Using the Extension Coordination Model to reproduce the Enthalpies of Transfer of Tetraethylurea From Water to Aqueous Ethanol, Propan-1-ol and Acetonitrile at 298 K.

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Abstract

The enthalpies of transfer of tetraethylurea, TEU, from water to aqueous ethanol, EtOH, propan-1-ol, PrOH, and acetonitrile, MeCN, are reported and analysed in terms of the Extension Coordination Model. The analyses show that the solvation of TEU is random in the considered solvent mixtures. It is also found that TEU interact more strongly with EtOH or PrOH than water.

Key words: titration calorimeter; preferential solvation; tetraethylurea; variable ($\alpha n + \beta N$)

1. Introduction

The Extension of the simple Coordination Model to take account of the effects of changes in solvent-solvent interactions is relatively straightforward and has been described in detail elsewhere.[1-2] Briefly a solute occupies a cavity in the solvent structure, surrounded by its coordination sphere of n solvent molecules. The solvation in mixed solvents is analogous to complexation, with the better solvent taking the role of the ligand. In order to complex to the solute each of these n molecules will have broken some fraction, α, of their bonds to other solvent molecules, resulting in endothermic enthalpy change of $-n\alpha\Delta\Delta H^{\circ*}$ where $\Delta\Delta H^{\circ*}$ associated with the broken bonds. Additionally there may be a modification of solvent-solvent bonds around the coordination sphere, affecting N (note $N \geq n$) solvent molecules. By postulating that the resulting enthalpy changes is proportional to $\Delta\Delta H^{\circ*}$ we can set it equal to an enthalpy change, $-n\beta\Delta\Delta H^{\circ*}$, where β is the average proportionality constant for the modified bonds and is negative if the bonds are strengthened (leading to an exothermic contribution to the enthalpy of solution). Finally the solute may be supposed to interact with the modified solvent giving rise to an enthalpy change $\Delta\Delta H_{12}^{\theta}$. After introducing the approximation that values of α and β are constant over a range of solvent compositions, and some manipulation this leads to:

$$\Delta H_t^{\theta} = (\frac{px_B}{x_A + px_B})\left[\Delta\Delta H_{12}^{\theta} + (\alpha n + \beta N)\Delta\Delta H^{\circ*}\right]$$
$$- \frac{(\alpha n + \beta N)}{x_A + px_B}(x_A L_A + px_B L_B) \qquad (1)$$

where ΔH_t^{θ} is enthalpy of transfer of the solute from pure solvent A to mixtures of A and a second solvent B. 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. 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:

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

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

$\Delta\Delta H^{\circ*}$ is the difference between the *A-A* and *B-B* interactions in the two pure solvents and is taken as the difference between the enthalpies of condensation of the pure components. $\Delta\Delta H_{12}^{\theta}$ is the difference between the solute-*B* and solute-*A* interactions in the pure solvents, 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. The parameter $(\alpha n + \beta N)$ reflects the net effect of the solute on the solvent-solvent bonding with αn resulting from the formation of a cavity wherein n solvent molecules become the nearest neighbours of the solute and βN reflecting the enthalpy change from strengthening or weakening of solvent-solvent bonds of N solvent molecules ($N \geq n$) around the cavity ($\beta < 0$ indicates a net strengthening of solvent-solvent bonds). The superscript θ in all cases refers to the quantities in

infinite dilution of the solute. Preferential solvation is accounted for by p, which is defined by:

$$\frac{N_A}{N_B} \approx \frac{n_A}{n_B} = \frac{x_A}{px_B}$$

$p<1$ or $p>1$ indicate a preference for solvent A or B respectively; $p=1$ indicates random solvation. Analyses of ΔH_t^θ for 2-methylpropane-2-ol, TBA and a series of teteraalkylammonium halides in mixed aqueous solvents revealed that ΔH_t^θ could not be reproduced by equation 1 over the whole range of solvent compositions.[3-6]

2. Experimental and Results

The solvents[7-10] were purified as described previously. The enthalpies of transfer of the solutes 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. The microcalorimeter was frequently calibrated electrically during the course of the study.

Enthalpies of transfer have been reported as kJ mol^{-1}. The precisions of enthalpies of solution at the infinite dilution of the solute were determined as the 95% confidence limits of intercepts of plots ΔH_S against solute concentration. Typically these were around 0.05 kJ mol^{-1}, or better with repeat abilities at the same level. The estimated precisions for enthalpies of 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 0.07 kJ mol^{-1}, or better. The enthalpies of transfer of TEU from water to aqueous EtOH, PrOH and MeCN mixtures are listed in Table 1.

