A New Equation To Reproduce The Enthalpies Of Transfer Of Tetrabutylammonium Bromide From Water To Aqueous Methanol, Ethanol, Propan-1-Ol And 1,4-Dioxane Systems At 298.15K

✉ *Corresponding Author*

G.Rezaei Behbehani
Department of Chemistry, Imam Khomeini
International University Qazvin, (IRAN)
E-mail: grb402003@yahoo.com

ABSTRACT

Enthalpies of transfer of tetrabutylammonium bromide from water to aqueous methanol, ethanol, propan-1-ol and 1, 4-dioxane systems are reported and analysed in terms of the old and 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 tetrabutylammonium bromide preferentially solvated by water the all considered solvent mixtures. The extent to which tetrabutylammonium bromide disrupts the solvent-solvent bonds increases systematically from aqueous methanol to propan-1-ol. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

All of this work pointed to the dominance of solute to near neighbor solvent molecules interactions. The observation of preferential solvation in mixed solvents was suggested that solvation was analogous to complexation, with the solvent taking role of the ligand. In this simple coordination model all thermodynamic changes result from the successive replacement of the molecules of one solvent, say A, by those of a second solvent, B, in the coordination sphere of the solute. The model used to analyze the enthalpies of transfer data has been presented in detail previously[1-4]. Briefly this takes account of preferential solvation by the components of a mixed solvent, the extent to which the solute

Full Paper

disrupts of enhances solvent-solvent bonding, and the interaction of the solute with the surrounding solvent molecules. This treatment leads to:

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

x_A' and x_B' are the local mole fractions of the components A and B in the coordination sphere of the solute which can be expressed as follow:

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

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, calculated from the mixing enthalpies of solvent A and B, ΔH^E, as follow:

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

$\Delta\Delta H^{\circ*}$ 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(-44.12, -37.43, -42.32, -47.45 and -38.6 kJ/mol for water, methanol, ethanol, propan-1-ol and 1,4-dioxane respectively). $\Delta\Delta H_{12}^\theta$ is the difference between the solute-B and solute-A interactions in the pure solvents, including any intramolecular contributions to $\Delta\Delta H_{12}^\theta$. 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 neighbors of the solute and βN reflecting the enthalpy change from strengthening or weakening of solvent-solvent bonds of N solvent molecules($N^3 n$) 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 $\Delta\Delta H_{12}^\theta$ values could not be reproduced quantitatively by equation 1 across the

whole range of solvent compositions[5-7]. The$(\alpha n + \beta N)$ values 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 equation 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 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, 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$(\alpha n + \beta N)$.

EXPERIMENTAL

Methanol, ethanol, propan-1-ol and 1, 4-dioxane[8-9] were purified as described previously. Enthalpy measurements were carried out with a four-channel commercial microcalorimeter(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. Tetrabutylammnium bromide solution(0.1mM) was injected by use of a Hamilton syringe into the calorimetric titration vessel, which contained 1.3mL pure methanol, ethanol, propan-1-ol and 1, 4-dioxane. The injection of tetrabutylammnium solution into these pure solvents was repeated 13 times with 0.2ml tetrabutylammnium bromide solution per injection. Results are the enthalpies of solution for ternary solvent mixtures including tetrabutylammonium bromide in aqueous methanol, ethanol, propan-1-ol or 1,4-dioxane. The mixing enthalpies for aqueous methanol, ethanol, propan-1-ol or 1,4-dioxane, ΔH^E,

were measured by injection of 0.2 mL water into 1.3 mL pure methanol, ethanol, propan-1-ol or 1,4-dioxane for 13 times.

