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Thermochemic properties of NaCl and KCl solutions in mixtures of water with *N,N*-dimethylacetamide at 25°C

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Abstract

Enthalpies of solution of NaCl and KCl in water–*N,N*-dimethylacetamide (DMA) mixtures (containing 0–20 mol.% of DMA) were measured at 25°C. The standard dissolution enthalpies for both investigated salts increase with increase in DMA content in the mixed solvent, in contrast with the dissolution enthalpies for other inorganic salts in the same mixtures examined so far. The calculated single-ion transfer enthalpies from water to water–DMA mixtures exhibit the opposite course with a distinct minimum for anions and a maximum for cations. The extrema of the ionic transfer enthalpies observed in all water–organic mixtures investigated thus far seem to be a consequence of the shape of the solvation enthalpy curves for Ph_4P^+ and BPh_4^- ions which are the basis for the calculation of individual ionic contributions and which are hydrophobically hydrated in water–organic solvents

INTRODUCTION

Calorimetric investigations on ternary electrolyte–organic solvent–water systems showed that in some water–organic mixtures the standard solution enthalpies of the electrolytes exhibited maxima in the high-water region of the mixed solvent compositions. These maxima were observed in water–alkanol [1–7], water–tetrahydrofuran [8] and water–hexamethylphosphoramide [9] mixtures. Their presence was explained as a result of water-structure stabilisation by the organic cosolvent or of hydrophobic hydration.

N,N-Dimethylacetamide (DMA), having three methyl groups in its molecule, is one of the organic solvents that undergoes hydrophobic hydration in aqueous solution. Thermochemical examinations of electrolyte solutions in DMA–water mixtures performed hitherto have demonstrated that the dissolution enthalpies, $\Delta H_s^{\ominus}$, of organic electrolytes, such as Bu_4NBr [10], $NaBPh_4$ [11] and Ph_4PBr [11], pass through a maximum within the high-water contents, while for inorganic electrolytes such as NaBr [11], NaI [12], KI [13] and CsI [12], the $\Delta H_s^{\ominus}$ function decreases monotonously with the decrease in the water content in the mixed solvent. The enthalpic pair interaction coefficients h_{xy} reported in the literature have negative values for

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NaI–DMA and CsI–DMA pairs in aqueous solution [12], whereas for NaCl–DMA and KCl–DMA pairs the h_{xy} values are positive [14]. This observation suggests that NaCl and KCl in DMA–water mixtures behave in a manner different from NaI and CsI. The standard solution enthalpies for NaCl and KCl should increase with decreasing water content in the mixed solvent. Therefore, we decided to determine calorimetrically the enthalpies of solution of NaCl and KCl in the mixtures of *N*,*N*-dimethylacetamide with water. The results obtained, together with the appropriate literature data, will enable us to calculate single-ion transfer enthalpies from water to water–DMA mixtures for K^+ and Cl^- ions.

EXPERIMENTAL

Sodium chloride, p.a. and potassium chloride, p.a., both POCh-Gliwice (Poland) were dried for several days in a vacuum drier at 100 °C. *N*,*N*-Dimethylacetamide, Merck (Germany), was kept over 4A-type molecular sieves and then distilled under a reduced pressure. Doubly distilled water was demineralised using ion exchangers. The mixtures were prepared by weight.

TABLE 1

Enthalpies of solution of NaCl in *N*,*N*-dimethylacetamide–water mixtures at 25 °C

