Thermodynamic and Viscosity *B*-coefficient Data for Single Ions derived from a New Analytical Approach

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A new approach enables provision of single ion thermodynamic data and viscosity *B*-coefficients for 1:1 electrolytes in aqueous solution and the results suggest that the widely criticised yet standard assumption that $B(K^+) = B(Cl^-)$ used to subdivide viscosity *B*-coefficients may need revision.

Given values of a combined thermodynamic property, P_{ij}, for a salt M_iX_j {where P_{ij} could be $[\Delta X^{\ominus}_{hyd}(M_i^+)(g) + \Delta X^{\ominus}_{hyd}(X_j^-)(g)]$ where $X = G$, H, or S, or the viscosity *B*-coefficient,[1] $B(M_iX_j)$} attempts can be made to separate this combined property into single ion components. To date five basic approaches have been used and identified by Conway[2] in a recent review article. The approaches he lists are (a) to split the combined value equally for a salt having ions of similar radii, (b) to extrapolate values for a salt to zero ionic radii or volume or zero reciprocal radius, (c) to use extrapolation techniques on plots involving differences of conventional (and hence experimentally accessible) values of ionic properties, (d) to use methods in which the individual ionic values of the property of a salt can be obtained in a relatively direct manner (*e.g.* e.m.f. measurements), or (e) to compare properties of a given ion with those of an isoelectronic neutral molecule of similar chemical constitution and size.

Thus for example in attempting to separate single ion values of the hydration enthalpy, Halliwell and Nyburg[3] and Morris[4,5] have employed an approach akin to method (b) while on the other hand to separate single ion values from the viscosity *B*-coefficient, Gurney[6] has employed an approach like method (d) based on ion mobility measurement. The technique applied here employs an assumption which, the authors believe, renders correlations between the various types of property more acceptable.

Our approach involves a standard statistical analysis which is based on the assumption that a combined property P_{ij} can be partitioned into single ion values, $P(M_i^+)$ and $P(X_j^-)$ consistent with achieving minimum error in the pairwise addition, equation (1).

$$P(M_i^+) + P(X_j^-) = P_{ij} \tag{1}$$

It can be shown that if we take a series of salts (*e.g.* the alkali halides having *m* different cations variously paired with *n* different anions) then the relative individual single ion values assignable, are given by the equations (2) and (3), where θ_P is a

$$P(M_i^+) = \frac{1}{n}\sum_{j=1}^{n} P_{ij} - \theta_P = P_{M_i^+} - \theta_P \tag{2}$$

and

$$P(X_j^-) = \frac{1}{m}\sum_{i=1}^{m} P_{ij} - \overline{P_{ij}} + \theta_P = P_{X_j^-} + \theta_P \tag{3}$$

Table 1. Absolute properties of alkali metal and halide ions at 298 K obtained from the analysis. Values shown in parentheses are results from other approaches (refs. 3—5, 10—13).

Ion M_i^+	$\Delta H^\ominus_{hyd}$ (M_i^+) (g) /kJ mol^{-1}	$\Delta G^\ominus_{hyd}$ (M_i^+) (g) /kJ mol^{-1}	$\Delta S^\ominus_{hyd}$ (M_i^+) (g) /J K^{-1} mol^{-1}	$B(M_i^+)$ /mol dm^{-3}
Li^+	−536.3 (−511.7)	−498.0 (−468.8)	−128.5 (−143.8)	0.136 (0.150)
Na^+	−420.8 (−396.2)	−392.2 (−363.0)	−96.1 (−111.4)	0.072 (0.086)
K^+	−337.1 (−312.5)	−319.2 (−290.0)	−60.1 (−75.4)	−0.021 (−0.007)
Rb^+	−312.5 (−287.9)	−297.4 (−268.2)	−50.7 (−66.0)	−0.043 (−0.029)
Cs^+	−287.3 (−262.7)	−274.3 (−245.1)	−43.6 (−58.9)	−0.059 (−0.045)
Ion X_j^-	$\Delta H^\ominus_{hyd}(X_j^-)$ (g) /kJ mol^{-1}	$\Delta G^\ominus_{hyd}(X_j^-)$ (g) /kJ mol^{-1}	$\Delta S^\ominus_{hyd}$ (X_j^-) (g) /J K^{-1} mol^{-1}	$B(X_j^-)$ /mol dm^{-3}
F^-	−513.6 (−538.1)	−468.2 (−497.4)	−151.8 (−136.5)	0.133 (0.119)
Cl^-	−362.8 (−387.4)	−336.0 (−365.2)	−89.8 (−74.5)	0.007 (−0.007)
Br^-	−331.8 (−356.4)	−309.8 (−339.0)	−73.7 (−58.4)	−0.018 (−0.032)
I^-	−291.5 (−316.1)	−275.0 (−315.8)	−55.2 (−39.9)	−0.055 (−0.069)