RESULTS AND DISCUSSION

Defining the enthalpy of solution for preparing a concentrated aqueous solution as $\Delta H_S^C(W)$, the standard enthalpy of solution for a solute in water, $\Delta H_S^\theta(W)$, and in the aqueous methanol, ethanol, propan-1-ol or 1, 4-dioxane mixtures, $\Delta H_S^\theta(mix)$, can be expressed as follow:

$$\Delta H_S^\theta(W) = \Delta H_S^C(W) + \Delta H_D^\theta(W)$$

$$\Delta H_S^\theta(mix) = \Delta H_S^C(W) + \Delta H_D^\theta(mix)$$

Both of which include equal value of $\Delta H_S^C(W)$, therefore the enthalpies of transfer of the solute (ΔH_t^θ) from water to aqueous methanol, ethanol, propan-1-ol or 1, 4-dioxane mixtures can be obtained as:

$$\Delta H_t^\theta = \Delta H_D^\theta(mix) - \Delta H_D^\theta(W)$$

Where $\Delta H_D^\theta(mix)$ is the enthalpy of dilution of the solute into methanol, ethanol, propan-1-ol or 1,4-dioxane, and $\Delta H_D^\theta(W)$ is the enthalpies of dilution of the solutes into pure water. ΔH_t^θ were listed in TABLE 1 and shown graphically in figure 1.

TABLE 1: Enthalpies of transfer of tetrabutylammonium bromide from water to aqueous methanol, ethanol, propan-1-ol and 1,4-dioxane mixtures at 298.15 K in kJ/mol

x_B	MeOH	EtOH	PrOH	Dioxane
0	0.00	0.00	0.00	0.00
0.05	7.16	15.15	26.50	18.00
0.10	14.25	26.20	40.00	25.20
0.15	20.15	32.80	39.60	28.00
0.20	24.21	36.50	39.40	28.30
0.30	28.13	38.02	37.20	27.30
0.40	29.23	35.86	35.00	25.50
0.50	28.41	33.90	31.20	23.42
0.60	26.70	33.00	27.50	24.54
0.70	25.46	32.00	25.00	29.90
0.80	24.21	31.23	25.50	37.00
0.90	24.31	31.75	26.00	45.80
1.00	28.81	28.85	26.50	51.40
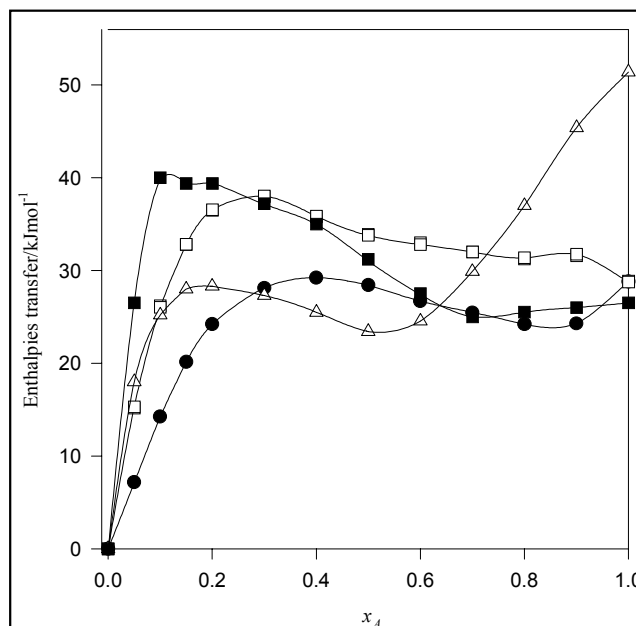
Figure 1: Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for tetrabutylammonium bromide in aqueous methanol (●), ethanol (□), propan-1-ol (■) and 1, 4-dioxane (Δ) via equation 9. x_B is the mole fraction of methanol, ethanol, propan-1-ol and 1,4-dioxane.