m (mol kg^{-1})	ΔH_s (kJ mol^{-1})	m (mol kg^{-1})	ΔH_s (kJ mol^{-1})	m (mol kg^{-1})	ΔH_s (kJ mol^{-1})
Water		$x^a = 0.02$		$x = 0.06$	
0.01712	3.96	0.01758	4.23	0.01546	4.90
0.02083	4.03	0.01762	4.25	0.02226	4.93
0.03203	4.07	0.02490	4.25	0.02349	4.94
0.03927	4.02	0.03492	4.25	0.03282	4.94
0.03977	4.11	0.03988	4.26	0.05044	5.05
0.05282	4.10	0.04989	4.27	0.05175	5.00
0.07647	4.13	0.06567	4.29	0.05462	5.04
0.09914	4.15	0.07602	4.31	0.07491	5.10
		0.08707	4.44	0.07640	5.06
$x = 0.10$		0.10213	4.35	0.07643	5.09
0.01547	5.94			0.09074	5.12
0.01749	5.99	$x = 0.15$		0.10037	5.16
0.01973	6.02	0.01302	7.67		
0.03209	6.03	0.01343	7.75	$x = 0.20$	
0.03609	6.10	0.01625	7.74	0.00978	8.50
0.03665	6.08	0.02632	7.76	0.01443	8.68
0.04325	6.06	0.02868	7.78	0.02181	8.71
0.05497	6.19	0.03987	7.82	0.02948	8.84
0.05541	6.13	0.04154	7.79	0.03320	8.84
0.06235	6.21	0.05323	7.86	0.04313	8.97
0.06672	6.23	0.05679	7.82	0.04421	8.99
				0.05636	9.10

[a] Mole fraction of *N*,*N*-dimethylacetamide.

TABLE 2

Enthalpies of solution of KCl in N,N-dimethylacetamide–water mixtures at 25 °C

m (mol kg^{-1})	ΔH_s (kJ mol^{-1})	m (mol kg^{-1})	ΔH_s (kJ mol^{-1})	m (mol kg^{-1})	ΔH_s (kJ mol^{-1})
water		$x^{a} = 0.02$		$x = 0.06$	
0.00501	17.34	0.00554	17.56	0.00476	18.00
0.00516	17.34	0.00571	17.51	0.00538	18.02
0.00613	17.34	0.01112	17.50	0.00981	18.05
0.01115	17.38	0.01355	17.61	0.01050	18.08
0.01194	17.36	0.01635	17.54	0.01411	18.07
0.01786	17.40	0.01995	17.65	0.01467	18.07
0.01836	17.36	0.02151	17.57	0.01809	18.08
0.02420	17.38	0.02747	17.66	0.02022	18.08
0.02714	17.43				
$x = 0.10$		$x = 0.15$		$x = 0.20$	
0.00291	18.66	0.00362	19.42	0.00316	19.78
0.00416	18.69	0.00391	19.43	0.00544	19.82
0.00707	18.67	0.00746	19.44	0.00671	19.86
0.00826	18.72	0.00804	19.46	0.01012	19.82
0.01153	18.70	0.01115	19.47	0.01363	19.94
0.01248	18.77	0.01189	19.49	0.01538	19.89
0.01611	18.73	0.01480	19.50	0.01933	20.01
0.01705	18.80	0.01566	19.53	0.02102	19.92

[a] Mole fraction of N,N-dimethylacetamide.

The measurements of solution enthalpies were performed using an "isoperibol" calorimeter as described in an earlier report [15]. The uncertainties in the measured enthalpies did not exceed ±0.5% of the measured value.

RESULTS AND DISCUSSION

Enthalpy of solution

The measured dissolution enthalpies of NaCl and KCl in water and in water–N,N-dimethylacetamide mixtures are presented in Tables 1 and 2 as a function of both electrolyte concentration and the mixed solvent composition. The standard solution enthalpies, $\Delta H_s^{\ominus}$, in the examined mixtures were determined graphically by extrapolation of the $\Delta H_s = f(m^{1/2})$ function to $m = 0$. Other extrapolation methods (such as the Criss and Cobble method [16]) could not be used for this purpose due to the lack of some of the data necessary for the calculations.

