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ENTHALPIES OF TRANSFER OF ALKALI METAL HALIDES FROM WATER TO WATER–ACETAMIDE MIXTURES

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ABSTRACT

The enthalpies of solutions of NaBr, KCl, KBr and CsI have been determined in water and water–acetamide mixtures at 333.15 K. The standard enthalpies of solution (ΔH^0) of the electrolytes investigated have been evaluated. The corresponding enthalpies of solvation (ΔH_s^0) and transfer (ΔH_{tr}^0) from water to water–acetamide mixed solvents have been calculated. Single ion enthalpies of transfer ($\Delta H^0_{tr(ion)}$) for Na^+, K^+, Cs^+, Cl^-, Br^- and I^- ions have been derived. The dependence of the ionic enthalpy of transfer on the solvent composition, temperature and size and nature of ions is discussed.

INTRODUCTION

The present study is a continuation of thermodynamic investigations on the water–acetamide–electrolyte ternary system. In previous papers [1–3] the enthalpies of solution of some electrolytes in water–acetamide mixtures at 298.15 and 313.15 K have been measured. Here we report the results from measurements of enthalpy of solution for NaBr, KCl, KBr and CsI in water and water–acetamide mixtures at 333.15 K. The present study aims to develop enthalpy of transfer data for alkali halides from water to water–acetamide mixtures at different temperatures. For the reason of lack of literature data the enthalpies of solution for the electrolytes investigated in water at 333.15 K have been also determined.

EXPERIMENTAL

Reagents.

Sodium bromide, KCl and KBr (POCH-Gliwice, p.a.) were recrystallized from deionized doubly-distilled water and dried for one day at 383 K.

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Caesium iodide (BDH, A.R.) was used without further purification and dried under vacuum for one day at 323 K. The salts were stored in a vacuum desiccator. Purification of acetamide was described previously [2]. The mixed solvents used for investigations were prepared by mixing the weighed amounts of acetamide with deionized doubly distilled water.

Calorimetry

The calorimeter and experimental procedure have been described earlier [2]. The calorimeter was placed in a thermostated water bath whose accuracy was ca 0.01 K. Two electrical calibrations were made for each run, one before breaking the ampoule and another after. The enthalpies of solution were determined at a series of concentrations covering the range 0.01–0.2 mol kg^{-1} in water and four water–acetamide mixtures. All enthalpies of solution were determined in triplicate, and only the average values are reported. The total uncertainty of ΔH_m is about $\pm 0.5\%$. All measurements were made at 333.15 ± 0.01 K.

RESULTS

The results of the measurements of the integral enthalpies of solution in water and water–acetamide mixtures are given in Tables 1–5. The plots $\Delta H_m = f(\sqrt{m})$ were found to be linear within experimental error and they have been extrapolated to zero concentration for evaluation of the standard

TABLE 1

Enthalpy of solution, ΔH_m, of some alkali halides in water at 333.15 K

NaBr		KCl		KBr		CsI	
m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
0.0144	4.60	0.0091	12.82	0.0082	14.81	0.0096	27.74
0.0251	4.52	0.0163	12.86	0.0144	14.87	0.0153	27.71
0.0355	4.48	0.0257	12.89	0.0216	14.95	0.0232	27.70
0.0449	4.39	0.0362	12.93	0.0339	15.01	0.0374	27.69
0.0544	4.35	0.0502	12.97	0.0498	15.10	0.0503	27.68
0.0660	4.31	0.0656	12.98	0.0647	15.19	0.0642	27.66
0.0755	4.27	0.0833	13.01	0.0809	15.27	0.0811	27.66
0.0904	4.25	0.1004	13.05	0.1003	15.36	0.1006	27.65
0.1120	4.20	0.1243	13.10	0.1209	15.41	0.1362	27.62
0.1361	4.14	0.1511	13.14	0.1431	15.52	0.1604	27.60
0.1540	4.10	–	–	0.1605	15.59	–	–

