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SOLUBILITY DATA OF SOME SODIUM SALTS IN MOLTEN UREA
Part I

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ABSTRACT

Liquid–solid equilibrium temperatures were measured over the concentration ranges allowed by the thermal stability of urea in binary systems between the amide and some sodium salts (NaSCN, $NaNO_3$, $NaClO_4$ and HCOONa). Experimental results are given in terms of phase diagrams and on the basis of the trend of $\Delta T/(\nu m K)$ vs. m.

INTRODUCTION

As a continuation of our studies concerning the properties of binary mixtures composed of molten amides and electrolytes [1–12], we have studied the cryoscopic behaviour of some sodium salts in molten urea.

Previous investigations have indicated that the Na^+ ion promotes supercooling phenomena in mixtures with molten amides, especially acetamide [3,6], and in such liquid solutions the existence of viscoelastic and dielectric relaxations was noted [13–17], as well as ultrasonic losses in the megahertz region [18], which may be due to polymeric aggregations produced by association phenomena of solvated ions.

In this paper we investigate the influence of different anions on the cryoscopic behaviour of these binary systems.

EXPERIMENTAL

The cryoscopic method used has been described previously [19]. In order to measure melting points near room temperature, we employed equipment as described by Braghetti et al. [20], in which an F40 JULABO cryostat was adopted for refrigeration.

The chemicals employed were: NH_2CONH_2 (99.8%; Carlo Erba RPE), $NaNO_3$ and $NaClO_4$ (both 99%; Carlo Erba RPE), NaSCN and HCOONa (both 99%; Fluka); all were used without further purification.

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The sodium salts were hot-dried under dynamic vacuum and the urea was dried at room temperature for several days under dynamic vacuum. In this paper, "1" denotes urea and "2" denotes the other component.

RESULTS AND DISCUSSION

Liquid–solid equilibrium temperatures are given in Tables 1–4. The crystallization curves are shown in Fig. 1, while Fig. 2 shows graphically the trend of $\Delta T/(\nu m K)$ vs. m, where ΔT is the cryoscopic lowering, m is the molality, ν is the total number of ions in the salt formula, and K is the thermodynamic cryoscopic constant of urea, the value of which, 5.58 K kg

TABLE 1

Liquid–solid equilibrium temperatures in the binary system urea–NaSCN

X_1 [a]	T(K)	X_1	T(K)
1.0000	406.0	0.9932	404.3
0.9900	404.2	0.9839	402.7
0.9763	401.4	0.9681	400.0
0.9582	397.9	0.9475	395.7
0.9377	394.1	0.9256	389.7
0.9124	387.5	0.8953	378.0
0.8764	377.4	0.8672	370.1
0.8492	358.9	0.8249	355.9
0.8127	340.5	0.7957	334.8
0.7753	336.1	0.7501	318.0
0.7468	329.8	0.7291	343.9
0.7259	347.4		

[a] Mole fraction of urea.

TABLE 2

Liquid–solid equilibrium temperatures in the binary system urea–$NaClO_4$

X_1 [a]	T(K)	X_1	T(K)
1.0000	406.0	0.9935	404.6
0.9883	403.8	0.9838	402.8
0.9788	403.1	0.9681	400.1
0.9593	398.7	0.9503	396.7
0.9401	394.6	0.9268	389.5
0.9119	381.5	0.8993	381.6
0.8792	365.8	0.8740	359.5
0.8450	354.3	0.8191	347.6
0.8003	353.4	0.7750	365.9
0.7490	375.2		

[a] Mole fraction of urea.

TABLE 3

Liquid–solid equilibrium temperatures in the binary system urea–$NaNO_3$

X_1 [a]	T(K)	X_1	T(K)
1.0000	406.0	0.9924	404.9
0.9877	404.4	0.9832	402.8
0.9760	401.9	0.9708	400.9
0.9680	400.2	0.9608	396.7
0.9567	398.4	0.9498	392.1
0.9268	389.5	0.9097	388.7
0.8949	385.6	0.8699	377.7
0.8506	373.9	0.8273	363.9
0.8124	358.7	0.7965	353.6
0.7795	364.0	0.7744	360.4
0.7593	384.5	0.7495	399.2

[a] Mole fraction of urea.

m^{-1}, was deduced from the literature [21]. The experimental data of $\Delta T/(\nu m)$, extrapolated to $m = 0$, for urea give the following values: 5.39 K kg m^{-1} (solute $NaClO_4$), 5.47 K kg m^{-1} (solute $NaNO_3$) and 5.56 K kg m^{-1} (solutes NaSCN and HCOONa).

