Thermochimica Acta, 137 (1989) 233–240
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPIES OF SOLVATION OF ALKALI AND HALIDE IONS IN WATER–ACETAMIDE MIXTURES IN THE RANGE 298.15–348.15 K

MARIAN WOLDAN

Research and Development Centre for Standard Reference Materials WZORMAT— Branch in Łódź, 90-132 Łódź (Poland)

(Received 10 February 1988)

ABSTRACT

The enthalpies of solution of NaBr, KCl, KBr and CsI have been determined in water and in four water–acetamide mixtures. The standard enthalpies of solution $\Delta H^{\ominus}$ of the investigated electrolytes have been evaluated. The corresponding enthalpies of solvation $\Delta H_s^{\ominus}$ have been calculated. Single ion enthalpies of solvation $\Delta H^{\ominus}_{s(ion)}$ and the ionic enthalpy of transfer $\Delta H^{\ominus}_{tr(ion)}$ from water to water–acetamide mixed solvent have been derived. The dependence of the ionic enthalpy of transfer on the solvent composition, size and nature of ions and temperature is discussed.

INTRODUCTION

The mixture water–acetamide ($AcNH_2$) is an interesting system the behaviour of which deviates slightly from ideality [1,2], showing a great compatibility between the components due to the similar hydrogen bond energies for water–water and water–acetamide [3]. Although various physico-chemical properties of water–acetamide mixtures have been reported in some papers, a literature survey revealed that studies of this system through enthalpy of solution of electrolyte measurements are lacking. In view of this it was desirable to study the enthalpy of solution of a number of electrolytes in water–acetamide mixtures at different temperatures. For this purpose the enthalpies of solution of chosen alkali halides in water–acetamide mixtures in the range 298.15–348.15 K have been measured and the corresponding enthalpies of solvation have been calculated. Previous papers [4] reported the results of enthalpy of solution measurements at 298.15, 313.15 and 333.15 K. Here results are reported from enthalpy measurements of these electrolytes at 348.15 K and single ion enthalpies of solvation of alkali and halide ions in the range 298.15–348.15 K.

0040-6031/89/$03.50

EXPERIMENTAL

Materials

Salts and acetamide were purified and dried using the procedure described in an earlier paper [4]. The mixed solvents used for investigations were prepared by weighing using deionized double distilled water and acetamide.

Calorimetry

The calorimeter and experimental procedure have been described earlier [4]. The enthalpies of solution were determined at a series of concentrations covering the range 0.01–0.2 mol kg^{-1}. All enthalpies of solution were determined in triplicate. The total uncertainty of enthalpy of solution is about $\pm 0.5\%$.

RESULTS

The values of the enthalpy of solution for investigated electrolytes in water and water–acetamide mixtures at 348.15 K are omitted as too extensive. The plots of $\Delta H_m = f(\sqrt{m})$ were found to be linear within experimental error and they have been extrapolated to zero concentration for evaluation of the standard enthalpies of solution $\Delta H^{\ominus}$. The lack of necessary data makes it impossible to calculate $\Delta H^{\ominus}$ by the Criss–Cobble method [5]. The values of the standard enthalpies of solution obtained for investigated electrolytes are given in Table 1. The enthalpies of solvation $\Delta H_s^{\ominus}$ for the

TABLE 1

Standard enthalpies of solution of some alkali halides in mixtures of $(1-x)H_2O + xAcNH_2$ at 348.15 K (kJ mol^{-1})

Salt	Water	$x = 0.0510$	$x = 0.1155$	$x = 0.2336$	$x = 0.4155$
NaCl	−1.0	−1.2	−1.6	−2.1	−3.2
NaBr	−6.1	−6.5	−7.0	−7.9	−9.2
NaI	−12.2	−13.0	−14.0	−15.9	−18.5
KCl	11.0	10.7	10.2	9.5	8.5
KBr	13.0	12.5	11.9	10.8	9.6
KI	14.4	13.5	12.4	10.3	7.8
CsCl	10.6	10.2	9.6	8.9	7.2
CsBr	18.0	17.4	16.7	15.6	13.7
CsI	26.1	25.1	23.9	21.8	18.6

