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A Method of Predicting Diffusion Coefficients of Solutes at Infinite Dilution

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The prediction of the diffusion coefficient of solutes in solution has been the subject of numerous studies and several equations which allow the coefficient to be estimated have been proposed (Reid et al., 1977). A recent report by Sridhar and Potter (1977) proposes two equations, one for liquid-liquid systems and another for gas-liquid systems.

A simpler relationship has been found between the limiting diffusion coefficient of the solute and the self-diffusion coefficient of the solvent, which is given by the symmetrical relationship

$$D^0{}_{21}(V_2{}^* - \bar{v}_2{}^0)^{1/2} = D_{11}(V_1{}^* - v_1)^{1/3} \qquad (1)$$

where $D^0{}_{21}$ and D_{11} are the limiting diffusion coefficient 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, and $\bar{v}_2{}^0$ is the partial molar volume of the solute in solution and v_1 is the molar volume of the solvent. This equation is suitable for both liquid-liquid and gas-liquid systems.

THE DATA

The extensive data in the literature pertaining to diffusion coefficients as surveyed by others (Dullien, 1972; Hayduk and Buckley, 1972; Reid et al., 1977; Sridhar and Potter, 1977; and Van Greet and Adamson, 1964) was used to test Equation (1). The data used included those for a total of thirteen different solvents and 126 solutes. For the solvent, V^* values were taken from the literature when available or otherwise estimated using a method proposed by Fedors (1978) which is simpler to apply and yields results comparable to the method of Lydersen (1955). The corresponding viscosities and densities were taken from the original data sources. V^* values for the solutes were estimated as for the solvents. $\bar{v}_2{}^0$ for liquid and solid solutes are generally unavailable, and so the value was taken equal to the molar volume of pure solute (in the liquid state). For solutes which are crystalline in the pure state, the volume corresponding to the liquid state was estimated using the method of Fedors (1974). For solutes which are in the gaseous state, $\bar{v}_2{}^0$ values were taken from the compilation of Hildebrand and Scott (1950).

RESULTS AND DISCUSSION

Table 1 summarizes the results obtained to date. The first column lists the solvent and the second column the number of different solutes whose diffusion coefficient at infinite dilution was determined in each solvent. Column 3 contains the average value of $D^0{}_{21}\ (V_2{}^* - \bar{v}_2{}^0)^{1/3}$, while the next column lists the values of the self-diffusion coefficient for the solvent calculated from the diffusion coefficient of the solute via Equation (1). The last column lists the value of the self-diffusion coefficient of the solvent as obtained from direct experimental measurement. As may be seen, the agreement between the two sets of values is satisfactory.

Data for five solutes in both ethanol and butanol as solvents did not follow Equation (1). For these two solvents, the calculated diffusion coefficients for symmetrically shaped solutes were higher than the equation would predict. These anomalous data are tabulated in Table 2. In column 5 of the table, there is listed the values of $D^0{}_{21}$ calculated on the straightforward applica-

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TABLE 1

Solvent	Number of solutes	$D^0_{21}(V_2^* - v_2^0)^{1/2} \times 10^5$ $\text{cm}^{7/2}/\text{s mole}^{1/2}$	$D_{11} \times 10^5$, cm^2/s calc	$D_{11} \times 10^5$, cm^2/s exptl	Ref.
Carbon tetrachloride	50	18.9	1.35	1.32	1, 3, 4
Chloroform	8	26.4	2.08	2.58	1, 4
Acetone	3	51.2	4.84	4.44	1, 4
Ethyl acetate	6	37.4	2.78	—	1, 4
Benzene	7	29.2	2.22	2.22	1, 4
Water	10	15.1	2.20	2.51	1, 4
Methanol	12	21.0	2.46	2.32	1, 3, 4
Ethanol	6	12.0	1.16	1.01	1, 4
Butanol	5	5.9	0.44	—	1, 4
Hexane	15	61.0	3.97	4.21	1, 2, 3, 4
Heptane	1	50.6	3.05	3.12	1, 4
Octane	1	34.0	2.10	2.37(2.0)[6]	4, 5
Dodecane	2	17.5	0.81	0.81	4, 5

TABLE 2

Solvent: ethanol

Solute	$D^0_{21} \times 10^5$ cm^2/s exptl	$(V_2^* - \bar{v}_2^0)^{1/2}$ $\text{cm}^{3/2}/\text{mole}^{1/2}$	$D^0_{21}(V_2^* - \bar{v}_2^0)^{1/2} \times 10^5$ $\text{cm}^{7/2}/\text{s mole}^{1/2}$	$D^0_{21} \times 10^5$ cm^2/s calc, monomer	$D^0_{21} \times 10^5$ cm^2/s calc, tetramer
Benzene	1.81	13.10	23.7	0.80	1.60
Carbon tetrachloride	1.50	13.67	20.5	0.76	1.50
Carbon dioxide	3.20	7.50	24.0	1.40	2.78
Solvent: butanol					
Benzene	0.99	13.10	12.96	0.46	0.92
p-dichlorobenzene	0.82	15.53	12.13	0.46	0.92

tion of Equation (1), while column 6 lists the calculated D^0_{21} value on the assumption that these two solvents exist as tetramers. These values may be compared with those obtained experimentally. These two sets of data are in good agreement. Association factors for solvents have been employed in the past for purposes of correlating diffusion data for solutes (Wilke and Chang, 1955).

In another paper, it was shown that the self-diffusion coefficient for a remarkably wide span of liquids ranging from the liquid metals to high molecular weight polymers could be expressed by (Fedors, 1978)

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

where η_1 is the viscosity of the liquid. Using this equation in combination with Equation (1), we get

$$D^0_{21} = \frac{4.5 \times 10^{-9}\, T(V_1^* - v_1)^{3/2}}{\eta_1 V_1^{*4/3}(V_2^* - v_2^0)^{1/2}} \tag{3}$$

from which the limiting infinite dilution diffusion coefficient can be calculated directly.

Here, T is expressed in degrees Kelvin; V_1^* and V_2^* are the volumes at the critical temperature of the solvent and solute, respectively, expressed in cubic centimeters per mole; v_1 and v_2^0 are the volumes of the solvent and the solute (at infinite dilution), respectively, expressed in cubic centimeters per mole and η_1 is the viscosity of the solvent expressed in poise.

Equation (3) was compared to the Wilke and Chang (1955) diffusion equation for some 52 solutes in eight different solvents using data provided by Reid et al. (1977). The average percent error calculated using $[D^0_{21}(\text{calc}) - D^0_{21}(\text{exptl})]/D^0_{21}(\text{exptl}) \times 100$ was 22.3% for Equation (3) and 22.4% using the Wilke Chang expression. Although the two equations thus provide about the same average deviations, the advantage of Equation (3) is that it is applicable over a much wider range of solvent viscosities.

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