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STANDARD ENTHALPIES OF TRANSFER OF ALKALI-METAL AND HALIDE IONS FROM WATER TO WATER–UREA MIXTURES

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ABSTRACT

The enthalpies of solution of NaI and KBr have been measured in four water–urea mixtures at 298.15 K. The standard enthalpies of solution (ΔH°) and solvation (ΔH_s°) of the electrolytes investigated have been evaluated. Single-ion enthalpies of solvation, ΔH_s°(ion), on going from water to water–urea mixtures for alkali-metal and halide ions have been derived. The effect of urea concentration on the ionic enthalpy of transfer has been investigated.

INTRODUCTION

Water–urea mixtures are interesting for several reasons and they have been the subject of many experimental and theoretical investigations. The polarity of urea, its hydrogen-bonding ability and its consequent high solubility in water provide intrinsic points of interest. The dielectric constant of water–urea mixtures does not change very much from that of pure water over a certain concentration range [1]. The importance of urea as a denaturant has led to numerous studies of its aqueous solutions. Considerable attention has been paid to the nature of water–urea mixtures [2–6]. A number of ternary systems, where an electrolyte or nonelectrolyte is added to the water–urea solution, have also been investigated [7–12].

Despite all these studies, however, the nature of the interactions between water and urea is still not fully understood: while urea usually appears to act as a "structure breaker" in ternary systems, there are some cases where its structural effects are not so clear. On the other hand, relatively little work on the thermodynamics of electrolytes dissolved in these solutions has been carried out. The thermodynamics of urea in water–alkali-metal halide mixtures have been studied by Schrier et al. [13], and recently the solvation of alkali-metal chlorides in water–urea mixtures has been reported [7,14,15].

In order to obtain the enthalpy of transfer for single alkali-metal and halide ions on going from water to water–urea mixtures, we have extended

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the thermochemical investigations to solutions of NaI and KBr in these mixtures. In the light of all these data, it is possible to discuss the effect of urea concentration and the effect of the size and nature of an ion on the enthalpy of transfer from water to water–urea mixtures. Since the net effect of ions on the structure of water has already been established, it was felt that such a study might throw some light on the nature of the urea–water interactions.

EXPERIMENTAL

Analytical reagent-grade samples of NaI and KBr were obtained from POCH (Gliwice, Poland). These were purified and dehydrated by the usual methods. AnalaR grade urea (POCH, Gliwice) was recrystallized twice from double-distilled water without heating above 340 K and dried under vacuum at room temperature. The melting point of the urea was 405.8 K, in accordance with literature data [16].

The mixed solvents used in the investigations were prepared by weighing, using double-distilled water and urea. The procedure used to measure the enthalpy of solution has been described previously [17]. The enthalpies of solution were determined at a series of concentrations in the range 0.01–0.15 mol kg^{-1} in four mixtures containing 10, 20, 30 and 40 wt.% urea in water, respectively. All enthalpies of solution were determined in triplicate and only the average values are reported here. The total uncertainty in ΔH_m is about $\pm 0.5\%$. All measurements were carried out in a calorimeter placed in a thermostatted water bath controlled to within ± 0.01 K.

RESULTS

The integral enthalpies of solution (ΔH_m) measured for NaI and KBr in water–urea mixtures are given in Tables 1 and 2. Within experimental error, they show a linear dependence on the square root of the molality and they have been extrapolated to zero concentration to evaluate the standard enthalpies of solution (ΔH°) for the electrolytes under study. The values of ΔH° obtained for NaI and KBr in water–urea mixtures at 298.15 K are given in Table 3: for comparison, literature values [15] of ΔH° for some alkali-metal chlorides are also included. The enthalpies of solvation (ΔH_s°) for alkali halides in water–urea mixtures have been calculated from ΔH° and the lattice enthalpy (ΔH_{cryst}) using the relation

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

The lattice enthalpies for the alkali halides at 298.15 K are taken from the literature [18]. Finally, Table 4 lists the enthalpies of solvation of alkali

