

Application of a New Method to Reproduce the Enthalpies of Transfer of NaI from Water to Aqueous Methanol, Ethanol and *i*PrOH Solvent Systems at 298 K

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The enthalpies of transfer, ΔH_t^θ , of NaI from water to aqueous methanol, ethanol and isopropanol, *i*PrOH, systems are reported. These data have been analysed in terms of the new solvation theory. These data are considered in terms of the new developed solvation theory including variable $(\alpha n + \beta N)$, the net effect of the solute on the solvent-solvent bonding, is positive if there is a net breaking or weakening of solvent-solvent bonds. The solvation parameters recovered from the analyses indicate that the net affect of NaI on solvent structure is a breaking of solvent-solvent bonds and that NaI is preferentially solvated by water in all aqueous alcohol systems considered. $(\alpha n + \beta N)$ values increase with increasing in the size of the alcohol alkyl residue from methanol to *i*PrOH.

Key Words : Variable $(\alpha n + \beta N)$, Solvent-solvent bond

Introduction

The thermodynamic parameters for transfer of a solute from pure solvent to mixed solvent show a number of different complex variations with the solvent composition. The form of the transfer parameter against solvent composition profiles, are sensitive to changes in both the solute and the solvent components of the mixture. Thus, for example, the enthalpies of transfer of LiCl pass through a sharp minimum in acetonitrile-water mixtures and through a broad maximum in methanol-water mixtures, while those of tetraphenylarsonium chloride pass through a sharp maximum in acetonitrile-water mixtures.¹⁻⁸ In this paper we present enthalpies of transfer for NaI in three aqueous solvent systems. The improved method including variable values, has been used to reproduce the enthalpies transfer data.

Experimental and Results

Methanol, Ethanol and *i*PrOH⁹⁻¹² were purified as described previously. The enthalpies of transfer of NaI were calculated from their enthalpies of solution, ΔH_s , into the different solvent systems. In all cases the enthalpies of solution were measured to ten solute concentrations (0.002-0.1 mol dm⁻³) and the data extrapolated to infinite dilution. The enthalpies of solution were measured using a 4 channel commercial microcalorimetric system, Thermal Activity monitor 2277, Thermometric, Sweden. The heat of each injection was calculated by the "Thermometric Digitam 3" software program.

Enthalpies of transfer have been reported as kJ mol⁻¹. The precisions of the infinite dilution enthalpies of solution were determined as the 95% confidence limits of intercepts of plots ΔH_s against solute concentration. Typically these were around ± 0.03 kJ mol⁻¹, or better with repeat abilities at the same level. The estimated precisions for enthalpies of

Table 1. Enthalpies of transfer of NaI from water to aqueous methanol, ethanol and *i*PrOH mixtures at 25 °C in kJ mol⁻¹

x_B	MeOH	EtOH	<i>i</i> PrOH
0	0	0	0
0.05	0.85	1.69	2.60
0.1	1.27	3.35	5.52
0.2	2.10	4.85	5.61
0.3	1.99	4.92	3.45
0.4	1.87	2.62	0.06
0.5	1.35	1.35	-1.71
0.6	0.83	0.00	-3.33
0.7	0.02	-1.50	-5.26
0.8	-0.80	-2.98	-7.13
0.9	-1.62	-4.41	-8.91
1	-2.43	-5.83	-10.58

transfer are determined by the absolute precisions of the infinite dilution enthalpies of solution in water and mixed solvent, and vary accordingly; thus, the precisions for enthalpies of transfer were about ± 0.05 kJ mol⁻¹, or better. The enthalpies of transfer for NaI in aqueous methanol, ethanol and *i*PrOH are listed in Table 1.

Discussion

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, $-n\alpha\Delta H^{0*}$, where α is the fraction of the molar enthalpy of solvent-solvent bonding, ΔH^{0*} , associated with the broken bonds. The solute may also cause changes in solvent-solvent bonding over a number of molecular diameters. On average N (note $N \geq n$) solvent molecules are affected giving rise to an enthalpy change, $-N\beta\Delta H^{0*}$, 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 $\Delta\Delta H_{12}^\theta$. This model leads to equation 1 for the enthalpy of transfer, ΔH_t^θ , of the solute from pure solvent A to mixtures of A and a second solvent B. In equation 1, L_A and L_B are the relative partial molar enthalpies, $\Delta\Delta H^{0*}$ is the difference between the A-A and B-B interactions in the two pure solvents, $\Delta H_A^{0*} - \Delta H_B^{0*}$, and is taken as the difference between the enthalpies of condensation of the pure components. The superscript θ in all cases refers to the quantities in infinite dilution of the solute.

