Diffusion Coefficients in Dilute Binary Liquid Mixtures

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A correlation for the estimation of diffusion coefficients at infinite dilution and self-diffusion coefficients is obtained by adapting the Stokes-Einstein equation to binary mixtures in which the size of molecules of the solute and the solvent is of the same order of magnitude. The ratios of the molecular sizes and of the parachors of the pure components are used to account for the intermolecular forces. The correlation is successfully tested with a considerable amount of available experimental data. The limits of the applicability of the correlation are indicated.

The theories of diffusion in the liquid state by Einstein, Eyring, and Hirschfelder (*1, 9*) have provided a foundation for numerous correlations. However, the search for satisfactory analytical correlations applicable generally, or at least to groups of chemical binary systems, has not yet produced any answer. While this search has been going on, some semiempirical correlations have been developed and have met with limited success. These are appreciated by engineers who prefer to have some means of estimating diffusion coefficients to waiting for an analytically established relationship.

The Stokes-Einstein (*9*) equation has provided a good basis for the development of a number of useful correlations for the prediction of diffusion coefficients in dilute solutions. Thus,

$$\frac{D_{AB}\mu_B}{kT} = \frac{1}{6\pi R_A} \tag{1}$$

was derived on the assumption of a physical model in which large rigid spheres diffuse through a medium of small particles. Such a situation exists in the diffusion of colloidal particles through a liquid. The equation agrees well with experimental data for colloidal solutions. The group $(D_{AB}\mu_B/T)$ is reasonably constant for a given colloidal system and is essentially independent of temperature. There are a few reasonably successful empirical adaptations of the Stokes-Einstein equation to dilute binary systems in which the sizes of the solute and of the solvent particles are of the same order of magnitude. Their relative sizes have a decisive effect on the solute–solvent intermolecular forces. This problem has been dealt with in various ways by many authors.

Wilke and Chang (*13*) introduced the molecular weight of the solvent and an empirical association factor. Empirically fitted constants resulted in the following equation:

$$\frac{D_{AB}\mu_B}{T} = 7.4 \times 10^{-8}\,\frac{(x_B M_B)^{1/2}}{V_A^{0.6}} \tag{2}$$

The association factor x_B is a property of every individual solvent and has to be estimated from experimental data.

Sitaraman et al. (*10*) suggested that the ratio of the latent heats of vaporization of the solute and the solvent would account better for the intermolecular forces and also for the association of the solvent molecules. The resulting equation with an empirical constant and an empirical exponent assumed the following form:

$$D_{AB} = 5.4 \times 10^{-8}\left[\frac{M_B^{1/2}\Delta L_B^{1/3} T}{\mu_B V_A^{0.5}\Delta L_A^{0.3}}\right]^{0.93} \tag{3}$$

King et al. (*3*) ascribed the same significance to the ratio of the latent heats of vaporization. But they suggested that the ratio of the molecular volumes would give a better representation of the molecular sizes than the use of the solvent molecular weight and of the solute molal volume. With the aid of experimental data, they obtained the equation:

$$\frac{D_{AB}\mu_B}{T} = 4.4 \times 10^{-8}\left[\frac{V_B}{V_A}\right]^{1/6}\left[\frac{\Delta H_B}{\Delta H_A}\right]^{1/2} \tag{4}$$

Another approach, in trying to develop an empirical correlation, was used by Ibrahim and Kuloor (*2*) and also by Olson and Walton (*7*) who initiated an investigation into the relationship between diffusivity and surface tension.

It emerges from this brief review that: the allowance for the variation in the intermolecular forces made in Equations 3 and 4 improves only marginally the Wilke and Chang equation, as can be seen by reference to Table I; and the property of surface tension is another physical property which is affected by the intermolecular forces, but its use for correlating purposes has not yet been fully investigated.

The complete Table I and a list of references have been deposited with the ACS Microfilm Depository Service. This table and references have been taken from ref. *12*.

