

Solution calorimetry of alkyl substituted ammonium bromides in aqueous and nonaqueous solvents

G. Somsen

Department of Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract - Enthalpies of solution at infinite dilution of electrolytes in several pure and mixed solvents, aqueous as well as non-aqueous, are discussed. Special attention is given to the peculiar properties of solutions of electrolytes containing alkyl groups, viz. tetraalkylammonium bromides. In water and highly aqueous mixed solvents, the enthalpies of solution of these compounds are strongly influenced by hydrophobic hydration. Attention will be given to the influence of size and nature of the substituting alkyl groups, to the influence of the temperature, and to the role of the cosolvent. Especially in mixtures of water and acetonitrile, the enthalpies of solution of tetraalkylammonium bromides with large alkyl groups are extremely dependent on solvent composition and temperature.

INTRODUCTION

The energetic aspects of solute–solvent interactions can be investigated directly by calorimetric measurements of the enthalpies of solution of a certain solute in different solvents. The difference in the enthalpies of solution at infinite dilution in two solvents reflects the change in solvation of the solute. On a molecular scale this change is due to different solute-solvent interactions as well as to alterations in solvent-solvent interactions in the vicinity of the solute molecule. The solvents involved may be pure liquids or liquid mixtures, where the solvent properties of the system can be varied by changing the composition.

This contribution will focus attention on the peculiar properties of tetraalkylammonium salts in water. It is well-known, that the large tetraalkylammonium ions are hydrated in a special way, called "hydrophobic hydration" (ref. 1). It involves a shift in the spatial and orientational correlations between the water molecules in the vicinity of the solute molecule. In most non-aqueous solvents, particularly in non-hydrogen bonded solvents, it is absent. In comparing solvents, *N,N*-dimethylformamide (DMF) has proven to be a suitable reference solvent in many cases. It is an aprotic, non-associated liquid with properties close to those of an ideal dipolar liquid. It is a good solvent for many solutes and completely miscible with many other solvents. Since the hydrophobic hydration of R_4N^+ ions eventually will disappear on addition of a non-aqueous cosolvent to water, we have used the enthalpies of solution of various tetraalkylammonium salts in mixtures of water and DMF to study the energetic aspects of hydrophobic hydration in a systematic way. For reason of comparison other solvent mixtures were investigated also.

The enthalpies of solution discussed in this paper have been measured calorimetrically using commercially available instruments. Details about the calorimetric procedure and the purification of solutes and solvents can be found in the original work (ref. 2). The enthalpies of solution presented refer to infinite dilution and, unless indicated otherwise, to 298.15 K.

ENTHALPIES OF SOLUTION AND ENTHALPIES OF TRANSFER

Standard enthalpies of solution of several alkali and tetraalkylammonium bromides in four different solvents are given in Table 1. Besides DMF, the solvents are dimethylsulphoxide (DMSO), like DMF an aprotic liquid, *N*-methylformamide (NMF), a protic and chain-wise associated liquid, and water, a liquid in which the molecules are highly associated by a three-dimensional network of hydrogen bonds. Inspection of Table 1 shows that the changes in the enthalpies of solution are almost equal for all solutes if we compare non-aqueous solvents. However, for transfers from NMF, DMF or DMSO to water differences occur between alkali bromides on the one hand and tetraalkylammonium bromides on the other. The enthalpies of solution of all alkali bromides are most endothermic in water, those of the tetraalkylammonium bromides (with an only exception for Me₄NBr) are most exothermic in water.

TABLE 1. Values of $\Delta_{\text{sol}}H^\circ/\text{kJ}\cdot\text{mol}^{-1}$ of alkali and tetraalkylammonium bromides in DMF, DMSO, NMF and water at 298.15 K.

