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ENTHALPIES OF SOLUTION OF NaI AND CsI IN *N,N*-DIMETHYLACETAMIDE–WATER MIXTURES AT 298.15 K

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ABSTRACT

The enthalpies of solution ΔH_s of NaI and CsI in *N,N*-dimethylacetamide–water mixtures at 298.15 K were measured. The standard enthalpies of solution of NaI determined in this study were compared with analogous functions for the systems containing formamide and *N,N*-dimethylformamide. The effect of cation size on the transfer enthalpy was analysed.

INTRODUCTION

N,N-Dimethylacetamide (DMA) is often used as a solvent in numerous chemical processes (in organic syntheses, in galvanic cells, in producing and processing of plastics, etc.) because of its chemical and thermal stability. Although thermodynamic functions of the dissolution of electrolytes can provide some information on the interactions of ions with solvent molecules, data are scarce in the literature. In this work the enthalpies of dissolution of NaI and CsI in DMA–water mixtures were measured at 298.15 K.

EXPERIMENTAL

Sodium iodide (P.O.Ch. Gliwice, Poland; pro Analysi) and caesium iodide (L.R., BDH) were dried in vacuo for several days at a temperature of 335 K. *N,N*-Dimethylacetamide (Merck; pro Analysi) was exposed to the action of KOH for several days and was then dried using molecular sieves of the 4A type. Finally, DMA was distilled under reduced pressure (boiling point, 64–65 °C/28 mm). Doubly distilled water was used. Water–organic mixtures were prepared by weight. The measurements of the enthalpy of solution were performed in the "isoperibol" calorimeter described elsewhere [1]. The temperature inside the calorimeter was determined using two thermistors (5 kohm $(298.15\ \mathrm{K})^{-1}$) working in the Wheatstone bridge system. The voltage of the unbalanced bridge was measured by means of a

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TABLE 1

Enthalpies of solution ΔH_s of NaI in water–dimethylacetamide mixtures at 298.15 K

$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
$x^a = 0.01$		$x = 0.05$	
4.35	7.704	3.57	9.433
4.49	7.704	5.62	9.399
5.11	7.666	6.77	9.387
9.95	7.679	8.60	9.395
13.27	7.662	12.13	9.366
15.97	7.645	13.66	9.370
21.43	7.637	15.64	9.345
21.56	7.633	20.75	9.337
30.82	7.569	24.88	9.307
		35.37	9.278
$x = 0.10$		$x = 0.15$	
4.25	11.20	6.48	12.87
5.83	11.17	8.81	12.82
9.36	11.15	13.22	12.79
12.28	11.12	18.61	12.72
15.30	11.12	24.81	12.67
20.63	11.08	28.46	12.64
21.59	11.07	36.96	12.59
$x = 0.30$		$x = 0.50$	
4.00	20.00	5.39	31.51
4.96	19.96	5.98	31.50
5.80	19.92	12.39	31.07
10.76	19.85	12.61	31.08
13.14	19.78	20.38	30.66
16.12	19.76	21.21	30.61
18.40	19.72	29.20	30.27
23.93	19.66	30.41	30.21
25.76	19.62		
$x = 0.65$		$x = 0.80$	
5.80	39.10	6.40	44.30
10.68	38.72	12.89	43.99
16.50	38.41	20.16	43.80
20.42	38.22	30.25	43.52
$x = 1.00$			
7.23	51.21		
14.95	50.85		
23.24	49.70		
31.57	49.72		
41.34	49.68		

[a] Mole fraction of DMA in mixed solvent.

TABLE 2

Enthalpies of solution ΔH_s of CsI in water–dimethylacetamide mixtures at 298.15 K

$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	ΔH_s (kJ mol^{-1})
$x^a = 0.0$		$x = 0.05$	
5.05	33.29	2.19	30.19
5.53	33.29	3.11	30.13
10.35	33.23	5.22	30.12
11.39	33.22	6.50	30.07
16.42	33.17	8.16	30.07
17.63	33.16	10.67	30.01
25.49	33.18	11.99	30.02
		15.23	29.95
$x = 0.10$		$x = 0.15$	
2.55	26.54	1.79	23.93
4.11	26.43	2.58	23.91
5.40	26.46	5.39	23.90
8.61	26.32	11.13	23.89
12.16	26.26	12.28	23.88
14.63	26.19	19.11	23.86
19.52	26.10	23.84	23.85
21.69	26.05		
$x = 0.30$		$x = 0.50$	
1.89	15.91	2.21	6.309
3.37	15.94	3.43	6.363
4.74	15.89	7.87	6.231
6.86	15.89	8.26	6.268
8.74	15.86	14.06	6.195
15.33	15.83	16.29	6.131
16.80	15.86	21.47	6.122
29.11	15.77	25.84	6.035
$x = 0.65$		$x = 0.80$	
2.58	−0.925	1.94	−7.614
3.43	−0.870	2.17	−7.506
8.76	−0.653	4.41	−7.256
9.92	−0.598	4.98	−7.330
15.22	−0.435	7.01	−6.986
16.48	−0.381	8.52	−6.798
19.15	−0.326	15.04	−6.160
22.02	−0.272	15.17	−6.202
$x = 1.00$			
1.75	−16.21		
2.20	−15.99		
4.57	−15.26		
9.97	−14.29		
12.19	−13.36		
19.10	−12.45		
22.65	−11.66		