Development of Correlation

From this review of the correlations based on the Stokes-Einstein equation, the following conclusions may be drawn:

The Stokes-Einstein equation itself agrees well with experimental data obtained with liquid-phase systems answering the description of the physical model assumed in the derivation of Equation 1. The size of the solute molecules is an important variable in Equation 1, and the solvent is treated as a continuum.

For most of the binary systems, the size of the solute and solvent molecules is of the same order of magnitude. Thus, any attempt to adapt the Stokes-Einstein equation would make it necessary to introduce the size of the solvent molecules as an additional variable. This could take the form of such ratios as $(R_A{}^l/R_B{}^t)$ or $(V_A{}^s/V_B{}^q)$.

An association factor, which is different for every polar solvent and almost certainly temperature dependent, was introduced in Equation 2. In Equations 3 and 4 a ratio of the latent heats of vaporization was introduced in the belief that it would account for the association phenomenon. Unfortunately, these equations do not show any marked improvement over Equation 2 as demonstrated in Table I.

It was pointed out earlier that surface tension has already been considered (*2, 7*) as a correlating factor, but the suggestion needs to be fully investigated. Surface

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Table I. Comparison of Correlations for Estimating Diffusion Coefficients at Infinite Dilution, $D_{AB} \times 10^5$ cm²/sec[a]

					% Error[c] in D_{AB} estimated by			
No.	Solvent	Temp range, °C	No. of systems[b]	No. of data points[b]	This work, Equation 8	W-C,[d] Equation 2	King, Equation 4	Sitar, Equation 3
1	Water	0–70	91 (75)	287 (253)	13.1	10.3	19.4	12.9
2	Methanol	5–55	90 (79)	104 (93)	14.0	17.2	13.1	13.3
3	Ethanol	7–65	27 (26)	43 (42)	18.1	25.8	18.5	16.7
4	*n*-Propanol	15–30	10	11	12.2	32.9	24.8	22.6
5	*i*-Propanol	30	5	5	5.3	24.6	36.7	29.9
6	*n*-Butanol	25–45	11 (9)	13 (11)	11.2	21.7	14.8	15.5
7	*i*-Butanol	20–30	7	8	19.1	33.7	19.0	19.0
8	*n*-Pentanol	25	3	3	11.7	48.6	48.0	51.5
9	Heptanol	25	3	3	12.3	47.3	44.3	51.1
10	Isoamyl alcohol	19	1	1	35.0	77.2	46.6	45.2
11	*n*-Hexane	0–80	25	35	9.3	11.5	13.9	18.8
12	*n*-Heptane	7–100	7	32	7.7	10.7	13.2	22.2
13	*n*-Octane	0–100	5	24	4.4	11.5	15.2	16.8
14	*n*-Decane	20–25	2	3	12.9	14.0	12.2	20.8
15	*n*-Dodecane	25	5	5	16.5	14.5	11.6	19.7
16	*n*-Tetradecane	25	2	2	25.3	18.4	9.1	23.1
17	*n*-Hexadecane	25	4	4	27.2	22.1	17.4	26.6
18	Benzene	5–85	59 (53)	110 (108)	10.1	12.2	10.8	17.8
19	Toluene	6–110	23	50	8.9	17.1	10.0	17.5
20	Cyclohexane	7–100	7	28	11.6	10.5	12.1	16.1
21	Methylcyclohexane	10–60	5	11	10.0	15.5	13.0	11.8
22	Acetone	6–55	11	19	6.4	11.9	12.9	10.8
23	Methyl ethyl ketone	25	1	1	13.5	15.9	26.0	14.3
24	Methyl isobutyl ketone	25	1	1	23.5	39.3	44.9	29.6
25	Cyclohexanone	25–90	2	4	9.7	15.6	5.2	17.9
26	Carbon tetrachloride	6–60	48	78	10.1	32.5	10.7	14.1
27	Chloroform	10–40	11	15	9.6	27.8	9.7	11.3
28	Bromoform	20–25	4	4	11.4	66.3	16.5	15.4
29	Methylene chloride	7.5	1	1	13.0	58.4	26.9	47.6
30	Ethylene chloride	7.3	1	1	1.8	22.2	7.9	26.1
31	Tetrachloroethane	50	1	1	11.9	51.3	25.2	60.6
32	Chlorobenzene	10–40	3	7	8.3	11.4	10.4	10.8
33	Bromobenzene	7–40	4	8	10.0	21.2	2.2	10.7
34	Ethylbenzene	7.3	1	1	1.1	8.0	10.5	6.7
35	Nitrobenzene	17–20	4	4	9.4	12.3	4.1	7.2
36	Ethylbenzoate	15–20	4	4	17.5	9.0	9.5	16.8
37	*m*-Xylene	7–25	2	3	18.7	44.9	20.7	43.9
38	Methyl acetate	30	1	1	14.6	14.9	17.8	6.9
39	Ethyl acetate	20–30	8	9	12.9	24.2	16.4	16.4
40	Isopropyl acetate	30	1	1	20.3	31.5	31.0	2.5
41	Butyl acetate	20–30	4	4	11.6	31.7	22.1	13.7
42	Ethyl ether	7–25	5	6	29.5	30.0	25.0	17.1
43	Aniline	20–60	5	7	27.5	25.0	21.2	23.2
44	Mesitylene	7.3	1	1	6.5	17.5	21.9	15.4
45	Tetralin	7	2	2	10.9	20.7	24.2	29.4
46	Transdecalin	7–25	3	3	12.6	11.4	9.0	12.9
47	Dioxane	25	2	2	2.6	13.4	9.0	24.2
48	*m*-Cymene	7.3	1	1	22.9	11.9	11.4	14.7
49	Acetic acid	20	1	1	32.4	3.2	3.4	35.2
50	Anisole	20	1	1	11.0	16.6	12.3	22.3
51	Methylnaphthalene	7.5	1	1	11.8	2.6	2.2	9.8
52	Carbon disulfide	16–19	2	2	6.2	15.9	20.4	21.1
53	Ethylene glycol	25–40	2	7	12.2	8.7	19.5	20.8
54	Diethylene glycol	25–40	2	6	5.6	9.7	13.3	18.7
55	Propylene glycol	25–50	2	7	13.7	10.3	23.3	24.1
Overall absolute average % error					12.0	16.5	15.2	15.9
Percentage of data points within ±30% accuracy limit					95.1	83.2	87.8	87.2

