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DETERMINATION OF COMPOSITIONS OF NaI SOLID SOLVATES OBTAINED FROM THE SOLUTIONS IN MIXTURES OF WATER WITH ACETONITRILE AND N, N-DIMETHYLFORMAMIDE AT 25°C

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The thermogravimetric method was applied to determine the compositions of solid NaI existing in equilibrium with saturated salt solutions over the whole range of the compositions of the mixtures of water with AN and DMF at 25°C. It was concluded that NaI is preferentially hydrated in water-rich region only for both investigated systems, i.e. for $x_{AN}<0.15$ and $x_{DMF}<0.25$. Above the mentioned organic solvent content the significant differences in solvation of NaI are observed for both systems. In water-AN system for $0.15<x_{AN}<0.95$ NaI is weakly preferentially hydrated and the composition of the solvate is: $NaI\cdot H_2O\cdot CH_3CN$. In pure AN, NaI is not solvated. In water-DMF system in the ranges of composition $0.25<x_{DMF}<0.50$ and $0.50<x_{DMF}<0.80$ two types of mixed solvates are observed: $NaI\cdot 4H_2O\cdot 2DMF$, and $NaI\cdot 2H_2O\cdot 2DMF$, respectively. So, NaI is strongly solvated by both components of mixed solvent. For $x_{DMF}>0.80$ like in pure DMF, NaI is solvated by two molecules of DMF.

Keywords: NaI solid solvates, TG

Introduction

The mixtures of water with acetonitrile (AN) or N, N-dimethylformamide (DMF) are almost isodielectric [1–3] ($\varepsilon_{AN} = 35.95$ and $\varepsilon_{DMF} = 37$) but their other properties differ [3–10]. Water-AN system exhibits a large positive deviation from Raoult's law [4], positive ΔH_M and ΔG^E_{12} [5, 6] and negative or small positive preferential solvation $\delta x_{2(1)}$ [7], so, the self-interactions of each component are favoured over the mutual ones [6, 7]. On the contrary water-DMF mixture shows negative ΔH_M [8] and ΔG^E_{12} [9] and large positive preferential solvation

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$\delta x_{2(1)}$ [7], so the mutual interactions of the components are stronger than their self-interactions [7].

Structural discontinuities in water–AN system [4–7, 10, 11] may significantly affect the solvation of ions. Two different opinions concerning the solvation of NaI in this system exist in literature. Preferential solvation of both ions by AN molecules above 15 mol% AN was concluded from self-diffusion [12] and B-viscosity coefficients [13] and Walden product [12, 14]. On the other hand, weak preferential hydration of I^- ions and preferential hydration of Na^+ ions were drawn from n.m.r. [15] and from the free energy of transfer [16, 17] studies.

In case of water–DMF system the exchange of water molecules in the first solvation shell of ions for DMF ones was suggested above 67 mol% DMF [18]. The free enthalpies of transfer of ions point out to solvation of Na^+ ions by DMF molecules in pure DMF [17].

The investigations of solid NaI obtained from its saturated solutions in both mixed solvents over the whole range of mixed solvent compositions can provide an insight into solvation processes in these systems and let the conclusions concerning the salt solvation in solid phase compare with dilute solutions of the investigated systems coming from different experimental methods.

Experimental

NaI (Merck, analytical grade) was dried under vacuum at 70°C. AN (Aldrich, pure) purified by successive distillation from P_2O_5 and CaH_2 after initial drying with CaH_2 [19]. DMF (Aldrich, pure) was dried over 4A molecular sieves and then distilled at reduced pressure [19].

TG method was applied to obtain the composition of solid NaI existing in equilibrium with saturated salt solutions in the mixtures of water with AN and DMF at 25°C. The saturated solution of NaI in the investigated mixed solvents were prepared by weight in order to obtain ca. 0.5 g of NaI in a solid phase. The solutions were kept in darkness in thermostat cell at constant temperature for about four days in order to reach the equilibrium between solid and liquid phases. Then, they were filtered off under vacuum and the precipitates were analyzed immediately without drying. The measurements were made with a 102/1500 derivatograph (MOM, Hungary) recording TG, DTG and DTA curves. Samples of 250 mg were heated in static air in ceramic crucibles, Al_2O_3 was a reference material, at a heating rate of 2.5 deg·min^{-1} and with sensitivities TG: 200 mg. The samples were heated to 300°C only, because the earlier measurements showed that above 250°C there was only pure NaI in the sample and it decomposed at ca. 630°C. The products of decomposition were calculated on the basis of TG curves weight losses.