TABLE 2

Enthalpy of solution, ΔH_m, of NaBr in water–acetamide mixtures at 333.15 K

Mole fraction of acetamide in mixed solvent							
0.0510		0.1155		0.2326		0.4155	
m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})
0.0141	4.96	0.0143	5.68	0.0140	6.88	0.0138	8.45
0.0248	4.88	0.0243	5.58	0.0248	6.80	0.0247	8.37
0.0350	4.84	0.0348	5.55	0.0344	6.76	0.0345	8.33
0.0452	4.75	0.0460	5.47	0.0461	6.69	0.0457	8.29
0.0546	4.71	0.0539	5.44	0.0539	6.65	0.0542	8.25
0.0653	4.67	0.0650	5.40	0.0642	6.60	0.0647	8.22
0.0752	4.61	0.0748	5.35	0.0750	6.56	0.0751	8.19
0.0907	4.54	0.0913	5.30	0.0909	6.50	0.0912	8.14
0.1135	4.53	0.1138	5.26	0.1110	6.44	0.1125	8.10
0.1347	4.50	0.1352	5.21	0.1335	6.41	0.1340	8.07
0.1560	4.41	0.1558	5.16	0.1517	6.35	0.1532	8.04
0.1795	4.33	0.1780	5.08	0.1788	6.28	0.1786	7.98

enthalpies of solution (ΔH^0). The lack of necessary data makes it impossible to calculate ΔH^0 by the Criss–Cobble method [4]. The values obtained for the standard enthalpies of solution of the electrolytes investigated at 333.15 K are given in Table 6. The enthalpies of solvation (ΔH_s^0) for the electrolytes have been calculated from the standard enthalpies of solution

TABLE 3

Enthalpy of solution, ΔH_m, of KCl in water–acetamide mixtures at 333.15 K

Mole fraction of acetamide in mixed solvent							
0.0510		0.1155		0.2336		0.4155	
m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
0.0097	12.48	0.0096	12.01	0.0095	11.07	0.0093	9.65
0.0172	12.55	0.0168	12.06	0.0159	11.13	0.0153	9.71
0.0273	12.60	0.0270	12.13	0.0268	11.21	0.0264	9.79
0.0380	12.63	0.0391	12.18	0.0385	11.26	0.0372	9.83
0.0513	12.68	0.0520	12.22	0.0518	11.30	0.0517	9.90
0.0661	12.75	0.0672	12.29	0.0669	11.38	0.0664	9.96
0.0846	12.80	0.0844	12.34	0.0840	11.43	0.0837	10.02
0.1013	12.84	0.1020	12.39	0.1021	11.48	0.1012	10.07
0.1251	12.89	0.1229	12.45	0.1222	11.54	0.1220	10.13
0.1503	12.95	0.1498	12.51	0.1505	11.60	0.1501	10.21

TABLE 4

Enthalpy of solution, ΔH_m, of KBr in water–acetamide mixtures at 333.15 K

Mole fraction of acetamide in mixed solvent							
0.0510		0.1155		0.2336		0.4155	
m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
0.0084	14.27	0.0085	13.56	0.0079	12.37	0.0081	10.60
0.0135	14.32	0.0139	13.63	0.0129	12.41	0.0132	10.63
0.0222	14.38	0.0234	13.66	0.0230	12.44	0.0245	10.68
0.0345	14.43	0.0358	13.73	0.0356	12.52	0.0352	10.71
0.0501	14.52	0.0495	13.81	0.0498	12.56	0.0501	10.75
0.0652	14.57	0.0647	13.86	0.0644	12.62	0.0650	10.79
0.0812	14.64	0.0809	13.90	0.0812	12.66	0.0816	10.83
0.1007	14.69	0.1011	13.98	0.1006	12.72	0.1007	10.86
0.1212	14.73	0.1205	14.02	0.1203	12.77	0.1217	10.89
0.1418	14.81	0.1411	14.11	0.1405	12.81	0.1417	10.92
0.1610	14.85	0.1602	14.15	0.1598	12.85	0.1604	10.94
0.1827	14.90	0.1820	14.17	0.1806	12.88	0.1813	10.97

(ΔH^0) and lattice entalpy (ΔH_{cryst}) using the relation

$$-\Delta H_s^0 = \Delta H_{cryst} - \Delta H^0 \tag{1}$$

The lattice enthalpies of the alkali halides are taken from the literature [5]. It is known that the enthalpy of solvation of the electrolyte is summed from the individual values of the ions. Hence, from values of ΔH_s^0 obtained for