TABLE 2

Enthalpies of solvation of some alkali halides in mixtures of $(1-x)H_2O+xAcNH_2$ at 348.15 K (kJ mol^{-1})

Salt	Water	$x = 0.0510$	$x = 0.1155$	$x = 0.2336$	$x = 0.4155$
NaCl	778.4	778.6	779.0	779.5	780.6
NaBr	745.0	745.4	745.9	746.8	748.1
NaI	700.5	701.3	702.3	704.2	706.8
KCl	695.7	696.0	696.5	697.2	698.2
KBr	662.3	662.8	663.4	664.5	665.7
KI	617.8	618.7	619.8	621.9	624.4
CsCl	638.8	639.2	639.8	640.5	642.2
CsBr	605.4	606.0	606.7	607.8	609.7
CsI	560.9	561.9	563.1	565.2	568.4

electrolytes under study have been calculated from the standard enthalpies of solution and lattice enthalpy ΔH_{cryst} using the relation

$$-\Delta H_s^{\ominus} = \Delta H_{\text{cryst}} - \Delta H^{\ominus} \tag{1}$$

The lattice enthalpies for alkali halides are taken from the literature [6]. It is known that the standard enthalpy of solvation of the electrolyte is additively built up from the individual values of the ions. Hence, from values of $\Delta H_s^{\ominus}$ obtained in this work it is possible to calculate the values of the enthalpies of solvation of some non-investigated salts. Thus

$$\begin{aligned}
\Delta H^{\ominus}_{s(\text{NaCl})} &= \Delta H^{\ominus}_{s(\text{NaBr})} + \Delta H^{\ominus}_{s(\text{KCl})} - \Delta H^{\ominus}_{s(\text{KBr})}\\
\Delta H^{\ominus}_{s(\text{KI})} &= \Delta H^{\ominus}_{s(\text{KBr})} + \Delta H^{\ominus}_{s(\text{NaI})} - \Delta H^{\ominus}_{s(\text{NaBr})}\\
\Delta H^{\ominus}_{s(\text{CsCl})} &= \Delta H^{\ominus}_{s(\text{CsI})} + \Delta H^{\ominus}_{s(\text{NaCl})} - \Delta H^{\ominus}_{s(\text{NaI})}\\
\Delta H^{\ominus}_{s(\text{CsBr})} &= \Delta H^{\ominus}_{s(\text{CsI})} + \Delta H^{\ominus}_{s(\text{NaBr})} - \Delta H^{\ominus}_{s(\text{NaI})}
\end{aligned} \tag{2}$$

The values $\Delta H^{\ominus}_{s(\text{NaI})}$ in water and water–acetamide mixtures are taken from the literature [7]. Table 2 lists the enthalpies of solvation of alkali halides in water-acetamide mixtures at 348.15 K.

DISCUSSION

In developing a theory dealing with electrolyte solutions much attention has been devoted to ion–solvent interactions, which are a controlling factor in infinitely dilute solutions where ion–ion interactions are absent. Ion–solvent interactions manifest themselves in all molal functions obtained by extrapolation to infinite dilution. By separating the limiting molal functions of solutes into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute–solvent interactions.

TABLE 3

Ionic ethalpies of solvation of alkali-metal and halide ions in mixtures of $(1-x)H_2O + xAcNH_2$ at several temperatures (kJ mol^{-1})