DISCUSSION

As the ΔH_t^θ values could not be reproduced quantitatively by equation 1 over the entire range of solvent compositions, we have extended 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), equation 1 simplifies to:

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

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:

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

Full Paper

TABLE 2: Solvation parameters for tetrabutylammo-nium bromide in the mixtures of water methanol, ethanol, propan-1-ol or 1,4-dioxane with via equation 9. $\Delta\Delta H_{12}^{\theta} > 0$ indicates stronger interaction of urea with water. * corrected $(\alpha n + \beta N)\theta_A$

Solvent system	p	$(\alpha n + \beta N)_A^{\theta}$	$(\alpha n + \beta N)_A^{\theta}{}^*$	$(\alpha n + \beta N)_B^{\theta}$	$\Delta\Delta H_{12}^{\theta}$ (kJ)
H_2O-MeOH	0.64	34.47	53.83	-5.63	-1723.14
H_2O-EtOH	0.64	43.8	68.43	43.86	-47.47
H_2O-PrOH	0.64	55.33	86.45	10.00	-1940.71
H_2O- Dioxane	1	37.61	37.61	8.16	-1291.06

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

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

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, $(\alpha n + \beta N)\theta_A$, and alcohol-rich domain, $(\alpha n + \beta N)\theta_B$, which can be written:

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

Comparing equations 5 and 6 leads to:

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

After reorganizing, leads to:

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

ΔH^E for the binary solvent mixtures is $x_A L_A + x_B L_B$. As the solutes were introduced into the binary solvent mixtures, the mole fractions of the components of A and B in the bulk solvent, x_A and x_B, and in the solvation sphere, x'_A and x'_B, are not necessarily the same. Thus ΔH^E in the solvation sphere can be expressed as follow:

$$\Delta H^E = x'_A L_A + x'_B L_B \qquad (8b)$$

Replacing ΔH^E with $x'_A L_A + x'_B L_B$ in equation 7, leads to:

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

Where $(\alpha n + \beta N)\theta_A$ and $(\alpha n + \beta N)\theta_B$ 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, $\overset{A \to B}{\Delta} H_t^{\theta}$, in equation 9 is:

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

$\Delta H_A^{\circ *}$ and $\Delta H_B^{\circ *}$ are the enthalpies of condensation for pure solvent A and B respectively. Applying equal value for $(\alpha n + \beta N)\theta_A$ and $(\alpha n + \beta N)\theta_B$ in equation 9 leads to equation 1.

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 tetrabutylammnium bromide in aqueous methanol, ethanol, propan-1-ol and 1,4-dioxane. Solvation parameters recovered via equation 9 were reported in TABLE 2.

p values for the aqueous alcohol systems are substantially the same and less than one, indicating weak preferential solvation by water in these systems, while the value for the 1,4-dioxane systems is close to one, indicating random solvation. In all cases the $(\alpha n + \beta N)\theta_A$ values are positive, indicating that the net effect of the solute is breaking of solvent-solvent bonds. The $(\alpha n + \beta N)\theta_A$ provides a measure of the effect of the organic cosolvent on the water structure. Thus, when an organic species is introduced into water there is an enhancement of the water structure, resulting from the interaction of water with the cosolvent's non-polar groups. This led to the suggestion that the $(\alpha n + \beta N)\theta_A$ values reflect to the extent of enhancement of water structure by the non-polar alkyl residues of the alcohol molecules. 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 $(\alpha n + \beta N)\theta_A$ value[12-16]. In the aqueous alcohols $(\alpha n + \beta N)\theta_A$ values for tetrabutylammonium bromide increase systematically from aqueous

