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ENTHALPIC PAIR INTERACTION COEFFICIENTS IN DMF SOLUTION

3. Thermochemistry of NaI solutions in mixtures of N,N-dimethylformamide with urea, formamide, acetamide and N,N-dimethylacetamide at 298.15 K

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Abstract

Dissolution enthalpies of NaI in mixtures of N,N-dimethylformamide with urea, formamide, acetamide and N,N-dimethylacetamide were measured. The results were compared with data measured earlier for other DMF – non-electrolyte mixtures. The enthalpic pair interaction coefficients, h_{xy} (Na^+I^- – non-electrolyte) in DMF were calculated and analysed together with the appropriate data concerning other Na^+I^- – non-electrolyte pairs in DMF. The group interaction coefficients illustrating the interactions of Na^+I^- with the CH_2, OH, O, CO, 'Pep' and 'iPep' groups were determined and discussed.

Keywords: acetamide, dissolution enthalpies of NaI, DMF mixtures, enthalpic pair interaction coefficients, formamide, N,N-dimethylacetamide, urea

Introduction

This work is a continuation of our earlier studies on interactions between electrolyte (NaI) and non-electrolyte in N,N-dimethylformamide (DMF) solution. The previous papers were devoted to the analysis of experimentally determined enthalpic pair interaction coefficients, h_{xy} (NaI – non-electrolyte) for pairs containing alkanols, acetone, tetrahydrofuran, dioxane, acetonitrile and dimethylsulfoxide as the non-electrolyte [1, 2]. Now, we have extended these studies on systems with urea and some amides. For this purpose, the dissolution enthalpies of NaI were measured in the mixtures of DMF with urea (U), formamide (FA), acetamide (AA) and N,N-dimethylacetamide (DMA) within a range of high DMF content at 298.15 K and the h_{xy} values were calculated for the appropriate NaI – non-electrolyte pairs in DMF.

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Experimental

Sodium iodide and urea, both Merck (p.a.), were dried for several days under vacuum at 333 K. Formamide, N,N-dimethylformamide and N,N-dimethylacetamide, all Aldrich (99%) were dried using 4A type molecular sieves and then distilled under reduced pressure, Acetamide (Aldrich 99%) was crystallized from ethanol+diethyl ether mixture and then dried under vacuum at 313 K.

The mixtures were prepared by weight in a dry box, using freshly distilled solvents. The enthalpies of solution were measured with an 'isoperibol' type calorimeter. The glass calorimetric vessel, capacity ca. 80 cm^3, was equipped with a calibration heater, a thermistor and a stirrer – ampoule holder. A thin-walled glass ampoule with the substance to be dissolved was attached to the ampoule holder and crushed against the bottom of the calorimetric vessel during the experiment. The 10 kΩ thermistor was connected to a Wheatstone bridge. A temperature change of approximately $3\cdot10^{-5}$ K could be detected. The ampoule breaking-heat effect in the reaction vessel was negligible. The calorimeter was placed in a hermetically closed brass jacket with a capacity of about 1 dm^3 and immersed into a water thermostat. The temperature stability of the thermostat was better than $1\cdot10^{-3}$ K. The error in the calorimetric measurements was estimated to be ±0.7%.

Results and discussion

Dissolution enthalpies

The measured molar dissolution enthalpies, $\Delta_{sol}H_m$ of NaI in mixtures of DMF with urea, formamide, acetamide and N,N-dimethylacetamide are presented in Table 1. They were then extrapolated as a function of the square root of NaI molality to infinite dilution, in order to obtain the standard dissolution enthalpies, $\Delta_{sol}H^o$ in the investigated mixtures.

The standard dissolution enthalpy of NaI in N,N-dimethylformamide, determined in this work was: –55.25±0.18 kJ mol^{-1}. It agrees reasonably well with our earlier result: –55.31 kJ mol^{-1} [2] and with the appropriate literature data (–55.0±0.3 kJ mol^{-1} [3], –56.82 kJ mol^{-1} [4]). From the $\Delta_{sol}H^o$ data determined as described above the molar enthalpies of transfer, $\Delta_{tr}H^o$ of NaI from pure DMF to the investigated mixtures were calculated according to the formula:

$$\Delta_{tr}H^o(\mathrm{DMF} \rightarrow \mathrm{DMF} + \mathrm{Y}) = \Delta_{sol}H^o(\mathrm{DMF} + \mathrm{Y}) - \Delta_{sol}H^o(\mathrm{DMF}) \qquad (1)$$

where $\Delta_{sol}H^o$(DMF) and $\Delta_{sol}H^o$(DMF+Y) denote the standard dissolution enthalpies of NaI in pure DMF and in DMF+non-electrolyte (Y) mixtures, respectively. The obtained values of the $\Delta_{tr}H^o$ as a function of the mixed solvent composition are presented in Table 2 and Fig. 1. For comparison, the enthal-

