Thermochimica Acta, 189 (1991) 261–269
Elsevier Science Publishers B.V., Amsterdam

Solubility data of some potassium salts in molten urea
Part 2

G. Vitali [a], G. Berchiesi [a] and S. Barocci [b]

[a] *Dipartimento di Scienze Chimiche Università degli Studi di Camerino, Via S. Agostino n. 1, 62032 Camerino (Italy)*
[b] *E.P.O. Patentlaan 2, 2288 EE Rijswijk (ZH) (The Netherlands)*

(Received 15th February 1991)

Abstract

Binary mixtures composed of urea and some potassium salts (KSCN, KNO_3, $KClO_4$, HCOOK) have been investigated, and the liquid–solid equilibrium temperatures were measured in the concentration range allowed by the thermal stability of urea. Experimental results are presented as phase diagrams and are given in terms of the trend of $\Delta T/\nu K_c m$ versus m.

INTRODUCTION

In previous papers [1–13], we have pointed out that the binary mixtures of some amides and electrolytes, principally those containing acetamide [3–6], show supercooling phenomena and that the Na^+ ion was primarily responsible for these phenomena; in fact some binary mixtures containing Na^+ even reached the glass-transition temperature. Moreover, these liquid solutions exhibit viscoelastic behaviour [14–17], ultrasonic losses in the megahertz region [18] and dielectric relaxations [19], which may be explained on the basis of polymeric structures built by an aggregation of solvated ions. In this paper we consider the binary systems between urea and KSCN, $KClO_4$, KNO_3, HCOOK in order to determine the influence of different anions on cryoscopic behaviour and to compare the results with those of the binary systems composed of urea and the sodium salts of the same acids [13].

EXPERIMENTAL

The experimental cryoscopic method used has been described in a previous paper [20]. In order to measure melting points near room temperature, we used the equipment described in ref. 21, refrigerated by thermostatted liquid with an F 40 JULABO cryostat. The chemicals employed were: NH_2CONH_2 (99.8% Carlo Erba RPE), KNO_3 and $KClO_4$ (99% Carlo Erba

0040-6031/91/$03.50

TABLE 1

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

X_1	T (K)	X_1	T (K)	X_1	T (K)
1.0000	406.0	0.8603	374.1	0.5803	352.3
0.9888	403.2	0.8401	369.9	0.5609	362.9
0.9817	401.7	0.8202	365.7	0.5357	367.4
0.9774	399.9	0.7980	358.4	0.5003	375.0
0.9718	398.8	0.7802	353.6	0.4791	379.6
0.9649	398.8	0.7605	347.8	0.4404	386.0
0.9553	396.1	0.7406	342.7	0.4010	393.0
0.9535	395.0	0.7342	341.7	0.3568	399.9
0.9495	394.6	0.7303	341.0	0.3047	408.5
0.9427	393.9	0.7298	339.8	0.2599	420.7
0.9331	390.4	0.7192	337.0	0.2419	417.2
0.9229	388.8	0.6997	330.6	0.2217	422.4
0.9093	386.3	0.6814	327.2	0.1992	423.9
0.9034	384.1	0.6635	330.2	0.1498	431.3
0.8979	383.2	0.6403	338.2	0.1097	437.7
0.8940	381.8	0.6196	345.5	0.0503	443.8
0.8799	380.1	0.5992	350.7	0.0000	450.4

RPE), KSCN and HCOOK (99% Fluka); all were used without further purification. The potassium 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 represents urea and 2 denotes the other components.

RESULTS AND DISCUSSION

Liquid–solid equilibrium temperatures, as a function of molar fraction of urea, are given in Tables 1–4. Crystallisation curves and the trends of $\Delta T/\nu K_c m$ versus m are given in Figs. 1–3 and Fig. 4, respectively, where

TABLE 2

Liquid–solid-equilibrium temperatures in the binary system urea–$KClO_4$

X_1	T (K)	X_1	T (K)
1.0000	406.0	0.9686	398.7
0.9943	403.8	0.9578	396.5
0.9902	403.5	0.9499	397.9
0.9881	403.0	0.9434	394.6
0.9826	401.9	0.9379	392.7
0.9772	399.3	0.9252	389.6
0.9715	399.6		