Ion	Water	$x = 0.0510$				$x = 0.1155$				$x = 0.2336$				$x = 0.4155$
298.15 K		MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	
Na^+	396.8	397.2	396.6	396.9	396.9	397.3	397.1	397.5	397.3	397.7	398.2	398.8	398.2	
K^+	312.3	312.8	312.4	312.7	312.6	313.2	313.0	313.4	313.2	313.7	314.1	314.7	314.2	
Cs^+	252.0	253.7	253.4	253.6	253.6	254.2	254.1	254.6	254.3	255.0	255.6	256.3	255.6	
		NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX		
Cl^-	376.3	376.9	377.3	378.9	377.7	376.8	377.3	379.4	377.8	376.7	377.4	380.3	378.1	
Br^-	343.7	343.3	343.7	345.3	344.1	343.8	344.3	346.4	344.8	344.9	345.6	348.5	346.3	
I^-	300.1	300.1	300.5	302.1	300.9	300.8	301.3	303.4	301.8	302.3	303.0	305.9	303.7	
313.15 K		MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	
Na^+		398.1	397.7	397.5	397.8	398.2	398.1	398.2	398.2	398.4	398.7	399.5	398.9	
K^+		313.8	313.4	313.3	313.5	314.0	314.0	314.1	314.0	314.5	314.8	315.6	315.0	
Cs^+		254.8	254.7	254.6	254.7	255.0	255.1	255.3	255.1	255.6	255.9	256.7	256.1	
		NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX		
Cl^-		377.8	378.3	380.7	378.9	377.6	378.4	380.8	378.9	377.4	378.5	381.1	379.0	
Br^-		344.4	344.9	347.3	345.5	344.7	345.5	347.9	346.0	345.2	346.3	348.9	346.8	
I^-		300.3	300.8	303.2	301.4	301.1	301.9	304.3	302.4	302.7	303.8	306.4	304.3	

333.15K	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	MCl	MBr	MeI	Average value	MCl	MBr	MI	Average value
Na^+	399.0	398.7	398.5	398.7	399.2	399.1	399.1	399.1	399.7	399.7	400.3	399.9	400.3	400.6	402.0	401.0
K^+	314.9	314.8	314.6	314.8	315.2	315.1	315.2	315.2	315.6	315.7	316.3	315.9	316.2	316.5	317.9	316.9
Cs^+	255.8	255.7	255.7	255.8	256.0	256.1	256.3	256.1	256.5	256.7	257.4	256.9	257.2	257.6	259.0	257.9
	NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX	
Cl^-	378.6	379.6	382.0	380.1	378.7	379.7	382.3	380.2	378.8	379.9	382.7	380.5	378.9	380.3	383.4	380.9
Br^-	345.4	346.4	348.8	346.9	345.7	346.7	349.3	347.2	346.1	347.2	350.0	347.8	346.5	347.9	351.0	348.5
I^-	301.2	302.2	304.6	302.7	301.9	302.9	305.5	303.4	303.2	304.3	307.1	304.9	305.1	306.5	309.6	307.1
348.15 K	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value	MCl	MBr	MI	Average value
Na^+	399.6	399.4	399.3	399.4	399.8	399.7	399.9	399.8	400.1	400.2	401.0	400.4	400.6	400.9	402.4	401.3
K^+	315.7	315.5	315.5	315.6	315.9	315.8	316.1	315.9	316.2	316.3	317.1	316.5	316.7	316.9	318.4	317.3
Cs^+	256.4	256.4	256.5	256.4	256.6	256.7	257.0	256.8	256.9	257.1	258.0	257.3	257.6	257.9	259.4	258.3
	NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX		NaX	KX	CsX	
Cl^-	379.2	380.4	382.8	380.8	379.2	380.6	383.0	380.9	379.1	380.7	383.2	381.0	379.3	380.9	383.9	381.4
Br^-	346.0	347.2	349.6	347.6	346.1	347.5	349.9	347.8	346.4	348.0	350.5	348.3	346.8	348.4	351.4	348.9
I^-	301.9	303.1	305.5	303.5	302.5	303.9	306.3	304.2	303.8	305.4	307.9	305.7	305.5	307.1	310.1	307.6

In this study the ionic enthalpies of solvation in water-acetamide mixtures were calculated on the assumption [8]

$$\Delta H^{\ominus\,\mathrm{cat}}_{\mathrm{s(w)}}/\Delta H^{\ominus\,\mathrm{an}}_{\mathrm{s(w)}} = \Delta H^{\ominus\,\mathrm{cat}}_{\mathrm{s(ms)}}/\Delta H^{\ominus\,\mathrm{an}}_{\mathrm{s(ms)}} \tag{3}$$

where $\Delta H^{\ominus\,\mathrm{cat}}_{\mathrm{s(w)}}/\Delta H^{\ominus\,\mathrm{an}}_{\mathrm{s(w)}}$ and $\Delta H^{\ominus\,\mathrm{cat}}_{\mathrm{s(ms)}}/\Delta H^{\ominus\,\mathrm{an}}_{\mathrm{s(ms)}}$ are the enthalpies of solvation at infinite dilution of cation/anion in water (w) and in the mixed solvent (ms), respectively.