3. Discussion

The significant reason for the failure of equation 1, is the approximation of constant value for ($\alpha n + \beta N$) over the entire range of solvent compositions. The sensitivity of ($\alpha n + \beta N$) to the solvent compositions and the unsuitable assumption of the constant value for ($\alpha n + \beta N$) in equation 1 led us to extend this equation. One goal of the development of the previous solvation model, is the prediction of the thermodynamics consequences of changes in the solvent system. A second approach is to use the extended equation analytically, to obtain information about the fundamental solvation process.

Table 1. Enthalpies of transfer of TEU from water to aqueous EtOH, PrOH and MeCN mixtures at 25 °C in kJ mol^{-1}.

x_B	EtOH	PrOH	MeCN
0	0	0	0
0.12	0.04	0.05	0.02
0.14	0.08	0.09	0.04
0.15	0.13	0.13	0.06
0.16	0.18	0.18	0.08
0.18	0.23	0.22	0.11
0.21	0.29	0.27	0.14
0.24	0.34	0.32	0.17
0.28	0.39	0.37	0.20
0.35	0.44	0.41	0.24
0.44	0.49	0.45	0.27
0.61	0.54	0.49	0.31
0.68	0.58	0.53	0.34
1.00	0.00	1.42	-0.1

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

$$\Delta H_t^\theta = x_B\left[\Delta\Delta H_{12}^\theta + (\alpha n + \beta N)\Delta\Delta H^{\circ*}\right] - (\alpha n + \beta N)\Delta H^E \qquad (2)$$

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

$$\overset{A\rightarrow B}{\Delta}H_t^\theta = \left[\Delta\Delta H_{12}^\theta + (\alpha n + \beta N)\Delta\Delta H^{\circ*}\right] \qquad (3)$$

So that equation 2 rearranges to:

$$\frac{\Delta H_t^\theta - x_B \overset{A\rightarrow B}{\Delta}H_t^\theta}{\Delta H^E} = (\alpha n + \beta N) \qquad (4)$$

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

$$\frac{\Delta H_t^\theta - x_B \overset{A\rightarrow B}{\Delta}H_t^\theta}{\Delta H^E} = (\alpha n + \beta N)^{mix} \qquad (5)$$

If the solvation is random, it is possible 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:

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

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Comparing equations 5 and 6 leads to:

$$\Delta H_t^\theta = \overset{A \to B}{\Delta} H_t^\theta x_B + (\alpha n + \beta N)_A^\theta \Delta H^E$$
$$- \left[(\alpha n + \beta N)_B^\theta - (\alpha n + \beta N)_A^\theta\right] x_B \Delta H^E \quad (8)$$

ΔH^E for non-random solvation is $x_A' L_A + x_B' L_B$ where x_A' and x_B' are the local mole fractions of the solvent A and B respectively. If we apply non-random conditions to equation 8,

$$\Delta H_t^\theta = \overset{A \to B}{\Delta} H_t^\theta x_B' + (\alpha n + \beta N)_A^\theta \left[x_A' L_A + x_B' L_B\right]$$
$$- \left[(\alpha n + \beta N)_B^\theta - (\alpha n + \beta N)_A^\theta\right] x_B' \left[x_A' L_A + x_B' L_B\right] \quad (9)$$

Where

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

ΔH_t^θ values were fitted to equation 9 over the solvent compositions. In the procedure the only adjustable parameter (p) was changed until the best agreement between the experimental enthalpies transfer and calculated data was approached over the whole range of solvent composition. $(\alpha n + \beta N)_A^\theta$ and $(\alpha n + \beta N)_B^\theta$ are the net effects of the solute on solvent-solvent bonds in water-rich region and cosolvent-rich region respectively which are recovered from the coefficients of the second and third terms of equation 9. The enthalpy of transfer from pure solvent A to pure solvent B, $\overset{A \to B}{\Delta} H_t^\theta$ which is the coefficient of the first term in equation 9 is as follow:

$$\overset{A \to B}{\Delta} H_t^\theta = \left[(\Delta H_{12}^\theta)_B - (\Delta H_{12}^\theta)_A\right]$$
$$+ (\alpha n + \beta N)_B^\theta \Delta H_B^{\circ *} - (\alpha n + \beta N)_A^\theta \Delta H_A^{\circ *} \quad (10)$$

Where $\left[(\Delta H_{12}^\theta)_B - (\Delta H_{12}^\theta)_A\right]$ 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. $\Delta H_A^{\circ *}$ and $\Delta H_B^{\circ *}$ 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 10 leads to:

$$\overset{A \to B}{\Delta} H_t^\theta = \Delta\Delta H_{12}^\theta + (\alpha n + \beta N)(\Delta H_A^{\circ *} - \Delta H_B^{\circ *}) \quad (11)$$