TABLE 1

Enthalpies of solution (ΔH_m) for NaI in water–urea mixtures at 298.15 K

10 wt.% (3.22 mol.%) U		20 wt.% (6.98 mol.%) U		30 wt.% (11.39 mol.%) U		40 wt.% (16.67 mol.%) U	
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})
0.0115	10.07	0.0120	11.58	0.0128	13.26	0.0131	14.36
0.0184	10.05	0.0191	11.56	0.0179	13.26	0.0201	14.35
0.0231	10.04	0.0257	11.55	0.0228	13.25	0.0270	14.32
0.0377	10.02	0.0344	11.54	0.0467	13.21	0.0395	14.24
0.0552	9.99	0.0506	11.53	0.0580	13.20	0.0516	14.20
0.0701	9.97	0.0659	11.51	0.0715	13.19	0.0674	14.18
0.0837	9.92	0.0893	11.52	0.0908	13.18	0.0800	14.14
0.1002	9.91	0.1007	11.51	0.1049	13.19	0.0980	14.13
0.1152	9.88	0.1149	11.51	0.1160	13.17	0.1104	14.10
0.1307	9.86	0.1222	11.50	0.1302	13.16	0.1204	14.07
0.1510	9.85	0.1472	11.50	0.1505	13.14	0.1491	14.04

halides in water and in water–urea mixtures, calculated in accordance with eqn. (1). It is known that the enthalpy of solvation of the salts is additively built up from the individual values of the ions concerned. Hence, from the values of ΔH_s° obtained for alkali halides in water–urea mixtures, it is possible to calculate the values of the enthalpies of solvation for other salts

TABLE 2

Enthalpies of solution (ΔH_m) for KBr in water–urea mixtures at 298.15 K

10 wt.% (3.22 mol.%) U		20 wt.% (6.98 mol.%) U		30 wt.% (11.39 mol.%) U		40 wt.% (16.67 mol.%) U	
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})
0.0118	18.10	0.0103	16.35	0.0107	15.09	0.0102	13.64
0.0180	18.12	0.0181	16.35	0.0165	15.10	0.0162	13.66
0.0240	18.13	0.0287	16.37	0.0280	15.11	0.0230	13.67
0.0377	18.15	0.0367	16.38	0.0401	15.12	0.0369	13.69
0.0522	18.18	0.0572	16.39	0.0604	15.13	0.0502	13.71
0.0677	18.20	0.0730	16.40	0.0734	15.14	0.0700	13.73
0.0801	18.23	0.0935	16.41	0.0900	15.15	0.0908	13.74
0.0995	18.24	0.1033	16.41	0.1017	15.15	0.1090	13.75
0.1172	18.24	0.1129	16.40	0.1144	15.15	0.1202	13.75
0.1303	18.22	0.1388	16.38	0.1390	15.13	0.1403	13.74
0.1566	18.20	0.1522	16.36	0.1520	15.11	0.1588	13.72

TABLE 3

Standard enthalpies of solution ($\Delta H°$, kJ mol^{-1}) for alkali halides in water–urea mixtures at 298.15 K

Salt	Mole fraction of urea in mixed solvent				
	0.0000	0.0322	0.0698	0.1139	0.1667
NaCl	3.85 [a] 3.89 [b]	2.24 [a]	0.92 [a]	−0.12 [a]	−0.88 [a]
NaBr	−0.5 −0.63 [b]	−2.4	−3.8	−5.2	−6.6
NaI	−7.58 [c] −7.57 [b]	−10.17	−11.61	−13.33	−14.56
KCl	17.22 [a] 17.23 [b]	15.54 [a]	14.10 [a]	13.08 [a]	12.20 [a]
KBr	20.05 [d] 20.04 [b]	18.03	16.52	15.06	13.59
KI	20.4	17.7	16.2	14.5	13.1
CsCl [a]	17.78	14.89	13.05	11.64	10.42
CsBr	26.0	22.8	20.9	19.0	17.2
CsI	33.1	29.2	27.3	25.1	23.4

[a] Ref. 15. [b] Ref. 21. [c] Ref. 22. [d] Ref. 17.