The solubility measurements were performed in the way described earlier [20]. The salt concentration in saturated solutions was determined by potentiometric titration. The results of solubility were the average values of three independent determinations. All solubility measurements were performed twice.

Results and discussion

TG, DTA and DTG curves for NaI obtained for water–AN system are shown in Fig. 1 for chosen mixed solvent compositions. Results of the composition of solid NaI are completed in Table 1. It was found that the mixed solvent composition can be divided into three areas with different solid NaI compositions.

i) For water-rich region i.e. $0<x_{AN}<0.15$ the character of TG, DTA and DTG curves is the same as in pure water (Figs 1a and 1b). The dehydration of NaI is a two-step process. The mass loss corresponds to the release of 1 mol of water in each step i.e. at 115° and 145°C. The first endothermic peak at 72°C is probably connected with the vaporization of unbounded water and AN molecules (no sharp changes on DTG curves are observed). All the samples were not dried in order to avoid the changes in their composition especially in the case of mixed solvates (it was found that time and temperature influenced the composition of the samples). The solid NaI was found to be $NaI \cdot 2H_2O$, so, NaI is preferentially hydrated in water-rich region.

ii) For $0.15<x_{AN}<0.95$ (Figs 1c–e) the mass loss in the first step (at 70°–80°C) corresponds to the release of more than 1 mole of AN i.e. 1.02–1.27 moles (the sharp peaks on DTG curves appeared which were not observed for pure water and in water-rich region). Too large mass losses are connected with overlaying of two processes: release of AN and vaporization of unbounded molecules of both components of the mixed solvent. In the next two steps of decomposition (at 115° and 150°C) of 0.5 mole of water is released in each step. So, the composition of the solid phase is: $NaI \cdot H_2O \cdot CH_3CN$ and AN molecules are weaker bonded with NaI than water ones.

iii) For $x_{AN} = 1$ (Fig. 1f) the observed total mass loss of about 5% is probably connected with the solvent vaporization. NaI is not solvated in solid phase.

So, it can be concluded that NaI is rather weakly preferentially hydrated for $0.15<x_{AN}<0.95$ what confirms the conclusions coming from ΔG_t^{12} and n.m.a. studies [15–17].

Thermogravimetric curves for NaI in water–DMF system are shown in Fig. 2a–f. It was found that the solvent composition is divided into four areas with different compositions of NaI (Table 1).

Table 1 Solubilities, s, (g/100 g of solvent) and solid phase compositions of NaI in water–AN and water–DMF mixtures at 25°C; x_s - mole fraction of aprotic solvent

x_s	s	ρ g/cm^3	Composition of solid NaI
	Water–AN system		
0.0	64.97	1.925	$NaI\cdot 2H_2O$
0.1	61.23	1.768	$NaI\cdot 2H_2O$
0.2	56.16	1.621	$NaI\cdot H_2O\cdot CH_3CN$
0.3	50.10	1.456	$NaI\cdot H_2O\cdot CH_3CN$
0.4	45.37	1.349	$NaI\cdot H_2O\cdot CH_3CN$
0.5	39.75	1.239	$NaI\cdot H_2O\cdot CH_3CN$
0.6	33.65	1.138	$NaI\cdot H_2O\cdot CH_3CN$
0.7	28.95	1.067	$NaI\cdot H_2O\cdot CH_3CN$
0.8	22.10	0.9780	$NaI\cdot H_2O\cdot CH_3CN$
0.9	14.63	0.8980	$NaI\cdot H_2O\cdot CH_3CN$
1.0	20.22	0.9460	NaI
	Water–DMF system		
0.1	58.22	1.726	$NaI\cdot 2H_2O$
0,20	54.78	1.647	$NaI\cdot 2H_2O$
0.25	52.86	1.618	$NaI\cdot 2H_2O$
0.30	46.77	1.500	$NaI\cdot 4H_2O\cdot 2DMF$
0.35	39.66	1.396	$NaI\cdot 4H_2O\cdot 2DMF$
0.40	31.74	1.285	$NaI\cdot 4H_2O\cdot 2DMF$
0.50	23.93	1.190	$NaI\cdot 4H_2O\cdot 2DMF$
0.60	18.50	1.130	$NaI\cdot 2H_2O\cdot 2DMF$
0.70	13.68	1.076	$NaI\cdot 2H_2O\cdot 2DMF$
0.80	10.74	1.042	$NaI\cdot H_2O\cdot 2DMF$
0.90	8.083	1.010	$NaI\cdot 2DMF$
1.00	5.888	0.9918	$NaI\cdot 2DMF$