This is equation 3. If $(\alpha n + \beta N)_A^\theta = (\alpha n + \beta N)_B^\theta = (\alpha n + \beta N)$, equation 9 reduces to equation 1.
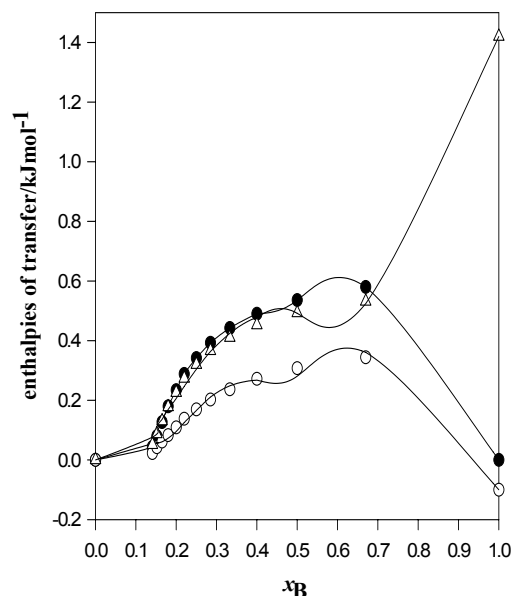

Figure 1. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer of TEU from water to aqueous EtOH (●), PrOH (∆) and MeCN(○) *via* equation 9.

Equation 9 has been shown to reproduce ΔH_t^θ for both electrolytes and non-electrolytes in a wide range of mixed aqueous and non-aqueous solvents.[10-11] Using equation 9 reproducing the enthalpies of transfer shows excellent agreement between the experimental and calculated data (Figure 1) over the whole range of solvent compositions for TEU in aqueous EtOH, PrOH and MeCN. Solvation parameters recovered *via* equation 9 were reported in Table 2. In the all cases, $(\alpha n + \beta N)_A^\theta$ values are negative, indicating that the net effect of TEU is a strengthening of solvent-solvent bonds in water-rich domains.

At low concentration, the shorter-chain alcohols, and other small organic molecules, enhance the structure of water.[11-15] In aqueous alcohols $(\alpha n + \beta N)_A^\theta$ values decrease from aqueous ethanol to propan-1-ol, indicating that the enhancement of water structure by propan-1-ol is more than that of by ethanol. Thus we can conclude that at very low alcohol concentrations alcohol monomers are present in an aqueous structure which has been rigidified by interactions with alcohol alkyl residue. This is supported by results from NMR measurements of relaxation times of water and organic molecules in the mixtures,[13] Xe NMR chemical shifts,[14] neutron scattering,[15] and dielectric relaxation.[16] The positive values of $(\alpha n + \beta N)_B^\theta$ indicates disruption of the alcoholic structure by TEU in the alcohol-rich region. The $(\alpha n + \beta N)_B^\theta$ value for aqueous acetonitrile is negative, indicating that urea strengthen the acetonitrile structure. Both $(\alpha n + \beta N)_A^\theta$ and $(\alpha n + \beta N)_B^\theta$ values for water-acetonirile mixtures is negative, indicating that the mobilities of both components decreases in

the mixtures. This is in agreement with the diffusion coefficients of water and acetonitrile in water-acetonirile mixtures.[17] *p* value for TEU in aqueous EtOH , PrOH and MeCN is one, indicating that solvation of TEU in these solvent mixtures is random. $\Delta\Delta H_{12}^{\theta}<0$ indicates weaker interaction of TEU with water.

Table 2 Solvation parameters for TEU in mixtures of water with EtOH, PrOH and MeCN *via* equation 9. $\Delta\Delta H_{12}^{\theta}>0$ indicates stronger interaction of TEU with water.

Solvent system	H$_2$O-EtOH	H$_2$O-PrOH	H$_2$O-MeCN
p	1	1	1
$(\alpha n+\beta N)_A^{\theta}$	-0.38	-0.59	-0.10
$(\alpha n+\beta N)_B^{\theta}$	3.06	2.50	-0.56
$\Delta\Delta H_{12}^{\theta}$ (kJ/mol)	134.06	130.09	-13.00

4. Conclusion

Using equation 9 reproducing the enthalpies of transfer of TEU from water to aqueous ethanol, propan-1-ol and acetonitrile shows excellent agreement between the experimental and calculated data (Figure 1) over the whole range of solvent compositions which is a good support for this equation. It is clear, from these few examples and the previous published cases,[10-11] that analysis of the enthalpies of transfer in this way can give remarkable insights into solvation in mixed solvents. Comparing these with the results of studies using other techniques supports this predictive theory.

5. References

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Povzetek

Določili smo entalpije prenosa, ΔH_t^{θ}, tetraetiluree (TEU) iz vode v različne vodne mešanice etanola, 1-propanola in acetonitrila. Rezultate smo analizirali s pomočjo razširjenega koordinacijskega modela solvatacije. Ugotovili smo, da je v obravnavanih mešanih topilih solvatacija TEU sicer naključna, da pa je interakcija TEU z etanolom in 1-propanolom močnejša kot z vodo.