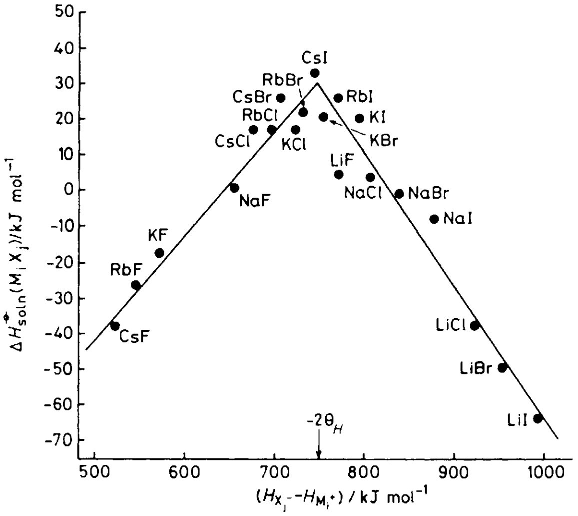

Figure 1. $\Delta H^\ominus_{soln}$ *vs.* $H_{X_j^-}—H_{M_i^+}$ for alkali metal halides.

constant, but undetermined, parameter and $\overline{P_{ij}}$ is the overall average value of the property P_{ij} for the total of the *mn* salts under consideration. The advantage of this approach is that the values of the parameters $P_{M_i^+}$ and $P_{X_j^-}$ in equations (2) and (3) may be evaluated *directly* from the source data P_{ij}. The second stage in our procedure is to attempt to determine the value of θ_P which then would permit absolute single ion assignments for $P(M_i^+)$ and $P(X_j^-)$. For a salt in which the enthalpy or free energy of hydration of the anion and cation are identical, Fajan's competition principle[7] dictates that the solubility will be a minimum and therefore $\Delta H^\ominus_{soln}(M_iX_j)(c)$ or $\Delta G^\ominus_{soln}(M_iX_j)(c)$ will be a maximum. This principle is employed in order to estimate the value θ_P for the various properties considered.

To illustrate the practical application of our approach we cite one example. The most recent and carefully analysed data for $[\Delta X^\ominus_{hyd}(M_i^+)(g) + \Delta X^\ominus_{hyd}(X_j^-)(g)]$ where $X = H, G$, or S are that of Morris,[4] recently published, and these data were used as a starting point in our analysis. We can obtain values of $P_{M_i^+}$ ($= H_{M_i^+}$) and $P_{X_j^-}$ ($= H_{X_j^-}$) using equations (2) and (3) and a plot of $\Delta H^\ominus_{soln}(M_iX_j)$[8,9] *versus* the parameter $(H_{X_j^-} - H_{M_i^+})$ yields the 'volcano' plot shown in Figure 1.

The left and right hand slopes of the 'volcano' were fitted by least squares analysis and the apex or intersection of the two curves was determined. On the basis of the Fajan's competition principle, at this apex: $P(M_i^+)$ $[= \Delta H^\ominus_{hyd}(M_i^+)(g)] =$ $P(X_j^-)$ $[= \Delta H^\ominus_{hyd}(X_j^-)(g)]$ and from equations (2) and (3), $(P_{X_j^-} - P_{M_i^+}) = -2\theta_P$ or in the specific case of the enthalpy of hydration data: $(H_{X_j^-} - H_{M_i^+}) = -2\theta_H$. Hence the undetermined parameter θ_P can be ascertained and used to generate absolute single ion values for the property under examination. The approach can be equally well applied to analyse viscosity *B*-coefficients and analogous plots can be made of $\Delta H^\ominus_{soln}$ *versus* parameters derived from viscosity data and the assumption made that at the apex of the plot the solvent equally 'competes' for the ions M_i^+ and X_j^-.

Table 1 gives the results obtained in these studies for absolute single ion properties which are broadly consistent with results obtained from other approaches.[3—5, 10—13] In the case of the viscosity *B*-coefficients however our method leads to interesting results which suggest that the Gurney assumption may not be valid in aqueous media [*i.e.* $B(K^+) \neq B(Cl^-)$] and consequently revision of single ion aqueous viscosity *B*-coefficients may be necessary.

Literature values of enthalpy of hydration of alkali metal and halide ions obtained by other workers[3—5, 10—13] correspond to values of θ_H in the range: $-399.5 \leqslant \theta_H \leqslant -363.3$ kJ mol^{-1} while the value of θ_H emerging for the present studies is -374.9 kJ mol^{-1} and corresponds to a value for the absolute enthalpy of the proton: $\Delta H^\ominus_{hyd}(H^+)$ (g) $= -1107.0$ kJ mol^{-1}.

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References

1 G. Jones and M. Dole, *J. Am. Chem. Soc.*, 1929, **51**, 2950.
2 B. E. Conway, *J. Solution Chem.*, 1978, **7**, 721.
3 H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126.
4 D. F. C. Morris, *Electrochim. Acta*, 1982, **27**, 1481.
5 D. F. C. Morris, *Struct. Bonding (Berlin)*, 1968, **4**, 63.
6 R. M. Gurney, 'Ionic Processes in Solution,' McGraw Hill, London, 1953.
7 K. Fajans, *Naturwissenschaften*, 1921, **9**, 729.
8 C. V. Krishnan and H. L. Freidman, 'Solute–Solvent Interactions,' vol. 2, Dekker, New York, 1977.
9 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, and R. L. Nuttall, 'Selected Values of Chemical Thermodynamic Properties,' Techn. Note 270—8, U.S. Dept. of Commerce, U.S.A., May 1981.
10 R. M. Noyes, *J. Am. Chem. Soc.*, 1962, **84**, 513.
11 D. R. Rosseinsky, *Chem. Rev.*, 1965, **65**, 467.
12 M. W. Lister, S. C. Nyburg, and R. B. Poyntz, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 685.
13 D. W. Smith, *J. Chem. Educ.*, 1977, **54**, 540.