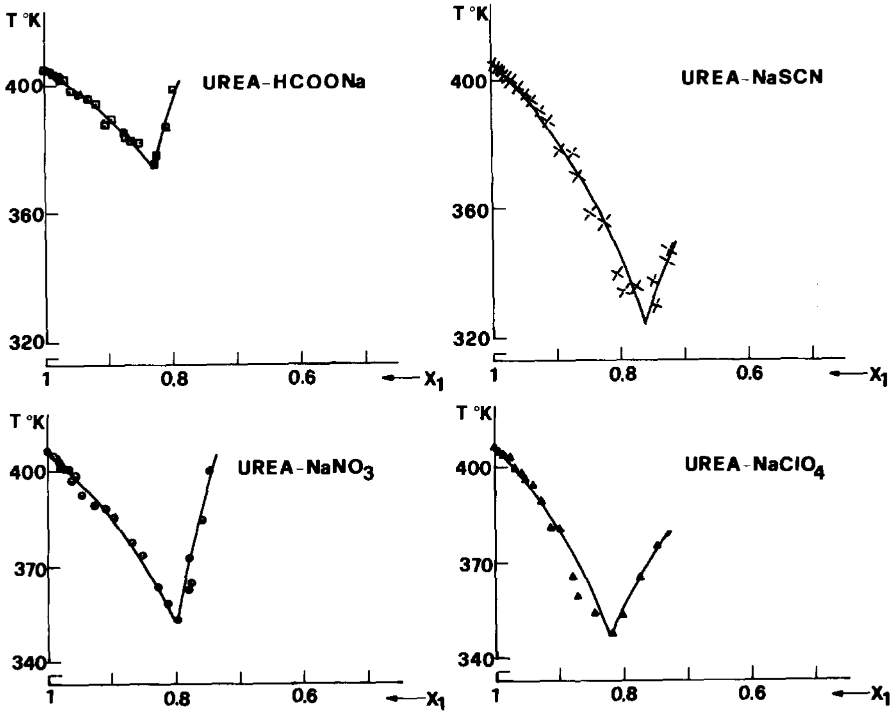

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems urea–HCOONa, urea–NaSCN, urea–$NaNO_3$ and urea–$NaClO_4$.

TABLE 4

Liquid–solid equilibrium temperatures in the binary system urea–HCOONa

X_1 [a]	T(K)	X_1	T(K)
1.0000	406.0	0.9917	404.6
0.9881	404.1	0.9819	402.8
0.9762	401.9	0.9732	401.6
0.9717	401.8	0.9617	398.0
0.9487	396.7	0.9341	395.6
0.9232	394.4	0.9068	387.3
0.8972	389.7	0.8759	384.6
0.8740	383.3	0.8695	382.8
0.8515	382.4	0.8269	375.0
0.8249	378.0	0.8103	386.4
0.8001	398.7		

[a] Mole fraction of urea.

From Fig. 2, which shows the experimental trend of $\Delta T/(\nu m K)$ vs. m, it is possible to deduce that all the electrolytes are completely dissociated at their experimental concentrations. This fact indicates that urea is a better solvent in comparison with acetamide [3] for sodium salts. The cause of this behaviour may be related to the presence of the NH_2 or CH_3 group.