i) For $x_{DMF}<0.25$ the hydrate: $NaI\cdot 2H_2O$ is found (Fig. 2a–b), decomposition of which goes in the same way as described above for pure water.

ii) For $0.25<x_{DMF}<0.50$ (Fig. 2c) three endothermic peaks are observed on DTA curves (at about 85°, 140° and 200°C). On DTG curves the first one is not observed, so this effect is probably connected with the vaporization process. The second one corresponds to the release of 4 moles of water and the third one of 2 moles of DMF (see, for comparison, TG and DTA curves for DMF in Fig. 2f).

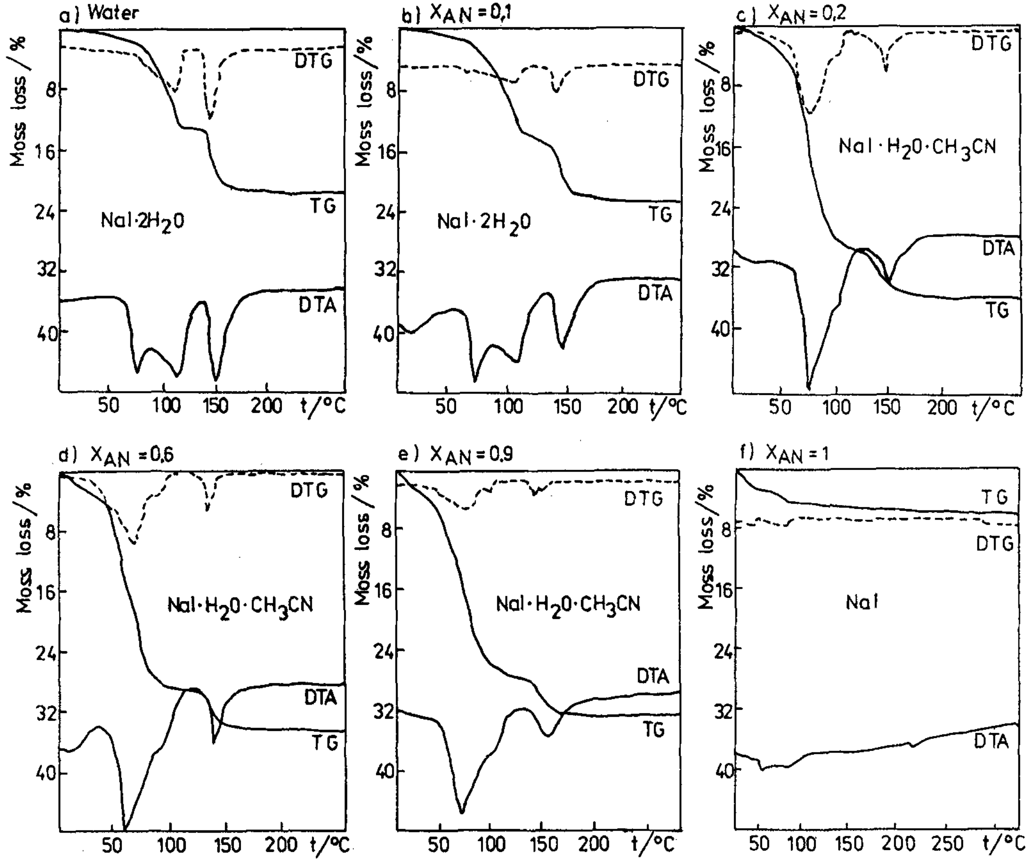

Fig. 1 TG, DTG and DTA curves of NaI obtained from water–AN mixed solvent over the whole range of mixed solvent compositions

