

Nomenclature

a_{ij} = factors defined by Equation 33
 a = distance between equilibrium positions
 C = total molar concentration
 C_i = molar concentration of species i
 D_{ij} = binary mutual diffusion coefficients
 D_{ij}^K = multicomponent diffusion coefficients defined by Equation 21
 D_{ij}^V = multicomponent diffusion coefficients defined in a volume average reference frame
 D^* = diffusion coefficient defined by Equation 32
 F_{ij} = friction coefficients defined by Equation 8
 f_{ij} = factors defined by Equation 33
 ΔG_i^\pm = free energy barrier for diffusion of species i
 ΔG_{io} = free energy barrier for diffusion of species i in a homogeneous mixture
 ΔG_{ij} = net activation energy for the $i - j$ frictional interaction
 h = Planck constant
 J_i^K = diffusional flux of i relative to K
 k = Boltzmann constant
 L_{ij}^K = phenomenological coefficients defined by Equation 20
 N = Avogadro's number
 R = gas constant
 T = absolute temperature
 V_{ix} = diffusional velocity of i in x direction
 \vec{V}_i = velocity vector of species i
 \bar{V}_i = molar volume of pure i
 \bar{V}_i = partial molar volume of i
 X = distance coordinate
 X_i = mole fraction of species i

GREEK LETTERS

α_{ij}^K = factor defined by Equation 28

γ_i = activity coefficient of species i
 δ_{ij} = Kronecker symbol
 μ_i = chemical potential of species i
 μ_{ij} = chemical potential composition derivative defined by Equation 22
 ν_i^\pm = frequency of jumps of species i

SUPERSCRIPIT

0 = infinite dilution of indicated species

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ESTIMATING LIQUID DIFFUSIVITY

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The Wilke-Chang correlation for predicting liquid diffusivities has been modified by replacing the association parameter of this equation by the square root of the solvent molar volume. Based on this, equations have been proposed for $V_2/V_1 \leq 1.5$ and $V_2/V_1 > 1.5$, which represent the experimental data with average deviations of 13.5 and 18%, respectively. V_1 and V_2 represent the molecular volumes of the solute and solvent, respectively.

THE most widely used equation for estimating liquid diffusivity is that of Wilke and Chang (6), which is based on the Stokes-Einstein equation. In this equation the so-called solvent factor of the earlier Wilke equation (5) was replaced by an association parameter, which could be taken as unity for unassociated solvents. Scheibel (3) proposed another equation in which the solvent factor was eliminated by the introduction of the molal volumes of the solvent and the solute. Subsequently Kuloor and coworkers (4) replaced the association parameter of the Wilke-Chang equation by the latent heats of the solvent and solute. In the present note new equations are proposed for estimating liquid diffusivity, which are largely free from the limitations of the Wilke equations.

In the Scheibel correlation the exponent of the solute molal volume is $1/3$ as against 0.6 in the Wilke-Chang equation. This exponent has been modified to 0.455 by Kuloor *et al.* By retaining the exponent of $1/3$ and introducing the solvent molal volume, also raised to the same power, the association parameter of the Wilke-Chang equation can be replaced, thus

eliminating the only drawback of this useful equation. [In Eyring's equation also (7), when the liquid free volume is expressed in terms of the liquid molal volume, an exponent of $1/3$ is obtained for V_2 .] This results in an equation of the form

$$D_{12} = (\text{constant}) \frac{M^{1/2} T}{\mu V_1^{1/3} V_2^{1/3}} \quad (1)$$

The constant of Equation 1 has been found to depend on the relative molecular volumes of the solvent and solute. Thus:

CASE 1

$$\frac{V_2}{V_1} \leq 1.5$$

$$D_{12} = 10 \times 10^{-8} \frac{M^{1/2} T}{\mu V_1^{1/3} V_2^{1/3}} \quad (2)$$