$$\Delta H_t^\theta = \frac{p x_B}{x_A + p x_B} [\Delta\Delta H_{12} + (\alpha n + \beta N) \Delta\Delta H^{0*}] - \frac{(\alpha n + \beta N)}{x_A + p x_B} (x_A L_A + p x_B L_B) \quad (1)$$

In mixed solvent systems, preferential solvation is accounted for by:

$$\frac{N_B}{N_A} \cong \frac{n_B}{n_A} = p \frac{x_B}{x_A}$$

Where x_A and x_B represent the mole fractions of the components, A and B, of the mixed solvent and n_A and n_B , N_A and N_B are the number of A and B components which are the nearest neighbours of the solute. p is an index of preferential solvation. $p < 1$ or $p > 1$ indicate a preference for solvent A or B respectively; $p = 1$ indicates random solvation. $\Delta\Delta H_{12}^\theta$ is the difference between the enthalpies of interaction of the solute with the two pure solvent A and B.

The parameter $(\alpha n + \beta N)$ reflects the net effect of the solute on the solvent-solvent bonding and it is positive if there is a net breaking or weakening of solvent-solvent bonds and is negative if the net effect of the solute is to cause a strengthening of these bonds.

L_A and L_B are the relative partial molar enthalpies for a binary mixtures of A and B components calculated from mixing enthalpies of solvent A and B, ΔH^E , as follow:

$$L_A = \Delta H^E + x_B \left(\frac{\partial \Delta H^E}{\partial x_B} \right)$$

$$L_B = \Delta H^E - x_A \left(\frac{\partial \Delta H^E}{\partial x_A} \right)$$

In the case of random solvation ($p = 1$), equation 1 simplifies to:

$$\Delta H_t^\theta = x_B [\Delta\Delta H_{12}^\theta + (\alpha n + \beta N) \Delta\Delta H^{0*}] - (\alpha n + \beta N) \Delta H_E \quad (2)$$

Where ΔH_E represents the excess enthalpy of the mixed solvent. The enthalpy of transfer from pure solvent A to pure solvent B, ${}^A \vec{\Delta} H_t^\theta$, is simply:

$${}^A \vec{\Delta} H_t^\theta = [\Delta\Delta H_{12}^\theta + (\alpha n + \beta N) \Delta\Delta H^{0*}] \quad (3)$$

So that equation 2 rearranges to:

$$\frac{\Delta H_t^\theta - x_B {}^A \vec{\Delta} H_t^\theta}{\Delta H_E} = (\alpha n + \beta N) \quad (4)$$

As $(\alpha n + \beta N)$ is not constant over the range of solvent composition, it is possible to change equation 4 to:

$$\frac{\Delta H_t^\theta - x_B {}^A \vec{\Delta} H_t^\theta}{\Delta H_E} = (\alpha n + \beta N)^{mix} \quad (5)$$

It is reasonable to define the net effect of the solute on solvent-solvent bonds in mixture, $(\alpha n + \beta N)^{mix}$, as a combination of these values in water-rich domain, $(\alpha n + \beta N)_A^\theta$, and alcohol-rich domain, $(\alpha n + \beta N)_B^\theta$, which can be written:

$$(\alpha n + \beta N)^{mix} = (\alpha n + \beta N)_A^\theta x_A + (\alpha n + \beta N)_B^\theta x_B \quad (6)$$

If we substitute $\frac{\Delta H_t^\theta - x_B {}^A \vec{\Delta} H_t^\theta}{\Delta H_E}$ ratio instead of $(\alpha n + \beta N)^{mix}$ in equation 6, after reorganising, leads to:

$$\frac{\Delta H_t^\theta - x_B {}^A \vec{\Delta} H_t^\theta}{\Delta H_E} = (\alpha n + \beta N)_A^\theta - [(\alpha n + \beta N)_B^\theta - (\alpha n + \beta N)_A^\theta] x_B \quad (7)$$

If we apply non-random conditions to equation 7, after reorganising,

$$\Delta H_t^\theta = x_B {}^A \vec{\Delta} H_t^\theta - (\alpha n + \beta N)_A^\theta [x_A' L_A + x_B' L_B] - x_B' [(\alpha n + \beta N)_B^\theta - (\alpha n + \beta N)_A^\theta] [x_A' L_A + x_B' L_B] \quad (8)$$

Where

$$x_A' = \frac{1}{x_A + p x_B}, \quad x_B' = \frac{p x_B}{x_A + p x_B}$$

Where $(\alpha n + \beta N)_A^\theta$ and $(\alpha n + \beta N)_B^\theta$ are the net effect of the solute on solvent-solvent bonds in water-rich region and alcohol-rich region respectively. The enthalpy of transfer from pure solvent A to pure solvent B, ${}^A \vec{\Delta} H_t^\theta$, in equation 8 is as follow:

$${}^A \vec{\Delta} H_t^\theta = [(\Delta H_{12})_B - (\Delta H_{12})_A] + (\alpha n + \beta N)_B^\theta \Delta H_B^{0*} - (\alpha n + \beta N)_A^\theta \Delta H_A^{0*} \quad (9)$$

Where $[(\Delta H_{12})_B - (\Delta H_{12})_A]$ is the relative strengths of solute-solvent bonds in the pure solvents including intramolecular contribution. For simplification it is written as $\Delta\Delta H_{12}^\theta$ and if it is positive the solute has weaker interaction with solvent B and the negative value of this parameter indicates stronger interaction of the solute with solvent B. ΔH_A^{0*} and ΔH_B^{0*} are the enthalpies of condensation for pure solvent A and B respectively.