TABLE 3

Liquid–solid equilibrium temperatures in the binary system urea–KNO_3

X_1	T (K)	X_1	T (K)
1.0000	406.0	0.9109	391.2
0.9943	404.4	0.8984	389.3
0.9885	403.6	0.8807	387.3
0.9797	402.1	0.8696	385.6
0.9697	399.8	0.8502	382.9
0.9592	398.0	0.8403	383.1
0.9517	397.3	0.8257	387.0
0.9438	395.8	0.8035	401.3
0.9336	394.7	0.7801	410.4
0.9207	392.7	0.7598	420.1

ΔT represents the cryoscopic lowering, m is the molality, ν is the total number of ions in the salt formula and K_c is the thermodynamic cryoscopic constant of urea, whose value, 5.58 K kg m^{-1}, was deduced from the literature [22]. The experimental data of $\Delta T/\nu m$, extrapolated to $m = 0$, give the following values: 5.72 K kg m^{-1} (solute $KClO_4$), 5.91 K kg m^{-1} (solute HCOOK), 5.68 K kg m^{-1} (solute KNO_3) and 6.09 K kg m^{-1} (solute KSCN).

The experimental trends shown in Fig. 4 demonstrate that all the electrolytes are completely dissociated at their experimental concentrations.

TABLE 4

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

X_1	T (K)	X_1	T (K)	X_1	T (K)
1.0000	406.0	0.8860	386.7	0.4994	352.0
0.9941	405.6	0.8692	383.7	0.4594	360.2
0.9928	403.7	0.8497	380.3	0.4297	368.1
0.9873	402.6	0.8188	372.7	0.4010	377.9
0.9823	403.1	0.7997	371.9	0.3698	377.3
0.9802	401.3	0.7697	365.5	0.3534	384.1
0.9759	401.9	0.7397	361.6	0.3393	388.4
0.9667	399.2	0.7170	358.0	0.3005	394.0
0.9626	398.8	0.7078	356.7	0.2603	398.8
0.9593	398.0	0.6700	351.1	0.2196	406.3
0.9541	397.2	0.6474	347.1	0.1800	413.7
0.9498	396.2	0.6248	344.4	0.1392	419.6
0.9447	396.4	0.6001	341.0	0.0986	427.2
0.9376	394.6	0.5701	328.9	0.0599	433.4
0.9264	393.8	0.5578	331.7	0.0000	440.8
0.9153	391.6	0.5396	329.6		
0.8993	388.3	0.5398	338.6		

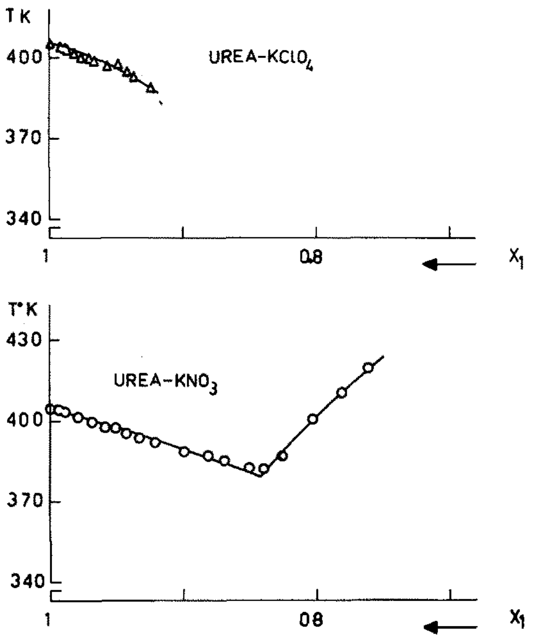

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems urea–$KClO_4$ and urea–KNO_3.

Once again, urea was shown to be a better solvent than acetamide [3] for potassium salts. As in the previous study [13], this may be related to the presence of the NH_2 or CH_3 group. By using the Gibbs–Duhem relation, we also evaluated approximately the mean ionic activity coefficient f_i for the various electrolytes; the respective trends as a function of the molar fraction of urea are shown in Fig. 5. This figure shows that in these binary systems, the solute–solvent interaction decreases in the order: $KClO_4 > KSCN > KNO_3 > HCOOK$. In general, urea–electrolyte mixtures do not exhibit supercooling phenomena: simply by cooling the mixtures without stirring, limited supercooling phenomena may be observed around the eutectic composition.