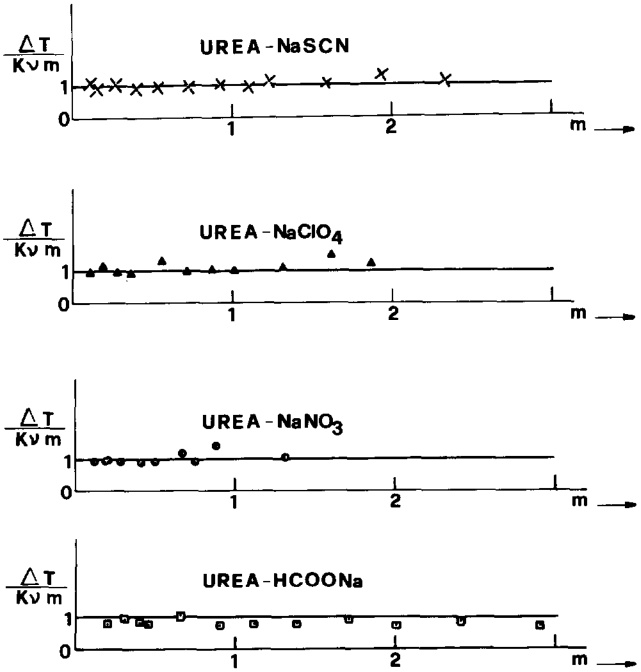

Fig. 2. Trend of $\Delta T/(\nu K m)$ vs. m for binary systems of urea with NaSCN, $NaClO_4$, $NaNO_3$ and HCOONa.

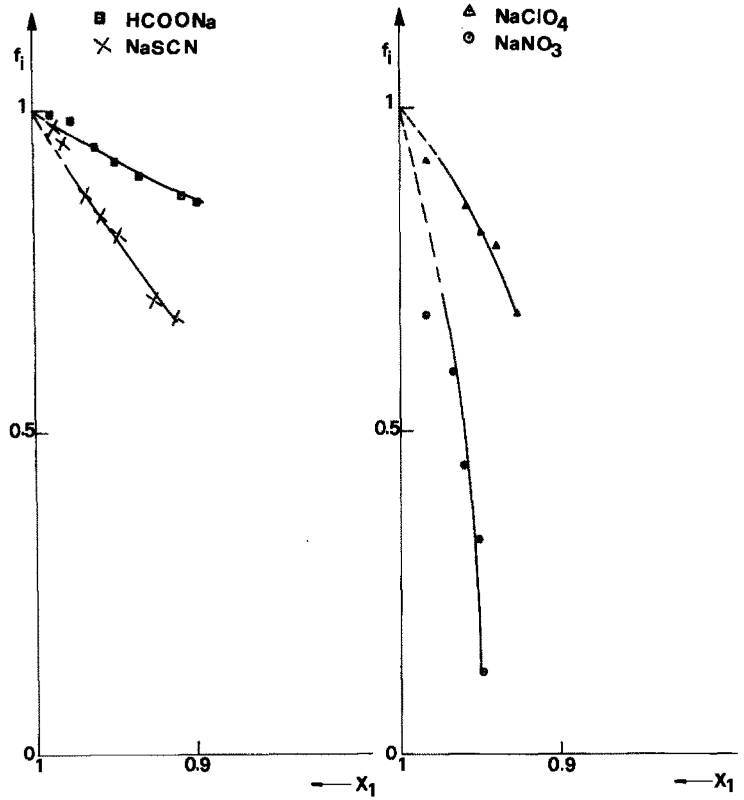

Fig. 3. Graphical trends of the mean ionic activity coefficient, f_i, as a function of the urea molar fraction for HCOONa, NaSCN, NaClO$_4$ and NaNO$_3$ solutions.

With the aid of the Gibbs–Duhem relation, we have also evaluated approximately the mean ionic activity coefficient, f_i, for various electrolytes, and the trends are shown in Fig. 3 as a function of the molar fraction of urea. From the data we may draw the following conclusions

1. In the urea–HCOONa system, the solute–solute interaction is stronger than in other systems.
2. In the urea–Na(NO$_3$, ClO$_4$, SCN) systems, the solute–solvent interaction is the dominant factor, according to the following scale: NaNO$_3$ > NaClO$_4$ ≃ NaSCN.

Urea–electrolyte mixtures do not exhibit noteworthy supercooling phenomena; in any event, the trend of the activity coefficient indicates that the behaviour of the anions derived from weak acids is different from that of anions derived from strong acids.

In the acetamide–electrolyte systems that have been studied previously [3], supercooling phenomena occur only when the salt has been derived from a strong acid. It is probable that supercooling depends on the cation–solvent interaction, which is competitive with the cation–anion interaction.

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