



Review

A high-performance theory for thermodynamic study of solvation in mixed solvents

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ABSTRACT

The enthalpies of transfer, ΔH_t^θ , of the solutes from pure solvent A to mixtures of A and a second solvent B were studied by isothermal titration calorimetry and analysed in terms of the new extended 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 and is positive if there is a net breaking or weakening of solvent–solvent bonds.

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1. Introduction

The thermodynamic parameters for transfer of a solute to mixed solvent show a number of different complex variations with the solvent composition [1–4]. All of this work pointed to the dominance of solute to near neighbour solvent molecule interactions in chemical changes which result from changes in solvent. Simply, if the interactions were strong the solute would be well solvated, while it was poorly solvated if they were weak. In mixed solvents, the solute was preferentially solvated by the component with which it interacted more strongly. The observation of preferential solvation in mixed solvents was particularly striking and suggested that solva-

tion in these media was analogous to complexation, with the better solvent taking the role of the ligand. In this review, the improved method including variable $(\alpha n + \beta N)$ values, have been used to reproduce the enthalpies transfer data. The agreement between experimental and calculated points *via* new method is excellent in all present cases and strikingly supports the new solvation model.

2. Experimental

2.1. Materials

All materials and reagents were of analytical grade, and solutions were made using double-distilled water.

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2.2. Method

Enthalpy measurements were carried out with a four-channel commercial microcalorimeter at 298 K (Thermal Activity Monitor 2277, Thermometric, Sweden). Each channel is a twin heat conduction calorimeter where the heat-flow sensor is a semi conducting thermopile (multi-junction thermocouple plates) positioned between the vessel holders and the surrounding heat sink. The insertion vessel was made from stain less steel. The solutes solutions (0.1 mM) were injected by use of a Hamilton syringe into the calorimetric titration vessel, which contained 1.3 mL pure solvent B. The injection of the solutes solutions into pure solvent B was repeated 13 times with 0.2 mL the solutes solutions per injection. Results are the enthalpies of solvation for ternary solvent mixtures including the solutes in aqueous solvent B. The enthalpies of dilutions for aqueous solvent B, ΔH^E , were measured by injection of 0.2 mL water into 1.3 mL pure solvent B with the exception of the solutes for 13 times. The calorimeter was frequently calibrated electrically during the course of the study.

3. Results and 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 Eq. (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:

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

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. $\Delta\Delta H^{0*}$ 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.

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.

This is not truly consistent with the derivation of Eq. (1), which incorporates the approximations that the values of α and β (the proportion of the total enthalpy of solvent–solvent bonding which is associated with the cavity formation and modification of sol-

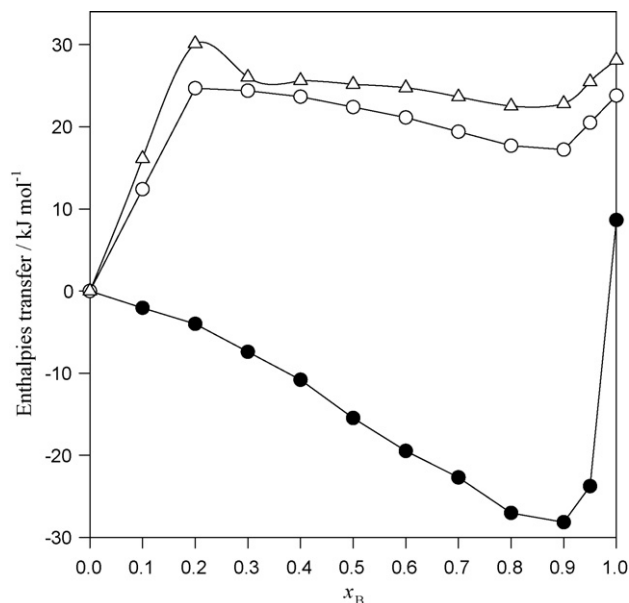


Fig. 1. Comparison between calculated (lines) and experimental (points) transfer enthalpies for LiBr (●), n -Bu₄NBr (○) and n -Pen₄NBr (△) in aqueous acetonitrile (B) mixtures at 298 K in kJ mol⁻¹.

vent structure around the cavity, respectively) are the same for each components of the mixed solvent and that both of these and n ($=n_A + n_B$) and N ($=N_A + N_B$) are constant over the range of solvent composition where Eq. (1) applies. The use of a common value of $(\alpha n + \beta N)$ effectively assumes that all of the solvent–solvent interactions are equally perturbed by the introduction of the solute or, all such interactions are equal. Clearly this would be the case for solvent systems such as mixtures of rare gases, where the solvent–solvent interaction would be symmetrical.

