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ENTHALPY OF SOLUTION OF SOME ELECTROLYTES IN WATER–ACETAMIDE MIXTURES AT 313.15 K

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ABSTRACT

The enthalpies of solution of NaCl, KCl, KBr, KNO_3 and CsI have been measured in water and mixtures of acetamide with water at 313.15 K in the miscibility range. The standard enthalpies of solution (ΔH^0) of the investigated electrolytes have been evaluated. The corresponding enthalpies of solvation (ΔH_s^0) and enthalpies of transfer (ΔH_t^0) from water to water–acetamide mixtures have been calculated. The dependence of the standard enthalpies of solution and enthalpies of transfer of the investigated electrolytes on the solvent composition is discussed.

INTRODUCTION

Much interest has been shown recently in the study of mixed aqueous solvents. In particular, we have been involved in systematic thermodynamic investigations of the water–acetamide mixtures. In a previous paper [1], the enthalpies of solution of some electrolytes in binary mixtures of acetamide and water in the miscibility range at 298.15 K have been measured. In this study we have examined the effect of acetamide concentration and the effect of size and nature of the electrolyte on the enthalpy of transfer from water to water–acetamide mixtures at 313.15 K. For this purpose the enthalpies of solution of NaCl, KCl, KBr, KNO_3 and CsI were measured in water and water–acetamide mixed solvents containing 15, 30 and 50% by weight of acetamide in water at 313.15 K.

EXPERIMENTAL

Acetamide (Xenon, A.R.) was recrystallized from methanol and dried under vacuum for 10 h at 313 K. The melting point of acetamide was 353–354 K which is in accordance with literature data [2,3]. Analytically pure NaCl, KCl and KBr (POCH, Gliwice) were recrystallized from

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double-distilled water and dried for a day at 383 K. Laboratory grade CsI (BDH, England) was used without further purification and dried under vacuum for 10 h at 323 K. The mixed solvents used for investigations were prepared by weighing using double-distilled water and acetamide. The procedure of measurements of the enthalpy of solution was described previously [1].

The calorimeter was placed in a thermostatted water bath whose accuracy was ca. 5×10^{-3} K. The enthalpies of solution were determined at a series of concentrations covering the range 0.01–0.2 mol kg^{-1} in water and mixtures containing 15, 30 and 50% by weight of acetamide in water, respectively. In general, two or more determinations were made for a particular concentration and the results were averaged. The total uncertainty of ΔH_m is about $\pm 0.5\%$. All measurements were made at 313.15 ± 0.01 K.

RESULTS

The results of the measurements of the integral enthalpies of solution in water and water–acetamide mixed solvents are given in Tables 1–5. The lack of the necessary data makes it impossible to calculate the standard enthalpies of solution (ΔH^0) by the Criss–Cobble method [4]. However, within the experimental error the integral enthalpies of solution show a linear dependence on the square root of the molality and they have been extrapolated to zero concentration for evaluation of the standard enthalpies of solution (ΔH^0) of the investigated electrolytes. The obtained values of the standard enthalpies of solution of the investigated electrolytes in water and

TABLE 1

The enthalpies of solution, ΔH_m, of NaCl in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

m (mol kg^{-1})	Water	m (mol kg^{-1})	15 wt% (5.10 mol%) $AcNH_2$	m (mol kg^{-1})	30 wt% (11.55 mol%) $AcNH_2$	m (mol kg^{-1})	50 wt% (23.36 mol%) $AcNH_2$
0.0278	2.22	0.0266	2.03	0.0274	1.81	0.0303	1.37
0.0392	2.29	0.0387	2.10	0.0365	1.85	0.0410	1.44
0.0518	2.32	0.0527	2.13	0.0505	1.90	0.0544	1.48
0.0676	2.37	0.0644	2.18	0.0641	1.95	0.0680	1.52
0.0855	2.40	0.0846	2.23	0.0798	1.97	0.0804	1.57
0.1010	2.44	0.0999	2.28	0.0945	2.01	0.0991	1.60
0.1207	2.48	0.1213	2.31	0.1178	2.05	0.1209	1.66
0.1501	2.53	0.1497	2.37	0.1485	2.11	0.1507	1.71
0.1699	2.57	0.1703	2.41	0.1671	2.16	0.1695	1.74
0.1877	2.60	0.1921	2.45	0.1882	2.19	0.1901	1.78

