

LIQUID DIFFUSIVITIES—THEIR MEASUREMENT AND PREDICTION

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KNOWLEDGE of liquid diffusivities is essential in understanding the mechanism of solute transport in liquid-liquid extraction, dissolution and crystallization processes. Literature records a vast amount of experimental work over the last century in relating solute transport property to molecular properties on the basis of hydrodynamic theory, Eyring's absolute reaction rate theory, statistical mechanics and irreversible thermodynamics. Experimental data are still fragmentary even for dilute solutions and there still remains uncertainty about the applicability of existing correlations for prediction of diffusivity data.

MEASUREMENT OF LIQUID DIFFUSIVITIES

Diaphragm cell technique as reported by Laddha *et al.*^{1,2} may be used to measure liquid diffusivities experimentally. According to Fick's law, unidirectional diffusion may be expressed as follows:

$$J = - D_{AB}^F \frac{dC_A}{dZ} = \frac{1}{A_e} \frac{dS}{dt}, \quad (1)$$

where

$$dS = - \bar{D}_{AB} A_e \frac{dC_A}{dZ} dt. \quad (2)$$

For quasi-steady state and linear concentration gradient,

$$\frac{dC_A}{dZ} = \frac{\Delta C_A}{l_e} = \frac{C_{A1} - C_{A2}}{l_e}, \quad (3)$$

D_{AB} , the space mean (integral) coefficient, is defined as:

$$\bar{D}_{AB} = \frac{1}{C_{A1} - C_{A2}} \int_{C_{A2}}^{C_{A1}} D_{AB}^F(C_A) dC_A. \quad (4)$$

Material balance on component A gives:

$$v_1 dC_{A1} = -v_2 dC_{A2} = dS, \quad (5)$$

$$dC_{A1} - dC_{A2} = -D_{AB} \frac{A}{l_e} \left(\frac{1}{v_1} + \frac{1}{v_2} \right)$$

where v_1 and v_2 are volumes of chambers 1 and 2 of the diffusion cell. Combining (2), (3) and (5) we get,

$$(C_{A1} - C_{A2}) dt. \quad (6)$$

Expressing $(A_e/l_e)[(1/v_1) + (1/v_2)]$ by a cell constant, β and $(C_{A1} - C_{A2})$ by ΔC_A , (6) may be integrated to give

$$D_{AB} = \frac{1}{\beta t} \ln (\Delta C_A^0 / \Delta C_A^F), \quad (7)$$

where ΔC_A^0 is the initial concentration difference $= C_{A1}^0 - C_{A2}^0$; ΔC_A^F is the final concentration difference $= C_{A1}^F - C_{A2}^F$; and

$$D_{AB} = (1/t) \int_0^t \bar{D}_{AB}(t) dt.$$

The diffusion coefficient defined by (7) represents the time-averaged integral diffusion coefficient. Gordon³ has shown that the time-averaged integral diffusion coefficient can be treated without any serious error as the ordinary integral diffusion coefficient as defined by the equation taken over the concentration range.

The cell constant β may be found by calibrating with 0.1 N HCl diffusing into pure water at 30°C using the diffusivity value of 3.078×10^{-5} cm²/sec from Stokes' data⁴.

PREDICTION OF DIFFUSIVITIES

The hydrodynamic theory of diffusion is based on Einstein's treatment of the Brownian move-

ment of colloids. The accuracy of the resulting Stokes-Einstein equation for liquid diffusivity decreases as the size of the diffusing particle decreases. According to the theory proposed by Eyring *et al.*⁵ diffusion may be described as a process in which molecules move from a given position into an adjacent hole in the liquid structure. Because of the inadequacy of theoretical equations based on hydrodynamic, kinetic and absolute reaction rate theories attempts have been made to correlate experimental data by empirical correlations. These equations have been summarised by Laddha and Degaleesan⁶. The Stokes-Einstein equation suggests that for dilute solutions

$$D_{AB}\mu_B/T = k/6\pi r_A, \quad (8)$$

where r_A , the radius of the solute molecule, is given by the following relationship assuming the molecule to be spherical

$$r_A = \left[\left(\frac{3}{4\pi} \right) \frac{V_A}{N} \right]^{1/3} \quad (9)$$

