**Heat Capacities; Isobaric; Salt Solutions**

The excess enthalpy $H^E$ of an aqueous salt solution prepared using 1 kg of water and $m_j$ moles of a 1:1 salt is related to $m_j$ using the DHLL. Because $C_p^E$ is the isobaric temperature dependence of $H^E$, then $C_p^E$ for this aqueous solution is given by equation (a) [1].

$$C_p^E(aq; w_1 = 1 \text{ kg}) = -(4/3) \cdot R \cdot m_j^{(3/2)} \cdot \left(\frac{m_j^0}{m_j}\right)^{1/2} \left[2 \cdot T \cdot S_H + T^2 \cdot \left(\frac{\partial S_H}{\partial T}\right)_p\right]$$

(b)

$S_{Cp}$ is the DHLL factor in the equation for the isobaric heat capacity.

$$C_p^E(aq; w_1 = 1 \text{ kg}) = -(4/3) \cdot R \cdot S_{Cp} \cdot m_j^{(3/2)} \cdot \left(\frac{m_j^0}{m_j}\right)^{1/2}$$

(c)

Using equation (c) [2], $\phi(J_j) = -(4/3) \cdot R \cdot S_{Cp} \cdot \left(\frac{m_j}{m_j^0}\right)^{1/2}$

(d)

We could perhaps have anticipated that according to DHLL, $\phi(J_j)$ is a linear function of $\left(\frac{m_j}{m_j^0}\right)^{1/2}$. An extensive literature describes the limiting partial molar isobaric heat capacities of ions in aqueous solution. One of the earliest investigations of the isobaric heat capacities of salt solutions was made by Randall and Ramage[3] and later by Randall and Taylor [4]. The groups lead by Hepler [5,6] and by Desnoyers [7] have made significant contributions in this area. However no agreement has been reached on a scale of absolute values.

Hepler reported relative estimates based on $C_p^\infty(H^+; aq; 298K)$ equal to zero.

Perhaps most attention has been directed at salts formed by alkylammonium cation [8,9] and hydrophobic anions; e.g. amino acids [10], phenylcarboxylates, t-butylcarboxylates[11] and cryptates[12]. Data [7] for $R_4N^+Br^- (aq)$ show that $C_p^\infty(aq_j)$ increases with increase in hydrophobic character of the $R$-group.

French and Criss argue [13] in favour of a scale which sets $C_p^\infty(Br^-; aq)$ at $-68 \text{ J} K^{-1} \text{ mol}^{-1}$. An attempt[14] has identified the various contributions to $C_p^\infty(\text{ion; aq})$. Certainly trends in $C_p^\infty(\text{ion; aq})$ point to characteristic features associated with the properties of ions in aqueous solution. Nevertheless, interpretation is not straightforward [14].
Footnotes

[1] $S_{cp} = 2 \cdot T \cdot S_H + T^2 \cdot (\partial S_H / \partial T)_P = [I] \cdot [K] \cdot [K^{-1}] + [K^2] \cdot [K^{-1}] \cdot [K]^{-1} = [I]

[2] $\phi(J_j) = [I] \cdot [J K^{-1} \text{ mol}^{-1}] \cdot [I] \cdot [I] = [I K^{-1} \text{ mol}^{-1}]

[15] For further details of heat capacities of salt solutions see—
(b) Alkali metal halides(aq); also solutions in D$_2$O; J.-L. Fortier, P. R. Philip and J.E.Desnoyers, J. Solution Chem., 1974, 3, 523.
(c) NaBPh$_4$(aq); and in urea(aq); B. Chawla, S. Subramanian and J. C. Ahluwalia, J. Chem. Thermodyn., 1972, 4, 575.
(d) Bu$_4$NBr(aq) and NaBPh$_4$(aq); and in aqueous mixtures; S. Subramanian and J. C.Ahluwalia, Trans. Faraday Soc., 1971, 67, 305.
(e) R$_4$NBr(aq; 382 to 363) K; M.J.Mastroianni and C. M. Criss, J. Chem. Thermodyn, 1972, 4, 321.


(n) Bu₄NB Br(aq); NaBPh₄(aq); (also binary aq. mixtures); R. K. Mohanty, T. S. Sarma, S. Subrahmanian and J. C. Ahluwalia, Trans. Faraday Soc., 1971, 67, 305.


(u) CH₃COOH(aq); CH₃COONa(aq), NH₃(aq); NH₄Cl(aq); 283, 298 and 313 K; G. Allred and E. M. Woolley, J. Chem. Thermodyn., 1981, 13, 155.

(v) Group III metal perchlorates;