Table 1 Molar dissolution enthalpies of NaI $\Delta_{sol}H_m$ in the mixtures of N,N'-dimethylformamide (DMF) with urea (U), formamide (FA), acetamide (AA) and N,N'-dimethylacetamide (DMA) at 298.15 K

m/mol kg^{-1}	$\Delta_{sol}H_m$/kJ mol^{-1}	m/mol kg^{-1}	$\Delta_{sol}H_m$/kJ mol^{-1}
DMF–U			
100 mol% DMF		5 mol% U	
0.00286	–54.77	0.00325	–52.40
0.00300	–54.73	0.00354	–52.31
0.00493	–54.61	0.00570	–52.11
0.00824	–54.42	0.00863	–51.61
0.00917	–54.35		
0.01425	–54.15		
10 mol% U		15 mol% U	
0.00306	–51.02	0.00352	–49.16
0.00365	–50.96	0.00376	–49.15
0.00599	–50.78	0.00745	–49.02
0.00770	–50.65	0.00749	–48.88
DMF–FA			
5 mol% FA		10 mol% FA	
0.00469	–52.43	0.00464	–51.32
0.00526	–52.03	0.00540	–51.02
0.00892	–52.02	0.01010	–50.91
0.01046	–51.83	0.01025	–50.92
15 mol% FA		20 mol% FA	
0.00382	–50.06	0.00400	–48.31
0.00421	–49.87	0.00464	–48.12
0.00892	–49.72	0.00885	–48.11
0.00972	–49.69	0.00904	–47.90
DMF–AA			
5 mol% AA		10 mol% AA	
0.00836	–51.34	0.00553	–50.83
0.00907	–51.04	0.00661	–50.56
0.01636	–50.47	0.01138	–50.36
0.01660	–50.70	0.01150	–50.31
15 mol% AA		20 mol% AA	
0.00515	–49.29	0.00295	–47.15
0.00535	–49.01	0.00506	–47.02
0.01073	–48.91	0.00625	–46.82
0.01223	–48.64	0.00859	–46.58

Table 1 Continued

m/mol kg^{-1}	$\Delta_{sol}H_m$/kJ mol^{-1}	m/mol kg^{-1}	$\Delta_{sol}H_m$/kJ mol^{-1}
	DMF–DMA		
5 mol% DMA		10 mol% DMA	
0.00432	–53.65	0.00325	–53.36
0.00473	–53.65	0.00433	–53.32
0.00832	–53.58	0.00679	–53.30
0.00881	–53.57	0.00837	–53.29
15 mol% DMA		20 mol% DMA	
0.00412	–53.71	0.00292	–54.91
0.00454	–53.69	0.00394	–54.91
0.00794	–53.67	0.00818	–54.88
0.00864	–53.62	0.00860	–54.87

pies of transfer of NaI from DMF to other, DMF – non-electrolyte mixtures investigated earlier are also given in Fig. 1. As it is seen, the transfer enthalpies of NaI in the investigated systems are positive and they increase with increasing cosolvent (non-electrolyte) content in the DMF – non-electrolyte mixtures. In this respect the discussed enthalpies behave differently than those in water – cosolvent mixtures, where different shapes of the $\Delta_{tr}H^{o}=f(x)$ curves are observed within the range of low cosolvent content [5]. The slope of the $\Delta_{tr}H^{o}$ function in DMF-cosolvent mixtures depends on the kind of the cosolvent and it grows in the following order: aprotic cosolvents < alcohols and secondary amides < primary amides and urea. This pattern qualitatively fulfils our expectations. As it was concluded in our earlier report [1], the shape of the NaI dissolution (and the transfer) enthalpy function in DMF-cosolvent mixtures reflects, to a large extent, the replacement of DMF molecules by the cosolvent in the solvation region of the electrolyte in these systems. This process, for DMF – aprotic cosolvent mixtures can be energetically unfavourable due to the lower

Table 2 Enthalpies of transfer of NaI $\Delta_{tr}H^{o}$ in kJ mol^{-1} from pure DMF to the mixtures of DMF with the cosolvents*

mol%	$\Delta_{tr}H^{o}$			
of cosolvent	U	FA	AA	DMA
5	1.65	1.65	2.47	1.39
10	3.65	3.15	3.60	1.77
15	5.61	4.65	5.29	1.43
20		6.45	7.56	0.27