Table I. Experimental and Estimated Liquid Diffusivities^a

<i>Solute</i>	<i>Temp.</i> , ° C.	<i>Solvent</i>	$D_{\text{exptl}} \times 10^5$	$D_{\text{calcd}} \times 10^5$	<i>Error</i> , %	
Case 1. $V_2/V_1 \leq 1.5$						
Acetic acid	12.5	Water	0.91	0.94	3.30	
Allyl alcohol	15.0		0.90	0.94	4.45	
Acetone	20.0		1.16	1.10	5.16	
Aniline	20.0		0.92 ± 0.04	0.98	2.09	
Bromine	12.0		0.90	0.98	8.90	
Butanol	15.0		0.77	0.86	11.69	
Carbon dioxide	18.0		1.71	1.36	20.41	
Diethylamine	20.0		0.97	0.98	1.03	
Ethanol	15.0		1.00	1.02	2.00	
Ethyl acetate	20.0		1.00 ± 0.07	0.99	0.00	
Glycerol	10.0		0.63	0.72	14.30	
Iodine	25.0		1.25	1.28	2.40	
Isoamyl alcohol	15.0		0.69	0.80	15.95	
Isobutyl alcohol	20.0		0.84 ± 0.10	0.99	16.50	
Methanol	15.0		1.28	1.17	8.60	
Nitrogen	22.0		2.02	1.55	23.30	
Allyl alcohol	15.0		Methanol	1.80	1.72	4.45
Acetone	18.8			2.22	1.85	16.70
Aniline	15.0			1.49	1.54	2.68
Carbon tetrachloride	15.0			1.70	1.58	7.06
Chloroform	15.0			2.07	1.64	20.80
Ethyl acetate	17.8			1.72	1.63	5.23
Ethyl benzoate	16.0			1.28	1.34	4.70
Ethyl bromide	15.0			2.40	1.75	27.06
Ethylene bromide	15.0			1.95	1.79	8.20
Furfural	15.0			1.70	1.64	3.53
Isoamyl alcohol	15.0			1.34	1.46	9.00
Methanol	25.0	2.27		2.53	10.95	
Nitrobenzene	16.8	1.48		1.53	3.38	
Nitromethane	16.0	2.23		1.96	12.10	
Phenol	15.0	1.40		1.56	11.42	
Benzene	15.0	Benzene		1.89	1.72	9.00
Bromine	12.0			2.00	1.97	1.50
Bromobenzene	7.3			1.41	1.34	4.96
Carbon tetrachloride	25.0			2.00	2.04	2.00
Chlorobenzene	15.0			1.42	1.63	14.80
Chloroform	15.0			2.11	1.76	16.60
Ethylene bromide	15.0		1.97	1.90	3.55	
Ethyl ether	15.0		2.21	1.67	24.40	
Iodine	20.0		1.95	2.08	6.66	
Isoamyl alcohol	15.0		1.48	1.57	6.10	
Nitrobenzene	15.0		1.84	1.58	14.12	
Phenol	15.0		1.27	1.67	31.50	
Propanol	15.0		1.60	1.82	13.80	
Aniline	18.5		Ethanol	2.70	0.84	69.00
Bromoform	20.0			0.97	0.89	8.25
Bromonaphthalene	20.0			0.76	0.74	2.64
Ethanol	25.0			1.05	1.18	12.40
Iodine	40.0			1.77	1.56	11.90
Isoamyl alcohol	20.0			0.78	0.8	2.56
Pyridine	20.0			1.12	0.91	18.80
Acetone	20.0			Isobutyl alcohol	0.74 ± 0.05	0.31
Diethylamine	20.0	0.34 ± 0.06			0.27	3.57
Acetic acid	25.0	Acetone		3.31	4.3	30.00
Benzoic acid	25.0		2.62	3.35	27.8	
Cinnamic acid	25.0		2.41	3.10	28.60	
Ethyl benzoate	20.0		2.47	2.90	17.40	
Nitrobenzene	20.0		2.94	3.28	11.60	
Acetone	20.0	Toluene	2.93 ± 0.03	2.28	21.40	
Benzoic acid	25.0		1.49	2.04	37.00	
Benzoic acid	20.0		1.74	1.90	9.20	
<i>m</i> -Bromotoluene	7.4		1.52	1.53	0.66	
Carbon tetrachloride	25.0		2.19	2.24	2.28	
Cinnamic acid	25.0		1.18	1.88	59.40	
Diethylamine	20.0		2.06	2.02	1.94	
Ethyl benzoate	20.0		1.85	2.26	22.20	
Acetone	20.0	Ethyl acetate	3.18 ± 0.04	2.94	6.05	
Nitrobenzene	20.0		2.25	2.53	12.40	
Nitrobenzene	20.0	Ethyl benzoate	0.73	0.58	20.50	
Acetone	20.0	Carbon tetrachloride	1.89	1.89	0.00	
Carbon tetrachloride	25.0		1.41	1.88	33.40	
Iodine	25.0		1.50	2.10	40.00	
Bromobenzene	7.3	Ethyl benzene	1.44	1.48	2.84	
Bromobenzene	7.3	<i>m</i> -Xylene	1.52	1.95	28.30	
Bromobenzene	7.3	<i>n</i> -Hexane	2.60	2.74	5.40	
2-Propanol	25.0	2-Propanol	0.65	0.60	7.70	

