Scientific Paper

Application of the New Solvation Theory to Reproduce the Enthalpies of Transfer of LiBr, Tetrabutylammonium Bromide and Tetrapentylammonium Bromide from Water to Aqueous Acetonitrile at 298 K

G. Rezaei Behbehani

Department of Chemistry, Imam Khomeini International University Qazvin Iran, E-mail: rezaeib@ikiu.ac.ir

Received 11-02-2005

Abstract

The enthalpies of transfer, ΔH^{θ}_{t}, of LiBr, tetrabutylammonium bromide, n-Bu_4NBr, and tetrapentylamonium bromide, n-Pen_4NBr, from water to aqueous acetonitrile solvent system are reported and analyzed in terms of the new developed solvation theory. The solvation parameters obtained from the analyses indicate that the net effect of tetraalkylammonium bromides on solvent structure is a breaking of solvent-solvent bonds and thus tetraalkylammonium bromides is preferentially solvated by acetonitrile. Preferential solvation of tetraalkylammonium bromides by acetonitrile is consistent with hydrophobisity of these compounds. LiBr is preferentially solvated by water.

Key words: preferential solvation, variable ($\alpha n + \beta N$), solvent-solvent bonds

Introduction

The solute-solvent interaction can be investigated by calorimetric measurement of the enthalpies of solution of a solute in different solvents. 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.[1–8] In this paper we present enthalpies of transfer for LiBr, n-Bu_4NBr and n-Pen_4NBr from water to aqueous acetonitrile. The improved method including variable ($\alpha n + \beta N$) values, has been used to reproduce the enthalpies transfer data.

Experimental and Results

The solvents were purified as described previously.[9–12] 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 at ten solute concentrations (0.002–0.1 mol dm^{-3}) and then the data were 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.

Enthalpies of transfer have been reported in 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 values of uncertainties were found to be around 0.03 kJ mol^{-1} or better. 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 were about 0.05 kJ mol^{-1}, or better. The enthalpies of transfer for LiBr, n-Bu_4NBr and n-Pen_4NBr from water to aqueous acetonitrile are listed in Table 1.

Table 1. Enthalpies of transfer of the solutes from water to aqueous acetonitrile mixtures at 25 °C in kJ mol^{-1}.

x_B	LiBr	n-Bu_4NBr	n-Pen_4NBr
0	0	0	0
0.1	–2.05	12.40	16.13
0.2	–4.00	24.70	30.13
0.3	–7.40	24.40	26.03
0.4	–10.81	23.67	25.63
0.5	–15.46	22.40	25.18
0.6	–19.47	21.13	24.75
0.7	–22.70	19.40	23.64
0.8	–27.03	17.70	22.53
0.9	–28.15	17.21	22.83
0.95	–23.76	20.50	25.48
1	8.65	23.80	28.13

Discussion

Extension of the simple coordination model taking into account the effects of changes in solvent-solvent interactions is relatively straightforward and has been described in detail elsewhere.[13] Briefly: a solute occupies a cavity in the solvent structure, surrounded by its coordination sphere of n solvent molecules. 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, $-n\alpha\Delta H^{*\circ}$ where α is the fraction of the molar enthalpy of solvent-solvent bonding, $\Delta H^{*\circ}$, 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 $\Delta H^{*\circ}$ we can set it equal to an enthalpy change, $-n\beta\Delta H^{*\circ}$, 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 $\Delta\Delta H^\theta_{12}$. This model leads to equation 1 for the enthalpy of transfer, ΔH^θ_t, of the solute from pure solvent A to mixtures of A and a second solvent B.

In equation 1, L_A and L_B are the relative partial molar enthalpies, $\Delta\Delta H^{*\circ}$ is the difference between the A-A and B-B interactions in the two pure solvents, $\Delta H^{\circ *}_A - \Delta H^{\circ *}_B$, 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.

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

In mixed solvent systems, preferential solvation is accounted for by:

$$\frac{N_B}{N_A} \cong \frac{n_B}{n_A} = p\frac{x_B}{x_A}$$

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 neighbors 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. $\Delta\Delta H^\theta_{12}$ is the difference between the enthalpies of interaction of the solute with the two pure solvent A and B.

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

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

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

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, $\overset{A\to B}{\Delta} H^\theta_t$, is simply:

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

So that equation 2 rearranges to:

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

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

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

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:

$$(\alpha n+\beta N)^{mix} = (\alpha n+\beta N)^\theta_A x_A + (\alpha n+\beta N)^\theta_B x_B \qquad (6)$$

We substitute $\dfrac{\Delta H_t^\theta - x_B \overset{A\to B}{\Delta} H_t^\theta}{\Delta H^E}$ ratio instead of $(\alpha n + \beta N)^{mix}$ in equation 6,

$$\frac{\Delta H_t^\theta - x_B \overset{A\to B}{\Delta} H_t^\theta}{\Delta H^E} = (\alpha n+\beta N)^\theta_A - \left[(\alpha n+\beta N)^\theta_B - (\alpha n+\beta N)^\theta_A\right] x_B \qquad (7)$$