*U – urea, FA – formamide, AA – acetamide, DMA – N,N-dimethylacetamide dipole moment of the cosolvent molecule (dioxane, acetone, THF, acetonitrile), or due to a less convenient electron density distribution in the molecule, which makes the ion solvation difficult (DMSO). Alcohols (*i*-butanol) and secondary amides (NMF) form single hydrogen bonds with DMF molecules. In this case, the ionic solvation shell formation in the mixtures of DMF with the mentioned non-electrolytes is connected with the destruction of the mixture structure which leads to a decrease in the exothermic effect of NaI dissolution. This phenomenon is even more evident in mixtures of DMF with primary amides and urea – the substances the molecules of which are capable of binding more than one DMF molecule and form more complicated structures. It is clear that in such cases the enthalpies of transfer of NaI from DMF to these mixtures have the highest positive values. The most striking shape of the $\Delta_{tr}H^0$ function is observed in DMF – DMA mixtures. Both solvents exhibit very similar physicochemical properties. The electric permittivity ($\varepsilon=37.8$), the donor number

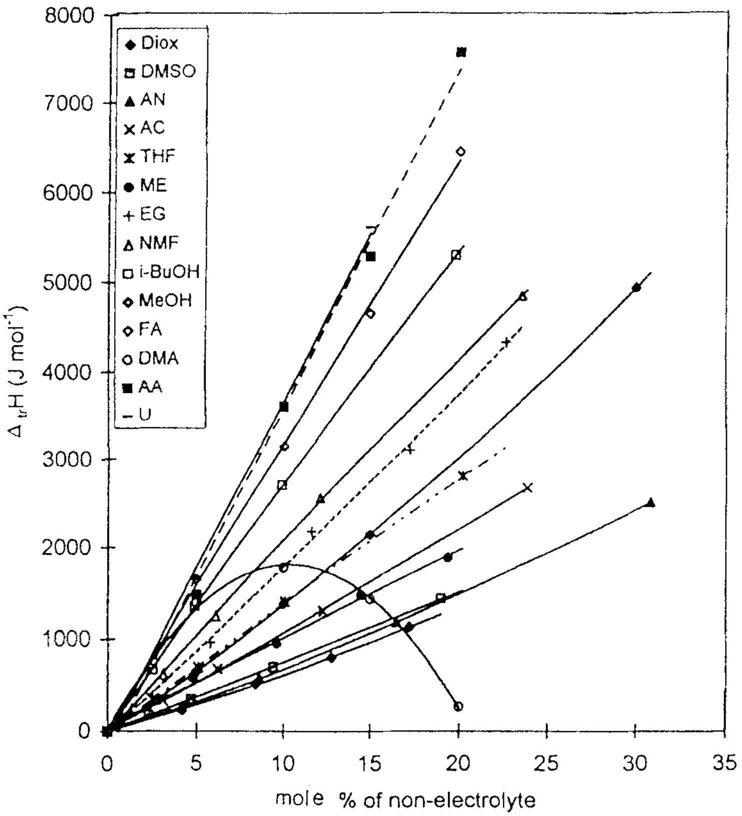

Fig. 1 Enthalpies of transfer of NaI from pure DMF to DMF – non-electrolyte mixtures at 298.15 K

(DN=27.8) and the acceptor number (A_N=13.6) of DMA are very close to the analogous functions characterising DMF (ε=36.7, DN=26.6, A_N=16.0 respectively) [6]. The dissolution enthalpies of NaI in pure DMF and DMA are also close to each other (–55.25 kJ mol^{-1} in DMF [this work] and –51.75 kJ mol^{-1} in DMA [7]). Therefore only small values of the $\Delta_{tr}H^o$ NaI could be expected. However, significant increase of $\Delta_{sol}H^o$ value was observed within the range of small DMA contents with a maximum at about 10 mol% of DMA. It can be supposed that addition of a small amount of DMA to DMF causes a reduction of empty space in the DMF structure. It is possible as the molecules of DMA although they have very similar properties, are somewhat larger than those of DMF. As the result, the cavity formation in the mixed solvent structure becomes more difficult and contributes endothermically to the dissolution enthalpy of NaI. Further increase in the DMA content, beyond the mixture composition corresponding to the maximum position destroys the structure of the mixture which facilitates the dissolution of NaI and makes it more exothermic.