Laddha and Smith⁷ suggested that the radius of the diffusing solute particle is influenced by the solvent species and hence suggested that 9 may be modified as follows:

$$r_A = \alpha \left[\left(\frac{3}{4\pi} \right) \left(\frac{V_A}{N} \right) \right]^{1/3} \left(\frac{V_A}{V_B} \right)^\beta, \quad (10)$$

where α is constant. Substitution of r_A according to (10) into (8) gives

$$\frac{D_{AB}\mu_B}{T} (V_A)^{1/3} = \left[\frac{k}{6\pi\alpha} \left(\frac{4\pi N}{3} \right)^{1/3} \right] \left(\frac{V_B}{V_A} \right)^\beta = \alpha_0 \left(\frac{V_B}{V_A} \right)^\beta, \quad (11)$$

where α_0 is a constant being equal to $(k/6\pi\alpha)(4\pi N/3)^{1/3}$. Based on the analysis of diffusivity data of 143 binary systems Laddha and Smith⁷ have proposed the following generalized equation for estimation of diffusivity.

$$\frac{D_{AB}\mu_B}{T} (V_A)^{1/3} = 1.892 \times 10^{-7} \left(\frac{V_B}{V_A} \right)^{0.16} \quad (12)$$

where D_{AB} is in cm^2/sec , μ_B is the viscosity of the solvent in centi poise, T in $^\circ\text{K}$.

The above equation may be used with confidence for binary systems which do not show appreciable association due to formation of hydrogen bonds between the solute and solvent species.

BINARY SYSTEMS FORMING ASSOCIATION COMPLEXES

If the solute and solvent of an organic binary system form an association complex, the diffusivity of solute as predicted by the various correlations reported in the literature may vary considerably from the experimentally measured value. Confining our attention to binary system capable of forming a simple association complex, we may assume that one molecule of solute A may combine with one molecule of solvent B to form the complex AB . Such a complex may be formed by hydrogen bonding in organic mixtures where one component contains a donor atom but no active hydrogen atom (such as in ethers, ketones and esters) while the other contains an active hydrogen atom but no donor atom (such as in chloroform). Ratcliff and Lusi⁸ have postulated that the law of mass action may be used to relate the monomer and complex concentrations in a ternary mixture consisting of solute and solvent monomers ($A1$ and $B1$) and the association complex ($A1B1$). Thus

$$\frac{X_{A1B1}}{X_{A1} X_{B1}} = K, \quad (13)$$

where X_{A1} , X_{B1} and X_{A1B1} are the mole fractions of the respective species in the ternary mixture and K is the association constant for the reaction.



At infinite dilution of the solute when $X_{B1} \rightarrow 1.0$, (13) becomes

$$X_{A1B1} = K X_{A1}. \quad (15)$$

Since the total flux of the solute must equal the sum of the monomer and complex fluxes the following relationship results at infinite dilution of the solute

$$D_{AB} = D_{A1} \frac{dX_{A1}}{dX_A} + D_{A1B1} \frac{dX_{A1B1}}{dX_A} \quad (16)$$

Taking into account the mass balance

$$X_A = X_{A1} + X_{A1B1}, \quad (17)$$

equation (16) may be expressed as

$$D_{AB} = \frac{1}{1+K} [D_{A1} + K D_{A1B1}] \quad (18)$$

Based on the analysis of experimental data for such binary systems forming simple association complexes Laddha and Kuppuswamy⁹ have proposed that D_{A1} and X_{A1B1} the diffusivities of the monomer the complex may be evaluated by the following relationships

$$D_{A1} = 2.0 \times 10^{-7} \left(\frac{T}{\mu_B} \right) \left(\frac{1}{V_A} \right)^{1/8} \left(\frac{V_B}{V_A} \right)^{0.15} \quad (19)$$

$$D_{A1B1} = 2.0 \times 10^{-7} \left(\frac{T}{\mu_B} \right) \left(\frac{1}{V_A + V_B} \right)^{1/3} \left(\frac{V_B}{V_A + V_B} \right)^{0.15} \quad (20)$$

With these relationships for D_{A1} and X_{A1B1} (6) has been found to predict satisfactory the value of D_{AB} , the diffusivity of solute A in solvent B taking into account the association constant K which may be estimated by the following relationship with the limiting value of the activity coefficient of the solute at infinite dilution γ_A^0

$$K = \frac{1 - \gamma_A^0}{\gamma_A^0} \quad (21)$$

The value of γ_A^0 may be estimated from vapour-liquid equilibria for the binary system. The above relationship for K is found valid for binary systems exhibiting negative deviations from Raoult's law.