TABLE 5

Enthalpy of solution, ΔH_m, of CsI in water–acetamide mixtures at 333.15 K

Mole fraction of acetamide in mixed solvent							
0.0510		0.1155		0.2336		0.4155	
m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
0.0093	26.69	0.0089	25.42	0.0088	23.03	0.0083	19.55
0.0162	26.68	0.0158	25.43	0.0154	23.04	0.0150	19.55
0.0240	26.67	0.0250	25.43	0.0249	23.05	0.0237	19.56
0.0377	26.67	0.0368	25.43	0.0364	23.05	0.0363	19.57
0.0511	26.66	0.0515	25.43	0.0517	23.06	0.0516	19.57
0.0660	26.66	0.0653	25.44	0.0656	23.07	0.0648	19.58
0.0822	26.65	0.0834	25.45	0.0831	23.08	0.0836	19.59
0.1035	26.65	0.1032	25.45	0.1027	23.07	0.1038	19.59
0.1337	26.65	0.1325	25.44	0.1322	23.05	0.1341	19.57
0.1599	26.64	0.1611	25.41	0.1603	23.02	0.1588	19.54

TABLE 6

The standard enthalpy of solution, ΔH^0, for some alkali halides in water–acetamide mixtures at 333.15 K (kJ mol^{-1})

Salt	Mole fraction of acetamide in mixed solvent				
	0.0000	0.0510	0.1155	0.2336	0.4155
NaCl	0.4	0.1	−0.4	−1.3	−2.5
NaBr	−4.8±0.1	−5.2±0.1	−5.9±0.1	−7.1±0.1	−8.6±0.1
NaI [a]	−10.7±0.2	−11.6±0.2	−12.7±0.2	−14.8±0.2	−17.8±0.2
KCl	12.7±0.2	12.3±0.2	11.8±0.2	10.9±0.2	9.5±0.2
KBr	14.6±0.2	14.1±0.2	13.4±0.2	12.2±0.2	10.5±0.2
KI	16.2	15.2	14.1	12.0	8.8
CsCl	12.2	11.7	11.0	9.8	8.1
CsBr	19.5	18.9	18.0	16.5	14.5
CsI	27.8±0.3	26.7±0.3	25.4±0.3	23.0±0.3	19.5±0.3

[a] From ref. 1.

the salts investigated it is possible to calculate the values of the enthalpies of solvation of some non-investigated salts. Thus

$$\Delta H^0_{s(NaCl)} = \Delta H^0_{s(NaBr)} + \Delta H^0_{s(KCl)} - \Delta H^0_{s(KBr)}$$

$$\Delta H^0_{s(KI)} = \Delta H^0_{s(KBr)} + \Delta H^0_{s(NaI)} - \Delta H^0_{s(NaBr)}$$

$$\Delta H^0_{s(CsCl)} = \Delta H^0_{s(CsI)} + \Delta H^0_{s(NaCl)} - \Delta H^0_{s(NaI)}$$

$$\Delta H^0_{s(CsBr)} = \Delta H^0_{s(CsI)} + \Delta H^0_{s(NaBr)} - \Delta H^0_{s(NaI)} \qquad (2)$$

The values of ΔH^0_s for NaI in water and water–acetamide mixtures are taken from the literature [1]. Finally, Table 7 lists the enthalpies of solvation of alkali halides both in water and water–acetamide mixtures at 333.15 K.

TABLE 7

The enthalpy of solvation, $-\Delta H^0_s$, for some alkali halides in water–acetamide mixtures at 333.15 K (kJ mol^{-1})

Salt	Mole fraction of acetamide in mixed solvent				
	0.0000	0.0510	0.1155	0.2336	0.4155
NaCl	777.0	777.3	777.8	778.7	779.9
NaBr	743.7	744.1	744.8	746.0	747.5
NaI	699.0	699.9	701.0	703.1	706.1
KCl	694.0	694.4	694.9	695.8	697.2
KBr	660.7	661.2	661.9	663.1	664.8
KI	616.0	617.0	618.1	620.2	623.4
CsCl	637.2	637.7	638.4	639.6	641.3
CsBr	603.9	604.5	605.4	606.9	608.9
CsI	559.2	560.3	561.6	564.0	567.5

From values of ΔH_s^0 for NaCl, KI, CsCl and CsBr it is possible to calculate in accordance with eqn. (1) the values of standard enthalpies of solution of these salts. The values of ΔH^0 for NaCl, KI, CsCl and CsBr calculated in this way are also included in Table 6.

DISCUSSION

In the studies of ion–solvent interactions, it is essential to consider the system at infinite dilution eliminating the effect of ion–ion interactions. Therefore we shall discuss the present results further on the basis of estimated standard enthalpies of solution. From Table 6 it can be seen that the standard enthalpies of solution of alkali halides in water–acetamide mixtures are more exothermic as the acetamide content in the mixed solvent increases. It can indicate a stronger interaction of the electrolyte with the water–acetamide mixtures than those in water.

