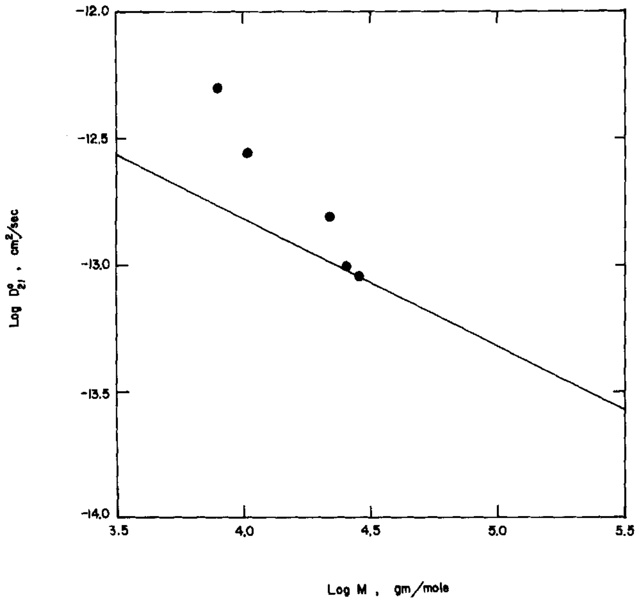

Figure 1. Comparison of the measured (ordinate) and calculated (abscissa) limiting diffusion coefficient of polystyrene in trans-decalin. Molecular weights ($\overline{Mn}$): ●, 1.5 × 10⁵ g/mole; ⊗, 4.5 × 10⁵ g/mole; ○, 7.7 × 10⁵ g/mole.

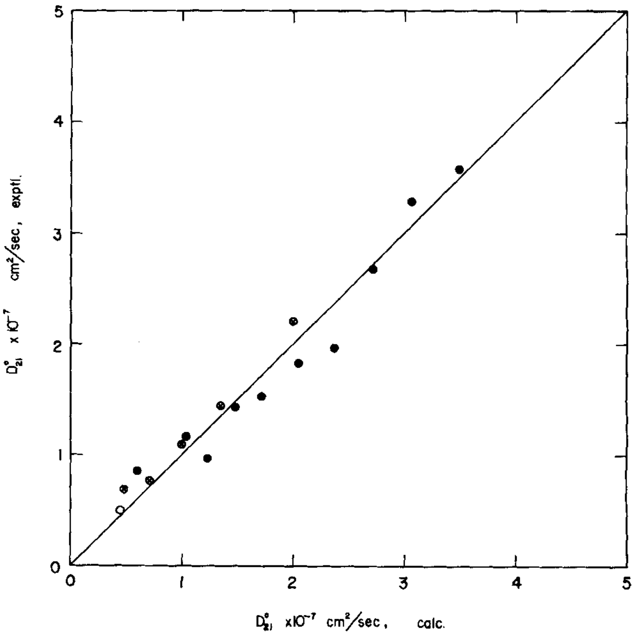

Figure 2. Diffusion coefficient of polyisoprene solute in natural rubber solvent as filled circles compared to response predicted by Equation (3) shown as line.

Equation (3) is apparently not applicable to the case of diffusion of a low molecular weight liquid solute into a high molecular weight liquid solvent. For example, the measured limiting diffusion coefficient of benzene into natural rubber (Pattle et al., 1967) at 25°C is 1.37×10^{-7} cm^2/s, whereas the value predicted by Equation (3) is 1.47×10^{-12} cm^2/s, five orders of magnitude lower. Similar discrepancies were found for other low molecular weight solutes. In fact, the discrepancies in most cases amount to the same factor, that is, 10^5. This aspect of the problem will be studied further.

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Tracer Analysis in Systems with Two-Phase Flow

P. L. MILLS, W. P. WU, and M. P. DUDUKOVIĆ

Chemical Reaction Engineering Laboratory
Department of Chemical Engineering
Washington University
St. Louis, Missouri 63130

Tracer analysis is an important tool in identification of many parameters in chemical engineering systems. The use of tracer impulse response techniques in single-phase systems leads to estimation of the active volume of the system, dead water regions, degree of backmixing, etc. (Levenspiel, 1972; Himmelblau and Bischoff, 1968; Wen and Fan, 1975). The same basic type of impulse or step response dynamic measurements can be applied to multiphase systems with only one flowing phase to estimate, besides the above-mentioned parameters, quantities such as fluid holdup, fluid-solid mass transfer coefficients, fluid-solid adsorption equilibrium constants, adsorption rate constants, surface kinetic constants, diffusivities in porous packings, etc. (Masamune and Smith, 1964; Suzuki and Smith, 1971; Misic and Smith, 1971; Haynes and Sarma, 1973; Haynes, 1975). Recently, the use of tracer dynamic measurements has been extended to systems with multiphase flow to evaluate fluid-fluid partition coefficients, holdup of each of the flowing phases, transport coefficients, effective areas of stagnant packing contacted by one of the flowing phases, degree of backmixing, etc. (Perilloux and Deans, 1972; Schwartz et al., 1976). The theory of tracer experiments has been extended to cover three-phase systems with two-phase flow, such as slurry reactors (Ramachandran and Smith, 1977) and a two-phase representation of the fluidized-bed reactor (Dayan and Levenspiel, 1970).

The interpretation of tracer dynamic experiments often relies on the analysis of moments of the response curve (Levenspiel, 1972; Suzuki and Smith, 1971). The advantages and disadvantages of this type of data analysis and comparison to other methods have been presented (Seinfeld and Lapidus, 1974). In spite of the possible pitfalls associated with the method of moments, the use of the technique is widely utilized owing to its simplicity. It is, therefore, of interest to evaluate the moments for the models of the system and by comparison of these expressions with experimentally calculated moments extract the values of desired system parameters.

The objective of this note is to outline the main differences in moments interpretation in single-phase and two-phase flow systems and to point out some results unique to the two-phase flow systems. Of particular interest is the effect of tracer volatility on the moments which was first observed and reported by Schwartz et al. (1976). The equations are presented for two-phase concurrent and countercurrent flow in packed beds.

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A packed bed with concurrent or countercurrent flow is considered. Both phases are assumed to be in plug flow, which is a reasonable approximation for most systems of practical interest. Let the two phases be liquid and gas, although the equations are applicable to two partially immiscible liquids also. The governing equations describing the response to an impulse injection of tracer are

$$H_L \frac{\partial C_L}{\partial t} = -u_L \frac{\partial C_L}{\partial z} - k_{LG} a_{LG} \left(C_L - \frac{C_G}{K_{LG}} \right)$$

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