Enthalpic pair interaction coefficients

In order to extend the analysis of NaI – non-electrolyte interactions in DMF solution the 'heterotactic' enthalpic pair interaction coefficients, h_{xy} were calculated. The details of the applied procedure have been described previously [8, 9]. The standard enthalpy of NaI solution in DMF+cosolvent mixtures, $\Delta_{sol}H^o$(DMF+Y) was presented as a function:

$$\Delta_{sol}H^o(\text{DMF} + \text{Y}) = \Delta_{sol}H^o(\text{DMF}) + bx_y + cx_y^2 \tag{2}$$

where xy is the mole fraction of cosolvent Y and b and c are coefficients that can be determined by the least-squares method. Parameter b in Eq. (2), which represents the limiting slope of the $\Delta_{sol}H^o$(DMF+Y) or $\Delta_{tr}H^o$(DMF→DMF+Y) function, is connected with the McMillan-Mayer [10] interaction coefficient h_{xy}.

$$b = 2h_{xy}(\delta m_y/\delta x_y)_{x_y\to 0} \tag{3}$$

Denoting the molar mass of the solvent (DMF) by M_s, we have for dilute solutions:

$$(\delta m_y/\delta x_y)_{x_y\to 0} = 1/M_s \tag{4}$$

Hence:

$$h_{xy} = 1/2\ M_s b \tag{5}$$

The h_{xy} values obtained in this way illustrate the sum of the enthalpic effects of the interactions between a molecule of the given non-electrolyte Y and the cation Na^+ and anion I^-:

$$h_{xy} = h(Na^+I^- - Y) = h(Na^+ - Y) + h(I^- - Y) \tag{6}$$

The enthalpic pair interaction coefficients determined in this work together with those of other NaI – non-electrolyte pairs in DMF investigated earlier [1, 2] are presented in Table 3.

Table 3 Enthalpic pair interaction coefficients h_{xy} in J kg mol^{-2} for NaI – non-electrolyte pairs in N,N-dimethylformamide at 298.15 K*

Non-electrolyte	h_{xy}	Non-electrolyte	h_{xy}
Water	1560^a	Urea	1378^d
Methanol	460^b	Formamide	1163^d
n-Propanol	860^a	N-methylformamide	760^a
i-Propanol	960^a	Acetamide	1313^d
i-Butanol	1000^a	N,N-dimethylacetamide	1258^d
Ethylene glucol	620^c	Acetone	420^a
2-Methoxyethanol	510^c	Dimethylsulfoxide	270^a
Tetrahydrofuran	500^a	Acetonitrile	240^a
1,4-Dioxane	190^c		

* The h_{xy} values presented here are twice as large as those given in our previous papers [1, 2]. This is so because they were presented previously as 'mean ionic' interaction coefficients which, for a 1-1 type electrolyte were defined as: $h_{xy} = 1/\nu\ h(MA\text{-}Y = 1/2\ [h(M^+\text{-}Y) + h(A^-\text{-}Y)]$.

a – Ref.[1], b – Ref.[17], c – Ref. [2], d – this work

The parameter c in Eq. (2) is related to a triplet interaction term, in our case to the h_{xy} coefficient. The interpretation of triplet interaction coefficients is obscured by the fact that they also contain a pairwise interaction term [10–12]. They will not be discussed in this paper.

