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Calorimetric investigations of NaCl, NaI and urea solutions in water–1,2-dimethoxyethane mixtures

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Abstract

Enthalpies of solution $\Delta_{\mathrm{sol}}H^{\ominus}$ of NaI, NaCl and urea in water–1,2-dimethoxyethane (DME) mixtures at 25°C were measured. The enthalpies of solution for NaCl, NaI and urea exhibit a maximum within the water-rich region. NaI and urea show a minimum in the range of high DME content. The maxima are apparently due to the hydrophobic hydration of DME molecules. The minima can be explained as a result of competition between water and DME molecules in the solute solvation shell.

Keywords: Dissolution enthalpies; NaCl; NaI; Urea; Water–1,2-dimethoxyethane mixtures

1. Introduction

Mixtures of water with aprotic solvents constitute an interesting group of liquid systems. Owing to the large variety of properties and molecular structures of the organic components, such mixtures exhibit a wide range of behaviour, which is particularly noticeable when these systems are used as solvents for electrolytes.

Among aprotic cosolvents, 1,2-dimethoxyethane (DME) is an interesting choice, because of the lack of self-association through hydrogen bonding and because the molecule contains two highly polar ether oxygen atoms which can be H-bonded to proton-donor groups. Moreover, DME forms complexes with the alkali metal cations Li^+ and Na^+ [1, 2]. 1,2-Dimethoxyethane has various uses, e.g. as a component of the mixed solvent in lithium batteries [3, 4]. Even so, the physico-chemical data on electrolyte solutions in water–DME mixtures are scarce (see, e.g. [5–8]). As part of

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a comprehensive study on thermochemical properties of 1:1 electrolytes and urea in water–organic solvent mixtures, the dissolution enthalpies of NaCl, NaI and urea in water containing small amounts of DME have previously been measured and the enthalpic pair interaction coefficients determined [9, 10]. This study extends our investigation over the whole available range of water–DME mixed solvent composition. The results are compared with analogous data on electrolytes in mixtures of water with other organic cosolvents with properties or molecular structures similar to DME.

2. Experimental

Sodium chloride and sodium iodide (both Merck, p.a.) were dried for several days under vacuum at 120°C (NaCl) or 60°C (NaI). Urea (POCh Poland, p.a.) was recrystallized from deionized, double-distilled water and dried under vacuum for several days at 60°C.

The 1,2-dimethoxyethane (Fluka AG) was kept for several days over KOH, refluxed for 24 h and distilled over sodium just prior to use (b.p. 85°C). The water–1,2-dimethoxyethane mixtures were prepared by weight.

Measurements of the dissolution enthalpies were made with the calorimetric system described elsewhere [11].

3. Results

Measurements of the enthalpy of solution of NaI were performed over the whole range of solvent composition. NaCl and urea were studied within a limited range of solvent composition because of their low solubility in mixtures with a high DME content.

Enthalpies of solution (NaCl and NaI) are given in Tables 1 and 2. Linear extrapolation against $m^{0.5}$ was performed to obtain the standard dissolution enthalpies $\Delta_{sol}H^{\ominus}$ at infinite dilution. Extrapolation based on Debye–Hückel theory was not possible owing to the lack of data on the temperature coefficient of the electric permittivity for water–DME mixtures.

For the urea–DME–water system, four to six independent measurements of the dissolution enthalpy were performed in each mixture. The final concentration ranged from 0.006 to 0.015 mol kg^{-1}. As no concentration dependence (within the error limits) of the solution enthalpies was observed, the measured enthalpies were regarded as the infinite dilution values $\Delta_{sol}H^{\ominus}$.

The standard enthalpies of solution for NaCl, NaI and urea in water–DME mixtures at 25°C are presented in Table 3. Table 3 also contains previously determined $\Delta_{sol}H^{\ominus}$ values for NaCl, NaI and urea in water–DME mixtures containing $<20\%$ of DME [9, 10].