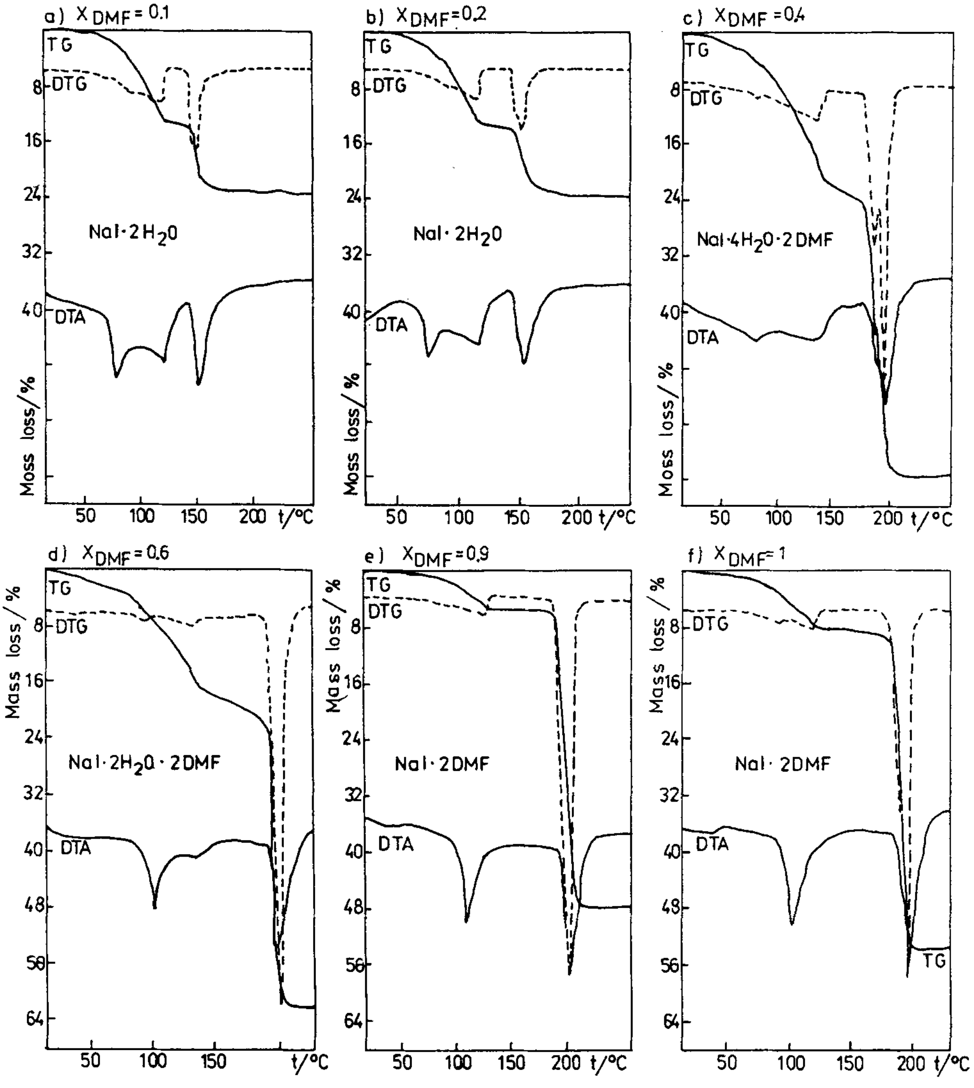

Fig. 2 TG, DTG and DTA curves of NaI obtained from water–DMF mixed solvent over the whole range of mixed solvent compositions

So, the composition of solid NaI is: NaI·4H_2O·2DMF and DMF molecules are more strongly bonded with NaI than water ones.

iii) For $0.50 < x_{DMF} < 0.80$ (Fig. 2d) NaI loses water and DMF molecules as described above in point ii) but the mass loss at 140°C corresponds to 2 moles of water. The composition of solid NaI is $NaI \cdot 2H_2O \cdot 2DMF$ and DMF molecules are more strongly bonded with NaI than water ones.

iv) Above $x_{DMF} > 0.8$, like in pure DMF, NaI loses DMF molecules at about 200°C and the mass loss corresponds to the release of 2 moles of DMF. The solid phase composition is: $NaI \cdot 2DMF$.