3.1. Introducing an improved method for reproducing enthalpy of transfer

The ΔH_t^{θ} values could not be reproduced quantitatively by Eq. (1) across the whole range of solvent composition [1–4]. The significant reason for the failure of Eq. (1) 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. (1) in most cases (Figs. 1–4) led us to introduce the new extended coordination model of solvation [5–11]. 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 different size of cosolvent molecules and different interactions between solvent molecules. Consider the case in which the solute transferred, it can not be assuring that the number of the molecules 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 and the net effect of solute on solvent–solvent bonds in mixtures, $(\alpha n + \beta N)^{\text{mix}}$, is change during the solvent compositions, led us to introduce a new solvation model. In the case of random solvation when $p = 1$, Eq. (1) is changed 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 represent the mixing enthalpies of solvents A and B. The enthalpy of transfer from pure solvent A to pure solvent B, $\Delta H_t^{\theta, A \rightarrow B}$, is simply

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

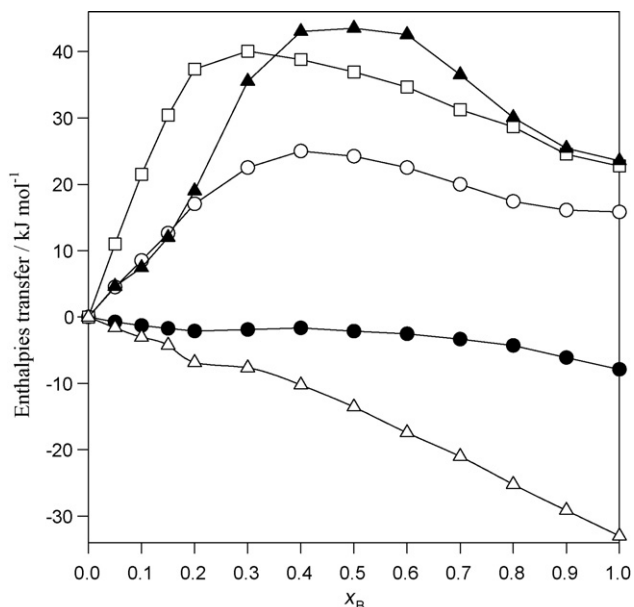


Fig. 2. Comparison between calculated (lines) and experimental (points) transfer enthalpies for Me₄NBr (●), Pr₄NBr (○), Bu₄NBr (□), Pen₄NBr (▲) and CsBr (Δ) in aqueous DMF (B) mixtures at 298 K in kJ mol⁻¹.

So that Eq. (2) rearranges to

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

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

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

It is reasonable to define the net effect of the solute on solvent–solvent bonds in mixture, $(\alpha n + \beta N)^{\text{mix}}$, as a combination of these values in A-rich domain, $(\alpha n + \beta N)_A^\theta$, and B-rich domain,

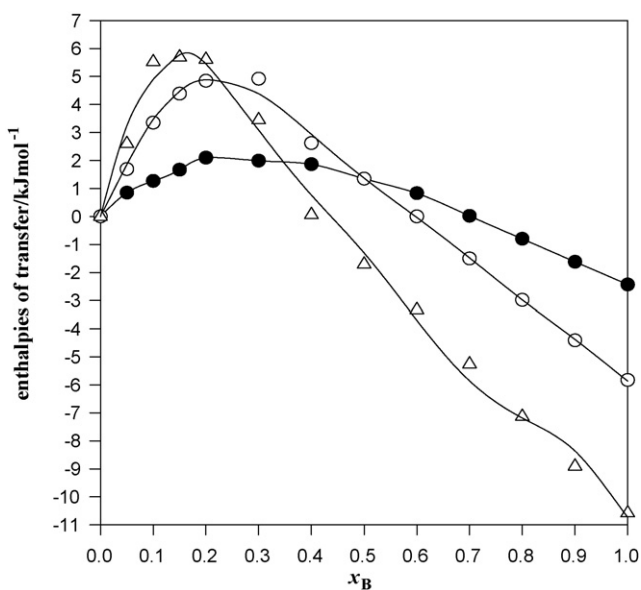


Fig. 3. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for NaI in aqueous methanol (●), ethanol (○) and iPrOH (Δ) via Eq. (8). x_B is the mole fraction of ethanol, methanol or iPrOH.

