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A new equation to reproduce the enthalpies of transfer of formamide, *N*-methylformamide and *N*,*N*-dimethylformamide from water to aqueous methanol mixtures at 298 K

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Abstract

The enthalpies of transfer of formamide (Form) *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF) from water to aqueous methanol mixtures are reported and analysed in terms of the new solvation theory. It was found that a previous equation could not reproduce these data over the whole range of solvent compositions. Using the new solvation theory to reproduce the enthalpies of transfer shows excellent agreement between the experimental and calculated data over the entire range of solvent compositions. The analyses show that the solvation of DMF is random in the aqueous methanol mixtures while Form and NMF are preferentially solvated by methanol. It is also found that the interaction of the solutes is stronger with methanol than with water.

Keywords: Titration calorimetry; Preferential solvation; DMF; Variable ($\alpha n+\beta N$)

1. Introduction

It has been shown previously [1,2] 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:

$$\Delta H_{\mathrm{t}}^{\theta} = x'_{\mathrm{B}}[\Delta\Delta H_{12} + (\alpha n + \beta N)\Delta\Delta H^{\circ *}] - (\alpha n + \beta N)(x'_{\mathrm{A}}L_{\mathrm{A}} + x'_{\mathrm{B}}L_{\mathrm{B}}), \qquad (1)$$

x'_{A} and x'_{B} are the local mole fractions of the components A and B in the solvation shell, where the solvent molecules are the nearest neighbours of the solute, which can be expressed as follow:

$$x'_{\mathrm{A}} = \frac{1}{x_{\mathrm{A}} + p x_{\mathrm{B}}}, \qquad x'_{\mathrm{B}} = \frac{p x_{\mathrm{B}}}{x_{\mathrm{A}} + p x_{\mathrm{B}}}.$$

$\Delta H_{\mathrm{t}}^{\theta}$ 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, calculated from the mixing enthalpies of solvent A and B, ΔH^{E}, as follow:

$$L_{\mathrm{A}} = \Delta H^{\mathrm{E}} + x_{\mathrm{B}}\left(\frac{\partial \Delta H^{\mathrm{E}}}{\partial x_{\mathrm{B}}}\right), \qquad L_{\mathrm{B}} = \Delta H^{\mathrm{E}} - x_{\mathrm{A}}\left(\frac{\partial \Delta H^{\mathrm{E}}}{\partial x_{\mathrm{B}}}\right).$$

$\Delta\Delta H^{\circ *}$ 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, including any intramolecular contributions to $\Delta H_{\mathrm{t}}^{\theta}$. 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

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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. (1) across the whole range of solvent compositions [3–6]. The ($\alpha n + \beta N$) values recovered from the analyses of transfer enthalpies using Eq. (1) depend on both of the components of the mixed solvent. That is, they appear to be properties of solvation by the mixed solvent rather than by the individual components of the mixture. This is not consistent with the derivation of Eq. (1), which incorporates the approximations that the values of αn and βN are the same for each of the components of the mixed solvent and that ($\alpha n + \beta N$) values are constant over the range of solvent compositions where equation 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, that all such interactions are equal. Clearly this would be the case for solvent systems such as mixtures of rare gases, where the solvent–solvent interactions would be symmetrical. Because the ($\alpha n + \beta N$) values are not constant over the range of solvent compositions, it led us to introduce a new solvation theory including variable ($\alpha n + \beta N$).

2. Experimental

2.1. Materials

Methanol [7–9] was purified as described previously. Form, NMF and DMF were obtained from Aldrich. The solutions were made in double-distilled water.

2.2. Method

Enthalpy measurements were carried out with a four-channel commercial microcalorimeter (Thermal Activity Monitor 2277, Thermometric, Sweden). The insertion vessel was made from stainless steel. Solutes solutions (0.1 mM) were injected by a Hamilton syringe into the titration vessel, which contained 1.3 ml pure methanol. The injection was repeated 13 times with 0.2 ml per injection. Results are the enthalpies of dilution for the solutes in aqueous methanol. The heat of dilution of water into methanol was measured as described above. The enthalpy of dilution of water into methanol was subtracted from the enthalpies of dilution of the solutes.