[a] Mole fraction of DMA in mixed solvent.

Keithley K-148 nanovoltmeter. The temperature sensitivity was ca. 5×10^{-5} K. The temperature in the thermostat was stable to $\pm 1 \times 10^{-3}$ K. The experimental precision was $\pm 0.5\%$.

RESULTS

The enthalpies of solution ΔH_s of NaI and CsI over the entire composition range of water–DMA mixtures were determined for salt concentrations between 4×10^{-3} and 4×10^{-2} mol kg^{-1} at a temperature of 298.15 K (Tables 1 and 2). The standard enthalpies of solution were obtained by the graphic extrapolation of ΔH_s up to infinite dilution. The lack of temperature derivatives of electric permittivity and density in the literature made it impossible to apply the extrapolation method of Criss and Cobble. The standard enthalpies of solution obtained here are included in Table 3 and are presented in Figs. 1 and 2 as a function of the composition of the mixed solvent.

DISCUSSION

The standard enthalpy of NaI dissolution vs. the composition of H_2O–DMA mixtures is presented in Fig. 1 together with the earlier data from our laboratory [3] concerning the NaI–H_2O–*N*,*N*-dimethylformamide (DMF) and NaI–H_2O–formamide (F) systems. Results of thermochemical and viscosimetric measurements for NaI–H_2O–DMF and NaI–H_2O–F [4]

TABLE 3

Standard enthalpies of solution $\Delta H_s^\ominus$ of NaI and CsI in aqueous mixtures of DMA at 298.15 K

x_{DMA}	$\Delta H_s^\ominus$(NaI) (kJ mol^{-1})	$\Delta H_s^\ominus$(CsI) (kJ mol^{-1})
0.0	−7.575 [a]	33.29
0.01	−7.758	32.64
0.025	−8.248	–
0.05	−9.483	30.33
0.10	−11.30	26.84
0.15	−13.03	23.96
0.30	−20.18	15.97
0.50	−32.53	6.514
0.65	−39.90	−1.158
0.80	−45.99	−8.425
1.00	−51.75	−18.09

[a] Value of $\Delta H_s^\ominus$(NaI) in water from ref. 2.

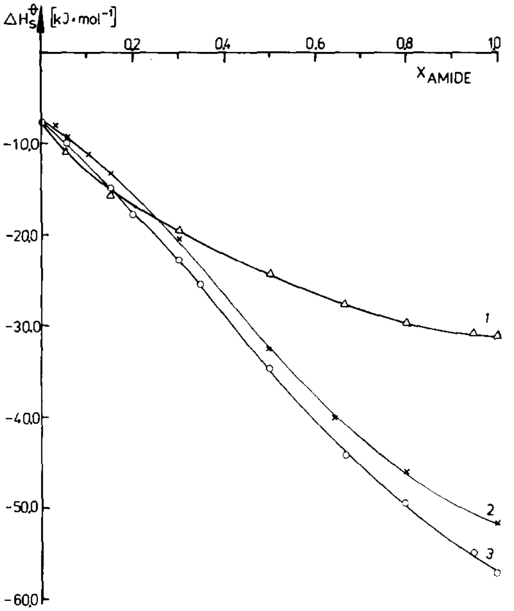

Fig. 1. Standard enthalpy of solution of NaI in the mixtures of water with amides as a function of solvent composition at 298.15 K: 1, formamide; 2, dimethylacetamide; 3, dimethylformamide.