4. Discussion

Fig. 1 presents the standard enthalpies of solution for NaCl, NaI and urea in water–DME mixtures as a function of solvent composition. The data for all three solutes

Table 1
Enthalpies of solution of NaCl in water–1,2-dimethoxyethane mixtures at 25°C

m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}	m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}	m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}
$x = 7.89$ [a]		$x = 11.76$		$x = 16.66$	
0.00384	5.95	0.00292	5.82	0.00316	5.11
0.00473	5.97	0.00356	5.85	0.00373	5.14
0.00494	5.97	0.00385	5.85	0.00386	5.14
0.00495	5.97	0.00448	5.86	0.00428	5.15
0.00923	6.00	0.00879	5.90	0.0083	5.22
0.01061	6.02	0.00909	5.91	0.00967	5.25
0.01103	6.03	0.00992	5.92	0.00983	5.25
0.01149	6.03	0.01026	5.92	0.01067	5.27
$x = 23.06$		$x = 31.80$		$x = 44.43$	
0.00277	3.67	0.00267	1.18	0.00112	−3.79
0.00304	3.68	0.00352	1.29	0.00389	−3.58
0.00346	3.72	0.01146	1.93	0.00565	−3.63
0.00394	3.76	0.01191	2.20	0.00789	−3.33
0.00693	3.85	0.02663	2.64		
0.00706	3.85	0.02782	2.81		
0.00803	3.90	0.04216	3.12		
0.00861	3.92	0.04437	3.32		

[a] x is the mol% of DME in the mixed solvent.

Table 2
Enthalpies of solution of NaI in water–1,2-dimethoxyethane mixtures at 25°C

m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}	m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}	m/ mol kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$/ kJ mol^{-1}
$x = 11.76$ [a]		$x = 23.06$		$x = 44.43$	
0.00828	−15.53	0.00659	−26.29	0.00169	−38.18
0.01049	−15.45	0.00914	−26.05	0.00198	−38.09
0.01385	−15.32	0.00939	−26.01	0.00414	−37.58
0.01894	−15.23	0.01387	−25.97	0.00509	−37.36
0.02528	−15.03	0.01958	−25.84	0.00674	−37.07
0.02831	−14.95	0.01978	−25.68	0.00823	−36.83
$x = 64.27$		0.02111	−25.73	0.00961	−36.63
0.00201	−47.63	0.02839	−25.51	0.01137	−36.38
0.00214	−47.57	$x = 79.15$		$x = 100.00$	
0.00484	−46.55	0.00232	−50.49	0.00136	−41.99
0.00497	−46.52	0.00453	−50.2	0.00217	−41.36
0.00784	−45.72	0.00688	−49.95	0.00301	−41.36
0.00854	−45.54	0.00749	−49.89	0.00487	−40.53
0.01138	−44.89	0.00985	−49.73	0.00619	−40.29
0.01243	−44.65	0.01436	−49.92	0.00813	−39.74
		0.01661	−49.29	0.00976	−39.44
				0.1192	−38.97

[a] x is the mol% of DME in the mixed solvent.

Table 3
Molal enthalpy of solution $\Delta_{sol}H^{\ominus}$ at infinite dilution in aqueous mixtures of 1,2-dimethoxyethane at 25°C

mass% of DME	mol% of DME	$\Delta_{sol}H^{\ominus}$/kJ mol^{-1}		
		NaCl	NaI	urea
0	0.00	3.85 [a]	−7.58 [a]	15.31 ± 0.03 [b]
5	1.04	4.17 [a]	−7.41 [a]	15.74 ± 0.03 [b]
10	2.17	4.48 [a]	−7.44 [a]	15.86 ± 0.02 [b]
15	3.41	4.90 [a]	−7.73 [a]	15.79 ± 0.03 [b]
20	4.76	5.38 [a]	−8.23 [a]	15.54 ± 0.03 [b]
30	7.89	5.84	–	–
40	11.76	5.73	−16.20	12.78 ± 0.02
50	16.66	4.94	–	–
60	23.06	3.39	−26.90	9.13 ± 0.02
70	31.80	0.50	–	–
80	44.43	−3.93	−39.19	6.41 ± 0.03
90	64.27	–	−49.66	4.42 ± 0.02
95	79.15	–	−51.73	3.74 ± 0.02
99	95.19	–	–	6.05 ± 0.02
100	100.00	–	−43.79	–

[a] Ref. [9].
[b] Ref. [10].

exhibit maxima within the water-rich region. Similar maxima were observed earlier for the inorganic electrolytes in mixtures of water and aliphatic alcohols [12–14], THF [15], HMPT [16] and 2-alkoxyethanols [14, 17–19]. It is generally accepted that the presence of these maxima is connected with the structure-making or -stabilizing effect of the added organic cosolvent on water. This effect probably results from hydrophobic hydration of the alkyl groups in the cosolvent. Formation of the solute solvation shell in the region of the hydrophobically ordered structure is more difficult than in pure water or in organic cosolvent-rich mixtures.