The values of the ionic enthalpies of solvation in water in the range 298.15–348.15 K are taken from the literature [9]. Table 3 lists the enthalpies of solvation of alkali and halide ions in water–acetamide mixtures. Notice that the ionic enthalpies of solvation increase as abs. values with increasing contents of $\mathrm{AcNH_2}$ in the mixture. This effect is smallest for the $\mathrm{Cl^-}$ ion. It can indicate a stronger ion–solvent interaction in water–acetamide mixtures than those in water. Similarly values of $\Delta H^{\ominus}_{\mathrm{s(ion)}}$ increase as abs. values with increasing temperature. As can be seen from Table 3 the effect of acetamide and temperature on the ionic enthalpies of solvation increases with increasing radius of ion as well as for cations and anions. On the basis of the above observations it may be supposed that on adding $\mathrm{AcNH_2}$ to water the three-dimensional network of H-bonds in water is gradually destroyed, and water–acetamide mixed associates with H-bonds are being formed continuously. A better insight into these questions may be expected from a consideration of the ionic enthalpy of transfer $\Delta H^{\ominus}_{\mathrm{tr(ion)}}$ from water to water–acetamide mixtures. The $\Delta H^{\ominus}_{\mathrm{tr(ion)}}$-values are obtained, by difference, from the relation

$$\Delta H^{\ominus}_{\mathrm{tr(ion)}} = \Delta H^{\ominus}_{\mathrm{s(ion)(ms)}} - \Delta H^{\ominus}_{\mathrm{s(ion)(w)}} \tag{4}$$

where $\Delta H^{\ominus}_{\mathrm{s(ion)(ms)}}$ and $\Delta H^{\ominus}_{\mathrm{s(ion)(w)}}$ are the enthalpies of solvation at infinite dilution of a given ion in the mixed solvent (ms) and in water (w), respectively. The changes observed in $\Delta H^{\ominus}_{\mathrm{tr(ion)}}$ can be explained on the basis of different structural behaviour of ions. It can be assumed that there are two contributions to $\Delta H^{\ominus}_{\mathrm{tr(ion)}}$

$$\Delta H^{\ominus}_{\mathrm{tr(ion)}} = \Delta H^{\ominus}_{\mathrm{tr(el)}} + \Delta H^{\ominus}_{\mathrm{tr(str)}} \tag{5}$$

where $\Delta H^{\ominus}_{\mathrm{tr(el)}}$ derives largely from the coulombic interaction between the ionic charge and the charge distributions on the solvent molecule and $\Delta H^{\ominus}_{\mathrm{tr(str)}}$ derives from the effect of an ion on the structure of the solvent. The solvent molecules in the region of dielectric saturation are strongly held by the ion and may be expected to contribute little to any variation of $\Delta H^{\ominus}_{\mathrm{tr(el)}}$ with increasing acetamide content and temperature. Therefore, it may be expected that

$$\Delta H_{\mathrm{tr(ion)}} \approx \Delta H^{\ominus}_{\mathrm{s(str)(ms)}} - \Delta H^{\ominus}_{\mathrm{s(str)(w)}} \tag{6}$$

where $\Delta H^{\ominus}_{\mathrm{s(str)(ms)}}$ and $\Delta H_{\mathrm{s(str)(w)}}$ are the structural contributions to $\Delta H^{\ominus}_{\mathrm{s(ion)}}$

in mixed solvent (ms) and water (w), respectively. It is known that an ion in solution is surrounded by one or more centrosymmetrically orientated shells of solvent molecules (region A). Region A is in turn surrounded by a region of collapse of solvent structure (region B). In region A, a structure-making process has taken place, tending to lower the structural enthalpy, and in region B a structure-breaking process has taken place, tending to increase the structural enthalpy. On transferring ions from a three-dimensional structure (water) to a water–acetamide mixture in which this structure has partially disappeared, the structure-breaking enthalpy will be lost. This is greater for larger ions, hence this effect will be such as to make $\Delta H^{\ominus}_{\mathrm{tr(str)}}$ most negative for the largest ion in a series. (a) Any steric hindrance to the