(e.g., NaBr, KI, CsBr, CsI) not experimentally studied. Thus

$$\begin{aligned}
\Delta H_s°(\text{NaBr}) &= \Delta H_s°(\text{NaCl}) + \Delta H_s°(\text{KBr}) - \Delta H_s°(\text{KCl})\\
\Delta H_s°(\text{KI}) &= \Delta H_s°(\text{NaI}) + \Delta H_s°(\text{KCl}) - \Delta H_s°(\text{NaCl})\\
\Delta H_s°(\text{CsBr}) &= \Delta H_s°(\text{CsCl}) + \Delta H_s°(\text{KBr}) - \Delta H_s°(\text{KCl})\\
\Delta H_s°(\text{CsI}) &= \Delta H_s°(\text{CsCl}) + \Delta H_s°(\text{NaI}) - \Delta H_s°(\text{NaCl}) \qquad (2)
\end{aligned}$$

From these values of $\Delta H_s°$ for NaBr, KI, CsBr and CsI in water–urea mixtures the standard enthalpies of solution for these salts were calculated and these are also given in Table 3. According to a literature report [19], the enthalpies of solvation for Cs^+ and I^- ions in water are equal. On the assumption that this relation is also true for water–urea mixtures in the water-rich region, the enthalpies of solvation for single ions were calculated (method a). On the other hand, the ionic enthalpies of solvation were determined using the technique employed by Latimer et al. [20] (method b). The values of $\Delta H_s°$(ion) obtained in this way are collected in Table 5. Utilizing the values of $\Delta H_s°$(ion) from Table 5, the ionic enthalpies of transfer ($\Delta H_{tr}°$(ion)) from water to water–urea mixtures were calculated from the relation

$$\Delta H_{tr}°(\text{ion}) = \Delta H_s°(\text{ion, ms}) - \Delta H_s°(\text{ion, w}) \qquad (3)$$

where $\Delta H_s°$(ion, ms) and $\Delta H_s°$(ion, w) are the enthalpies of solvation at infinite dilution for a given ion in the mixed solvent (ms) and in water (w), respectively. It is interesting to note that the values of $\Delta H_{tr}°$(ion) calculated

TABLE 4

Enthalpies of solvation ($-\Delta H_s^\circ$, kJ mol^{-1}) for alkali halides in water–urea mixtures at 298.15 K

x_U	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl	CsBr	CsI
0.0000	773.6	739.4	695.9	689.5	655.3	611.8	631.6	597.4	553.9
0.0322	775.2	741.3	698.5	691.2	657.3	614.5	634.5	600.6	557.8
0.0698	776.5	742.7	699.9	692.6	658.8	616.0	636.3	602.5	559.7
0.1139	777.5	744.1	701.6	693.6	660.2	617.7	637.8	604.4	561.9
0.1667	778.3	745.5	702.9	694.5	661.7	619.1	639.0	606.2	563.6

TABLE 5

Ionic enthalpies of solvation ($-\Delta H_s^\circ$(ion), kJ mol^{-1}) for alkali-metal and halide ions in water–urea mixtures at 298.15 K, using methods a and b

Ion	Mole fraction of urea in the mixture									
	0.0000		0.0322		0.0698		0.1139		0.1667	
	a	b	a	b	a	b	a	b	a	b
Na^+	396.9	418.95	397.5	419.6	398.0	420.05	398.5	420.65	399.0	421.1
K^+	312.8	334.85	313.5	335.6	314.1	336.15	314.6	336.75	315.2	337.3
Cs^+	254.9	276.95	256.8	278.9	257.9	279.85	258.8	280.95	259.7	281.8
Cl^-	376.6	354.65	377.7	355.6	378.5	346.45	379.0	356.85	379.3	357.2
Br^-	342.5	320.45	343.8	321.7	344.7	322.65	345.6	323.45	346.5	324.4
I^-	299.0	276.95	301.0	278.9	301.9	279.85	303.1	280.95	303.9	281.8

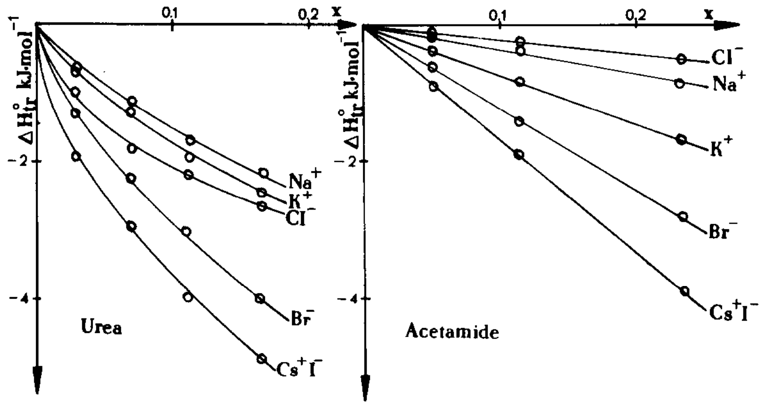

Fig. 1. Enthalpies of transfer of alkali-metal and halide ions as a function of mole fraction of nonelectrolyte in the mixed solvent at 298.15 K.

from the ΔH_s°(ion) values estimated using methods a and b are almost identical. A plot of ΔH_{tr}°(ion) vs. mole fraction (x) of urea in water–urea mixtures is presented in Fig. 1.