Full Paper

methanol to aqueous propan-1-ol. The clear implication of this is that the extent to which the alcohols enhance the aqueous structure increase with the size of the alcoholic alkyl residue. In the alcohol-rich region$(\alpha n+\beta N)\theta_B$ for each of the solvent systems falls, as would be expected for solvation in a less structure medium. The $(\alpha n+\beta N)\theta_A$ value in the aqueous 1,4-dioxane is similar to that for aqueous methanol, indicating that the structural enhancement by 1,4-dioxane and methanol are comparable, in contrast of the Xe NMR chemical shift studies[15]. This difference may result from the preferential solvation of tetrabutylammonium bromide by water. Tetrabutylammonium bromide preferentially solvated by water in the aqueous alcohol systems, leading to an increase in the alcohol mole fractions in the bulk solvents. Increasing the alcohol concentrations in the bulk solvents leads to a small transition from the water structure to one of less structured medium based on that of the alcohol, leading to lower value of $(\alpha n+\beta N)\theta_A$. Thus we conclude that$(\alpha n+\beta N)\theta_A$ values in the absence of the solute is more than that of including solute. To approach to the corrected values of$(\alpha n+\beta N)\theta_A$, we have to multiply$(\alpha n+\beta N)\theta_A$ values by a factor of $1/p$. The corrected values of$(\alpha n+\beta N)\theta_A$ are 37.61, 53.86, 68.43 and 86.45 for 1,4-dioxane, methanol, ethanol and propan-1-ol respectively, indicating that the extent of water structural enhancement increasing in the order 1,4-dioxane < methanol < ethanol < propan-1-ol. For the aqueous alcohol systems, the interactions between the alcohol molecule and the surrounding water are two types, hydrogen bonding with the alcoholic OH group and a hydrophobic interaction with the alkyl residue, the latter leading to structural enhancement. In effect, an increase in the size of the alkyl residue will shift the balance between these two types of interaction in favour of the hydrophobic contribution. Since 1,4-dioxane has two polar sites, the ether oxygens, for hydrogen bonding to water molecules, the balance of interactions will be shifted, with the relative hydrophobic contribution reduced.

CONCLUSION

Using equation 9 reproducing the enthalpies of transfer of tetrabutylammonium bromide from water to aqueous methanol, ethanol, propan-1-ol and 1,4-dioxane mixtures 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.

REFERENCES

[1] G.Rezaei Behbehani, M.Dillon, J.Smyth, W.E. Waghorne; J.Solution Chem., **31**, 811-822 **(2002)**.

[2] G.Rezaei Behbehani, D.Dunnion, P.Falvey, K.Hickey, M.Meade, Y.McCarthy, C.R.Symon, W.E.Waghorne; J.Solution Chem., **29**, 521-539 **(2000)**.

[3] E.de Valera, D.Feakin, W.E.Waghorne; J.Chem.Soc. Faraday Trans., **79**, 1061-1066 **(1983)**.

[4] E.de Valera, D.Feakins, W.E.Waghorne; J.Chem.Soc. Faraday Trans., **76**, 560-569 **(1980)**.

[5] B.G.Cox, W.E.Waghorne, C.K.Pigott; J.Chem.Soc. Faraday Trans., **75**, 227-233 **(1979)**.

[6] B.G.Cox, A.J.Parker, W.E.Waghorne; J.Phys.Chem., **78**, 1731-1740 **(1974)**.

[7] A.Costigan, D.Feakins, I.McStravick, C.O' Duinn, J.Ryan, W.E.Waghorne; J.Chem.Soc.Faraday Trans., **87**, 2443-2446 **(1991)**.

[8] P.Hogan, I.Mcstravick, J.Mullally, W.E.Waghorne; J.Chem.Soc.Faraday Trans., **90**, 2691-2695 **(1994)**.

[9] D.Feakins, P.Hogan, C.O' Duinn, W.E.Waghorne; J. Chem.Soc.Faraday.Trans., **88**, 423-425 **(1992)**.

[10] G.Rezaei Behbehani; J.Bull.Korean Chem.Soc., **2**, 238-240 **(2005)**.

[11] G.Rezaei Behbehani; Acta Chimica Slov., 288-291 **(2005)**.

[12] G.Rezaei Behbehani; J.Bull.Korean Chem.Soc., **2**, 208-210 **(2006)**.

[13] G.Rezaei Behbehani, S.Ghamamy; J.Thermochimica acta, **444**, 71 **(2006)**.

[14] D.Feakins, E.de Valera, W.E.Waghorne; J.Chem.Soc. Faraday Trans., **81**, 2702-2709 **(1985)**.

[15] J.A.Ripmeester, D.W.Davidson; J.Mol.Struct., **75**, 67-76 **(1981)**.

[16] D.Feakins, J.Mullally, W.E.Waghorne; J.Chem.Soc. Faraday Trans., **87**, 89-91 **(1991)**.