[a] This table is a summary of a larger table in ref. *12*, giving the individual solutes employed in calculating the constant and exponents in Equation 8. [b] The total number of data points = 996 (946), and the total number of systems = 535 (499). The quantities in the brackets indicate the data points and the systems used with Equations 3 and 4. [c] Error % = (calculated − experimental) × 100/experimental. [d] The Wilke and Chang association parameter x_B was assumed to be 2.6 for water, 1.9 for methanol, and 1.5 for other alcohols. All the other solvents were allocated unity as the association parameter. Water was treated as a tetramer in Equation 2 when diffusing in organic solvents.

tension reflects the strength of the intermolecular forces, probably better than the latent heats of vaporization if it is considered as a component of a parachor. A parachor is a secondary derived function dependent on the primary properties of surface tension, density, and molecular weight (*8*). It can be regarded as a sum of constants characteristic of the individual atoms or groups within the molecule (*1*). According to Sugden (*11*), a parachor is in some degree a measure of the effect of the forces due to molecular attraction on the molecular volumes. There are a number of quantitative definitions of the parachor which reflect the above features. Thus, in Hirschfelder et al. (*1*), it is defined as

$$P = 7.1 \times 10^{23} \epsilon^{1/4} \delta^{5/2} \tag{5}$$

Quayle (*8*) also defines parachors as molecular volumes at corresponding states of the same value of surface tension and suggests the following definition:

$$P = \gamma^{1/4} V \tag{6}$$

According to Hirschfelder et al. (*1*), the parachor for any given substance remains nearly independent of temperature over a wide temperature range. The last property makes it possible to use the parachor in conjunction with the group $(D_{AB}\mu_B/T)$. Thus, it is obvious that the parachors are more dependent on molecular structures and sizes than the latent heats of vaporization and would be expected to be more sensitive indicators of the intermolecular forces, particularly with polar compounds. It is therefore suggested that the correlating equation should assume the form:

$$\frac{D_{AB}\mu_B}{T} = K \frac{V_A{}^s}{V_B{}^q} \left[\frac{P_B}{P_A} \right]^m \tag{7}$$