The values obtained for $\Delta H_s^{\ominus}$ for NaCl and KCl in water and in water–DMA mixtures are collected in Table 3. The standard enthalpies of solution in pure water determined in this work ($\Delta H_s^{\ominus}$(NaCl) = 3.89 kJ

TABLE 3

Standard dissolution enthalpies of NaCl and KCl in water–N,N-dimethylacetamide mixtures at 25 °C

mol.% DMA	$\Delta H_s^\ominus$(NaCl) (kJ mol^{-1})	$\Delta H_s^\ominus$(KCl) (kJ mol^{-1})
0	3.89	17.29
2	4.11	17.42
6	4.73	17.95
10	5.72	18.58
15	7.39	19.33
20	8.13	19.67

mol^{-1}; $\Delta H_s^\ominus$(KCl) = 17.29 kJ mol^{-1}) are in very good agreement with the literature data: 3.78 [8], 3.80 [16], 3.88 [17,18] and 3.90 [19] kJ mol^{-1} for NaCl; and 17.18 [20] 17.19 [21], 17.22 [18], 17.28 [22] and 17.41 [23] kJ mol^{-1} for KCl. Figure 1 presents the transfer enthalpies, $\Delta H_t^\ominus$, of NaCl and KCl from water to water–DMA mixtures calculated according to the

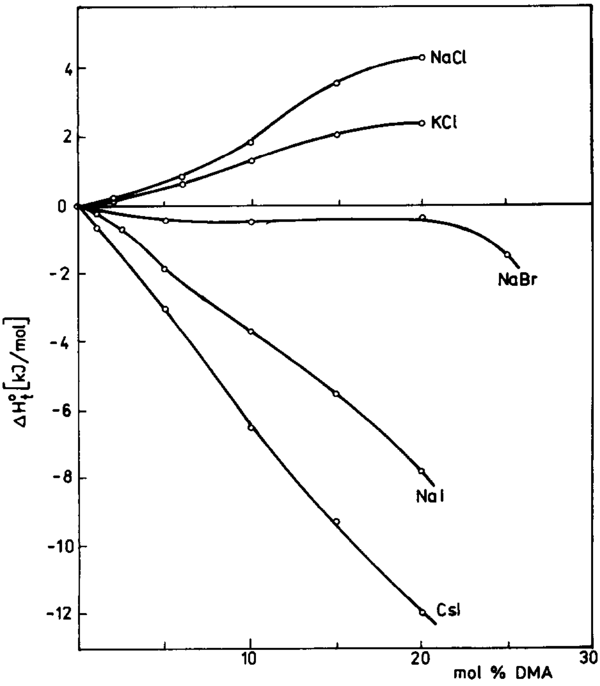

Fig 1. Enthalpies of transfer of electrolytes from water to water–N,N-dimethylacetamide mixtures at 25 °C.

formula

$$\Delta H_t^{\ominus} = \Delta H_s^{\ominus}(\mathrm{M}) - \Delta H_s^{\ominus}(\mathrm{W}) \tag{1}$$

where $\Delta H_s^{\ominus}(\mathrm{M})$ and $\Delta H_s^{\ominus}(\mathrm{W})$ are the standard solution enthalpies of the electrolyte in the mixture and in pure water, respectively. For comparison, Fig. 1 also gives analogous data for NaBr, NaI and CsI taken from the literature [12].

It can be seen from the data presented that the standard solution enthalpy for NaCl and KCl salts in the mixtures of water with DMA increases with increase in DMA content over the whole range of the mixed solvent composition examined. Because of the limited solubility of NaCl and KCl in the mixtures investigated, it was not possible to determine if the maximum of the $\Delta H_s^{\ominus}$ (and $\Delta H_t^{\ominus}$) function characteristic for electrolyte solutions in mixtures of water with alkanols [1–7], with THF [8], or with HMPT [9], also appears in the inorganic salt–water–DMA system. Nevertheless, the course of the $\Delta H_t^{\ominus}$ function observed here for NaCl and KCl solutions seems to be an effect of the hydrophobic hydration of DMA molecules in water–DMA mixtures.