TABLE 2

The enthalpies of solution, ΔH_m, of KCl in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

m (mol kg^{-1})	Water	m (mol kg^{-1})	15 wt% (5.10 mol%) $AcNH_2$	m (mol kg^{-1})	30 wt% (11.55 mol%) $AcNH_2$	m (mol kg^{-1})	50 wt% (23.36 mol%) $AcNH_2$
0.0098	15.40	0.0093	15.00	0.0089	14.43	0.0097	13.34
0.0191	15.44	0.0187	15.05	0.0175	14.49	0.0181	13.41
0.0307	15.47	0.0301	15.09	0.0290	14.56	0.0292	13.46
0.0502	15.53	0.0498	15.16	0.0475	14.64	0.0483	13.55
0.0698	15.57	0.0687	15.21	0.0680	14.72	0.0691	13.62
0.0877	15.59	0.0885	15.26	0.0891	14.79	0.0885	13.68
0.1074	15.61	0.1049	15.29	0.1057	14.83	0.1077	13.73
0.1285	15.63	0.1289	15.33	0.1273	14.87	0.1286	13.77
0.1502	15.67	0.1498	15.38	0.1483	14.92	0.1497	13.83
0.1732	15.70	0.1712	15.41	0.1699	14.96	0.1702	13.87
0.1994	15.72	0.1965	15.44	0.1911	15.04	0.1938	13.92

water–acetamide mixtures are given in Table 6 and they are presented as a function $\Delta H^0 = f(x_{AcNH_2})$ in Fig. 1. The enthalpies of solvation (ΔH_s^0) for all the investigated electrolytes have been calculated from the standard enthalpies of solution (ΔH^0) and lattice enthalpy (ΔH_{cryst}) using the relation

$$-\Delta H_s^0 = \Delta H_{cryst} - \Delta H^0 \qquad (1)$$

The lattice enthalpy of the alkali halides are taken from the literature [5],

TABLE 3

The enthalpies of solution, ΔH_m, of KBr in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

m (mol kg^{-1})	Water	m (mol kg^{-1})	15 wt% (5.10 mol%) $AcNH_2$	m (mol kg^{-1})	30 wt% (11.55 mol%) $AcNH_2$	m (mol kg^{-1})	50 wt% (23.36 mol%) $AcNH_2$
0.0102	17.84	0.0104	16.98	0.0103	15.95	0.0099	14.14
0.0205	17.88	0.0212	17.02	0.0207	16.01	0.0202	14.20
0.0317	17.90	0.0313	17.06	0.0319	16.06	0.0303	14.25
0.0421	17.95	0.0431	17.10	0.0425	16.11	0.0424	14.30
0.0582	17.98	0.0577	17.14	0.0568	16.15	0.0555	14.35
0.0722	18.01	0.0726	17.17	0.0731	16.20	0.0741	14.40
0.0932	18.04	0.0942	17.22	0.0935	16.24	0.0918	14.46
0.1115	18.06	0.1108	17.24	0.1102	16.26	0.1099	14.50
0.1349	18.10	0.1363	17.29	0.1341	16.32	0.1355	14.56
0.1568	18.13	0.1555	17.31	0.1526	16.35	0.1537	14.59
0.1732	18.15	0.1747	17.34	0.1742	16.38	0.1751	14.63
0.1941	18.17	0.1950	17.38	0.1933	16.41	0.1938	14.67

TABLE 4

The enthalpies of solution, ΔH_m, of KNO_3 in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

m (mol kg^{-1})	Water	m (mol kg^{-1})	15 wt% (5.10 mol%) $AcNH_2$	m (mol kg^{-1})	30 wt% (11.55 mol%) $AcNH_2$	m (mol kg^{-1})	50 wt% (23.36 mol%) $AcNH_2$
0.0071	33.17	0.0070	32.27	0.0073	31.20	0.0068	29.49
0.0102	33.20	0.0104	32.30	0.0101	31.20	0.0099	29.50
0.0155	33.23	0.0147	32.32	0.0154	31.21	0.0163	29.55
0.0190	33.25	0.0180	32.34	0.0189	31.22	0.0202	29.57
0.0239	33.27	0.0235	32.35	0.0250	31.23	0.0270	29.60
0.0362	33.31	0.0340	32.37	0.0339	31.24	0.0385	29.63
0.0482	33.29	0.0501	32.40	0.0504	31.25	0.0520	29.65
0.0706	33.23	0.0703	32.40	0.0712	31.25	0.0730	29.62
0.0945	33.17	0.0936	32.37	0.0909	31.20	0.0942	29.60
0.1135	33.10	0.1122	32.33	0.1107	31.15	0.1119	29.57
0.1412	33.00	0.1383	32.30	0.1370	31.10	0.1377	29.51
0.1677	32.95	0.1608	32.25	0.1615	31.06	0.1629	29.45

however, the value of ΔH_{cryst} for KNO_3 was calculated from Krestov and Zverev's data [6]. The values of the enthalpies of solvation of the investigated electrolytes calculated in accordance with eqn. (1) both in water and water–acetamide mixtures are given in Table 7. Using the values of ΔH^0 or ΔH_s^0 of the investigated electrolytes in water and water–acetamide mixtures