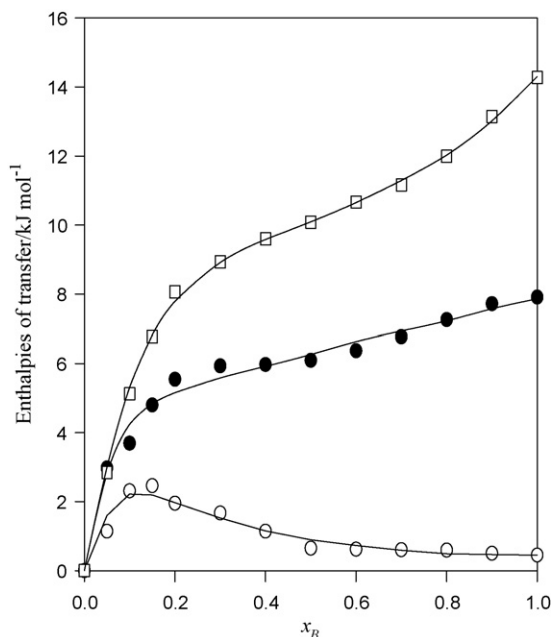


Fig. 4. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for FA (○), NMF (●) and DMF (□) from water to aqueous methanol via Eq. (8). x_B is the mole fraction of methanol.

$(\alpha n + \beta N)_B^\theta$, which can be written:

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

If we substitute $(\Delta H_t^\theta - x_B \Delta H_t^{\theta A \rightarrow B})/\Delta H^E$ ratio instead of $(\alpha n + \beta N)^{\text{mix}}$ in Eq. (6), after reorganising, leads to

$$\frac{\Delta H_t^\theta - x_B \Delta H_t^{\theta A \rightarrow B}}{\Delta H^E} = (\alpha n + \beta N)_A^\theta x_A + (\alpha n + \beta N)_B^\theta x_B \quad (7)$$

In non-random conditions, $\Delta H^E = x'_A L_A + x'_B L_B$ and x_A and x_B , change to x'_A and x'_B which represent the local mole fractions of the components, A and B in the solvation sphere. Therefore in the non-random cases Eq. (7), leads to

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

where

$$x'_A = \frac{x_A}{x_A + p x_B}, \quad x'_B = \frac{p x_B}{x_A + p x_B} \quad (9)$$

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 A-rich region and B-rich region, respectively. The enthalpy of transfer from pure solvent A to pure solvent B, $\Delta H_t^{\theta A \rightarrow B}$, in Eq. (8) is as follows:

$$\Delta H_t^{\theta A \rightarrow B} = [(\Delta H_{12})_B - (\Delta H_{12})_A] + (\alpha n + \beta N)_B^\theta \Delta H_B^{0*} - (\alpha n + \beta N)_A^\theta \Delta H_A^{0*} \quad (10)$$

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.

Table 1
Solvation parameters for solutes in water–acetonitrile mixtures using Eq. (8)

Solute	$(\alpha n + \beta N)_A^\theta$	$(\alpha n + \beta N)_B^\theta$	$\Delta \Delta H_{12}$	p
LiBr	-18.56	-13.23	352.09	0.30
<i>n</i> -Bu ₄ NBr	33.00	73.75	905.51	1.85
<i>n</i> -Pen ₄ NBr	29.52	64.16	751.78	3.00

$p < 1$ indicates preferential solvation of the solute by water and $p > 1$ shows preferential solvation by acetonitrile. $\Delta \Delta H_{12} > 0$ indicates that the interactions of the solutes with acetonitrile are weaker than with water.

Table 2
Solvation parameters for Me₄NBr, Pr₄NBr, Bu₄NBr, Pen₄NBr and CsBr in water–DMF mixtures using Eq. (8)

Solute	$(\alpha n + \beta N)_A^\theta$	$(\alpha n + \beta N)_B^\theta$	$\Delta \Delta H_{12}$	p
Me ₄ NBr	-0.28	1.08	55.39	1.00
Pr ₄ NBr	5.65	0.60	-205.12	0.76
Bu ₄ NBr	7.60	3.64	-141.84	1.50
Pen ₄ NBr	9.88	-0.78	-448.89	0.39
CsBr	0.47	0.82	-15.89	1.00

$p < 1$ indicates preferential solvation of the solute by water and $p > 1$ shows preferential solvation by DMF. $\Delta \Delta H_{12} < 0$ indicates that the interactions of the solute with DMF are stronger than with water.