salt	DMF	DMSO	NMF	water	salt	DMF	DMSO	NMF	water
LiBr	-77.5	-71.5	-63.2	-48.8	Me ₄ NBr	16.4	12.8	27.4	24.6
NaBr	-30.9	-24.9	-17.4	-0.6	Et ₄ NBr	9.4	13.6	21.1	6.2
KBr	-16.3	-11.3	-3.5	19.9	<i>n</i> -Pr ₄ NBr	9.9	16.0	20.8	-4.3
RbBr	-13.7	-8.1	-0.1	21.9	<i>n</i> -Bu ₄ NBr	12.5	20.8	22.5	-8.4
CsBr	-7.5	-2.5	6.0	26.3	<i>n</i> -Pen ₄ NBr	22.9	36.0		2.7
NH ₄ Br	-15.7			17.3					

In comparison with the alkali salts the hydration of the tetraalkylammonium ions results in exothermic contributions to the enthalpies of solution. These contributions increase in magnitude with the size of the alkyl groups and can be correlated with the hydrophobic hydration of these solute particles. Differences in the enthalpies of solution of alkali bromides and tetraalkylammonium bromides are also present in aqueous *mixed* solvents. Figure 1 presents enthalpies of solution of CsBr and *n*-Bu₄NBr in DMF + water as a function of the mole fraction of water, x_w . Whereas the enthalpy of solution of CsBr changes gradually from pure DMF to pure water, that of *n*-Bu₄NBr shows at higher x_w a pronounced exothermic shift toward the value in pure water. In non-aqueous mixed solvents this exothermic shift is absent, as shown in Fig. 2 where enthalpies of solution of *n*-Bu₄NBr in DMF + water are compared with those in mixtures of two aprotic non-aqueous solvents (DMF + DMSO) and those in mixtures of an aprotic and a protic non-aqueous solvent (DMF + NMF). The enthalpies of solution in both non-aqueous mixtures change practically linearly with the solvent composition.

The comparison of the enthalpies of solution of *n*-BuNH₃Br and NH₄Br in DMF + water in Fig. 3 clearly demonstrates that the exothermic shift in the aqueous solvent systems is due to the presence of alkyl groups. From the evidence that the enthalpies of solution are influenced by the hydrophobic hydration of

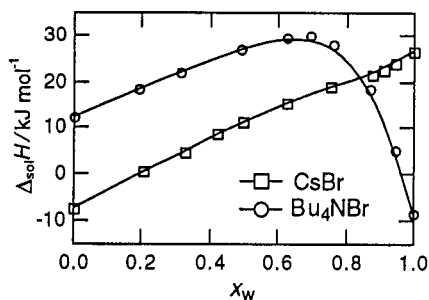


Fig. 1. Enthalpies of solution of CsBr and *n*-Bu₄NBr in DMF + water.

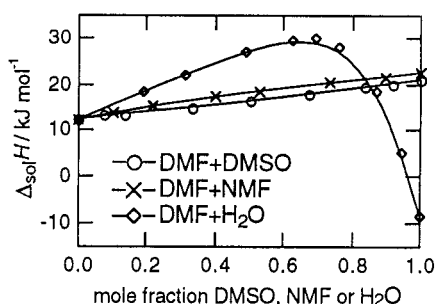


Fig. 2. Enthalpies of solution of *n*-Bu₄NBr in mixtures of DMF with DMSO, NMF and water.

the alkyl groups in pure water and in water-rich mixtures, changes in the enthalpies of solution in a mixture of DMF and water can be described as the result of two contributions. The first is due to the solvation that should occur if hydrophobic effects would be absent. It will give rise to a linear change of the enthalpy of solution as found for CsBr and NH_4Br and visualized in Fig. 4 by line a. The second contribution is due to hydrophobic hydration. It is exothermic and maximal in pure water. Due to the cooperative character of hydrophobic hydration the magnitude of this contribution decreases rapidly with decreasing water content. It is reflected in Fig. 4 by curve b. The sum of these contributions is the enthalpy of solution, given in Fig. 4 by curve c. For clarity this curve is shifted slightly downwards.

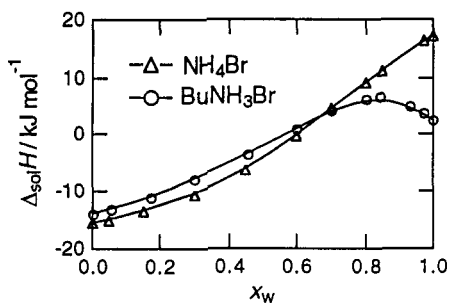


Fig. 3. Enthalpies of solution of $n\text{-BuNH}_3\text{Br}$ and NH_4Br in DMF + water.