suggest a similar destruction by both amides of the three-dimensional water structure. The similar values of $\Delta H_s^\ominus$(NaI) for the three systems considered (Fig. 1) in the range 0–30 mol.% of amide seems to suggest that an analogous effect is exerted by DMA on the water structure. The amide molecules enter the water having destroyed its primary structure and possibly create mixed associates of various compositions and shapes with the water molecules as proposed by several workers [5–13]. The presence of alkyl groups in the disubstituted amides decreases the exothermic effect of the enthalpies of dissolution of the electrolytes. Therefore diminishing slopes of the function $\Delta H_s^\ominus(\mathrm{NaI}) = \mathrm{f}(\mathrm{mol.\%\ amide})$ are observed in the order: F > DMF > DMA. This is reflected by the enthalpic pair interaction coefficients $h_{xy}[(\mathrm{Na}^+ + \mathrm{I}^-) - \mathrm{amide}]$ in water

$h_{xy}[(\mathrm{Na}^+ + \mathrm{I}^-) - \mathrm{F}] = -348\ \mathrm{J\ kg\ mol}^{-2}$ (from ref. 14)

$h_{xy}[(\mathrm{Na}^+ + \mathrm{I}^-) - \mathrm{DMF}] = -212\ \mathrm{J\ kg\ mol}^{-2}$ (from ref. 14)

$h_{xy}[(\mathrm{Na}^+ + \mathrm{I}^-) - \mathrm{DMA}] = -62\ \mathrm{J\ kg\ mol}^{-2}$ (our data)

(In order to calculate the h_{xy} coefficients, the method described in ref. 15 was used.)

In the range of mixed solvent compositions exceeding 30 mol.% of amide, the $\Delta H_s^\ominus$(NaI) values for the three systems differ. The exothermic effects of

TABLE 4

Physical properties of F, DMF and DMA and standard enthalpies of solution of the amides in water and of NaI in the amides

Amide	DN [a]	ϵ [a]	η (cP)	μ [d] (D)	$\Delta H^{\ominus}_{\text{in H}_2\text{O}}$ (kJ mol^{-1})	$\Delta H_s^{\ominus}$(NaI) (kJ mol^{-1})
F	24.0	109.6	3.260 [b]	3.73	2.05 [e]	−31.28 [g]
DMF	26.6	36.7	0.7902 [b]	3.86	−14.74 [f]	−57.15 [g]
DMA	27.8	37.8	0.927 [c]	3.81	−20.38 [f]	−51.75

[a] Reference 17. [b] Reference 4. [c] Reference 18. [d] Reference 19. [e] Reference 20. [f] Reference 21. [g] Reference 3.

NaI dissolution in formamide and in mixtures containing a high content of formamide are much smaller than the $\Delta H_s^{\ominus}$(NaI) values for the systems containing disubstituted amides. This observation is probably due to the ability of formamide molecules to form numerous hydrogen bonds with each other. In pure formamide two-dimensional folded surfaces exist formed by molecules bound with hydrogen bonds [16]. Formamide creates more complicated associates with water than do DMA and DMF. Therefore the ions Na^+ and I^- which enter the system containing formamide have to destroy more hydrogen bonds, and this is accompanied by an endothermic effect.

Table 4 presents some physical properties of the three amides together with the standard enthalpies of solution of the amides in water and of NaI in the amides. From the analysis of the data it can be seen that the largest interaction of amide with water is observed for DMA, probably because of the hydrophobic hydration effect. This effect is more evident in DMA than in DMF owing to the additional methyl group in the DMA molecule. A slightly higher electric permittivity and donor number also indicate a smaller $\Delta H_s^{\ominus}$(DMA) value than $\Delta H_s^{\ominus}$(DMF) value in water. As regards the standard enthalpy of solution of NaI in the amides (Table 4) it can be seen that the steric hindrance of the additional $-\mathrm{CH}_3$ group causes a smaller exothermic effect (compare $\Delta H_s^{\ominus}$(NaI) in DMA with $\Delta H_s^{\ominus}$(NaI) in DMF). In the mixtures of DMA and DMF with water the hydrophobic hydration effect appears, but the difference between the $\Delta H_s^{\ominus}$(NaI) values in systems containing the disubstituted amides is smaller than the difference between the corresponding values in pure DMA and pure DMF.

Figure 2 shows the dependence of $\Delta H_s^{\ominus}$ of the two electrolytes NaI and CsI measured here and KI measured by Khrenova [22] on the DMA content in the mixtures with water. The character of all the curves is similar. In contrast with systems containing water and alcohols no extrema are observed in the systems studied here. The exothermic effect of the dissolution of the investigated alkali metal iodides in DMA–water mixtures decreases in the order NaI > KI > CsI. This is expected due to the decrease in surface charge density of the cations.