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

To prove Eq. (8) experimentally we reproduced several data using the new model and compared them with those of recovered from Eq. (1) (Figs. 1–4). The solvation parameters recovered from these equations were reported in Tables 1–3. Using Eq. (8) for reproducing the enthalpies of transfer shows excellent agreement between the experimental and calculated data (Figs. 1–4) over the whole range of solvent compositions [5–11]. The values in the water-rich domains increase systematically with the size of non-polar alkyl residues on the solute and, for the bulkier solutes, are relatively large.

The analysis of the thermodynamic transfer parameters using Eq. (8) can give remarkable insight into solvation in mixed solvents.

$(\alpha n + \beta N)$ values in MeCN-rich regions, $(\alpha n + \beta N)_B^\theta$ are more than those of in water-rich domains, $(\alpha n + \beta N)_A^\theta$, which indicate the solutes disrupts solvent–solvent bonds in MeCN more than those of in water. The large tetraalkylammonium ions are hydrophobic and in most non-aqueous solvents, particularly non-hydrogen bonded solvents, it is absent. Since the hydrophobic property of tetraalkylammonium ions eventually will vanish with addition of MeCN to water, it has been expected that *n*-Bu₄NBr and *n*-Pen₄NBr prefer to leave water structure in aqueous MeCN. p values recovered from Eq. (8) are more than unity for *n*-Bu₄NBr and *n*-Pen₄NBr which means these solutes preferentially solvated by MeCN. These results are consistent with hydrophobicity of these solutes which are good support for the new developed solvation theory. Using Eq. (8) reproducing the enthalpies of transfer LiBr, Bu₄NBr and *n*-Pen₄NBr from water to aqueous MeCN shows excellent agreement between the experimental and calculated data (Fig. 1) over the whole range of solvent composition which is a good support for this equation.

Table 3
Solvation parameters for NaI in mixtures of water with methanol, ethanol and *i*PrOH via Eq. (8)

Solvent system	p	$(\alpha n + \beta N)_A^\theta$	$(\alpha n + \beta N)_B^\theta$	$\Delta \Delta H_{12}^\theta$ (kJ mol ⁻¹)
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

$p < 1$ indicates preferential solvation of NaI by water and $\Delta \Delta H_{12}^\theta < 0$ indicates stronger interaction of NaI with alcoholic components.

The comparison between experimental and calculated enthalpies transfer for tetramethylammonium bromide, Me₄NBr, tetrapropylammonium bromide, Pr₄NBr, tetrabutylammonium bromide, Bu₄NBr, tetrapentylammonium bromide, Pen₄NBr and cesium bromide, CsBr in aqueous dimethylformamide, DMF, mixtures at 298 K have shown in Fig. 2. The solvation parameters for Me₄NBr, Pr₄NBr, Bu₄NBr, Pen₄NBr in and CsBr in water–DMF mixtures recovered from Eq. (8) were listed in Table 2 In the all cases, with the exception of Me₄NBr $(\alpha n + \beta N)_A^\theta$ values are positive, indicating that the net effect of the solute is the breaking of solvent–solvent bonds. $(\alpha n + \beta N)_A^\theta$ values reflect the hydrophobic hydration of the alkylresidues, leading to the enhancement of the water structure by the non-polar alkyl groups of the tetraalkylammonium bromide molecules. The greater is the extend of this enhancement, the greater will be the disruption of the structure of the mixed solvent resulting from the introduction of the solute and the greater will be the $(\alpha n + \beta N)_A^\theta$ values. $(\alpha n + \beta N)_A^\theta$ values increase from Me₄NBr to Pen₄NBr, indicating that the hydrophobic contributions increase with the size of alkyl groups of these solutes. The clear implication of this is that the extent to which the tetraalkylammonium bromides enhance the aqueous structure increases with the size of alkyl residues from Me₄NBr to Pen₄NBr. In the DMF-rich region, the values of $(\alpha n + \beta N)_B^\theta$ for each of the solvent system decrease (with the exception of Me₄NBr), as would be expected for solvation in a less structured medium. Because the hydrophobic hydration is rapidly decreased by the addition Me₄N⁺ ions eventually will disappear as increasing amounts of DMF are added to water, we can attribute $(\alpha n + \beta N)_B^\theta$ values to the loss of this property in the DMF-rich region. The $(\alpha n + \beta N)_B^\theta$ value for Me₄NBr is -0.28, indicating that Me₄NBr is not hydrophobic at all. The enthalpy of transfer curve for Me₄NBr resembles that of the non-hydrophobic solute CsBr (Fig. 2). The Pr₄NBr and Pen₄NBr are preferentially solvated by water ($p < 1$) whereas Bu₄NBr ($p > 1$) is preferentially solvated by DMF. The solvation of Me₄NBr and CsBr is random ($p = 1$).