After reorganizing, leads to:

$$\Delta H_t^\theta = \overset{A\to B}{\Delta} H_t^\theta x_B + (\alpha n+\beta N)_A^\theta \Delta H^E$$

$$-\left[(\alpha n+\beta N)_B^\theta - (\alpha n+\beta N)_A^\theta\right] x_B \Delta H^E \qquad (8)$$

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,

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

$$-\left[(\alpha n+\beta N)_B^\theta - (\alpha n+\beta N)_A^\theta\right] x'_B \left[x'_A L_A + x'_B L_B\right] \qquad (9)$$

where $\quad x'_A = \dfrac{1}{x_A + p x_B}, \; x'_B = \dfrac{p x_B}{x_A + p x_B}$

ΔH^θ_t 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. $(\alpha n + \beta N)^\theta_A$ and $(\alpha n + \beta N)^\theta_B$ 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, $\overset{A\to B}{\Delta} H^\theta_t$ which is the coefficient of the first term in equation 9 is as follow:

$$\overset{A\to B}{\Delta} H_t^\theta = \left[(\Delta H_{12})_B - (\Delta H_{12})_A\right]$$

$$+(\alpha n+\beta N)_B^\theta \Delta H_B^{\circ *} - (\alpha n+\beta N)_A^\theta \Delta H_A^{\circ *} \qquad (10)$$

where $\left[(\Delta H_{12})_B - (\Delta H_{12})_A\right]$ is the relative strengths of solute-solvent bonds in the pure solvents including intramolecular contribution. For simplification it is written as $\Delta\Delta H^\theta_{12}$ 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 $(\alpha n + \beta N)^\theta_A$ and $(\alpha n + \beta N)^\theta_B$ in equation 10 leads to:

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

which is equation 3. If $(\alpha n + \beta N)^\theta_A = (\alpha n + \beta N)^\theta_B = (\alpha n + \beta N)$, equation 9 reduces to equation 1. Using equation 9 reproducing the enthalpies of transfer LiBr, n-Bu$_4$NBr and n-Pen$_4$NBr from water to aqueous MeCN shows excellent agreement between the experimental and calculated data (Figure 1) over the whole range of solvent composition, which is a good support for this equation.

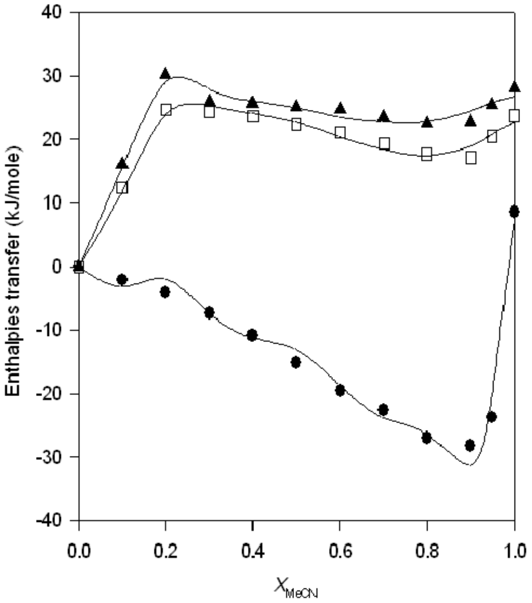

Figure 1. Comparison of the experimental (symbols) and calculated (lines) enthalpies of transfer for LiBr (●), n-Bu$_4$NBr (□) and n-Pen$_4$NBr (▲) *via* equation 9.

Solvation parameters obtained by the help of equation 9 were reported in Table 2. $(\alpha n + \beta N)$ values for n-Bu$_4$NBr and n-Pen$_4$NBr are positive, which indicates disruption of the solvent-solvent bonds by these solutes. These values for LiBr are negative which means that LiBr strengthens solvent-solvent bonds in aqueous acetonitrile. It could be seen that $(\alpha n + \beta N)^\theta_A$ and $(\alpha n + \beta N)^\theta_B$ values for LiBr in aqueous MeCN are –18.56 and –13.53 respectively, very close together thus and therefore a conclusion could be made that LiBr residues are surrounded by water structure over the whole range of solvent composition. These interpretations are consistent with preferential solvation of LiBr by water as $p<1$ ($p=0.3$).

