

Topic 2930

Viscosities; Salt Solutions

The (shear) viscosities of salt solutions have been extensively studied [1,2]. A frequently cited paper (always worth reading in terms of the care taken in the experimental study) was published by Jones and Dole [3]. The dependence of the viscosity of an aqueous salt solution $\eta(\text{aq})$ (at fixed temperature and pressure) on concentration of salt j is described by the Jones-Dole equation; equation (a) where $\eta_1^*(\ell)$ is the viscosity of water (ℓ) at the same T and p [3,4].

$$\eta(\text{aq})/\eta_1^*(\ell) = 1 + A \cdot c_j^{1/2} + B \cdot c_j \quad (\text{a})$$

Equation (a) is re-expressed as follows. By definition;

$$\psi = [\eta(\text{aq}) - \eta_1^*(\ell)]/[\eta_1^*(\ell) \cdot c_j^{1/2}] \quad (\text{b})$$

$$\text{Hence } \psi = A + B \cdot c_j^{1/2} \quad (\text{c})$$

A plot of ψ against $(c_j)^{1/2}$ has intercept A and slope B , the Jones-Dole B -viscosity coefficient [5]. The A coefficient describes the impact of charge-charge interactions on the viscosity of a solution, being generally positive and estimated using the Falkenhagen equation [6-8]. The B coefficient characterises ion-solvent interactions at defined T and p . For a 1:1 salt j , the B_j coefficient for salt j is expressed as the sum of ionic B coefficients.

$$B_j = B_+ + B_- \quad (\text{d})$$

For example, B_j for a series of salts with a common anion, the changes in B_j reflect changes in B_+ for the cations. The pattern in $B(\text{R}_4\text{N}^+ \text{I}^-; \text{aq}; 298.2 \text{ K})$ reflects the changes in $B(\text{R}_4\text{N}^+; \text{aq}; 298.2 \text{ K})$ through the series from $R = \text{methyl}$ to $R = \text{n-butyl}$. In fact the change in this case is indicative of the change in character from 'structure breaking' Me_4N^+ to hydrophobic 'structure forming' Bu_4N^+ ions [9]. In broad terms a positive B coefficient indicates a tendency for the solute to enhance water-water interactions and thus raise the viscosity whereas a negative coefficient indicates a tendency to induce disorder [10].

Ionic B-viscosity coefficients are linked to the hydration properties of ions. An important link was suggested by Gurney [11]. On the grounds that K^+ and Cl^- ions are roughly the same size, Gurney argued that for aqueous solutions, $B(K^+) = B(Cl^-)$. Hence one can estimate single-ion B-viscosity coefficients. A negative B-ionic coefficient indicates that the ion is a 'structure breaker' and a positive B-ionic viscosity coefficient indicates that the ion is a 'structure former'.

The terms 'structure breaker' and 'structure former' were extensively used in the decades from 1950 to 1990. However their popularity waned towards the end of the century as more precise descriptions of ionic hydration were sought.

Footnotes

[1] We confine attention to shear viscosities (i.e. resistance to shear). The related bulk viscosities (i.e. resistance to compression) are rarely discussed in the present context.

[2] Units; dynamic viscosity; traditional unit = poise, symbol P
 $P = 10^{-1} \text{ Pa s}$. But $\text{Pa} = \text{kg m}^{-1} \text{ s}^{-2}$ Then $P = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$
 SI unit; $\eta = [\text{kg m}^{-1} \text{ s}^{-1}]$

[3] G. Jones and M. Dole, J. Am. Chem. Soc., 1929, **51**, 2950.

[4] Other equations have been suggested as alternatives to the Jones-Dole equation.

(a) The concentration c_j is replaced by the ionic strength of the salt solution; C. Wu, J. Phys Chem., 1968, **72**, 2663.

(b) For non-electrolytes, the coefficient A is zero but a new term is usually added linear in the concentration of solute.

(i) R. Robinson and R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon, London, 1965.

(ii) W. Devine and B. M. Lowe, J. Chem. Soc., A, 1971, 2113.

(c) The ratio $\eta(\text{aq})/\eta_1^*(\ell)$ is expressed as a function of the volume fraction of the solute.

(i) D. G. Thomas, J. Colloid. Interface Sci., 1965, **20**, 267.

(ii) B. R. Breslau and I. F. Mikker, J. Phys. Chem., 1970, **74**, 1056.

(iii) J. Vand, J.Phys.Chem.,1948,**52**,277.

(iv) D. Eagland and G. Pilling, J. Phys. Chem., 1972,**76**,1902.

(d) Add a term linear in $(c_j)^2$ to equation (a).

N. Martinus, C. D. Sinclair and C. A. Vincent,

Electrochim. Acta, 1977,**22**,1183.

(e) Somewhat outside the terms of reference of the account developed here is a treatment of viscosity in terms of kinetic phenomena; e.g. in terms of Transition State Theory.

S. Glasstone, K. J. Laidler and H. Eyring, Theory of Rate Processes, McGraw-Hill, New York,1941.

For application of this model see for example,

(i) W. Good, Electrochim. Acta, 1964, **9**, 203; 1965, **10**,1; 1966, **11**, 759,767; 1967, **12**,103 1.

(ii) J. C. MacDonald, Electrochim. Acta, 1972,**17**,1965.

[5] See for example,

(i)R. L. Kay, K. T. Vituccio, C. Zawoyski and D. F. Evans.

J. Phys. Chem.,1966, **70**, 2336.

(ii)Y. Tamaki, Y. Ohara, M. Inabe, T. Mori and F. Numata,

Bull. Chem. Soc. Jpn.,1983,**56**,1930.

[6] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold, New York, 3rd. edition, 1958,p.240.

[7] See for example;

(a)A. Kacperska, S. Taniewska-Osinska, A. Bald and S. Szejgis,

J. Chem. Soc. Faraday Trans.1,1989,**85**,4147.

(b)A. Sacco, G. Petrella, A. Dell'Atti and A. de Giglio,

J. Chem. Soc. Faraday Trans.1, 1982,**78**,1507.

[8] An alternative approach involves calculating the A coefficient using the Falkenhagen theory and hence writing the Jones-Dole equation as follows.

$$\eta(\text{aq})/\eta_{\Gamma}^*(\ell) - 1 - A \cdot (c_j)^{1/2} = B \cdot c_j$$

In a plot of the LHS of this equation against c_j , the slope equals B. See for example, K. Tamaki, K. Suga and E. Tanihara,

Bull. Chem. Soc. Jpn.,1987,**60**,1225.

[9] B. M. Lowe and G. A. Rubiensi, Electrochem. Acta, 1974,**19**,393.

[10] E. R. Nightingale, J. Phys. Chem.,1959,**63**,1381;1962,**66**,894.

See also, D. T. Burns, Electrochim Acta, 1965,**10**,985.

[11] R. W. Gurney, Ionic Processes in Solution, McGraw-Hill,
New York, 1953.