Applying equal value for $(\alpha n + \beta N)_A^\theta$ and $(\alpha n + \beta N)_B^\theta$ in equation 8 leads to:

$${}^A \vec{\Delta} H_t^\theta = \Delta\Delta H_{12}^\theta + (\alpha n + \beta N) \Delta H_A^{0*} - \Delta H_B^{0*} \quad (10)$$

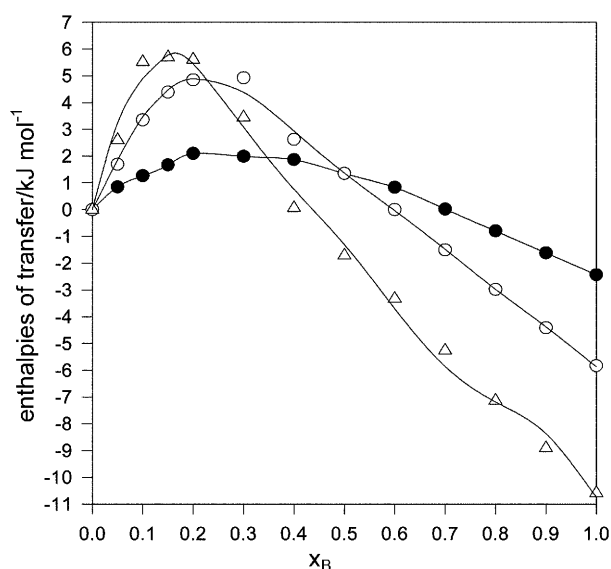


Figure 1. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for NaI in aqueous methanol (●), ethanol (○) and *i*PrOH (△) via equation 8. x_B is the mole fraction of ethanol, methanol or *i*PrOH.

Table 2. Solvation parameters for NaI in mixtures of water with methanol, ethanol and *i*PrOH via equation 8. $p < 1$ indicates preferential solvation of NaI by water and $\Delta\Delta H_{12}^\theta < 0$ indicates stronger interaction of NaI with alcoholic components.

Solvent system	p	$(\alpha n + \beta N)_A^\theta$	$(\alpha n + \beta N)_B^\theta$	$\Delta\Delta H_{12}^\theta$ (kJ/mole)
H ₂ O-MeOH	0.58	3.60	0.71	-96.29
H ₂ O-EtOH	0.47	8.36	0.52	-266
H ₂ O- <i>i</i> PrOH	0.40	10.25	-3.34	-479

Which is equation 3. If $(\alpha n + \beta N)_A^\theta = (\alpha n + \beta N)_B^\theta = (\alpha n + \beta N)$, equation 8 reduces to equation 1.

Using equation 8 reproducing the enthalpies of transfer shows excellent agreement between the experimental and calculated data (Figure 1) over the whole range of solvent composition for NaI in aqueous methanol, ethanol and *i*PrOH which is a good support for this equation.

Solvation parameters recovered via equation 8 were reported in Table 2. $(\alpha n + \beta N)$ values in the most of considered cases in this work are positive, which indicates

disruption of the solvent-solvent bonds by the solute (NaI). As it is shown in Table 2, $(\alpha n + \beta N)$ values in organic-rich regions, $(\alpha n + \beta N)_B^\theta$ are smaller than those of in water-rich domains, $(\alpha n + \beta N)_A^\theta$, which indicate a tendency of going to negative values from pure water to pure co-solvent components. We can suggest that the increase in $(\alpha n + \beta N)_A^\theta$ observed in the water-rich region results from the increase in the size of the non-polar alkyl groups of the alcohols. This led to the suggestion that the $(\alpha n + \beta N)_A^\theta$ values reflected the extend of enhancement of water structure by the non-polar alkyl residues of the alcohol molecules. Thus, as the size of the alkyl group increases, the solute interacts with a more structured solvent and $(\alpha n + \beta N)_A^\theta$ increases. p values via equation 8 are being 0.58, 0.47 and 0.40 for NaI in aqueous methanol, ethanol and *i*PrOH respectively, which indicate that NaI preferentially solvated by water in these solvent systems.¹³⁻¹⁵

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