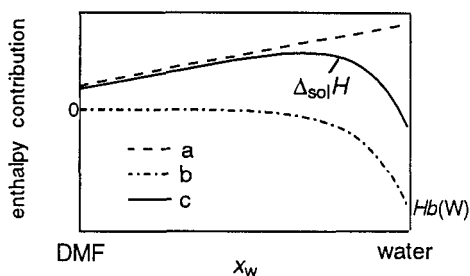


Fig. 4. Generalized picture of the enthalpy of solution and its contributions (see text).

Generally it is assumed that hydrophobic particles in water are surrounded by a clathrate-like "cage" of water molecules. Indeed a number of organic substances, including some tetraalkylammonium salts do form clathrate hydrates in the solid state. Starting from this point of view and assuming that this type of hydration is strongly affected by addition of a cosolvent to water, several model approaches (ref. 3,4) lead to an equation which describes the experimental enthalpies of solution over the complete mole fraction range with only two adjustable parameters :

$$\Delta_{\text{sol}}H(M) = (1 - x_w)\Delta_{\text{sol}}H(\text{DMF}) + x_w\Delta_{\text{sol}}H(W) + (x_w^n - x_w)Hb(W) \quad (1)$$

In this equation, $\Delta_{\text{sol}}H(M)$, $\Delta_{\text{sol}}H(\text{DMF})$, and $\Delta_{\text{sol}}H(W)$ are the enthalpies of solution of the salt in the solvent mixture, pure DMF, and pure water, respectively. $Hb(W)$ is the enthalpic contribution of hydrophobic hydration in pure water, and n is a parameter related to the number of water molecules involved in the hydration of one alkyl group.

The enthalpies of solution of $n\text{-Pr}_4\text{NBr}$, $n\text{-Bu}_4\text{NBr}$ and $n\text{-Pen}_4\text{NBr}$ in DMF + water can be described by eq. (1) very well. Least squares analysis in terms of this equation leads to values of $Hb(W)$ and n presented in Table 2, where also the mean deviations of the fits are given. Figure 5 shows the experimental results as well as the curves calculated using eq.(1). For Et_4NBr the experimental enthalpies of solution in DMF + water do not obey eq. (1) at all compositions. Values of $Hb(W)$ and n given in Table 2 are approximated from data

TABLE 2. The enthalpic effect of hydrophobic hydration in water, $Hb(W)$, the parameter n , and the mean deviation δ between calculated and experimental enthalpies of solution at 298.15 K.

solute	$Hb(W) / \text{kJ}\cdot\text{mol}^{-1}$	n	$\delta / \text{kJ}\cdot\text{mol}^{-1}$	solute	$Hb(W) / \text{kJ}\cdot\text{mol}^{-1}$	n	$\delta / \text{kJ}\cdot\text{mol}^{-1}$
Et_4NBr	-29.3	(2.3) ^a	-	[4.4]Br	-23.8	(1.9) ^a	-
$n\text{-Pr}_4\text{NBr}$	-39.6	4.2	0.17	[5.5]Br	-25.2	(2.3) ^a	-
$n\text{-Bu}_4\text{NBr}$	-52.8	6.4	0.23	[6.6]Br	-27.3	2.8	0.18
$n\text{-Pen}_4\text{NBr}$	-58.0	8.6	0.37				

^abased on data with $x_w < 0.75$.

with $x_w < 0.75$. The model approach fails completely for Me_4NBr (see Fig. 11), where the hydrophobic contribution is much less and the ionic charge much more dominant.

Although the trends in the values of $Hb(W)$ and n are in mutual agreement, the magnitudes of n are too small to identify this parameter with the number of water molecules involved in the hydrophobic hydration of one alkyl group, as was done in the simplest model approach (ref. 3). However, this can be remedied by introducing additional model assumptions (see ref. 2). The success of the model suggests that at least in mixtures with high water content the alkyl groups are independently solvated and contribute additively to the total changes.