The position and height of the maxima for the electrolytes in water–DME depend strongly on the anion, as was found previously for salts in mixtures of water with THF [16], HMPT [16] and 2-alkoxyethanols [14, 17–19]. Hence, the position of the maximum does not seem to indicate any particularly stable structure in the mixed solvent as was postulated for electrolytes in water–alkanol mixtures [12–14]. The positions of the maxima probably result from the superimposition of (a) an endothermic effect of breaking of the water–cosolvent mixture structure, i.e. the destruction of the cosolvent molecule hydration shell, and (b) an exothermic effect of the change in an ionic solvation shell composition, ensuing from the ion–dipole interaction. The structure of the DME molecule with its two strongly polar ether groups prevents the creation of a monolithic and stable hydrophobic cage surrounding the whole molecule. Therefore the first of the above mentioned effects, depending on the hydrophobic properties of the cosolvent molecule, does not seem to be large. The second effect is

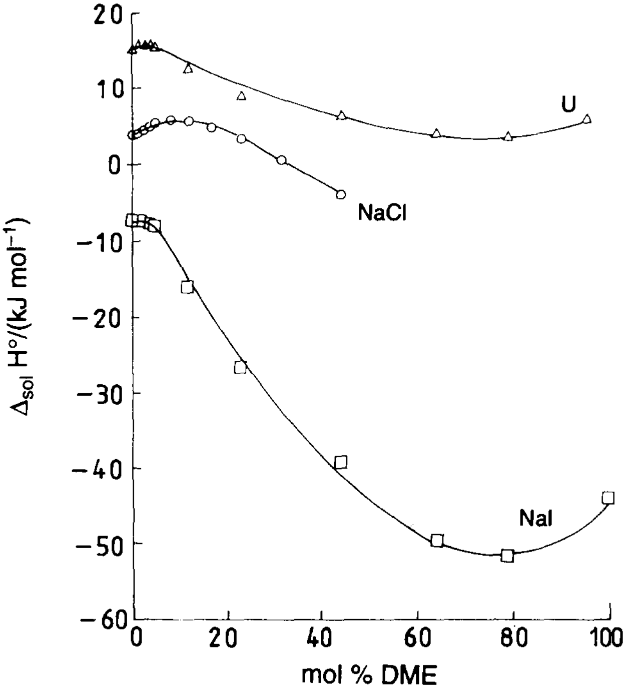

Fig. 1. Standard enthalpy of solution of NaCl, NaI and urea in DME–water mixtures as a function of the solvent composition at 25°C.

probably more pronounced for the iodide ion because of its higher polarizability and more effective interaction with the polar group in comparison with the chloride anion. This suggestion agrees well with Parker's observation [20] and also with the results of analysis of the enthalpic pair interaction coefficients for electrolyte–non-electrolyte pairs in aqueous solution [9]. As a consequence, in the systems under examination, the $\Delta_{sol}H^{\ominus} = f(x)$ curve for NaI changes its course in the range of smaller DME content, and the height of the $\Delta_{sol}H^{\ominus}$ maximum for NaI solution is lower than in the case of NaCl.

The $\Delta_{sol}H^{\ominus} = f(x)$ function for NaI and urea exhibits a minimum in the DME-rich region. The analogous minima of the $\Delta_{sol}H^{\ominus}$ of electrolytes with a high organic cosolvent content were observed earlier for mixtures of water with butyl alcohols [13], acetonitrile [21,22] and tetrahydrofuran [15] (Fig. 2). The presence of these extrema was attributed to the change of the mixed solvent structure (water–butyl alcohol [13], water–THF [15]) or to ion–water–cosolvent complex formation (water–acetonitrile [22]). In our opinion, the shape of the dissolution enthalpy function for NaI in the water–DME mixtures investigated here results from a superimposition of several energetic effects. The most important ones seem to be (a) changes in the ionic solvation and in water–DME interactions, resulting from the change in the mixed solvent