Comparing these results with those of urea–sodium salt binary mixtures containing the same anions, it is possible to point out that the urea–HCOONa and urea–HCOOK systems show the same activity coefficient, the same as for urea–NaSCN and urea–KSCN systems. In urea–$NaNO_3$ mixtures, the activity coefficient deviates from 1 more than in urea–KNO_3 mixtures, which is the inverse of the behaviour of mixtures containing Na and K. Thus, anions derived from strong acids and those derived from weak acids behave differently.

Indeed, the acetamide–electrolyte systems already studied [3] indicate that supercooling occurs when the salt is derived from a strong acid. We believe that the cation–solvent and cation–anion interactions are probably

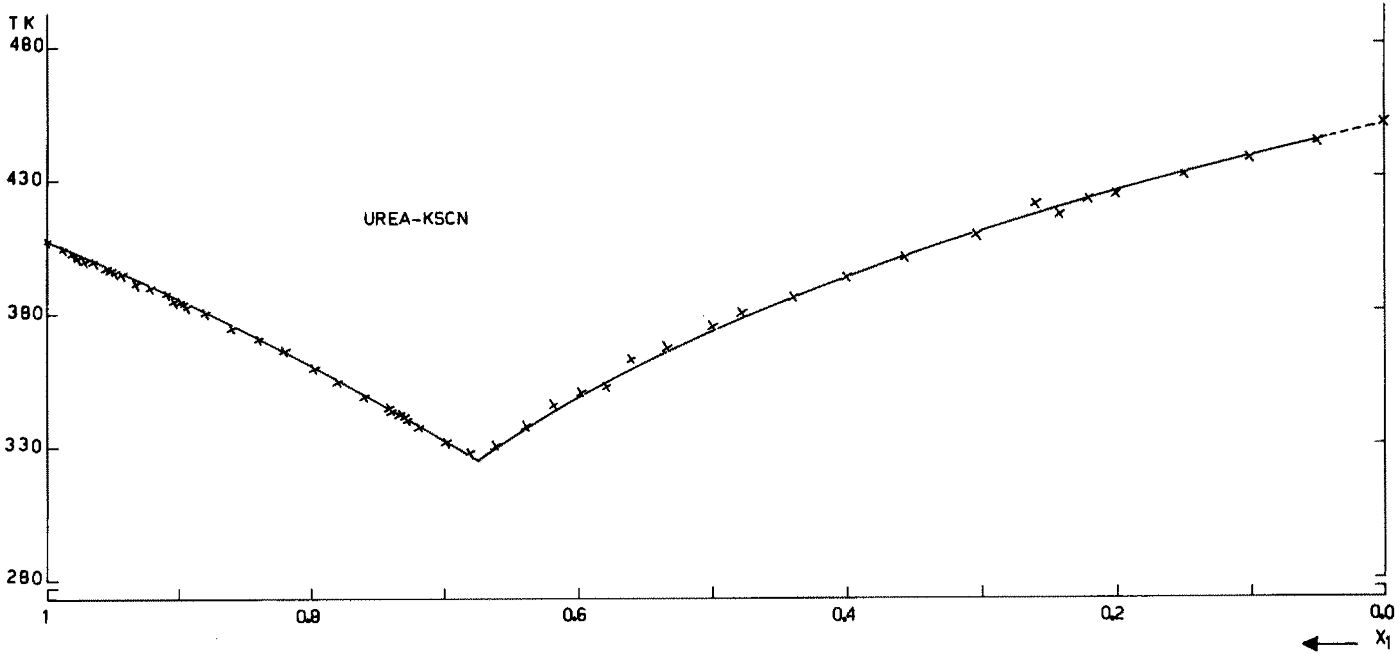

Fig. 2. Liquid–solid equilibrium temperatures in the binary system urea–KSCN. Broken line represents the thermal instability zone.