The increase of both the cation and the anion size involves a change in the slope and even in the direction of the $\Delta H_t^{\ominus}$ curve (see Fig. 1).

Enthalpic pair interaction coefficients

Having determined experimentally the enthalpies of transfer of NaCl and KCl from pure water to water–DMA mixtures, we calculated the enthalpic pair interaction coefficients h_{xy} in order to compare them with the analogous literature data. The calculations were performed using the method proposed by Heuvelsland et al. [24]. The h_{xy} values obtained for NaCl–DMA and KCl–DMA pairs in water solution agree very well with those calculated by Lilley and coworkers [14] from heat of mixing data (Table 4).

Single-ion transfer enthalpies

Using the data obtained and the appropriate literature values (Table 5), the electrolyte standard transfer enthalpies were split into ionic contribu-

TABLE 4

Enthalpic pair interaction coefficients h_{xy} (J kg mol^{-2}) for NaCl–DMA and KCl–DMA pairs in water

	Our data	Literature data [9]
h_{xy}(NaCl–DMA)	75	99
h_{xy}(KCl–DMA)	45	43

TABLE 5

Standard enthalpies of transfer $\Delta H_t^\ominus$ (kJ mol^{-1}) of salts from water to water–DMA mixtures at 25 °C

	Mol % DMA							
	5	10	15	20	40	60	80	100
$NaClO_4$ [11]	0.25	−2.51	−6.61 [a]	−10.71	−29.66	−44.60	−52.55	−56.94
NaBr [11]	−0.45	−0.49	−0.45 [a]	−0.40	−4.80	−12.52	−19.98	−25.59
Ph_4PBr [11]	15.94	17.06	18.37 [a]	19.68	12.82	6.46	0.31	−2.91
$NaBPh_4$ [11]	25.06	27.28	19.68 [a]	12.06	−21.68	−41.17	−51.47	−55.48
Bu_4NBr [10]	14.65	26.16	35.29 [a]	40.71 [a]	43.97 [a]	37.67 [a]	31.24 [a]	24.10
NaI [12]	−1.91	−3.73	−5.46	−7.84 [a]	−18.79	−31.13 [a]	−38.42	−44.18
CsI [12]	−2.96	−6.45	−9.33	−11.99 [a]	−22.05 [a]	−31.89 [a]	−41.72	−51.38
KI [13]	−2.87 [a]	−5.74	−7.60 [a]	−9.46	−20.02 [a]	−31.48	−41.56	−49.53
NaCl [b]	0.69 [a]	1.83	3.50	4.24				
KCl [b]	0.55 [a]	1.29	2.04	2.38				

[a] Interpolated values.

[b] This work

tions by applying the well-known Parker assumption [25]

$$\Delta H_t^\ominus(Ph_4P^+) = \Delta H_t^\ominus(BPh_4^-) \tag{2}$$

In order to calculate the single-ion transfer enthalpies, the multiple linear regression method was used. Owing to the small number of data for mixtures above 20 mol.% DMA, the $\Delta H_t^\ominus$ values for single ions in these systems were calculated from the formula

$$\begin{aligned}\Delta H_t^\ominus(Ph_4P^+) &= \Delta H_t^\ominus(BPh_4^-)\\ &= 0.5\left[\Delta H_t^\ominus(Ph_4PBr) + \Delta H_t^\ominus(NaBPh_4) - \Delta H_t^\ominus(NaBr)\right]\end{aligned} \tag{3}$$

TABLE 6

Single-ion transfer enthalpies $\Delta H_t^\ominus$ (kJ mol^{-1}) from water to water–DMA mixtures at 25 °C