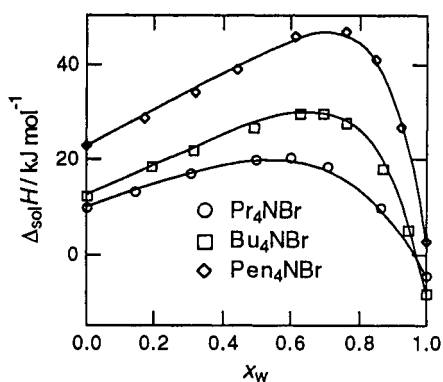


Fig. 5. Enthalpies of solution of $n\text{-Pr}_4\text{NBr}$, $n\text{-Bu}_4\text{NBr}$, and $n\text{-Pen}_4\text{NBr}$ in DMF + water.

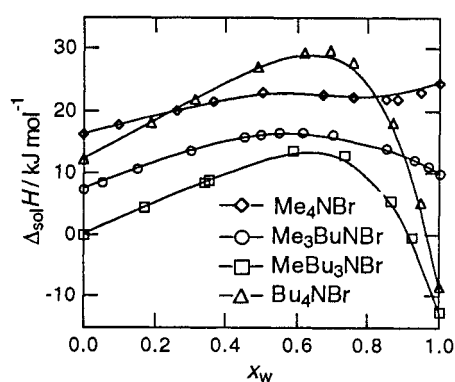
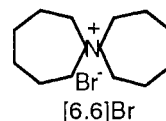
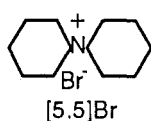


Fig. 6. Enthalpies of solution of asymmetrically substituted ammonium bromides in DMF + water.

The independent solvation of the alkyl groups in the solute molecules can be investigated by studying asymmetric tetraalkylammonium bromides. One example is already given in Fig. 3, where $Hb(W)$ of $n\text{-Bu}_3\text{NH}_3\text{Br}$ is approximately $1/4$ of that of $n\text{-Bu}_4\text{NBr}$. Other examples are presented in Fig. 6 by the enthalpies of solution of Me_4NBr , $n\text{-BuMe}_3\text{NBr}$, $n\text{-Bu}_3\text{MeNBr}$ and $n\text{-Bu}_4\text{NBr}$. The shape of their curves changes gradually from Me_4NBr to $n\text{-Bu}_4\text{NBr}$. Actually, the curves of the asymmetric compounds can be calculated quantitatively from those for Me_4NBr and $n\text{-Bu}_4\text{NBr}$ by simple additivity.

Evidence has been presented (ref. 5,6) that the hydrophobic hydration of n -alkyl groups in water is related to their conformational flexibility. We have studied this aspect through the enthalpies of solution of several azoniaspiroalkane bromides. These compounds can be regarded as tetraalkylammonium salts in which the side chains are terminally interconnected. Enthalpies of solution were obtained for 5-azoniaspiro-[4.4]-nonane bromide, 6-azoniaspiro-[5.5]-undecane bromide, and 7-azoniaspiro-[6.6]-tridecane bromide, for which we use the abbreviations [4.4]Br, [5.5]Br and [6.6]Br, respectively.



The compound [4.4]Br can be compared with Et_4NBr , [6.6]Br with $n\text{-Pr}_4\text{NBr}$.

Figure 7 shows that in DMF + NMF the enthalpies of solution of these compounds change linearly with composition. In DMF + water, they give curves with the familiar exothermic shift at higher x_w (see Fig. 8). However, the magnitude is much smaller than for the corresponding aliphatic ammonium bromides. It appears that only the results for [6.6]Br can be described satisfactorily by eq. (1) with parameters as given in Table 2. For [4.4]Br and [5.5]Br only approximated values can be obtained. This outcome indicates that the reduced flexibility of the hydrocarbon groups in the azoniaspiroalkane bromides leads to smaller hydrophobic contributions, in agreement with conclusions given in refs. 5 and 6.