This equation was tested with a large variety of experimental data to evaluate the constant K and the exponents s, q, and m. The optimization routine NELM (*6*) and an ICL 1904A computer were used. With a total of 883 data points at infinite dilution and 113 data points for self-diffusion (*12*), the constants were established giving the following correlation:

$$\frac{D_{AB}\mu_B}{T} = 8.93 \times 10^{-8} \frac{V_A{}^{1/6}}{V_B{}^{1/3}} \left[\frac{P_B}{P_A} \right]^{0.6} \tag{8}$$

The constant of the equation has dimensions; therefore, the set of units defined in the nomenclature should be used with Equation 8.

Table I gives a summary of the binary systems used to establish the constant and the exponents in Equation 8. The parachors required in Equation 8 were obtained either from Quayle (*8*) or were calculated by the Sugden (*11*) additive method. Also, the deviations of the diffusivities predicted by Equations 2–4 and 8 from the experimental values are reported in Table I. A comparison of the values predicted by Equation 8 with the experimental values is made in Figure 1. It follows from Table I that Equation 8 compares favorably with Equations 2–4.

Discussion of Correlation

Table I shows that Equation 8 was tested on a wide variety of binary systems. There are binary systems to which this equation is not applicable and others which require the use of association parameters either for the solutes or for the solvents.

Highly viscous solvents. All the equations tested (Table I) underpredict the diffusion coefficients in highly viscous solvents, such as glycerol, chrysene, hendecane, and others of similarly high viscosity. The predicted coefficients were up to 80% below the experimental ones. Thus, Equation 8 is not recommended for this type of binary system. Of the solvents in Table I, propylene glycol has the highest viscosity of 43 cP at 25°C. The upper limit of solvent viscosity for which Equation 8 may be used is probably higher if a larger deviation than 13.7% in the predicted coefficient can be tolerated.

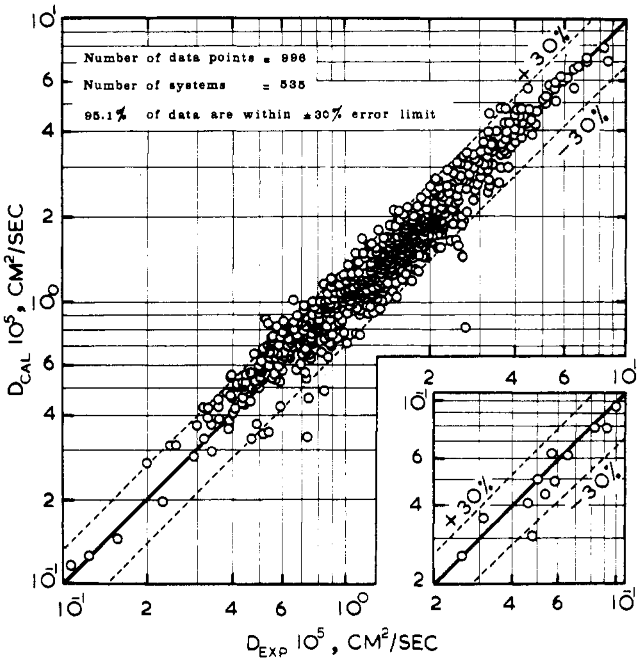

Figure 1. Comparison of experimental diffusion coefficients with coefficients predicted by Equation 8

Diffusion of water in organic solvents. Equation 8 predicts coefficients within ±10% accuracy limits for these systems, provided that water molecules are treated as dimers, i.e., a double molal volume (2 V_A) and double parachor (2 P_A) are used in Equation 8.