Table I. Continued

Solute	Temp., ° C.	Solvent	$D_{\text{exptl}} \times 10^5$	$D_{\text{calcd}} \times 10^5$	Error, %
Case 2. $V_2/V_1 > 1.5$					
Acetic acid	20.0	Ethyl acetate	2.18	2.67	22.50
Acetone	17.0	Ethyl benzoate	0.83	0.55	34.40
Ethyl acetate	15.7		0.68	0.49	27.90
Acetic acid	20.0	Isobutyl alcohol	0.30 ± 0.04	0.27	10.00
Diethylamine	20.0		0.34 ± 0.06	0.23	17.90
Formic acid	25.0	Acetone	3.77	4.00	6.10
Acetic acid	25.0	Toluene	2.26	2.22	1.78
Formic acid	25.0		2.65	2.46	7.20
Methyl iodide	7.4		2.23	1.70	26.90
Formic acid	13.9	Benzene	2.31	1.87	19.05
Acetic acid	25.0	Carbon tetrachloride	1.49	1.85	24.20
Formic acid	25.0		1.89	2.06	9.00
Iodine	25.0	Heptane	3.42	2.80	18.15
Iodine	15.0	Cyclohexane	1.54	1.04	32.40

^a Data from (4, 5, 6).

Table II. Proposed Equation and Wilke-Chang Equation for Systems Involving Water as Solute^a

(Case 2)

Solvent	Temp., ° C.	$D_{\text{exptl}} \times 10^5$	Wilke-Chang		Present Work	
			$D \times 10^5$	Dev., %	$D \times 10^5$	Dev., %
Acetone	25	4.56	8.70	90.8	5.40	18.4
Furfural	20	0.90 ± 0.1	2.14	138	1.29	43.3
Aniline	20	0.70 ± 0.1	0.83	18.6	0.40	42.8
Isobutyl alcohol	20	0.36 ± 0.03	0.81	125	0.41	13.9
Ethyl alcohol	18	1.10	2.58	134	1.23	11.8
Ethyl acetate	20	3.20 ± 0.15	7.52	135	4.00	25.0

^a Data from (2, 4).

CASE 2

$$\frac{V_2}{V_1} > 1.5$$

$$D_{12} = 8.5 \times 10^{-8} \frac{M^{1/2} T}{\mu V_1^{1/3} V_2^{1/3}} \quad (3)$$

In addition to molecular weight the only properties involved in estimating liquid diffusivity from the above equations are viscosity and molal volumes of solvents and solute, which are easy to estimate. In these correlations the viscosity of the solvent is used compared to that of the solution in the Wilke-Chang equation.

The proposed correlations have been tested for 96 systems (Table I and II) and found to hold satisfactorily. The average errors are: case 1, 13.5% based on estimated deviations for 76 systems; and case 2, 18% based on estimated deviations for 20 systems.

Under case 2 are also included the systems in which water diffuses into an organic liquid. This is a situation in which the Wilke-Chang equation fails completely, as pointed out by Olander (2). With the proposed equation (case 2) the diffusion coefficient of water in organic liquids can be predicted with an average deviation of about 25%, as against 100% by the Wilke-Chang equation (Table II). However,

the correlation does not hold satisfactorily for highly viscous liquids. The calculated diffusion coefficient of water in ethylene glycol (26 centipoises at 20° C.) shows a deviation of about 100% (comparable to the deviations normally obtained with the Wilke-Chang equation for water as solute).

Nomenclature

D_{12} = diffusion coefficient of 1 in 2, sq. cm./sec.
 M = molecular weight of solvent
 V_1 = molecular volume of solute, cc./g.-mole
 V_2 = molecular volume of solvent, cc./g.-mole
 μ = viscosity of solvent (or solution), centipose

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