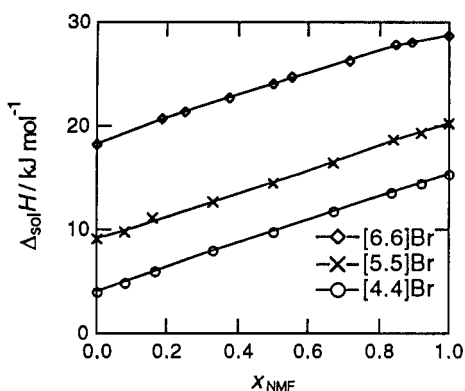


Fig. 7. Enthalpies of solution of azoniaspiroalkane bromides in DMF + NMF.

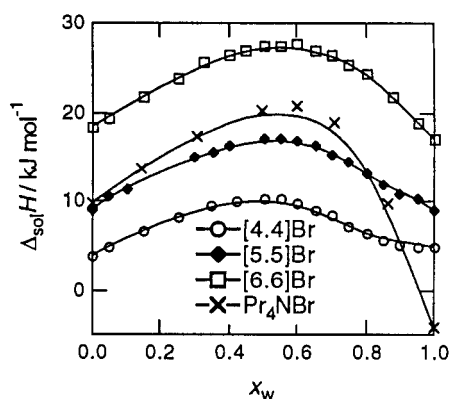


Fig. 8. Enthalpies of solution of *n*-Pr₄NBr and azoniaspiroalkane bromides in DMF + water.

Substitutions in one or more of the alkyl groups may also affect the nature of the R₄N⁺ ion. The influence of terminal OH groups is revealed by the enthalpies of solution of (2-hydroxyethylammonium) bromides. Figure 9 presents enthalpies of transfer of tetra(2-hydroxyethyl)ammonium bromide, (EtOH)₄NBr, triethyl(2-hydroxyethyl)-ammonium bromide, Et₃(EtOH)NBr, and (for comparison) Et₄NBr. For reason of clarity the results for Et₂(EtOH)₂NBr and Et(EtOH)₃NBr are not shown, but they lie between the curves for Et₃(EtOH)NBr and (EtOH)₄NBr. The results indicate that the hydrophobic contributions decrease with the number of 2-hydroxyethyl groups. The enthalpies of transfer of the compound with four terminal OH groups, (EtOH)₄NBr, show no sign of hydrophobic contributions at all and the curve in Fig. 9 resembles that of non-hydrophobic CsBr (see Fig. 1).

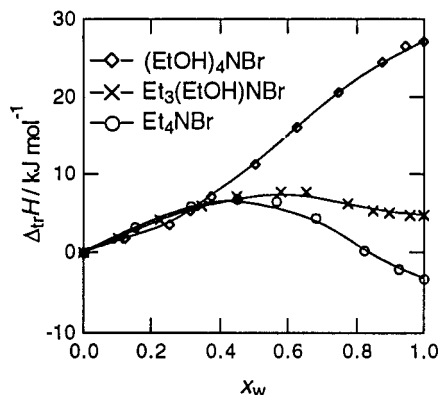


Fig. 9. Enthalpies of transfer of several OH substituted tetraalkylammonium bromides in DMF + water.

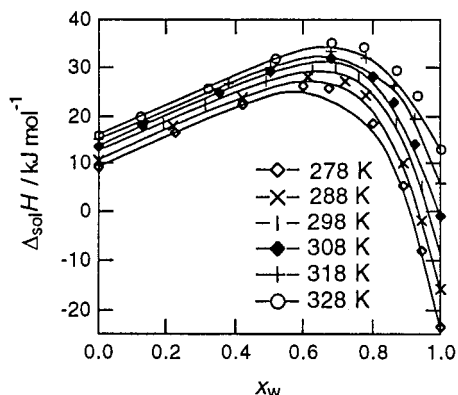


Fig. 10. Enthalpies of solution of *n*-Bu₄NBr in DMF + water at different temperatures.

The structural properties of liquid water change considerably with temperature and so will hydrophobic hydration. The enthalpies of solution of *n*-Bu₄NBr in DMF + water at different temperatures reflect this change. Figure 10 gives values at 5, 15, 25, 35, 45, and 55 °C. All curves can be described by eq. (1) with a rather constant value of *n* (6.4±0.4) and values of *Hb*(W) ranging from -65.6 kJ·mol⁻¹ at 5 °C to -34.4 kJ·mol⁻¹ at 55 °C.