TABLE 5

The enthalpies of solution, ΔH_m, of CsI in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

m (mol kg^{-1})	Water	m (mol kg^{-1})	15 wt% (5.10 mol%) $AcNH_2$	m (mol kg^{-1})	30 wt% (11.55 mol%) $AcNH_2$	m (mol kg^{-1})	50 wt% (23.36 mol%) $AcNH_2$
0.0068	30.47	0.0061	29.26	0.0064	27.76	0.0066	24.73
0.0099	30.50	0.0095	29.29	0.0098	27.80	0.0101	24.80
0.0169	30.53	0.0164	29.35	0.0167	27.88	0.0172	24.89
0.0204	30.56	0.0211	29.38	0.0212	27.91	0.0221	24.96
0.0305	30.60	0.0299	29.41	0.0303	28.00	0.0312	25.03
0.0468	30.60	0.0403	29.45	0.0404	28.04	0.0403	25.11
0.0590	30.57	0.0576	29.42	0.0563	28.05	0.0570	25.16
0.0731	30.51	0.0711	29.37	0.0707	28.03	0.0703	25.16
0.0906	30.46	0.0902	29.32	0.0906	28.00	0.0908	25.13
0.1147	30.40	0.1125	29.25	0.1111	27.95	0.1103	25.08
0.1385	30.31	0.1331	29.16	0.1407	27.90	0.1416	24.91
0.1617	30.20	0.1607	29.06	0.1625	27.81	0.1670	24.77

TABLE 6

The standard enthalpies of solution, ΔH^0, of some electrolytes in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

Electrolyte	Water	15 wt% (5.10 mol%) $AcNH_2$	30 wt% (11.55 mol%) $AcNH_2$	50 wt% (23.36 mol%) $AcNH_2$
NaCl	2.01 ± 0.05	1.80 ± 0.05	1.59 ± 0.05	1.13 ± 0.05
NaI [7]	-8.9 ± 0.1	-9.8 ± 0.1	-11.0 ± 0.1	-13.3 ± 0.1
KCl	15.3 ± 0.15	14.8 ± 0.15	14.3 ± 0.15	13.2 ± 0.15
KBr	17.7 ± 0.15	16.9 ± 0.15	15.8 ± 0.15	14.0 ± 0.15
KNO_3	33.1 ± 0.3	32.2 ± 0.3	31.2 ± 0.3	29.4 ± 0.3
CsI	30.4 ± 0.3	29.1 ± 0.3	27.6 ± 0.3	24.5 ± 0.3

TABLE 7

The enthalpies of solvation, $-\Delta H_s^0$, of some electrolytes in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

Electrolyte	Water	15 wt% (5.10 mol%) $AcNH_2$	30 wt% (11.55 mol%) $AcNH_2$	50 wt% (23.36 mol%) $AcNH_2$
NaCl	775.4	775.6	775.8	776.3
NaI	697.2	698.1	699.3	701.6
KCl	691.4	691.8	692.4	693.5
KBr	657.6	658.4	659.5	661.3
KNO_3	650.1	651.0	652.0	653.8
CsI	556.6	557.9	559.4	562.5

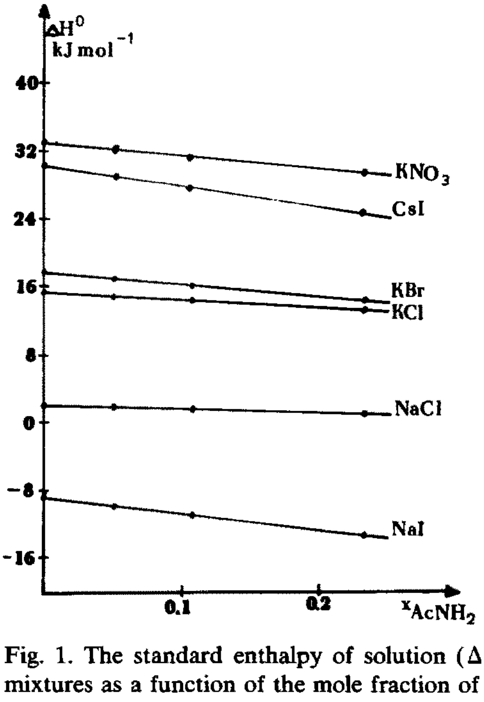

Fig. 1. The standard enthalpy of solution (ΔH^0) of some electrolytes in water–acetamide mixtures as a function of the mole fraction of $AcNH_2$ at 313.15 K.