The enthalpic pair interaction coefficients, h_{xy} for all NaI – non-electrolyte pairs in DMF investigated so far are positive in contrast to aqueous solutions where the analogous h_{xy} coefficients assume both positive and negative values [12, 14]. According to the model of interactions presented in our earlier papers [9, 12, 14] it means that in DMF solution the endothermic effects of desolvation dominate over ion – cosolute attraction forces. As the result, the analysed interactions in DMF solution which are illustrated by h_{xy} coefficients are thermochemically unfavourable. The postulated significant contribution of the desolvation effect to the enthalpic interaction coefficients suggests that similarly as in aqueous solution the h_{xy} (NaI – non-electrolyte) values in DMF can be correlated with some functions characterizing the solvation process of the investigated non-electrolytes [9, 12]. However, there is no simple correlation between h_{xy} and the enthalpy or molar heat capacity for the solvation of non-electrolyte in DMF which were so characteristic in aqueous solutions [13, 14]. It is possible that the strong solvation of non-electrolytes and NaI in DMF makes the effects of partial desolvation of the interacting species less differentiated than in water. Owing to this, the energetic effects connected with the solvation do not constitute the main contribution to the variation of the h_{xy} coefficient in DMF. It has been shown in previous papers of one of the authors that the enthalpic pair interaction coefficients h_{xy} in DMF can be presented as a sum of group contributions (SWAG model [15]) similarly as in aqueous solution [2]. In the mentioned paper the effects of interaction between NaI and CH_2, OH and ether (–O–) groups were determined. Now we extended these calculations including additionally the h_{xy} values for NaI-formamide, NaI–acetamide and NaI–DMA pairs, determined in this work, which also permitted calculation of the effect of interaction between NaI and the amide groups. In order to avoid any casual error, we included into the calculation only those functional groups which are present in the molecules of at least two non-electrolytes. In our case they were: alkyl group (CH_2), hydroxy group (OH), ether group (–O–) and according to a suggestion found in some papers [12] –CONH– group, characteristic of primary and secondary amides, denoted 'Pep'. The values of group additivity coefficient that refer to the non-electrolytes listed in Table 3 and containing in their molecules the particular functional group were calculated using the multiple linear regression method. The results of calculations are presented in Table 4. The tertiary amide function (denoted 'iPep') and carbonyl group (CO) appear only once among the investigated non-electrolytes (DMA and acetone). In that case the NaI – 'iPep' and NaI–CO group contributions were calculated by subtracting from the total h_{xy} value the sum of contributions referring to the other functional groups present in the given molecule. The results are also presented in Table 4. As can be seen from the Table, the interaction coefficient of NaI with the apolar group CH_2 is positive, as expected. It represents a thermochemical repulsion between a solvated ion and the solvated apolar group [8, 9, 12, 16]. The interaction coefficients which describe the interactions between ions and carbonyl (CO) or ether (–O–) groups are negative, similarly as in aqueous systems [12, 14]. It points to the relatively strong attraction forces of the ion-dipole type, which occur in the investigated system. In contrast to aqueous solutions [12, 14], the interactions between NaI and hydroxy (OH) or amide ('Pep') groups are thermochemically unfavourable in DMF. However, this surprising phenomenon can be explained by taking into account that the strongly polar groups mentioned above are capable of forming hydrogen bonds with the solvent (DMF) molecules. It is possible that in the im-

Table 4 Functional group interaction coefficients $h_{NaI\text{-}j}$ inJ kg mol^{-2} in DMF solutions*

Functional group combinations *j*	$h_{NaI\text{-}j}$
$Na^{+}I^{-}$ – CH_2	201± 8[a]
$Na^{+}I^{-}$ – OH	120±18[a]
$Na^{+}I^{-}$ – O	–308±22[a]
$Na^{+}I^{-}$ – 'Pep'	1037±24[a]
$Na^{+}I^{-}$ – 'Pep'	353
$Na^{+}I^{-}$ – CO	–183
r	0.995
std. error of fit	32.40

* See footnote for Table 3

a – values calculated using the multiple linear regression method

mediate vicinity of the interacting particles the H-bonds are broken, which gives a strong endothermic impact to the corresponding group interaction coefficients. The above conclusion in confirmed by the nature of NaI–'iPep' interaction which is less endothermic than the NaI–'Pep' interaction. The tertiary amide group is not capable of forming hydrogen bonds with the solvent molecule, and therefore the endothermic effect of the cosolute desolvation is relatively small.

References

1 H. Piekarski, J. Chem. Soc., Faraday Trans. 1, 84 (1988) 591.
2 H. Piekarski and W. Kobierski,Thermochim. Acta, 164 (1990) 323.
3 L. Weeda and G. Somsen, Recl. Trav. Chim., 86 (1967) 893.
4 G. A. Krestov and V. A. Zverev, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., 14 (1971) 528.
5 S. Taniewska-Osińska, Chem. Soc. Reviews, (1993) 205.
6 M. Koidel and S. Ishiguro, J. Solution Chem., 24 (1995) 511.
7 S. Taniewska-Osińska and M. Tkaczyk, Thermochim. Acta. 141 (1989) 131.
8 H. Piekarski and M. Tkaczyk, Thermochim. Acta, 112 (1987) 377.
9 H. Piekarski, Can. J. Chem., 64 (1986) 2127.
10 W. G. McMillan Jr. and J. E. Mayer, J. Chem. Phys., 13 (1954) 276.
11 R. H. Wood, T. H. Lilley and P. T. Thompson, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 1301.
12 H. Piekarski and M. Tkaczyk, J. Chem. Soc., Faraday Trans. 1, 87 (1991) 3661.
13 H. Piekarski and M. Tkaczyk, J. Chem. Soc., Faraday Trans. 1, 91 (1995) 2299.
14 H. Piekarski, Wiad. Chem., 47 (1993) 129.
15 J. J. Savage and R. H. Wood, J. Solution Chem., 5 (1976) 733.
16 P. J. Cheek, M. A. Gallardo-Jimenez and T. H. Lilley, J. Chem. Soc., Faraday Trans. 1, 84 (1988) 3435.
17 A. Piekarska, H. Piekarski and S. Taniewska-Osińska, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 513.