Acids diffusing in organic solvents. The best results were obtained if the acid solutes, such as acetic acid, formic acid, benzoic acid, and similar acids were treated as dimers (*4, 5*), when diffusing in such solvents as benzene, toluene, carbon tetrachloride, acetone, ethanol, and others. But an exception should be made for acids diffusing in water, methanol, and butanol, when the acids should be treated as monomers (*5*).

Diffusion of inert solutes in monohydroxy alcohol solvents. For the diffusion of such inert solutes as benzene and carbon tetrachloride in monohydroxy alcohols, all the equations predict coefficients about 45% lower than the experimental ones. This is ascribed to the association of the solvent molecules. For these systems an empirical formula was devised for the estimation of the association factor:

$$n = 8\,\mu_B \tag{9}$$

where the viscosity of the solvent is in centipoises (*12*). The factor n is used in Equation 8 as a multiplier to the molal volume and to the parachor of the solvent. The application of this association factor reduced the prediction error from 45 to 10% for the appropriate systems in Table I.

With these limitations Equation 8 predicts diffusion coefficients at infinite dilution and self-diffusion coefficients which are slightly more accurate than those predicted by Equations 2–4. This is demonstrated in Table I. Moreover, Figure 1 shows that 95.1% of the data points fall within the ±30% accuracy lines. The corresponding percentages for the other equations are: 83.2% for the Wilke and Chang Equation 2, 87.2% for the Sitaraman et al. Equation 3, and 87.8% for the King et al. Equation 4.

Equation 8, besides giving more accurate predictions, is also more convenient to use because of the ease of estimating the parachors. These can be obtained by means of such relationships as Equation 6 or by the addition of the parachors of the individual atoms and groups of a given compound (*11*). These authors have no knowledge of the relative merits of Equation 5, besides the information given on page 356 of ref. *1*.

It is sometimes not possible to use Equations 3 and 4 for the prediction of diffusion coefficients, because some solutes do not form a liquid phase; therefore, their latent heat of vaporization cannot be defined uniquely. This difficulty does not arise with Equation 8 as it employs parachors instead which can be defined uniquely.

Out of the total of 996 data points in Table I, 113 represent self-diffusion coefficients. The values predicted by Equation 8 are more accurate because the molal volumes of the solute and the solvent are fitted with different exponents.

Conclusion

The semiempirical correlation developed here predicts diffusion coefficients at infinite dilution and self-diffusion coefficients with better accuracy than the other correlations based on the Stokes-Einstein equation. Like any semiempirical correlation, it has a limited field of application. The improved performance in the correlation was achieved by the introduction of the parachors in place of the latent heats of vaporization.

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Nomenclature

D_{AB} = binary liquid diffusion coefficient at infinite dilution of solute A, cm^2/sec
D_{cal} = values of D_{AB} calculated from Equation 8 in Figure 1
D_{exp} = experimental values of D_{AB} in Figure 1
ΔH_A, ΔH_B = latent heats of vaporization of A and B, respectively, at their normal boiling points, cal/g mol
ΔL_A, ΔL_B = latent heats of vaporization of A and B, respectively, at their normal boiling points, cal/g
M_B = molecular weight of B
P = parachor, g$^{1/4}$ cm^3/g mol sec$^{1/2}$
P_A, P_B = parachors of A and B, respectively, g$^{1/4}$ cm^3/g mol sec$^{1/2}$
R_A, R_B = molecular radius of A and B, respectively
T = temperature, K
V = molal volume, cm^3/g mol, at T, K
V_A, V_B = molal volumes of A and B, respectively, at their normal boiling points, cm^3/g mol
k = Boltzman's constant, erg/molecule K
K, m, q, s, t, l = constants
n = self-association factor in Equation 9
μ_B = viscosity of pure solvent at T, K, cP
γ = surface tension of pure liquid at T, K, dynes/cm
ϵ, δ = Lennard-Jones parameters, erg/molecule and Å, respectively

Subscripts

A = solute
B = solvent

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Supplementary Material Available. The complete Table I and a list of references will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $6.00 for photocopy or $2.00 for microfiche, referring to code number JCED-75-106.