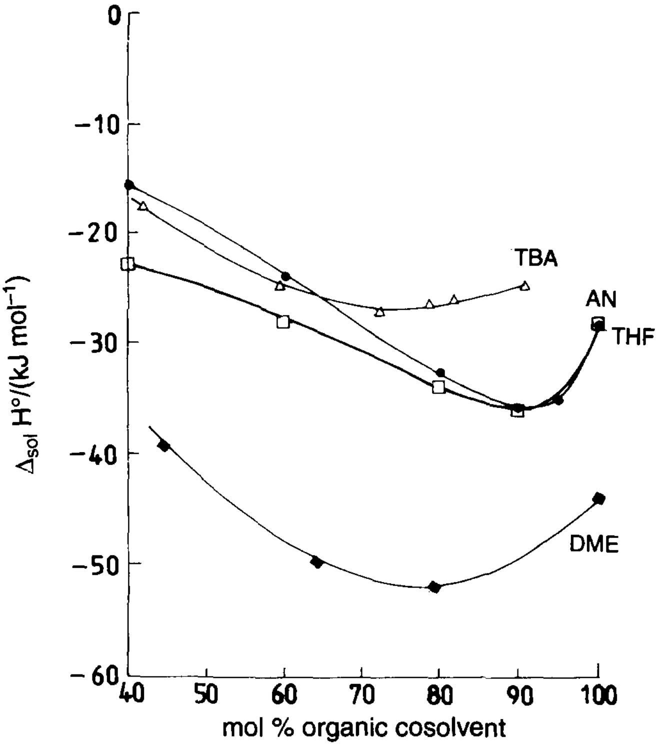

Fig. 2. Standard enthalpy of solution of NaI in mixtures of water with 1,2-dimethoxyethane (DME), acetonitrile (AN), tert-butanol (TBA) and $NaClO_4$ in water-tetrahydrofuran (THF) mixtures at 25°C.

composition, (b) Na^+-DME complex formation [1, 2], and (c) ionic association due to the low electric permittivity of DME ($\varepsilon = 7.2$ [4]). An addition of even small amounts of water to DME decreases the ionic association owing to the increase in the electric permittivity of the mixture. As a result, a greater number of "free" Na^+ ions appear in the solution, which, in turn can be "chelated" by the DME molecules. This phenomenon probably makes an additional exothermic contribution into the ionic solvation effect at small water contents up to the minimum of the $\Delta_{sol}H^{\ominus}$. A further increase in the water content in the system further decreases the ionic association. However, now the Na^+-DME complex formation is more difficult because of the competitive effects of water-DME and ion-water interactions. As a result of such competition the $\Delta_{sol}H^{\ominus}$ of the salts increases (exothermic effect of the dissolution decreases) beyond the minimum of $\Delta_{sol}H^{\ominus}$. The above presumptions are convergent with the conclusions drawn from the analysis of the results of thermochemical investigations of electrolyte solutions in mixtures of DME with γ-butyrolactone and propylene carbonate [23]. It can also be assumed that analogous reasons are responsible for the presence of the minimum mentioned earlier of the $\Delta_{sol}H^{\ominus} = f(x)$ function for $NaClO_4$ in water-THF mixtures [15]. The position of the $\Delta_{sol}H^{\ominus}$ minimum for NaI in water-DME mixtures corresponds to a smaller mole fraction of the organic cosolvent in the mixture than that for $NaClO_4$ in the mixtures of water with THF. The finding is probably connected with the different stoichiometry of the Na^+–ether molecule complexes, which are 1:4 for THF and 1:2 for DME [24].

A minimum of the urea dissolution enthalpy in the water–DME mixtures seems to be also a result of competition between water and DME molecules in the urea solvation process. Because of its molecular structure, urea is able to interact through dipole–dipole attraction forces as well as through hydrogen bond formation with the molecules of both components of the mixed solvent. Therefore, it can be supposed that, in the region of low water content in the mixed solvent, some water molecules join the urea–DME associates, which results in an exothermic shift of the urea dissolution enthalpy in the DME-rich region. Further increase of water content in the mixed solvent (beyond the $\Delta_{sol}H^{\ominus}$ minimum) causes a gradual expulsion of the DME molecules from the mixed associates. As a result, the $\Delta_{sol}H^{\ominus}$ of urea increases up to the earlier mentioned maximum in the water-rich region. The energetically unfavourable urea–DME interactions in the presence of water are confirmed by an analysis of the enthalpic pair interaction coefficients h_{xy} in water [11].

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