TABLE 4

Ionic enthalpy of transfer $\Delta H^{\ominus}_{\mathrm{tr(ion)}}$ for alkali-metal and halide ions in water–acetamide mixtures (kJ mol^{-1})

Ion	$x = 0.0510$	$x = 0.1155$	$x = 0.2336$	$x = 0.4155$
298.15 K				
Na^+	0.1	0.5	1.4	–
K^+	0.3	0.9	1.9	–
Cs^+	1.6	2.3	3.6	–
Cl^-	1.4	1.5	1.8	–
Br^-	0.4	1.1	2.6	–
I^-	0.8	1.7	3.6	–
313.15 K				
Na^+	0.3	0.7	1.4	–
K^+	0.4	0.9	1.9	–
Cs^+	0.4	0.8	1.8	–
Cl^-	0.0	0.0	0.1	–
Br^-	0.4	0.9	1.7	–
I^-	0.7	1.7	3.6	–
333.15 K				
Na^+	0.3	0.7	1.5	2.6
K^+	0.3	0.7	1.4	2.4
Cs^+	0.3	0.7	1.5	2.5
Cl^-	0.1	0.2	0.5	0.9
Br^-	0.2	0.5	1.1	1.8
I^-	0.7	1.4	1.9	5.1
348.15 K				
Na^+	0.1	0.3	0.9	1.8
K^+	0.3	0.6	1.2	2.0
Cs^+	0.3	0.7	1.2	2.2
Cl^-	0.1	0.2	0.3	0.7
Br^-	0.3	0.5	1.0	1.6
I^-	0.7	1.4	2.9	4.8

solvation of the smaller ions by acetamide molecules will also tend to cause $\Delta H^{\ominus}_{tr(str)}$ to decrease as ionic radius increases. (b) All ions should make more centrosymmetric structures in water–acetamide mixtures than in water. (c) The biggest increase in structure-making should be shown by the smallest ion, hence this effect would make $\Delta H^{\ominus}_{tr(str)}$ decrease as ionic radius decreases. The total dependence of $\Delta H^{\ominus}_{tr(ion)}$ upon ionic radius arises from a balance between above mentioned effects. It seems that for Cs^+, Br^- and I^- ions effect (a) is the most important. The course of the function $\Delta H^{\ominus}_{tr(ion)} = f(x, T)$ for Na^+ and K^+ ions arises from a balance between effects (b) and (c). In the case of the Cl^- ion, all effects mentioned are probably small and $\Delta H^{\ominus}_{tr(ion)}$ is the smallest. Thus, the variation of $\Delta H^{\ominus}_{tr(ion)}$ with ionic radius is of greater complexity than its variation with solvent composition.

REFERENCES

1 M. Woldan and S. Taniewska-Osińska, Acta Univ. Łódź. Folia Chim., 1 (1982) 3.
2 M. Woldan, Acta Univ. Łódź. Folia Chim., 8 (1988), in press.
3 A. Johanson and F.A. Kolman, J. Am. Chem. Soc., 94 (1972) 8196.
4 M. Woldan, Thermochim. Acta, 94 (1985) 345; 105 (1986) 41; 111 (1987) 175.
5 C.M. Criss and J.W. Cobble, J. Am. Chem. Soc., 83 (1961) 3223.
6 E. Somsen, Recl. Trav. Chim., 85 (1966) 517.
7 S. Taniewska-Osińska and M. Woldan, Acta, Univ. Łódź Folia Chim., 3 (1984) 41.
8 K.P. Mishchenko, Acta Phys. Chim., 3 (1935) 693.
9 G.A. Krestov and W.K. Abrosimov, Izv. Vyshh. Uncheb. Zaved. Khim. Khim. Tekh., 12 (1969) 127.