Temperature has much less influence on the enthalpies of solution of Me₄NBr (see Fig. 11). The difference between *n*-Bu₄NBr and Me₄NBr is more clearly demonstrated by the partial molar heat capacities calculated from the enthalpies of solution and visualized in Fig. 12. With respect to heat capacities Me₄NBr is not hydrophobic at all, whereas *n*-Bu₄NBr is strongly hydrophobic. The contribution to C_{p,2} due to hydrophobic hydration of *n*-Bu₄NBr in pure water is about 600 J·K⁻¹·mol⁻¹.

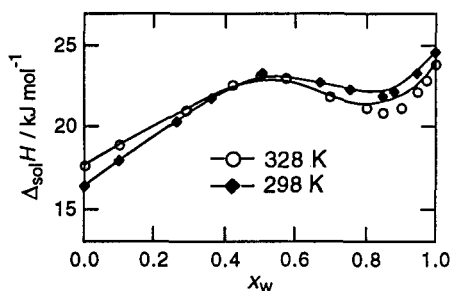


Fig. 11. Enthalpies of solution of Me_4NBr in DMF + water at different temperatures.

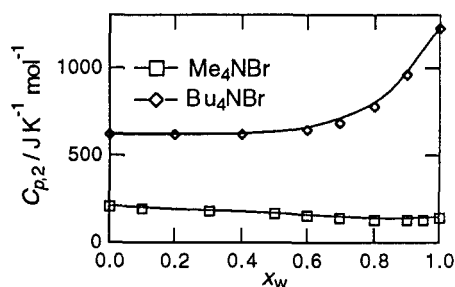


Fig. 12. Partial molar heat capacities of Me_4NBr and $n\text{-Bu}_4\text{NBr}$ in DMF + water.

Up to now, mainly mixtures of water and DMF have been considered. In the model approach of aqueous mixtures by eq. (1) no specific influence is attributed to the cosolvent. For this reason the model becomes less satisfactory for protic cosolvents (ref.7). In Figs. 13 and 14 enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ are presented for several aprotic cosolvents. For DMSO and N,N -dimethylacetamide (DMA) the picture is similar to that in mixtures of water and DMF. With DMSO as cosolvent $Hb(W)$ is $-51.5 \text{ kJ}\cdot\text{mol}^{-1}$, with DMA it is $-59.9 \text{ kJ}\cdot\text{mol}^{-1}$. Deviating results are obtained in mixtures of water and acetonitrile (AN) and water and 1,3-dioxolan-2-one (ethylene carbonate, EC). Figure 14 gives results for $n\text{-Bu}_4\text{NBr}$ in AN + water at 25°C and in EC + water at 45°C . At low mole fractions of water the results are clearly incompatible with eq. (1).

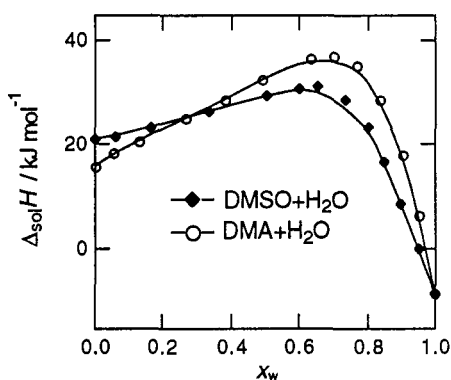


Fig. 13. Enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ in DMSO + water and DMA + water.

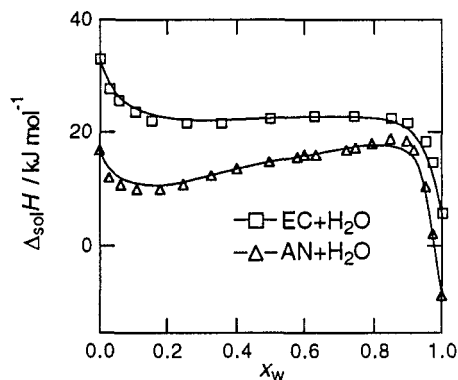


Fig. 14. Enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ in EC + water and AN + water.