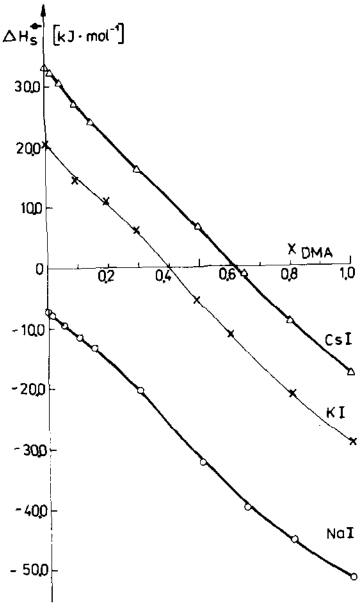

Fig. 2. Standard enthalpies of solution of NaI, KI and CsI in the mixtures of water with DMA as a function of solvent composition at 298.15 K (data for KI from ref. 7).

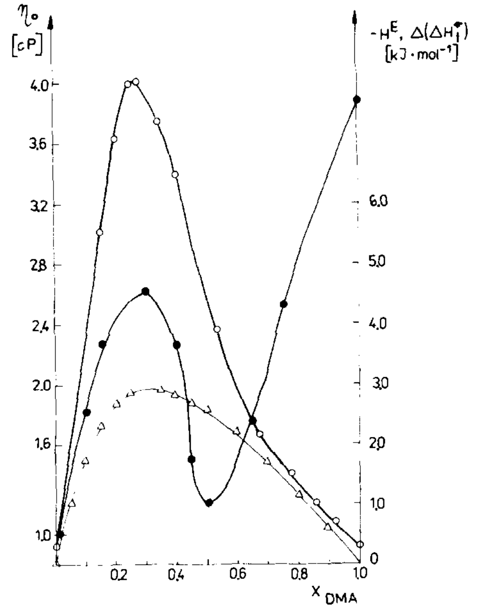

Fig. 3. Viscosity (○——○), enthalpy of mixing (△——△) and $\Delta(\Delta H_{tr}^{\ominus})(Na^+ - Cs^+)$ (●——●) for water–DMA mixtures at 298.15 K.

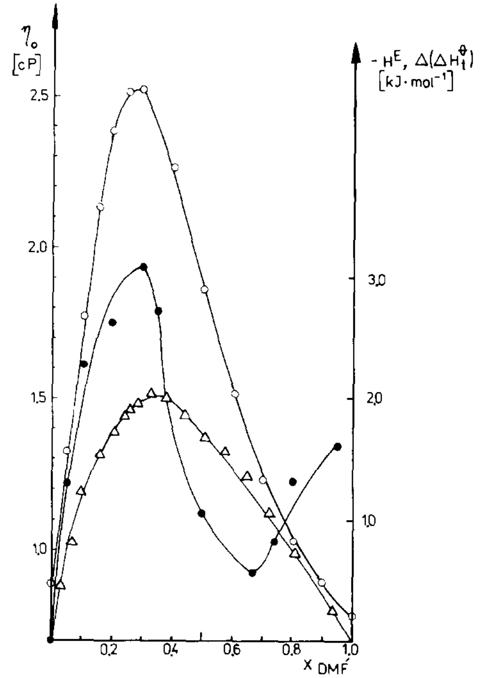

Fig. 4. Viscosity (o——o), enthalpy of mixing (△——△) and $\Delta(\Delta H_{tr})(Na^+ - Cs^+)$ (●——●) for water–DMF mixtures at 298.15 K.

In an earlier paper from our laboratory [23] maxima were observed in the differences between the transfer enthalpies from water to water–organic mixed solvent for two cations. The positions of these maxima corresponded to the viscosity maxima and to the maximum enthalpy of mixing of the binary solvent components. Maxima were also observed in mixtures of water with tetrahydrofuran, dimethyl sulphoxide and acetone. The above-mentioned functions for water–DMA and water–DMF binary mixtures are given in Figs. 3 and 4. The system containing formamide could not be used owing to the lack of necessary data for $\Delta H_s^\ominus$(CsI).

In mixtures containing DMA and DMF with water, the viscosity, heat of mixing, and difference between the enthalpies of transfer $\Delta(\Delta H_{tr}^\ominus)(Na^+ - Cs^+)$ exhibit maxima corresponding to a certain content of chosen amide. It can be supposed that the compositions of the binary mixtures corresponding to the maxima above are connected with the most stable structures of the mixed solvents. The formation of associates with a definite or varying stoichiometry cannot be excluded.

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