DISCUSSION

As can be seen from Table 5, the ionic enthalpies of solution increase with increasing concentration of urea in the mixed solvent. This may indicate the existence of stronger ion–solvent interactions in water–urea mixtures than in water. The effect of urea on the ionic enthalpies of solvation increases continuously with increasing ionic radius, both for cations and for anions. On this basis it may be supposed that, on adding urea to water, the three-dimensional network of hydrogen bonds in water is progressively destroyed and water–urea mixed associates with hydrogen bonds are formed. The present results suggest a reduction in the degree of structure in water–urea mixtures as compared to that existing in pure water. This view, namely that urea acts as a "structure breaker", is supported by various recent studies [7,9,23,24].

A better insight into these questions may be expected from a consideration of the ionic enthalpy of transfer (ΔH_{tr}°(ion)) on going from water to water–urea mixtures. Figure 1 shows the development of the enthalpy of transfer for alkali-metal and halide ions as a function of the mole fraction of urea. ΔH_{tr}°(ion) values for water–acetamide mixtures calculated on the basis of literature data [17] are also included for comparison.

The dielectric properties of water [25] and of aqueous urea [26] and acetamide [27] solutions are quite similar. Therefore, as a first approximation, we may assume that all electrostatic ion–solvent interactions are equal

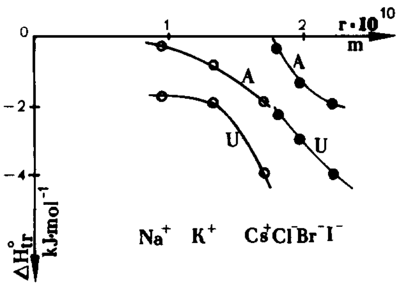

Fig. 2. Enthalpies of transfer of alkali-metal and halide ions as a function of ionic radii in water–urea (U) and water–acetamide (A) mixtures at 298.15 K.

in water and in these mixed solvents, and that the transfer functions primarily reflect structural changes. As can be seen from Fig. 1, the ionic enthalpies of transfer in water–acetamide mixtures are smaller than those in water–urea mixtures, suggesting that the effect of urea on the water structure is larger than the effect of acetamide. This leads one to conclude that acetamide molecules fit more closely to the water structure than do urea molecules. These observations can probably be explained by taking into account the triangular shape of the urea molecule. The picture obtained here is very different from that reported for a water–*t*-butyl alcohol(TBA) mixture [28], for which the enthalpies of transfer of the alkali-metal chlorides are positive, showing a maximum for a specific composition of the water–TBA mixture. The enthalpies of transfer of LiCl and NaCl on going from water to water–dioxan mixtures have also been reported as negative [29], the size effect, however, being the reverse of that observed here. Figure 2 shows the variation in ΔH_{tr}°(ion) with ionic radii for cations and anions in water–urea (U) and water–acetamide (A) mixtures. It is clear that ΔH_{tr}°(ion) increases with increasing ionic radii, both for cations and for anions. It may also be observed that the interaction of Cs^+ ion with the water–urea mixture is considerably larger than those for K^+ and Na^+ ions. In the water–acetamide mixture these cation interactions vary more smoothly than in the case of the water–urea mixture. For anions the relation $\Delta H_{tr}^{\circ}(\text{ion}) = f(r)$ is similar in both mixtures.