As it is shown in Table 2, $(\alpha n + \beta N)$ values in MeCN-rich regions, $(\alpha n + \beta N)^\theta_B$, are bigger than those in water-rich domains, $(\alpha n + \beta N)^\theta_A$, indicating that the solutes break MeCN structure is greater than that in the water structure. We can suggest that the increase in $(\alpha n + \beta N)^\theta_A$ observed in the water-rich region results from the increase in the size of the alkyl groups of the alkylamonium bromides. It is well-known, that the large tetraalkylammonium ions are hydrated in a special way, called "hydrophobic hydration". In most non-aqueous solvents, particularly non-hydrogen bonded solvents, there is no it hydrophobic hydration. Since the hydrophobic hydration of R$_4$N$^+$ ions eventually will disappear by addition of a non-aqueous cosolvent to water, it has been anticipated that n-Bu$_4$NBr and n-Pen$_4$NBr prefer to leave water structure. p values obtained from equation 9 are 1.85 and 3 for *n*-Bu_4NBr and *n*-Pen_4NBr respectively which means that these solutes are preferentially solvated by MeCN. These results are in consistence with known hydrophobicity of these solutes, which are good support for the new developed solvation theory.[14–16]

Table 2. Solvation parameters for the solutes in mixtures of water with acetonitrile *via* equation 9. $p<1$ indicates preferential solvation of the solutes by water and $\Delta\Delta H^{\theta}_{12}>0$ indicates stronger interaction of the solutes with water.

Solutes	LiBr	*n*-Bu_4NBr	*n*-Pen_4NBr
P	0.3	1.85	3.00
$(\alpha n+\beta N)^{\theta}_{A}$	–18.56	33.00	29.52
$(\alpha n+\beta N)^{\theta}_{B}$	–13.23	73.75	64.16
$\Delta\Delta H^{\theta}_{12}$ (kJ/mol)	352.09	905.51	751.78

Conclusion

The large tetraalkylammonium ions are hydrophobic. Since the hydrophobic property of tetraalkylammonium ions eventually should vanish with addition of MeCN to water, it has been expected that *n*-Bu_4NBr and *n*-Pen_4NBr prefer to leave water structure in aqueous MeCN. p values obtained from equation 9 are more than unity, $p>1$, for *n*-Bu_4NBr and *n*-Pen_4NBr which means that these solutes are preferentially solvated by MeCN. These results are in consistence with known hydrophobicity of these solutes and actually a good confirmation of the new developed solvation theory. The enthalpies of transfer LiBr, *n*-Bu_4NBr and *n*-Pen_4NBr from water to aqueous MeCN obtained from equation 9 are in excellent agreement with the experimental data (Figure 1) over the whole range of solvent composition.

References

1. G. Rezaei Behbehani, M. Dillon, J. Smyth, W. E. Waghorne, *J. Solution Chem*. **2002**, *31*, 811–822.
2. G. Rezaei Behbehani, D. Dunnion, P. Falvey, K. Hickey, M. Meade, Y. McCarthy, C. R. Symon, W. E. Waghorne, *J. Solution Chem*. **2000**, *29*, 521–539.
3. E. de Valera, D. Feakin, W. E. Waghorne, *J. Chem. Soc., Faraday Trans*. **1983**, *79*, 1061–1066.
4. E. de Valera, D. Feakins, W. E. Waghorne, *J. Chem. Soc., Faraday Trans*. **1980**, *76*, 560–569.
5. B. G. Cox, W. E. Waghorne, C. K. Pigott, *J. Chem. Soc., Faraday Trans*. **1979**, *75*, 227–233.
6. B. G. Cox, A. J. Parker, W. E. Waghorne, *J. Phys. Chem.* **1974**, *78*, 1731–1740.
7. G. Carthy, D. Feakins, W. E. Waghorne, *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 2585–2592.
8. D. Feakins, J. Mullally, W. E. Waghorne, *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1–5.
9. A. Costigan, D. Feakins, I. McStravick, C. O' Duinn, J. Ryan, W. E. Waghorne, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2443–2446.
10. P. Hogan, I. Mcstravick, J. Mullally, W. E. Waghorne, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2691–2695.
11. D. Feakins, P. Hogan, C. O' Duinn, W. E. Waghorne, *J. Chem. Soc. Faraday. Trans*. **1992**, *88*, 423–425.
12. P. A. Leighton, R. W. Crary, L. T. Schipp, *J. Am. Chem. Soc*. **1953**, *53*, 3017–3025.
13. D. Feakins, E. de Valera, W. E. Waghorne, *J. Chem. Soc., Faraday Trans*. **1985**, 81, 2702–2709.
14. E. V. Goldammer, H. G. Hertz, *J. Phys. Chem*. **1970**, *74*, 3734–3755.
15. J. A. Ripmeester, D. W. Davidson, *J. Mol. Struct*. **1981**, *75*, 67–76.
16. D. Feakins, J. Mullally, W. E. Waghorne *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 89–91.

Povzetek

Določili smo entalpije prenosa, ΔH^{θ}_{t}, za LiBr, tertabutilamonijev bromid, *n*-Bu_4NBr, in tetrapentilamonijev bromid, *n*-Pen_4NBr, iz vode v mešanice acetonitrila in vode. Izmerjene vrednosti smo obravnavali s pomočjo nove solvatacijske teorije. Dobljeni parametri solvatacije kažejo, da *n*-Bu_4NBr ruši medmolekulske vezi topilo-topilo in da je preferenčno solavtiran z acetonitrilom, kar je v skladu z znano hidrofobnostjo spojine. LiBr je preferenčno solvatiran z vodo.