3. Results and discussion

Defining the enthalpy of solution for preparing a concentrated aqueous solution as ΔH_S^C (W), the standard enthalpy of solution for solutes in water, ΔH_S^θ (W), and in the aqueous methanol mixtures, ΔH_S^θ (mix), can be expressed as follow:

$$\Delta H_S^\theta(\mathrm{W}) = \Delta H_S^C(\mathrm{W}) + \Delta H_D^\theta(\mathrm{W}),$$

$$\Delta H_S^\theta(\mathrm{mix}) = \Delta H_S^C(\mathrm{W}) + \Delta H_D^\theta(\mathrm{mix}).$$

Both of which include equal value of ΔH_S^C (W), therefore the enthalpies of transfer of the solutes (ΔH_t^θ) from water to aqueous methanol mixtures can be obtained as:

$$\Delta H_t^\theta = \Delta H_D^\theta(\mathrm{mix}) - \Delta H_D^\theta(\mathrm{W}),$$

where ΔH_D^θ(mix) is the enthalpy of dilution of the solutes into methanol, and ΔH_D^θ(W) is the enthalpies of dilution of the solutes into pure water. ΔH_t^θ were listed in Table 1 and shown graphically in Fig. 1. ΔH_t^θ values evaluated from

Table 1
Enthalpies of transfer of Form, NMF and DMF from water to aqueous methanol mixtures at 25 °C in kJ/mol

x_B	Form	NMF	DMF
0.00	0.00	0.00	0.00
0.05	1.14	2.97	2.84
0.10	2.31	3.69	5.12
0.15	2.46	4.80	6.77
0.20	1.95	5.54	8.06
0.30	1.67	5.93	8.93
0.40	1.14	5.97	9.60
0.50	0.65	6.09	10.08
0.60	0.62	6.37	10.60
0.70	0.60	6.77	11.16
0.80	0.59	7.26	11.99
0.90	0.50	7.72	13.14
1.00	0.45	7.91	14.27

Standard error is ± 0.02 kJ/mol or better.

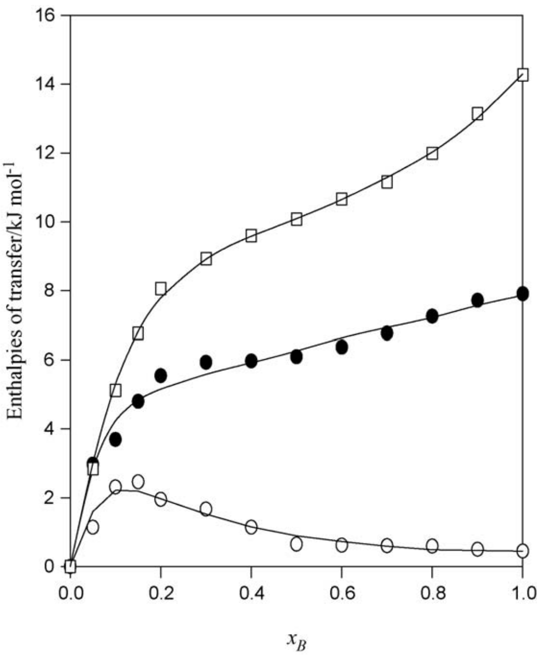

Fig. 1. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for Form (◯), NMF (●) and DMF (☐) from water to aqueous methanol via Eq. (9). x_B is the mole fraction of methanol.

this method are consistent with the previously reported data [5].