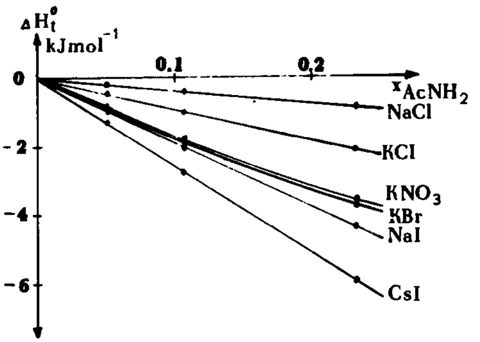

Fig. 2. The enthalpy of transfer (ΔH_t^0) of some electrolytes in water–acetamide mixtures as a function of the mole fraction of $AcNH_2$ at 313.15 K.

the enthalpies of transfer, ΔH_t^0, from water to water–acetamide mixed solvents can be calculated. Thus

$$\Delta H_t^0 = \Delta H^0_{(ms)} - \Delta \mathrm{H}^0_{(w)} = \Delta H^0_{s(ms)} - \Delta \mathrm{H}^0_{s(w)} \tag{2}$$

where $\Delta H^0_{(ms)}(\Delta H^0_{s(ms)})$ and $\Delta H^0_{(w)}(\Delta H^0_{s(w)})$ are the enthalpies of solution (solvation) at infinite dilution of the salt in the mixed solvent, ms, and in water, w, respectively. The dependence of the enthalpies of transfer, ΔH_t^0, of the investigated electrolytes in water–acetamide mixtures on the solvent composition is presented in Fig. 2. It is known that the enthalpy of solvation of the electrolyte at infinite dilution is built up additively from the individual values of the ions. Hence, it is possible to calculate the values of the enthalpies of solvation of non-investigated salts (NaBr, $NaNO_3$, KI, CsCl and CsBr) from the values of ΔH_s^0 obtained for the electrolytes investigated in water–acetamide mixtures. Thus

$$\begin{aligned}
&\Delta H^0_{s(NaBr)} = \Delta H^0_{s(NaCl)} + \Delta H^0_{s(KBr)} - \Delta H^0_{s(KCl)}\\
&\Delta H^0_{s(KI)} = \Delta H^0_{s(KCl)} + \Delta H^0_{s(NaI)} - \Delta H^0_{s(NaCl)}\\
&\Delta H^0_{s(CsCl)} = \Delta H^0_{s(CsI)} + \Delta H^0_{s(NaCl)} - \Delta \mathrm{H}^0_{s(NaI)}\\
&\Delta H^0_{s(CsBr)} = \Delta H^0_{s(CsI)} + \Delta H^0_{s(KBr)} - \Delta H^0_{s(KI)}\\
&\Delta H^0_{s(NaNO_3)} = \Delta H^0_{s(NaCl)} + \Delta H^0_{s(KNO_3)} - \Delta H^0_{s(KCl)}
\end{aligned} \tag{3}$$

From these values of ΔH_s^0 for NaBr, $NaNO_3$, CsCl and CsBr in water–acetamide mixtures and ΔH_{cryst} it is possible to calculate the standard enthalpies of solution of NaBr, $NaNO_3$, KI, CsCl and CsBr in water and water–acetamide mixtures at 313.15 K. The values of the standard enthalpies of solution for NaI in water–acetamide mixtures are taken from the literature [7]. The values of ΔH_s^0 and ΔH^0 calculated in this way for non-investigated salts in water and water–acetamide mixtures are given in Table 8.