Any changes in the solvent–solute interactions may be considered to be contained in the coefficients of interactions between the solute molecules, as proposed by MacMillan and Mayer [30]. For this reason we thought it advisable to calculate, on the basis of the data obtained, the enthalpic pair-interaction coefficient (h_{IN}) for alkali and halide ions with urea in aqueous solution: this was done, expressing the dependence of ΔH_{tr}°(ion) on urea concentration by the equation

$$\Delta H_{tr}^{\circ}(\text{ion}) = h_{IN}^{(0)} \cdot m_U + h_{IN}^{(1)} \cdot m_U^{3/2} + h_{IN}^{(2)} \cdot m_U^2 + \ldots \quad (5)$$

where m_U is the molality of urea in solution. The coefficient $h_{IN}^{(0)}$ represents

TABLE 6

Values of the coefficients $h_{\mathrm{IN}}^{(0)}$, $h_{\mathrm{IN}}^{(1)}$, $h_{\mathrm{IN}}^{(2)}$ of eqn. (5) for alkali and halide ions at 298.15 K

Ion	$h_{\mathrm{IN}}^{(0)}$ (J kg mol^{-2})	$h_{\mathrm{IN}}^{(1)}$ (J kg$^{3/2}$ mol$^{-5/2}$)	$h_{\mathrm{IN}}^{(2)}$ (J kg^{2} mol^{-3})
Water – urea			
Na^+	−545.83	176.45	−21.737
K^+	−578.90	165.10	−17.311
Cs^+	−2023.44	885.66	−123.465
Cl^-	−718.37	138.52	2.621
Br^-	−1173.34	421.39	−53.335
I^-	−2023.44	885.66	−123.465
Water – acetamide			
Na^+	−180.78	91.09	−14.601
K^+	−210.52	57.05	−7.361
Cs^+	−408.29	75.42	−7.820
Cl^-	12.75	−38.68	6.903
Br^-	−193.13	−12.61	4.702
I^-	−392.07	60.00	−4.336

the enthalpy of transfer of 1 mol of a given ion at infinite dilution in water to a water–urea mixture of unit molality. Hence, $h_{\mathrm{IN}}^{(0)}$ provides some measure of the primary enthalpy of interaction of a urea molecule with a given ion in the aqueous environment. The pair-interaction parameter $h_{\mathrm{IN}}^{(0)}$ is not only a measure of the new interaction between an ion and urea (nonelectrolyte); it also includes contributions for all modifications of the ion–water and water–urea interactions brought about by the presence of the third component. The values of the coefficients $h_{\mathrm{IN}}^{(0)}$, $h_{\mathrm{IN}}^{(1)}$ and $h_{\mathrm{IN}}^{(2)}$ calculated for alkali-metal and halide ions in water–urea and water–acetamide mixtures by the least squares method using an Odra 1305 computer are summarized in Table 6. The trends in the $h_{\mathrm{IN}}^{(0)}$ values in Table 6 are marked. The results indicate that the exothermicity of the $h_{\mathrm{IN}}^{(0)}$ values increases with increasing ionic size, both for cations and for anions. Moreover, the $h_{\mathrm{IN}}^{(0)}$ coefficients as absolute values for water–urea mixtures are larger than those for the water–acetamide system. It may be supposed that this difference is in keeping with the difference in dipole moments between urea (4.20 D) and acetamide (3.90 D), or it could be an effect of the substitution of one of the $-NH_2$ groups present in urea molecule by the $-CH_3$ group of acetamide. Correlations of $h_{\mathrm{IN}}^{(0)}$ with ionic radii suggest the possible significance of ion–dipole interactions in these mixtures. Moreover, in our view, the trends in $h_{\mathrm{IN}}^{(0)}$ are also due to perturbations of the water structure by the nonelectrolyte. If we assume, following Desrosiers et al. [24], that urea does not penetrate the hydration cosphere of the ions, the increase in $h_{\mathrm{IN}}^{(0)}$ would correspond to an increase in the number of water molecules in the hydration cosphere. It is known that the hydration cosphere of an ion in solution may be thought of as a layer of water molecules around the ion (the hydration complex) and the "broken-structure" region. It is obvious that the dimensions of the hydration complex and the "broken-structure" region depend upon the size and nature of the ion. Urea (and similarly acetamide) is assumed to give rise to a cosphere in which the water contains fewer hydrogen bonds than does bulk water. As the two hydrated molecules approach one other, there will be some changes in the hydration of the molecules. Overlap of the cosphere of urea (acetamide) with that of the ion will lead to a net destruction of some of the cosphere material. The sum of these solution effects leads to a net gain in enthalpy of transfer. This effect is largest for the Cs^+ ion. The $h_{\mathrm{IN}}^{(0)}$ values suggest that the effect of acetamide on water structure is smaller than that of urea. It may be supposed that the hydrophobic methyl group present in the acetamide molecule reduces the hydration of ions as compared with the $-NH_2$ group in urea.

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