The obtained results are compared with the results of NaI solubility – the property closely connected with electric permittivity (Fig. 3). The shapes of the solubility curves in both mixed solvents differ. In water–AN system the solubility curve changes almost monotonously (with a slight breakdown at about 15 mol% AN) up to minimum at about 90 mol% AN. So, the mixed solvent composition is divided into three areas corresponding to the different solid phase compositions.

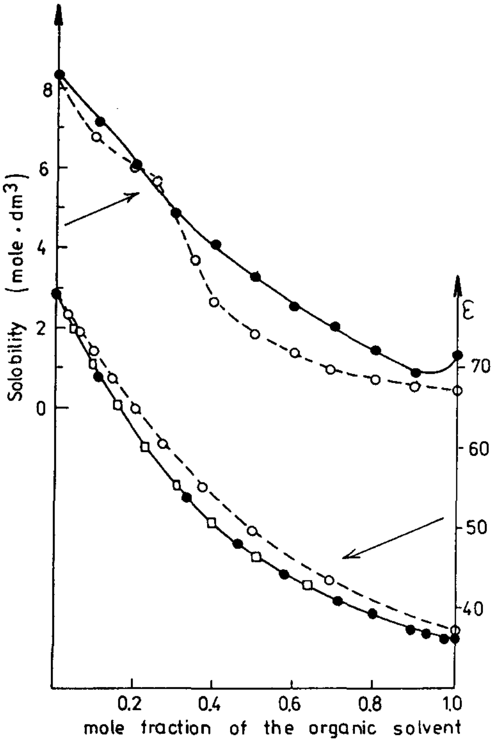

Fig. 3 Solubility of NaI in water-AN and water–DMF mixtures and electric permittivities [2–3] of mixed solvents at 25°C; (———) water–AN, (– – –) water–DMF; ε data (•) from Ref. [3] and (o □) from Ref. [2]

For water–DMF system the sharp change of the solubility curve is observed at 25 mol% DMF and significant ones at 50 and 80 mol% DMF dividing the mixed solvent composition into four areas with different solid phase compositions. So, the changes of the plot of solubility curves are closely connected with the changes of the solid phase composition.

The obtained results shows significant differences in solvation of NaI observed for both systems connected with different properties of both aprotic solvents.

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Zusammenfassung — Mittels TG wurde bei 25°C im gesamten Mischbereich von Wasser mit AN und DMF die Zusammensetzung von festem NaI bestimmt, welches im Gleichgewicht mit den entsprechenden gesättigten Salzlösungen steht. Es wurde geschlußfolgert, daß NaI in beiden Systemen nur in wasserreichen Regionen (x_{AN} und x_{DMF}) präferiert hydratiert wird. Oberhalb der erwähnten Alkoholgehalte werden für das Auflösen von NaI in beiden Systemen signifikante Unterschiede beobachtet. Im Wasser-AN-System ist NaI im Bereich 0.15_{AN} schwach präferiert hydratiert und die Zusammensetzung des Solvates ist: $NaIH_2OCH_3CN$. In reinem AN wird NaI nicht solvatiert. Im System Wasser-DMF werden im Zusammensetzungsintervall 0.25 und 0.50 zwei Typen von Mischsolvaten beobachtet: $NaI\cdot 4H_2O\cdot 2DMF$ und $NaI\cdot 2H_2O\cdot 2DMF$. NaI wird also in Lösungsmittelgemischen von beiden Lösungsmitteln stark solvatiert. Für $x_{DMF}0.80$, wie zum Beispiel in reinem DMF, wird NaI durch zwei Moleküle DMF solvatiert.