If the solute and solvent are individually capable of forming three-dimensional network of hydrogen bonds as they may each contain both donor and active hydrogen atoms, diffusion coefficients for such systems cannot be predicted with certainty with the available correlations. There is need to study the transport properties of such systems. Laddha and Karthikeyan¹⁰ have suggested that the following modified Lüscher equations

$$\frac{D_{AB} \mu_B}{T} = 5.857 \times 10^{-8} \left(\frac{\mu_B \Delta H_B}{\mu_A \Delta H_A} \right)^{0.217} \quad (22)$$

may be used effectively to predict the diffusivities of glycols and glycerol in aliphatic higher alcohols. In (17) ΔH_A and ΔH_B are the latent heats of vaporisation of solute and solvent respectively while μ_A and μ_B are the respective viscosities at the temperature of diffusion.

More studies are necessary to evaluate the effect of association due to hydrogen bonding on the diffusivities for the following typical situations: (a) solute species capable of forming dimer or higher complexes while diffusing into non-associating solvents and (b) associating solutes in associating solvents. Such studies will further our understanding of the complex nature of the diffusion processes.

List of symbols

- A_e — total effective cross-sectional area of the diaphragm pores, cm^2
- C — concentration of the diffusing solute, mole/ cm^3
- D_{AB} — diffusion coefficient (time averaged integral value) at infinite dilution [defined in eq. (7)], cm^2/sec
- \bar{D}_{AB} — space mean (integral) diffusion coefficient, eq. (4), cm^2/sec
- D_{AB}^F — binary diffusivity defined by Fick's Law, eq. (1), cm^2/sec
- K — association constant eq. (13)
- k — Boltzmann constant
- l_e — effective pore length of the diaphragm, cm
- N — Avogadro's Number, $6.023(10^{23})$ molecule/mole

- J — molar flux with respect to fixed co-ordinate system, mole/cm²/sec
 r — radius of solute molecule, cm eq. (9)
 S — moles of diffusing solute, mole/sec
 T — absolute temperature, °K
 t — time of diffusion, sec
 v_1, v_2 — volumes of Chambers 1 and 2 respectively of the diffusion cell
 V — molar volume (Kopp's law values by LeBas Method), cm³/mole
 Z — distance in the direction of diffusion, cm
 β — cell constant
 γ° — activity coefficient at infinite dilution
 Δ — difference
 μ — viscosity, centi poise

Subscripts

- 1, 2 — of compartments 1 and 2 respectively
 A, B — of diffusing solute and solvent respectively
 AB — of solute in solvent
 A_1, B_1 — solute and solvent monomers, respectively

- $A_1 B_1$ — simple complex of the monomer A_1 and monomer B_1

Superscripts

- $0, F$ — initial and final, respectively

1. Krishnan, K. S. and Laddha, G. S., *Indian Chem. Engr.*, 1965, 7, 83.
2. Amourdam, M. J. and Laddha, G. S., *J. Chem. Eng. Data*, 1967, 12, 389.
3. Gordon, A. R., *Ann. N.Y., Acad. Sci.*, 1945, 46, 285.
4. Stokes, R. H., Dunlop, P. J. and Hall, J. R., *Trans. Faraday Soc.*, 1953, 49, 886.
5. Eyring, H., Glasstone, S. and Laidler, K. J., *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
6. Laddha, G. S. and Degaleesan, T. E., *Transport phenomena in liquid extraction*, Ch. 3, Tata McGraw-Hill, 1976.
7. Laddha, G. S. and Smith, J. M., *Indian Chem. Engr.*, 1969, 11, T109.
8. Ratcliff, G. A. and Lysis, M. A., *Ind. Eng. Chem. (Fund)*, 1971, 10, 474.
9. Kuppuswamy, K. and Laddha, G. S., *Indian J. Technol.*, 1979, 17, 35.
10. Karthikeyan, K. and Laddha, G. S., *Indian Chem. Eng.*, 1976, 18, 7.

ANNOUNCEMENT

FIRST NATIONAL ENVIRONMENT CONGRESS

The First National Environment Congress will be held at the Indian Agricultural Research Institute, New Delhi from December 28 to 30, 1982. The focal theme for the congress will be the "State of Environment in India Today". The discussions will relate to what has happened since the Stockholm Conference on the Human Environment held in 1972 with regard to the protection and conservation of basic life support system. The Congress will be attended by a large number of participants from all parts of India.

Further particulars may be had from the Congress Secretary: Dr. Desh Bandhu, Secretary, IECA, School of Planning and Architecture, 1. P. Estate, New Delhi 110 002.