

Enthalpies of transfer of acetonitrile from water to aqueous methanol, ethanol and dimethylsulphoxide mixtures at 298.15 K

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Abstract

Previous studies have established that the extended coordination model of solvation can satisfactorily account for the variation in the transfer enthalpies of solutes in mixed-solvent systems. The model parameter relating to the solute-induced disruption of the solvent structure shows a marked dependence on the nature of the mixed solvent. In the present paper we report the transfer enthalpies of acetonitrile from water to aqueous methanol, ethanol and dimethylsulphoxide (DMSO) systems. Analysis of these in terms of the extended coordination model confirms both the model's ability to account for the experimental data, and the variability of the structural disruption parameter. The solvation parameters recovered from the analyses indicate that the net effect of acetonitrile on the solvent structure is a breaking of solvent–solvent bonds. The extent of bond breaking of the solvent increases from MeOH to EtOH.

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1. 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 [1–7]. These studies have revealed the existence of a transition in the solvating properties of the aqueous systems. They also showed that the extent to which solutes disrupt the solvent structure, as measured by the model parameter ($\alpha n + \beta N$), varied with the organic component. This second result was interpreted as indicating that the organic components had effect of rigidifying of the water structure, with the extent of rigidification increasing in the order

1,4-dioxane, methanol < ethanol < 2-methylpropan-2-ol (TBA), propan-1-ol [3]. However, this explanation, while plausible, cannot be strictly correct and, rather, poses a theoretical problem.

The variation in ($\alpha n + \beta N$) has implications for the other solvation model, which led us to introduce a new solvation theory including variable ($\alpha n + \beta N$). We have recently reported the enthalpies transfer of several solutes from water to aqueous organic solvent mixtures. These data were considered in terms of the new extended coordination model of Refs. [15–18].

2. Experimental and results

DMSO was dried over anhydrous CaSO₄ and twice fractionally distilled under reduced pressure. Methanol, ethanol and acetonitrile were purified as described previously [8]. The enthalpies of transfer of acetonitrile were calculated from their enthalpies of solution, ΔH_S^θ , into the different solvent systems. In all cases the enthalpies of solution were measured to 10 solute concentrations (0.005–0.2 mol dm⁻³) and the data extrapolated to infinite dilution. The enthalpies of solution were measured using the automated adiabatic bath calorimeter described previously [9]. Enthalpies of solution have been reported in Table 1 (in kJ mol⁻¹). The estimated precisions for enthalpies of

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Table 1
Enthalpies of solution of acetonitrile in aqueous methanol, ethanol and DMSO mixtures at 25 °C in kJ mol⁻¹

x_B	MeOH	EtOH	DMSO
0	-1.61	-1.61	-1.61
0.05	1.84	3.93	-0.11
0.1	4.34	7.39	1.49
0.2	6.27	8.59	3.34
0.3	6.59	8.00	4.29
0.4	6.24	6.79	4.41
0.5	5.82	6.04	4.09
0.6	5.29	5.99	3.39
0.7	4.89	5.94	2.54
0.8	4.69	5.89	1.64
0.9	4.49	5.84	0.79
1	4.51	5.79	-0.02

Table 2
Enthalpies of transfer of acetonitrile from water to aqueous methanol, ethanol and DMSO mixtures at 25 °C in kJ mol⁻¹

x_B	MeOH	EtOH	DMSO
0	0	0	0
0.05	3.45	5.54	1.50
0.1	5.95	9.00	3.10
0.2	7.88	10.20	4.95
0.3	8.20	9.61	5.90
0.4	7.85	8.40	6.02
0.5	7.43	7.65	5.70
0.6	6.90	7.60	5.00
0.7	6.50	7.55	4.15
0.8	6.30	7.50	3.25
0.9	6.10	7.45	2.40
1	6.12	7.40	1.59

solution were about 0.07 kJ mol⁻¹, or better. The enthalpies of transfer for acetonitrile in aqueous methanol, ethanol and DMSO are listed in Table 2.

3. Discussion

The enthalpies of transfer of acetonitrile, ΔH_t^θ , from water to aqueous methanol, ethanol and DMSO mixtures can be obtained as

$$\Delta H_t^\theta = \Delta H_S^\theta(\text{mix}) - \Delta H_S^\theta(W) \quad (1)$$

$\Delta H_S^\theta(\text{mix})$ values are the enthalpies of solution of acetonitrile into aqueous methanol, ethanol and DMSO mixtures. $\Delta H_S^\theta(W)$ is the enthalpy of solution of acetonitrile into pure water.