The significant reason for the failure of Eq. (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 Eq. (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. In the case of random solvation ($p=1$), Eq. (1) simplifies to:

$$\Delta H_{\mathrm{t}}^{\theta}=x_{\mathrm{B}}\left[\Delta\Delta H_{12}^{\theta}+(\alpha n+\beta N)\Delta\Delta H^{\circ *}\right] \\ -(\alpha n+\beta N)\Delta H^{\mathrm{E}}. \tag{2}$$

The enthalpy of transfer from pure solvent A to pure solvent B, $\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}$, is simply:

$$\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}=[\Delta\Delta H_{12}^{\theta}+(\alpha n+\beta N)\Delta\Delta H^{\circ *}]. \tag{3}$$

So that Eq. (2) rearranges to:

$$\frac{\Delta H_{\mathrm{t}}^{\theta}-x_{\mathrm{B}}\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}}{\Delta H^{\mathrm{E}}}=-(\alpha n+\beta N). \tag{4}$$

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

$$\frac{\Delta H_{\mathrm{t}}^{\theta}-x_{\mathrm{B}}\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}}{\Delta H^{\mathrm{E}}}=(\alpha n+\beta N)^{\mathrm{mix}}. \tag{5}$$

If the solvation is random, it is possible to define the net effect of the solute on solvent–solvent bonds in mixture, $(\alpha n+\beta N)^{\mathrm{mix}}$, as a combination of these values in water-rich domain, $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$, and alcohol-rich domain, $(\alpha n+\beta N)_{\mathrm{B}}^{\theta}$, which can be written:

$$(\alpha n+\beta N)^{\mathrm{mix}}=(\alpha n+\beta N)_{\mathrm{A}}^{\theta}x_{\mathrm{A}}+(\alpha n+\beta N)_{\mathrm{B}}^{\theta}x_{\mathrm{B}}. \tag{6}$$

Comparing Eqs. (5) and (6) leads to:

$$\Delta H_{\mathrm{t}}^{\theta}=\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}x_{\mathrm{B}}+(\alpha n+\beta N)_{\mathrm{A}}^{\theta}\Delta H^{\mathrm{E}} \\ -[(\alpha n+\beta N)_{\mathrm{B}}^{\theta}-(\alpha n+\beta N)_{\mathrm{A}}^{\theta}]x_{\mathrm{B}}\Delta H^{\mathrm{E}}. \tag{7}$$

ΔH^{E} for the binary solvent mixtures is $x_{\mathrm{A}}L_{\mathrm{A}}+x_{\mathrm{B}}L_{\mathrm{B}}$. As the solutes were introduced into the binary solvent mixtures if the solvation process is not random, the mole fractions of the components of A and B in the bulk solvent, x_{A} and x_{B}, and in the solvation shell, x'_{A} and x'_{B}, are not the same. Thus ΔH^{E} in the solvation shell can be expressed as follow:

$$\Delta H^{\mathrm{E}}=x'_{\mathrm{A}}L_{\mathrm{A}}+x'_{\mathrm{B}}L_{\mathrm{B}}. \tag{8}$$

Replacing ΔH^{E} with $x'_{\mathrm{A}}L_{\mathrm{A}}+x'_{\mathrm{B}}L_{\mathrm{B}}$ in Eq. (7), leads to:

$$\Delta H_{\mathrm{t}}^{\theta}=\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}x'_{\mathrm{B}}+(\alpha n+\beta N)_{\mathrm{A}}^{\theta}[x'_{\mathrm{A}}L_{\mathrm{A}}+x'_{\mathrm{B}}L_{\mathrm{B}}] \\ -x'_{\mathrm{B}}[(\alpha n+\beta N)_{\mathrm{B}}^{\theta}-(\alpha n+\beta N)_{\mathrm{A}}^{\theta}][x'_{\mathrm{A}}L_{\mathrm{A}}+x'_{\mathrm{B}}L_{\mathrm{B}}]. \tag{9}$$

Table 2
Solvation parameters for Form, NMF and DMF in aqueous methanol mixtures via Eq. (9)

Solutes	p	$(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$	$(\alpha n+\beta N)_{\mathrm{B}}^{\theta}$	$\Delta\Delta H_{12}^{\theta}$ (kJ)
Form	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.