The agreement between the calculated and experimental transfer enthalpies is, in all cases, close to the limit of experimental precision and provides striking support for Eq. (8). The elegant feature of Eq. (8) is that it is including the structural changes in the solvent systems over the whole range of solvent compositions as $(\alpha n + \beta N)$ value are not constant in this equation. Eq. (1) is not including solvent structural changes because of approximation of constant value for $(\alpha n + \beta N)$ over the entire range of solvent compositions.

3.2. Enthalpies of transfer for NaI in aqueous methanol, ethanol and *i*PrOH

Comparison between the enthalpies of transfer of NaI from water to aqueous methanol, ethanol and *i*PrOH mixtures were shown in Fig. 3. The solvation parameters recovered via Eq. (8) were reported in Table 3. $(\alpha n + \beta N)$ values in most cases are positive, which indicates disruption of the solvent–solvent bonds by the solute (NaI). As it is shown in Table 3, $(\alpha n + \beta N)$ 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.

Table 4

Solvation parameters for FA, NMF and DMF in aqueous methanol mixtures via Eq. (8)

Solutes	p	$(\alpha n + \beta N)_A^\theta$	$(\alpha n + \beta N)_B^\theta$	$\Delta\Delta H_{12}^\theta$ (kJ mol ⁻¹)
FA	2.25	2.93	0.17	-91.17
NMF	2.15	3.54	0.43	-94.70
DMF	1.00	7.93	-0.13	-255

$\Delta\Delta H_{12}^\theta < 0$ indicates that the interactions of the solutes are stronger with methanol than with water.

p values via Eq. (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 [11–15].

3.3. Enthalpies of transfer of formamide, *N*-methyl formamide and *N,N*-dimethyl formamide from water to aqueous methanol mixtures

Using Eq. (8) reproducing the enthalpies of transfer shows excellent agreement between the experimental and calculated data (Fig. 4) over the whole range of solvent compositions for FA, NMF and DMF in aqueous methanol. Solvation parameters recovered via Eq. (8) were reported in Table 4. In the all cases, $(\alpha n + \beta N)_A^\theta$ values are positive, indicating that the net effect of the solutes is a weakening of the solvent–solvent bonds in water-rich domains. $(\alpha n + \beta N)_A^\theta$ provides a measure of the effect of the organic cosolvent on the aqueous structure. Thus, when an organic species is introduced into water there is an enhancement of the aqueous structure, resulting from the interaction of water with the cosolvent, non-polar groups. The greater the extent of this enhancement, the greater will be the disruption of the structure of the mixed solvent resulting from the introduction of the solute and the greater the value of $(\alpha n + \beta N)_A^\theta$. The values of $(\alpha n + \beta N)_A^\theta$ increase, and those of p decrease, systematically from formamide to DMF. The variation in $(\alpha n + \beta N)_A^\theta$ has been attributed to changes in the size of the non-polar alkyl group of the amides. $(\alpha n + \beta N)_A^\theta$ values in increase from FA to DMF, indicating that the disruption of solvent–solvent

bonds by the solutes increases in the same order in the water-rich domain. The $(\alpha n + \beta N)_B^\theta$ value for DMF in aqueous methanol is negative, indicating that DMF strengthens the solvent–solvent bonds in the methanol-rich domain. $(\alpha n + \beta N)_B^\theta$ values for FA and NMF in aqueous methanol mixtures is positive, indicating that these solutes disrupt solvent–solvent bonds in the methanol-rich region. p value for DMF in aqueous methanol is 1, indicating that solvation of DMF in this solvent mixtures is random while, FA and NMF are preferentially solvated by methanol. $\Delta\Delta H_{12}^\theta < 0$ indicates that the interaction of the solutes are stronger with methanol than with water [11–18].

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