It has been shown previously [1–7] that the enthalpies of transfer of a solute from a pure solvent into a mixed-solvent system can be accounted for quantitatively in terms of three factors: preferential solvation by the components of the mixed solvent, weakening or strengthening of solvent–solvent bonds by the solute and the change in the enthalpy of the solute–solvent interactions. This treatment leads to

$$\Delta H_t^\theta = \overset{A \rightarrow B}{\Delta} H_t^\theta x'_B - (\alpha n + \beta N)(x'_A L_A + x'_B L_B) \quad (2)$$

$\overset{A \rightarrow B}{\Delta} H_t^\theta$ is the enthalpy of transfer from pure solvent A to pure solvent B. x'_A and x'_B are the local mole fractions of the components A and B in the solvation sphere, where the solvent molecules are the nearest neighbours of the solute, which can be expressed as follows:

$$x'_A = \frac{x_A}{x_A + p x_B}, \quad x'_B = \frac{p x_B}{x_A + p x_B} \quad (3)$$

ΔH_t^θ is the enthalpy of transfer of the solutes from solvent A to the mixtures of solvent A and B. x_A and x_B represent the bulk mole fractions of the components A and B in the binary mixtures. L_A and L_B are the relative partial molar enthalpies for the binary mixtures of A and B components. $\Delta \Delta H_{12}^\theta$ is the difference between the solute–B and solute–A interactions in the pure solvents, including any intramolecular contributions to ΔH_t^θ . 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). α and β represent the fraction of the enthalpy of solvent–solvent bonding associated with the cavity formation or restructuring, respectively. The superscript θ in all cases refers to the quantities in infinite dilution of the solute. $p < 1$ or $p > 1$ indicate a preference for solvent A or B, respectively; $p = 1$ indicates random solvation. The ΔH_t^θ values could not be reproduced quantitatively by Eq. (2) across the whole range of solvent compositions [1–7]. The significant reason for the failure of Eq. (2) is the approximation of constant values for α , β , n , N and $(\alpha n + \beta N)$ over the entire range of solvent compositions.

The failure of Eq. (2) in most cases [1–7] led us to introduce the new extended coordination model of solvation [15–18]. However, it is unreasonable to suppose that the number of the molecules neighbouring the solute and the molecules around the cavity is the same in the solvent mixtures with different concentrations of cosolvent, due to the different size of the molecule of cosolvent and the different interactions between the solvent molecules. Consider the case in which the solute transferred from pure solvent A to pure solvent B, it cannot be assure that the number of the molecules of A neighbouring the solute is the same as that of B. As the parameters α , β , n , N and $(\alpha n + \beta N)$ are not constant over the whole range of solvent compositions and the net effect of the solute on solvent–solvent bonds in mixture, $(\alpha n + \beta N)^{\text{mix}} = \delta^{\text{mix}}$, is changed during the solvent compositions, we suggested to express this parameter as follow:

$$\delta^{\text{mix}} = \delta_A^\theta x'_A + \delta_B^\theta x'_B = \delta_A^\theta + (\delta_B^\theta - \delta_A^\theta) x'_B \quad (4)$$

x'_A and x'_B mole fractions of the components A and B in the vicinity of the solute or solvation sphere. $(\alpha n + \beta N)_A^\theta = \delta_A^\theta$ and $(\alpha n + \beta N)_B^\theta = \delta_B^\theta$ are the net effects of the solute in water-rich domain and cosolvent-rich region, respectively. Therefore Eq. (2) changes to

$$\Delta H_t^\theta = \overset{A \rightarrow B}{\Delta} H_t^\theta x'_B - \delta^{\text{mix}}(x'_A L_A + x'_B L_B) \quad (5)$$

Substituting δ^{mix} from Eq. (4) into Eq. (5), leads to

$$\Delta H_t^\theta = \frac{A \rightarrow B}{\Delta} H_t^\theta x'_B - \delta_A^\theta (x'_A L_A + x'_B L_B) - (\delta_B^\theta - \delta_A^\theta) (x'_A L_A + x'_B L_B) x'_B \quad (6)$$