Moreover, the plots of ΔH° against mole fraction of acetamide in the mixed solvent show that the enthalpy of solution at infinite dilution of alkali halides in water–acetamide mixtures is proportional to the mole fraction of acetamide. Therefore, one can draw the conclusion that the interactions between water and acetamide molecules are probably very weak. It may be supposed that on adding $AcNH_2$ to water the three-dimensional network of H-bonds in water is gradually destroyed and water–amide mixed associates with H-bonds are being formed continuously. It seems that the enthalpy of transfer (ΔH_{tr}^0) better reflects the interactions water–acetamide–electrolyte. By difference, the ΔH_{tr}^0 values are obtained from the relation

$$\Delta H_{tr}^0 = \Delta H_{ms}^0 - \Delta H_w^0 \qquad (3)$$

where ΔH_{ms}^0 and ΔH_w^0 are the enthalpies of solution at infinite dilution of a given electrolyte in the mixed solvent, ms, and in water, w, respectively. The plots of ΔH_{tr}^0 against mole fraction of acetamide (x) show that ΔH_{tr}^0 may be expressed by the equation

$$\Delta H_{tr}^0 = a x_{AcNH_2} \qquad (4)$$

The numerical values for coefficient a are given in Table 8. For comparison, the values of a at 298.15 and 313.15 K from literature data [3] are also included in this table. Coefficient a may be regarded as some measure of the effect of acetamide on the ion–water interactions. As can be seen from Table 8, for both cations and anions, the absolute value of a increases with increasing ionic radius. From this it follows that the effect of acetamide on the ion–water interactions is the greatest for CsI and smallest for NaCl. This behaviour of alkali halides can be explained in terms of different structure-breaking and structure-making effects of ions on the structure of water and water–acetamide mixtures. It is readily observed that transfer parameter

TABLE 8

Transfer parameter, a, for alkali halides from water to water–acetamide mixtures

Salt	$-a$ (kJ mol^{-1})		
	298.15 K	313.15 K	333.15 K
NaCl	5.5 ± 0.5	4.0 ± 0.5	6.5 ± 0.5
NaBr	13 ± 1	11 ± 1	9 ± 1
NaI	19 ± 1	18 ± 1	17 ± 1
KCl	9.5 ± 1	9 ± 1	7.5 ± 1
KBr	18 ± 2	16 ± 1	10 ± 1
KI	24 ± 2	23 ± 2	18 ± 1
CsCl	20 ± 2	11 ± 1	10 ± 1
CsBr	29 ± 3	17 ± 2	12 ± 1
CsI	32 ± 3	25 ± 2	20 ± 2

decreases (except NaCl) with increasing temperature. It seems that it is caused by disordering of solvent structure by stronger thermal motions of molecules. On the other hand, the enthalpy of transfer eliminates the crystal term and measures the contributions from individual ions at infinite dilution:

$$\Delta H^0_{\mathrm{tr(MX)}} = \Delta H^0_{\mathrm{tr(M^+)}} + \Delta H^0_{\mathrm{tr(X^-)}} \tag{5}$$

Wu and Friedman [6] deduced the individual ionic transfer values from an extra thermodynamic assumption by putting

$$\Delta H^0_{\mathrm{tr(Cs^+)}} = \Delta H^0_{\mathrm{tr(I^-)}} = \tfrac{1}{2}\,\Delta H^0_{\mathrm{tr(CsI)}} \tag{6}$$

By following the same procedure, the individual ionic values calculated are presented in Figs. 1 and 2. As can be seen from Fig. 1, the absolute negative ionic enthalpy of transfer increases with increase in the content of acetamide in the mixed solvent. The effect of acetamide is smallest for $\mathrm{Cl^-}$ and largest for $\mathrm{Cs^+}$ and $\mathrm{I^-}$. The influence of temperature on $\Delta H^0_{\mathrm{tr(ion)}}$ increases with increasing content of acetamide in the mixture (see Fig. 2). The plots of $\Delta H^0_{\mathrm{tr(ion)}}$ against reciprocal of ionic radius show that cations give a parabolic variation, whereas anions vary linearly and sharply. The ionic enthalpy of transfer can be calculated from the Born equation [7], but it has been found that the predicted values differ significantly from the experimental ones as observed in other systems studied previously [8–12].