Since strong preferential solvation of ions in AN + water has been reported (ref.8,9) which is at variance with the assumptions underlying eq. (1), these deviations are not unexpected. Preferential solvation could also imply that enthalpies of solution of non-hydrophobic compounds in AN + water will not change proportional to solvent composition. This has been confirmed by the results for LiBr given in Fig. 15, which shows large changes in the enthalpy of solution at low water content and an almost linear change between $x_w = 0.2$ and $x_w = 1$.

Closer inspection of the curve for AN + water in Fig. 14 reveals an inflection between $x_w = 0.5$ and $x_w = 0.8$. It appears that the magnitude of the inflection is strongly temperature dependent. As visualized in Fig. 16, it changes into a local minimum at lower temperatures and at 0°C its magnitude is about $4 \text{ kJ}\cdot\text{mol}^{-1}$. At temperatures above 25°C the inflection disappears. Similar results have been obtained for other R_4NBr salts (ref.10). While the enthalpies of solution of $n\text{-Pr}_4\text{NBr}$ do not show any peculiarities down to 5°C , the results for tetra- n -pentyl- and tetra- n -heptylammonium bromide ($n\text{-Hept}_4\text{NBr}$) show very pronounced effects at low temperatures. They are given in Figs. 17 and 18, which show that at 0°C the local minimum for $n\text{-Pen}_4\text{NBr}$ has a magnitude of about $10 \text{ kJ}\cdot\text{mol}^{-1}$, for $n\text{-Hep}_4\text{NBr}$ about $35 \text{ kJ}\cdot\text{mol}^{-1}$. The results may be connected with the strongly positive values of G^E and H^E of AN + water (ref.11, 12), which has an upper critical solution temperature of 271.8 K at about $x_w = 0.64$ (ref.13). Recently, Marcus and Migron (ref.14)



Fig. 15. Enthalpies of solution of LiBr in AN + water at 25 °C..

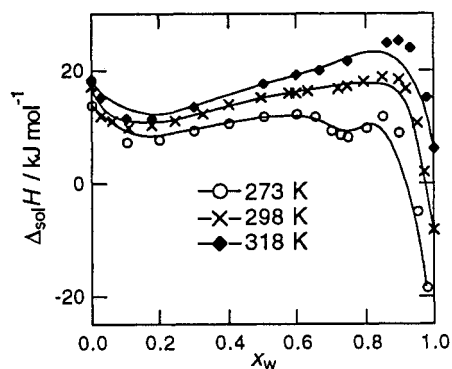


Fig. 16. Enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ in AN + water at different temperatures.

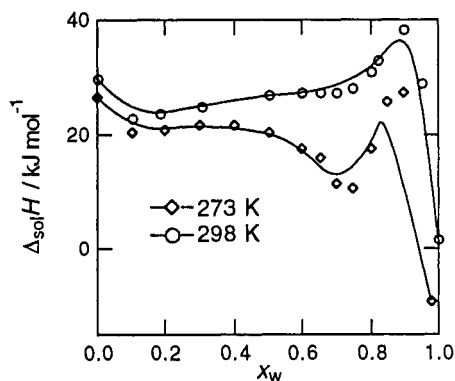


Fig. 17. Enthalpies of solution of $n\text{-Pen}_4\text{NBr}$ in AN + water at different temperatures.

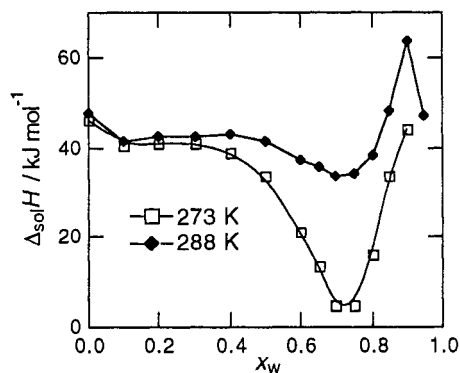


Fig. 18. Enthalpies of solution of $n\text{-Hept}_4\text{NBr}$ in AN + water at different temperatures.

presented evidence for microheterogeneity in AN + water between $x_w = 0.3$ and 0.7 . This might be compatible with these results.