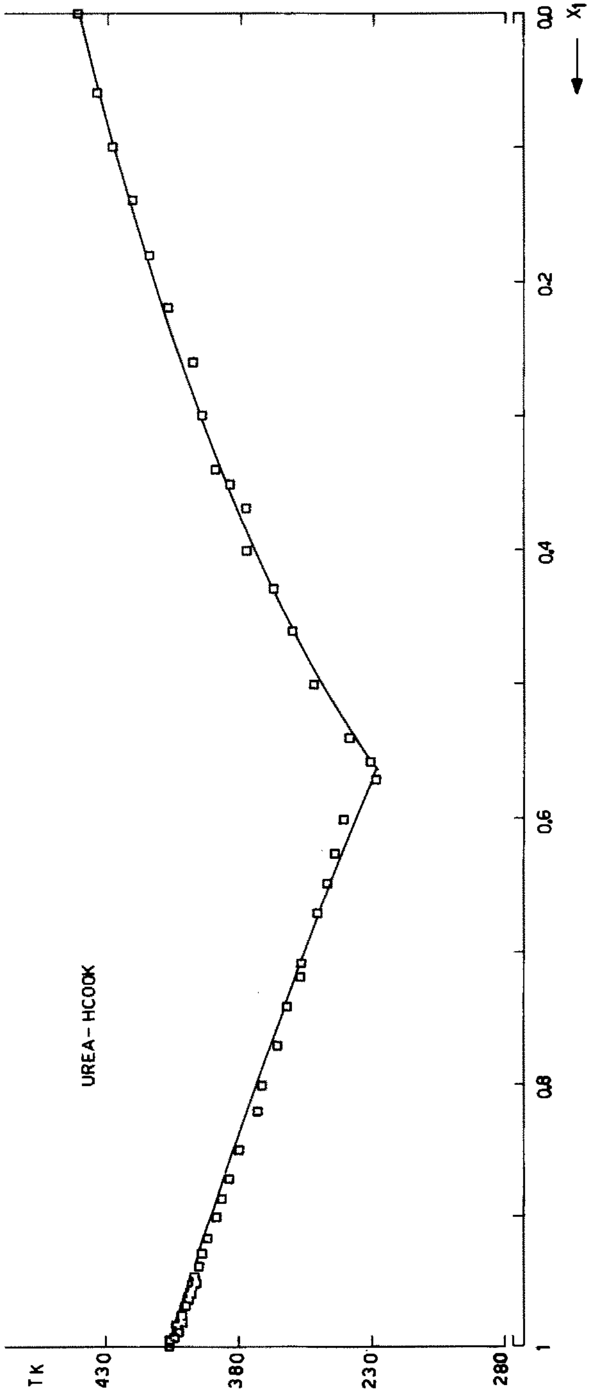

Fig. 3. Liquid–solid equilibrium temperatures in the binary system urea–HCOOK.

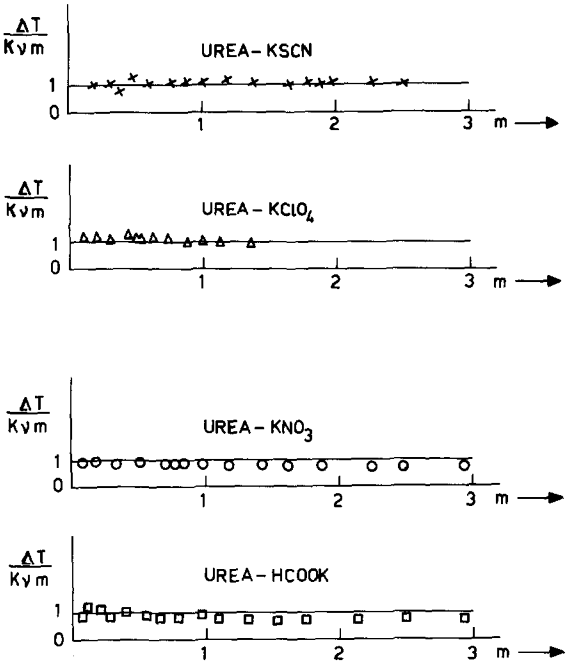

Fig. 4. Trend of $\Delta T/\nu K_c m$ vs. m for binary systems of urea with KSCN, $KClO_4$, KNO_3 and HCOOK.

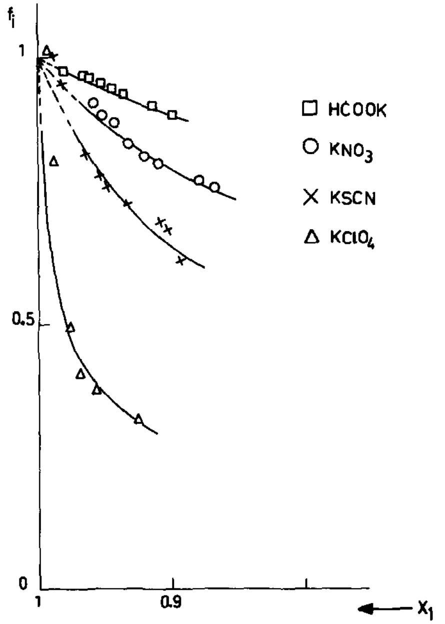

Fig. 5. Graphic trends of the mean ionic activity coefficient f_i as a function of the urea molar fraction for the HCOOK, KNO_3, KSCN and $KClO_4$ solutions.