ΔH_t^θ values were fitted to Eq. (6) 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. δ_A^θ and δ_B^θ 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 Eq. (6). $\frac{A \rightarrow B}{\Delta} H_t^\theta$ which is obtained from the coefficient of the first term of Eq. (6) can be expressed as follows:

$$\frac{A \rightarrow B}{\Delta} H_t^\theta = \Delta \Delta H_{12}^\theta + \delta_B^\theta \Delta H_B^{\circ*} - \delta_A^\theta \Delta H_A^{\circ*} \quad (7)$$

where $\Delta \Delta H_{12}^\theta$ is the relative strengths of solute–solvent bonds in the pure solvents including intramolecular contribution and if it is positive the solute has stronger interaction with solvent A and the negative value of this parameter indicates weaker interaction of the solute with solvent A. $\Delta H_A^{\circ*}$ and $\Delta H_B^{\circ*}$ are the enthalpies of condensation for pure solvent A and B, respectively (-44.9 , -37.43 , -38.7 and -53.7 kJ mol $^{-1}$ for water, methanol, ethanol and DMSO, respectively). If $\delta_B^\theta = \delta_A^\theta = (\alpha n + \beta N)$, Eq. (6) reduces to Eq. (2), as it is for acetonitrile in aqueous DMSO. Eq. (6) reproduces the enthalpies of transfer for acetonitrile in aqueous methanol, ethanol and DMSO over the whole range of solvent compositions accurately. The solvation parameters recovered from these analyses were listed in Table 3. It was found that δ_A^θ in the water-rich region was markedly dependent on the size of alkyl residue groups, the values, being 9.55, 14.76 and 1.86 for methanol, ethanol and DMSO, respectively. In the all cases δ_A^θ and δ_B^θ values are positive, indicating that the net effect of the solute is a breaking solvent–solvent bonds. p -Values are being 1.15, 1.00 and 1.00 for acetonitrile in aqueous methanol, ethanol and DMSO, respectively, indicating that the solvation of acetonitrile in aqueous ethanol and DMSO solvent systems is random solvation while for that of in aqueous methanol is preferential solvation by methanol.

When an organic species is introduced into water there is an enhancement of the aqueous structure, resulting from the interaction of water with the non-polar groups of the cosolvent. The greater the extent of this enhancement, the greater will be the disruption of the structure of the mixed solvent by the solute and

Table 3
Solvation parameters for acetonitrile in mixtures of water with methanol, ethanol and DMSO via Eq. (6)

Solvent system	p	δ_A^θ	δ_B^θ	$\Delta \Delta H_{12}^\theta$
H ₂ O–MeOH	1.15	9.55	2.13	–342.27
H ₂ O–EtOH	1.00	14.76	1.58	–593.72
H ₂ O–DMSO	1.00	1.86	1.82	16.20

$\Delta \Delta H_{12}^\theta < 0$ (in kJ mol $^{-1}$) indicates weaker interaction of acetonitrile with water.

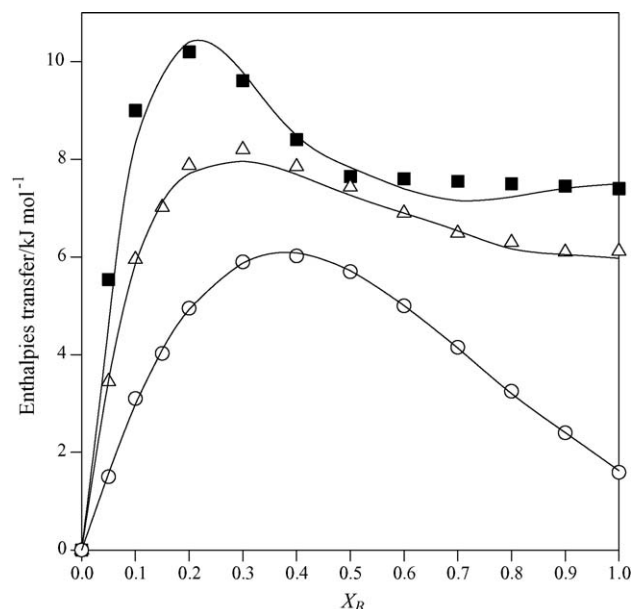


Fig. 1. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for acetonitrile in aqueous ethanol (■), methanol (Δ) and DMSO (\circ) via Eq. (6). x_B is the mole fraction of ethanol, methanol or DMSO.

the greater the value of δ_A^θ [10–14]. The δ_A^θ value in aqueous ethanol is greater than that of in aqueous methanol, indicating that ethanol enhances water structure more than methanol. In the alcohol-rich domain, where the solvent structure is less rigid, solvation of non-polar groups will involve less disruption of solvent structure and δ_B^θ values decrease in this region. $\Delta \Delta H_{12}^\theta < 0$ indicates that acetonitrile has weaker interaction with water.

4. Conclusion

Operationally it has been confirmed that the extended coordination model, via Eq. (6) will satisfactorily reproduce the transfer enthalpies of acetonitrile from water to aqueous methanol, ethanol and DMSO mixtures. Analysis of these in terms of the new extended coordination model confirms both the model's ability and the variability of the structural disruption parameters. Eq. (6) reproduces the enthalpies transfer accurately over the whole range of solvent compositions (Fig. 1).

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