$\Delta H_{\mathrm{t}}^{\theta}$ values were fitted to Eq. (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. $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$ and $(\alpha n+\beta N)_{\mathrm{B}}^{\theta}$ 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 Eq. (9). The enthalpy of transfer from pure solvent A to pure solvent B, $\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}$ which is the coefficient of the first term in Eq. (9) is as follow:

$$\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}=[(\Delta H_{12})_{\mathrm{B}}-(\Delta H_{12})_{\mathrm{A}}]+(\alpha n+\beta N)_{\mathrm{B}}^{\theta}\Delta H_{\mathrm{B}}^{\circ *} \\ -(\alpha n+\beta N)_{\mathrm{A}}^{\theta}\Delta H^{\circ *}_{\mathrm{A}}, \tag{10}$$

where $[\Delta H_{12}]_{\mathrm{B}}-(\Delta H_{12})_{\mathrm{A}}]$ 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. $\Delta H^{\circ *}_{\mathrm{A}}$ and $\Delta H^{\circ *}_{\mathrm{B}}$ are the enthalpies of condensation for pure solvent A and B, respectively.

Applying equal value for $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$ and $(\alpha n+\beta N)_{\mathrm{B}}^{\theta}$ in Eq. (10) leads to:

$$\overset{\mathrm{A}\rightarrow\mathrm{B}}{\Delta} H_{\mathrm{t}}^{\theta}=\Delta\Delta H_{12}^{\theta}+(\alpha n+\beta N)(\Delta H^{\circ *}_{\mathrm{A}}-\Delta H^{\circ *}_{\mathrm{B}}) \tag{11}$$

This is Eq. (3). If $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}=(\alpha n+\beta N)_{\mathrm{B}}^{\theta}=(\alpha n+\beta N)$, Eq. (9) reduces to Eq. (1).

Eq. (9) has been shown to reproduce $\Delta H_{\mathrm{t}}^{\theta}$ for both electrolytes and non-electrolytes in a wide range of mixed aqueous and non-aqueous solvents [10,11]. Using Eq. (9) reproducing the enthalpies of transfer shows excellent agreement between the experimental and calculated data (Fig. 1) over the whole range of solvent compositions for Form, NMF and DMF in aqueous methanol. Solvation parameters recovered via Eq. (9) were reported in Table 2. In the all cases, $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$ values are positive, indicating that the net effect of the solutes is a weakening of the solvent–solvent bonds in water-rich domains.

It has been shown previously that $(\alpha n+\beta N)_{\mathrm{A}}^{\theta}$ 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 $(\alpha n + \beta N)^{\theta}_{\mathrm{A}}$ [10,11]. The values of $(\alpha n + \beta N)^{\theta}_{\mathrm{A}}$ increase, and those of p decrease, systematically from fromamide to DMF. The variation in $(\alpha n + \beta N)^{\theta}_{\mathrm{A}}$ has been attributed to changes in the size of the non-polar alkyl group of the amides [3,5]. $(\alpha n + \beta N)^{\theta}_{\mathrm{A}}$ values in increase from Form to DMF, indicating that the disruption of solvent–solvent bonds by the solutes increases in the same order the water-rich domain [12–16]. The $(\alpha n + \beta N)^{\theta}_{\mathrm{B}}$ value for DMF in aqueous methanol is negative, indicating that DMF strengthens the solvent–solvent bonds in the methanol-rich domain. $(\alpha n + \beta N)^{\theta}_{\mathrm{B}}$ values for Form 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 one, indicating that solvation of DMF in this solvent mixtures is random while, Form and NMF are preferentially solvated by methanol. $\Delta\Delta H^{\theta}_{12}$ indicates that the interaction of the solutes are stronger with methanol than with water.

4. Conclusion

In this paper we have reported the enthalpies transfer for Form, NMF and DMF from water to aqueous methanol mixtures. It was found that Eq. (1) could not reproduce these data. Using Eq. (9) reproducing these data shows excellent agreement between the experimental and calculated data (Fig. 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.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.02.028.

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