always competitive; the latest relaxation studies [23] support the hypothesis that the salts are associated and that the salt aggregates are dispersed in the amorphous solvent. At present, this structure seems to be responsible for the supercooling phenomena. In the urea–salt systems, the cryoscopic behaviour suggests a complete dissociation of the salt. This is the fundamental difference compared with the acetamide–salt systems, and the probable reason that supercooling is not observed in urea systems.

As a consequence, the structure of urea systems is more simple (in comparison with acetamide systems), and the cryoscopic curve or derived quantities (such as activity coefficient) may be more easily interpreted on the basis of classical concepts of solute–solute or solute–solvent interactions.

While cryoscopic behaviour in electrolyte–acetamide systems is related to the presence of polymeric structures, and the components are present in different aggregates, in urea–electrolyte systems the cryoscopic behaviour shows a trend which seems to support the hypothesis that the charge/radius ratio is the factor which affects the activity coefficient, i.e. the structure is non-polymeric.

ACKNOWLEDGEMENTS

We are grateful to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support and to R. Borgarucci for technical assistance.

REFERENCES

1 F. Castellani, G. Berchiesi, F. Pucciarelli and V. Bartocci, J. Chem. Eng. Data, 26 (1981) 150.
2 F. Castellani, G. Berchiesi, F. Pucciarelli and V. Bartocci, J. Chem. Eng. Data, 27 (1982) 45.
3 G. Berchiesi, G. Gioia Lobbia, V. Bartocci and G. Vitali, Thermochim. Acta, 70 (1983) 317.
4 G. Gioia Lobbia and G. Berchiesi, Thermochim. Acta, 72 (1984) 391.
5 G. Gioia Lobbia, G. Berchiesi and G. Poeti, Thermochim. Acta, 74 (1984) 247.
6 G. Gioia Lobbia and G. Berchiesi, Thermochim. Acta, 74 (1984) 251.
7 G. Gioia Lobbia, G. Berchiesi and G. Poeti, Thermochim. Acta, 78 (1984) 297.
8 G. Gioia Lobbia and A. Amico, Thermochim. Acta, 87 (1985) 257.
9 G. Gioia Lobbia and G. Berchiesi, J. Chem. Eng. Data, 109 (1987) 52.
10 G. Gioia Lobbia and G. Berchiesi, Themochim. Acta, 118 (1987) 223.
11 G. Vitali and G. Berchiesi, Thermochim. Acta, 142 (1989) 13.
12 G. Vitali, G. Berchiesi and S. Barocci, Thermochim. Acta, 143 (1989) 205.
13 G. Vitali, G. Berchiesi and F. Castellani, Thermochim. Acta, 179 (1991) 231.
14 G. Berchiesi, G. Vitali, P. Passamonti and R. Płowiec, J. Chem. Soc., Faraday Trans. II, 79 (1983) 1255.
15 R. Płowiec, A. Amico and G. Berchiesi, J. Chem. Soc., Faraday Trans. II, 81 (1985) 217.
16 G. Berchiesi, G. Vitali and A. Amico, J. Mol. Liquids, 32 (1986) 99.

17 G. Berchiesi, G. Vitali and R. Płowiec and S. Barocci, J. Chem. Soc., Faraday Trans. II, 85(6) (1989) 635.
18 G. Berchiesi, F. Castellani and F. Pucciarelli, J. Pure Appl. Ultrason., 5 (1983) 66.
19 A. Amico, G. Berchiesi, A. Di Biasio and C. Cametti, J. Chem. Soc., Faraday Trans. II, 89 (1987) 277.
20 M. Braghetti, D. Leonesi and P. Franzosini, Ric. Sci., 38 (1968) 116.
21 M. Braghetti, G. Berchiesi and P. Franzosini, Ric. Sci., 39 (1969) 576.
22 G. Della Gatta and D. Ferro, Thermochim. Acta, 122 (1987) 143.
23 G. Berchiesi, M. De Angelis, G. Rafaiani and G. Vitali, J. Mol. Liq., in press.