TABLE 8

The values of standard enthalpies of solution, ΔH^0, and enthalpies of solvation, ΔH_s^0, for NaBr, $NaNO_3$, KI, CsCl and CsBr calculated from eqns. (3) and (1) in water–acetamide mixtures at 313.15 K (kJ mol^{-1})

Electrolyte	Water		15 wt% (5.10 mol%) $AcNH_2$		30 wt% (11.55 mol%) $AcNH_2$		50 wt% (23.36 mol%) $AcNH_2$	
	ΔH^0	$-\Delta H_s^0$	ΔH^0	$-\Delta H_s^0$	ΔH^0	$-\Delta H_s^0$	ΔH^0	$-\Delta H_s^0$
NaBr	−2.7	741.6	−3.3	742.2	−4.0	742.9	−5.2	744.1
$NaNO_3$	22.9	734.1	22.2	734.8	21.6	735.4	20.2	736.8
KI	19.0	613.2	17.9	614.3	16.3	615.9	13.4	618.8
CsCl	14.6	634.8	14.0	635.4	13.5	635.9	12.2	637.2
CsBr	22.4	601.0	21.4	602.0	20.4	603.0	18.4	605.0

DISCUSSION

As can be seen from Fig. 1 the course of the function $\Delta H^0 = f(x_{AcNH_2})$ of the investigated electrolytes in water–acetamide mixed solvents is linear. It may suggest that the interactions between water and acetamide molecules in the mixed solvent are very weak and that the enthalpy of solution at infinite dilution of the electrolytes is proportional to the mole fraction of acetamide in the mixed solvent. Therefore, one can suppose that the structure of water–acetamide mixtures changes gradually. Moreover, it can be noted (see Table 6) that the standard enthalpies of solution of the electrolytes in water–acetamide mixed solvents are more exothermic as the acetamide content in the mixed solvent increases. These more exothermic enthalpies of solution of the electrolytes in water–acetamide mixtures indicate a stronger interaction of the electrolyte with the mixed solvent than those in water. Moreover, the standard enthalpies of solution of the investigated electrolytes in water- acetamide mixtures at 313.15 K are more exothermic than those at 298.15 K [1]. It may be supposed that the interactions of the electrolyte with the water–acetamide mixed solvent increase with the rise of temperature. The course of the functions $\Delta H^0 = f(x_{AcNH_2})$ are expressed by monotonous curves with no extrema as at 298.15 K. Probably, on adding acetamide to water, the three-dimensional network of H-bonds in water is gradually destroyed and water–amide mixed associates with H-bonds are continuously being formed. It seems that the enthalpy of transfer (ΔH_t^0) is the function which better reflects the influence of acetamide on interaction between dissolved electrolyte and water–acetamide mixed solvent. As is seen from Fig. 2 the values of the enthalpy of transfer for the electrolytes investigated are more exothermic in the water–acetamide mixed solvents than those in water and they increase as the content of acetamide in the mixed solvent rises. The course of the dependence $\Delta H_t^0 = f(x_{AcNH_2})$ is linear and may be expressed by the equation $\Delta H_t^0 = a x_{AcNH_2}$ where x_{AcNH_2} is the mole fraction of acetamide in the mixed solvent. From Fig. 4 the slopes (coefficient "*a*") of these lines can be calculated. They are summarized in Table 9. The values

TABLE 9

Transfer parameter (coefficient "*a*") for some electrolytes from water to water–acetamide mixtures (kJ mol^{-1})

Electrolyte	298.15 K	313.15 K	Electrolyte	298.15 K	313.15 K
NaCl	−5.5 ± 0.5	−4.0 ± 0.5	KBr	−18 ± 2	−16 ± 1
NaBr	−13 ± 1	−11 ± 1	KI	−24 ± 2	−23 ± 2
NaI	−19 ± 1	−18 ± 1	KNO_3	−18 ± 1	−16 ± 1
$NaNO_3$	−15 ± 1	−12 ± 1	CsCl	−20 ± 2	−11 ± 1
KCl	−9.5 ± 1	−9 ± 1	CsBr	−29 ± 3	−17 ± 2
			CsI	−32 ± 3	−25 ± 2

of the coefficient "a" for non-investigated electrolytes were calculated using the values of the standard enthalpy of solution from Table 8. For comparison in Table 9 the values of this coefficient at 298.15 K are also included [1]. The coefficient "a" may be regarded as a measure of the influence of acetamide on the electrolyte–solvent interaction. From the values of coefficient "a" obtained it follows that the influence of acetamide on the interactions between the dissolved electrolyte and mixed solvent rises as the size of the ion grows, and for cations and anions. Therefore, one can draw the conclusion that CsI introduced into water–acetamide mixed solvents strongly disturbs the structure of water–acetamide mixture but NaCl acts only weakly. It is readily observed that the negative values of coefficient "a" decrease with the increase in temperature. From this it follows that the influence of acetamide on the solvent–electrolyte interactions decrease with the increase in temperature. Probably the interactions between water and acetamide decrease with the increase of temperature because of a stronger thermal motion of molecules.

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