Very recently we started to investigate the influence of dissolved electrolytes on the enthalpies of solution of tetraalkylammonium halides in water (ref. 16). In aqueous solutions of KCl as solvent, Chawla and Ahluwalia (ref. 15) found positive shifts in the enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ at increasing molality of KCl. We got a similar result in aqueous KBr only at higher molalities. Below 2 molal the shift in the enthalpy of solution of $n\text{-Bu}_4\text{NBr}$ is negative.

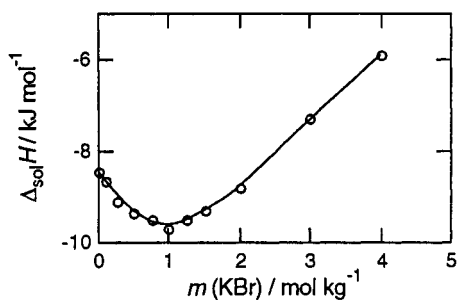


Fig. 19. Enthalpies of solution of $n\text{-Bu}_4\text{NBr}$ in aqueous solutions of KBr.

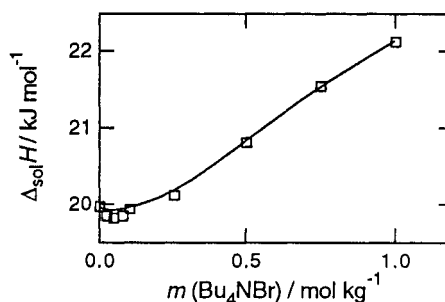


Fig. 20. Enthalpies of solution of KBr in aqueous solutions of $n\text{-Bu}_4\text{NBr}$.

This sign was substantiated by values of the enthalpy of solution of KBr in aqueous solutions of $n\text{-Bu}_4\text{NBr}$. Theoretically, the limiting slopes are determined by the pairwise interactions of the two solutes and are consequently equal. Within experimental error this is confirmed by the results (Figs. 19 and 20).

REFERENCES

1. F. Franks, Water, a Comprehensive Treatise, volume 2, Plenum Press, New York (1973).
2. W.J.M. Heuvelsland, Hydrophobic hydration in aqueous solvent mixtures, Doctoral thesis, Vrije Universiteit, Amsterdam (1980).
3. M.J. Mastroianni, M.J. Pikal and S. Lindenbaum, J. Phys. Chem., **76**, 3050 - 3057 (1972).
4. W.J.M. Heuvelsland, C. de Visser and G. Somsen, J. Phys. Chem., **82**, 29 - 32 (1978).
5. Wen-Yang Wen and U. Kaatze, J. Phys. Chem., **81**, 177 - 181 (1977).
6. A. LoSurdo, Wen-Yang Wen, C. Jolicoeur and J.-L. Fortier, J. Phys. Chem., **81**, 1813 - 1817 (1977).
7. C. de Visser and G. Somsen, J. Solution Chem., **3**, 847 - 855 (1974).
8. A.K. Covington and J.M. Thain, J. Chem. Soc., Faraday Trans. I, **70**, 1879 - 1887 (1974).
9. B.G. Cox, R. Natarajan and W.E. Waghorne, J. Chem. Soc., Faraday Trans. I, **75**, 86 - 95 (1979).
10. N. van Meurs, Th.W. Warmerdam and G. Somsen, Fluid Phase Equil., **49**, 263 - 269 (1989).
11. M.A. Villamanán and H.C. Van Ness, J. Chem. Engin. Data, **30**, 445 - 446 (1985).
12. H.T. French, J. Chem. Thermodynamics, **19**, 1155 - 1161 (1987).
13. G. Benter and H. Schneider, Ber. Bunsenges. Physik. Chem., **77**, 997 - 999 (1973).
14. Y. Marcus and Y. Migron, J. Phys. Chem., **95**, 400 - 406 (1991).
15. B. Chawla and J.C. Ahluwalia, J. Phys. Chem., **76**, 2582 - 2585 (1972).
16. A. Dupal and G. Somsen, to be published.