Enthalpies of Transfer and 'Hydrophobic Hydration.' Tetrabutylammonium Bromide in the Propan-1-ol + Water System

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Analysis of the enthalpies of transfer, ΔH°_t, of tetrabutylammonium bromide in the propan-1-ol + water system using a recently developed relationship between ΔH°_t and the thermodynamic properties of the mixed solvent, shows that the characteristic $\Delta H^\circ_t - x_2$ profile arises from a net breaking of solvent–solvent bonds by the solute, rather than a strengthening of them as in a hydrophobic interaction.

Recently,[1] we showed how the enthalpy of transfer of a solute in a binary mixed solvent, ΔH°_t, was related to the enthalpies of solvent–solvent bonding. The ΔH°_t values for tetrabutylammonium bromide in the propan-1-ol + water system (Table 1) are of particular interest when analysed in this way.

In the model used, a solute occupies a cavity in which n solvent molecules are its nearest neighbours. When this cavity is formed each of these n molecules must break some of its solvent–solvent bonds, giving rise to an increase in enthalpy, $-n\alpha\Delta\bar{H}^*$, where α is the fraction of the molar enthalpy of solvent–solvent bonding, $\Delta\bar{H}^*$, associated with the broken bonds. The solute may also cause changes in solvent–solvent bonding over a number of molecular diameters. On average N solvent molecules are affected giving rise to an enthalpy change $-N\beta\Delta\bar{H}^*$ where β is the average proportionality constant for the different modified bonds and is negative if the bonds are strengthened. Finally the solute may be supposed to interact with the modified solvent giving rise to an enthalpy change ΔH°_{12}.

Table 1. Enthalpies of transfer, ΔH°_t, of tetrabutylammonium bromide from water to propan-1-ol + water mixtures at 25 °C.

x_2[a]	ΔH°_t/ kcal mol^{-1}[b]	x_2[a]	ΔH°_t/ kcal mol^{-1}[b]
0.0322	4.12	0.4114	8.41
0.0696	6.50	0.5447	6.88
0.1138	9.56	0.7294	5.93
0.1663	9.46	1.0000	6.24
0.2305	9.27		

[a] x_2 = Mole fraction of propan-1-ol. [b] 1 kcal = 4.18 kJ.

This model leads to equation (1) for ΔH°_t from solvent A to a mixture of A and a second solvent B. In equation (1): L_A and L_B are the relative partial molar enthalpies, $-\Delta\bar{H}^\circ{}_A{}^*$ and $-\Delta\bar{H}^\circ{}_B{}^*$ the enthalpies of vaporization to zero pressure, and x_A and x_B the mole fractions of A and B respectively. The coefficient p takes account of preferential solvation and is defined by equation (2).

$$\begin{aligned}\Delta H^\circ_t = {} & \frac{px_B}{(x_A + px_B)}\{(\Delta H^\circ_{12})_B - (\Delta H^\circ_{12})_A\} \\ & - \frac{(\alpha n + \beta N)}{(x_A + px_B)}\{x_A L_A + px_B L_B\} \\ & + \frac{(\alpha n + \beta N)px_B}{(x_A + px_B)}\{\Delta\bar{H}^\circ{}_A{}^* - \Delta\bar{H}{}_B{}^*\} \end{aligned} \qquad (1)$$

$$\frac{n_A}{n_B} \approx \frac{N_A}{N_B} = \frac{1}{p}\frac{x_B}{x_B} \qquad (2)$$

The present data were fitted to equation (1) by an iterative technique. The best fit is shown by the solid line in Figure 1. The values of the coefficients obtained from the fitting are given in Table 2.

The plot of ΔH°_t against solvent composition (Figure 1) is typical of those found for large organic ions and non-electrolytes in mixed aqueous solvents.

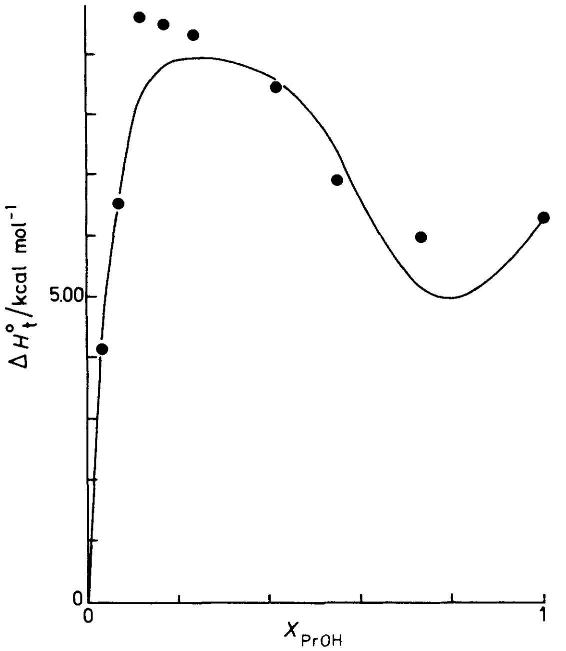

Figure 1. Enthalpies of transfer, ΔH°_t, (1 kcal = 4.18 kJ) of tetrabutylammonium bromide in water + propan-1-ol mixtures. The circles represent experimental data and the solid line values calculated *via* equation (1) (see text).

Table 2. Constants from equation (1) for tetrabutylammonium bromide.

	p	$\alpha n + \beta N$	$(\Delta H^\circ_{12})_{PrOH} - (\Delta H^\circ_{12})_{H_2O}$/ cal mol^{-1} [a]
NBu_4^+	0.24	28	−26 100
Br^-	12	1.9	7 600

[a] 1 cal = 4.18 J.

The interpretation of the characteristic $\Delta H^\circ_t - x_2$ profile has usually involved the concept of hydrophobic interaction,[2] that is, a solute in an essentially aqueous medium is supposed to strengthen solvent–solvent bonds around it. The characteristic maximum in ΔH°_t at low x_2 then reflects a structural maximum in the solvent mixture at which the solute makes a minimum of structure.

The present results contradict this view. A net strengthening of solvent–solvent bonds requires a negative value for (αn + βN), while the experimental value is positive showing that the net effect of the solute is to break solvent–solvent bonds. The value of 28 is large compared with those found for alkali-metal halides, for example 5.9 for Cs^+Cl^- in the methanol + water[1] system. While the possibility of a region of enhanced structure (βN negative) cannot be excluded, as it may be masked by the effects of cavity formation (αn), the $\Delta H^\circ_t - x_2$ profile offers no evidence for it.

In a later paper we shall show that these results are typical of those for tetra-alkylammonium halides in several mixed aqueous solvent systems and so the conclusion is general.

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References

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