	Mol.% DMA							
	5	10	15	20	40	60	80	100
Na^+	4.3±0.3	4.9±0.6	0.4±0.3	−4.0±0.1	−19.65	−30.07	−35.88	−39.08
K^+	3.8±0.5	3.6±1.0	−1.4±0.4	−5.8±0.2	−20.88	−30.42	−39.02	−44.43
Cs^+	3.5±0.6	2.5±1.1	−3.3±0.5	−8.2±0.2	−22.91	−30.83	−39.18	−46.28
Cl^-	−3.4±0.5	−2.7±0.9	3.2±0.4	8.2±0.2				
Br^-	−4.8±0.3	−5.4±0.6	−0.9±0.3	3.6±0.1	14.85	17.56	15.90	13.49
I^-	−6.5±0.5	−9.0±0.9	−6.1±0.4	−3.8±0.2	0.86	−1.06	−2.54	−5.10
ClO_4^-	−4.1±0.5	−7.4±1.0	−7.0±0.4	−6.7±0.2	−10.01	−14.53	−16.67	−17.86
Bu_4N^+	19.4±0.5	31.5±1.0	36.2±0.4	37.1±0.2	29.12	20.11	15.34	10.61
Ph_4P^+/ BPh_4^-	20.7±0.3	22.4±0.6	19.3±0.3	16.0±0.1	−2.03	−11.10	−15.59	−16.40

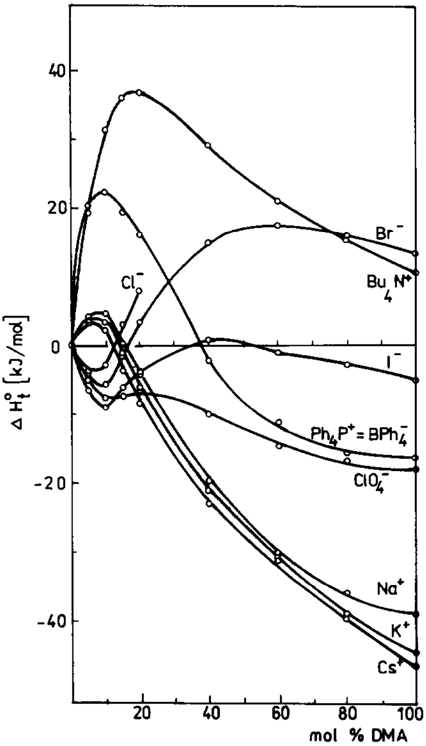

Fig 2 Ionic enthalpies of transfer from water to water–*N*,*N*-dimethylacetamide mixtures at 25 °C.

The ionic transfer enthalpies are shown in Table 6 and plotted in Fig. 2 as a function of the mixed solvent composition. They are in good agreement with data for Na^+, ClO_4^-, Br^- and Ph_4P^+ ions published by Gusev et al. [11].

The opposite behaviour of cations and anions is seen in the DMA–water mixtures (Fig. 2). The $\Delta H_t^{\ominus}$ curves present mirror images in the water-rich region, with a distinct minimum for anions and a maximum for cations. The minimum becomes deeper as the anion size increases, but for the cations the maximum decreases with the increase in ionic diameter. The position of the extremum depends on the type of ion. For large organic ions it corresponds to 10–20 mol.% DMA, whereas for inorganic ions the extrema appear within 5–10 mol.% DMA. No characteristic changes in the physicochemical properties of the DMA–water system are observed in the water-rich region of the mixture. Therefore one can suppose that the observed extrema of the ionic transfer enthalpies are a consequence of the hydrophobic hydration of Ph_4P^+ and BPh_4^- ions, which are assumed as the basis of the division of the enthalpies of transfer into individual ionic contributions. The dependence of the single ionic transfer enthalpies on the mixed solvent composition in DMA–water mixtures is similar to that observed in water–*t*-butanol [26], water–THF [8] and water–HMPT [9] mixtures. It can therefore be supposed that the so-called "TATB" method always gives similar shapes for the ionic $\Delta H_t^\ominus$ functions, with the maximum for cations and the minimum for anions in the water-rich region. These extrema on the ionic transfer enthalpies occur independently of whether or not the enthalpy of the salt dissolution function has an extremum within the same range of the mixed solvent composition.

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