The observed changes in $\Delta H^0_{\mathrm{tr(ion)}}$ can be explained on the basis of different structural behaviour of cations and anions. It can be assumed that the enthalpy of transfer depends on the difference between electrical and structural enthalpy effects in mixed solvent and water. The electrical enthalpy of transfer is compared with the change in enthalpy which will take place in the primary solvation sheath and would primarily be governed by the ion–dipole interaction, which decreases with increase in ionic radii. In water–amide mixtures, a cation will interact more strongly with the solvent

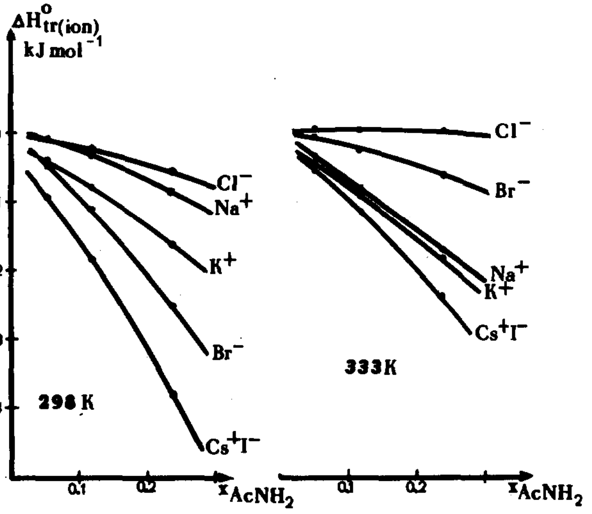

Fig. 1. The ionic enthalpy of transfer in water–acetamide mixtures as a function of mole fraction of acetamide.

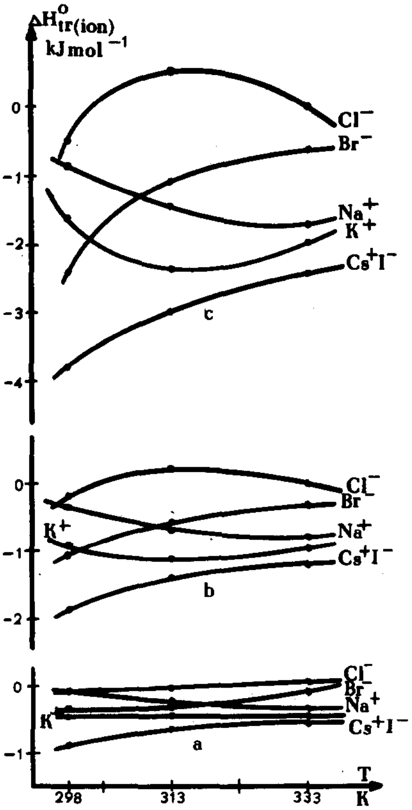

Fig. 2. The ionic enthalpy of transfer in water–acetamide mixtures as a function of temperature: (a) 5.10 mol% of $AcNH_2$; (b) 11.55 mol% of $AcNH_2$; (c) 23.36 mol% of $AcNH_2$.

molecules and an anion would interact weaker than in pure water [13,14]. Consequently the electrical enthalpy of transfer for a cation will be negative (exothermic) and for an anion positive. Outside the primary solvation sheath, the centrosymmetric structure imposed by the ion is not compatible with the normal solvent structure. If the structure of mixed solvent is less ordered than the structure of pure water, all ions would be able to create more order in the secondary solvation sheath in the mixture than in pure water. The enthalpy of transfer due to this effect would be negative (exothermic) and would increase with increasing size of ions because of the ability to accomodate more of the solvent molecules by the larger ions. This effect may be called the structural enthalpy. For cations the electrical enthalpy of transfer becomes less negative and the structural enthalpy becomes more negative as the radius of the ion increases. The addition of acetamide to water probably causes the increase of the electrical enthalpy of transfer and the decrease of structural transfer enthalpy for cations. The structural transfer enthalpy becomes less negative with increasing temperature and electrical enthalpy becomes more negative. Hence, the ionic enthalpy of transfer for Na^+ decreases (more negative) with increasing temperature and for Cs^+, increases. The balance between the two effects produces a minimum in the case of K^+. For the mixture containing more acetamide the effect of temperature is stronger. For anions, the electric and structural transfer enthalpy increase with increasing ions radius. The balance between the changes of these two effects with increasing temperature produces a maximum of $\Delta H^0_{\mathrm{tr(ion)}}$ in the case of Cl^-. Unfortunately the lack of necessary data over a wider range of temperature makes it impossible to compare water–acetamide mixtures with other mixed solvents.

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