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SUPERCOOLING PHENOMENA IN ELECTROLYTIC MIXTURES OF 2-KETOBUTYRAMIDE

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ABSTRACT

The liquid–solid equilibrium temperature is determined for binary mixtures of 2-ketobutyramide (acetoacetamide) + electrolyte in order to investigate the occurrence of supercooling phenomena. The composition range where supercooling occurs is given for all the binaries studied. The presence of the keto group on the chain of the amide increases the supercooling phenomena, which are more extended in these systems in comparison with those in the corresponding systems in butyramide.

INTRODUCTION

In recent papers we showed that alkali (principally Na^+) or alkali earth salts may cause irregularities in the crystallization behaviour of amides if the salts are derived from strong acids [1]. Strong supercooling phenomena may occur and in some cases the mixtures do not crystallize at all.

Ultrasonic and dielectric studies [2–6] have shown that these mixtures must be considered polymeric in the sense that polymeric structures, formed by association of amide molecules or solvated ions, must exist within the system. Some researchers have discussed the presence of open or closed dimeric structures [7,8] in liquid formamide. From our results [2–6] it seems that the association of acetamide may reach polymeric dimensions below room temperature.

The stability of these structures depends on two factors: (1) the type of amide; (2) the nature of the ions. The second factor has been discussed previously [1] and we showed that a low cation–anion interaction (where the anion is derived from strong acids) stabilizes the structures and the supercooled liquid, probably because the solvated ions associate according to the model outlined in a previous paper [3].

However, we have not reached any firm conclusions concerning the first factor. We noted that with increasing amide chain length the supercooled mixtures become less stable and crystallization becomes more regular [9,10].

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The other solvents investigated did not show this behaviour and if they did it was only to a very limited extent [11].

In this note we present the results of measurements of liquid–solid equilibrium temperatures in binary systems of 2-ketobutyramide + various salts.

EXPERIMENTAL

The method employed is widely described elsewhere [12] and for this reason is not reported here. The chemicals used are: 2-ketobutyramide (Fluka, 98%); NaCNS (Baker, 99%); $NaClO_4$ (C. Erba, 98%); $KClO_4$ (C. Erba, 98%); $LiNO_3$ (Alfa, 98.8%). They were used without further purification and dried under dynamic vacuum at a temperature some degrees below the melting point.

The systems investigated were the binaries consisting of acetoacetamide and NaCNS, $NaClO_4$, $KClO_4$, $LiNO_3$ respectively.

The mixtures were used not more than 3 h after preparation and, to avoid decomposition, were not heated over 110 °C.

For the system acetoacetamide + $NaClO_4$ the density was also measured with a digital vibrating microdensimeter manufactured by Paar (Austria).

RESULTS AND DISCUSSION

The values of the liquid–solid equilibrium temperatures are given in Tables 1 and 2, where X_2 stands for mole fraction of the electrolyte.

TABLE 1

Liquid–solid equilibrium temperatures in the binary systems $CH_3COCH_2CONH_2$–$NaClO_4$ and $CH_3COCH_2CONH_2$–$KClO_4$

$CH_3COCH_2CONH_2$–$NaClO_4$		$CH_3COCH_2CONH_2$–$KClO_4$	
X_2	T (K)	X_2	T (K)
0.0000	326.2	0.0000	326.2
0.0119	325.2(5)	0.0081	324.7
0.0158	323.6	0.0148	323.7
0.0245	322.1	0.0268	319.9
0.0412	319.3(5)	0.0441	315.7
0.0558	317.0		
0.0695	314.4		
0.0918	310.5		
0.1169	305.2(5)		
0.1359	300.5		
0.1570	294.4		
0.1748	287.8(5)		
0.1851	283.7		

TABLE 2

Liquid–solid equilibrium temperatures in the binary systems $CH_3COCH_2CONH_2$–NaCNS and $CH_3COCH_2CONH_2$–$LiNO_3$

$CH_3COCH_2CONH_2$–NaCNS		$CH_3COCH_2CONH_2$–$LiNO_3$	
X_2	T (K)	X_2	T (K)
0.0000	326.2	0.0000	326.2
0.0071	325.8(5)	0.0095	325.7(5)
0.0143	325.4(5)	0.0125	325.3
0.0263	324.4	0.0261	322.9
0.0444	321.7	0.0370	321.2
0.0660	319.7	0.0470	319.5
0.0918	315.4(5)	0.0792	314.0(5)
0.1143	311.3	0.0902	310.8(5)
0.1197	309.7	0.1112	312.6(5)
0.1399	304.7	0.1219	315.8
0.1630	298.2	0.1295	318.7
0.1656	296.7	0.1413	322.9
0.1746	292.2	0.1560	324.9(5)
0.1878	289.4	0.1889	330.2
0.2029	280	0.2206	332.0

NaCNS

This system exhibits supercooling phenomena in the mole fraction range $0.1 \leqslant X_2 \leqslant 0.2$, where X_2 is the salt concentration, when the liquid mixture is cooled without stirring (see Fig. 1). In the range $0.2 \leqslant X_2 \leqslant 0.4$ the mixture appears very dense and vitreous, and as the agitation was not efficient,

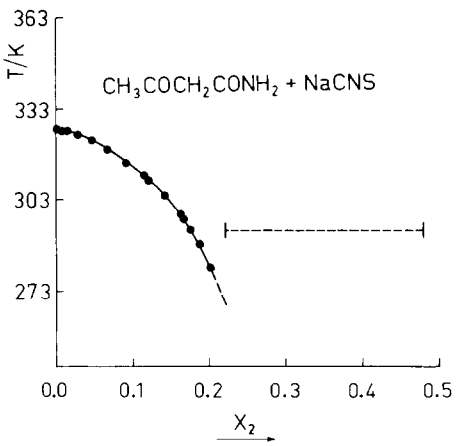

Fig. 1. Liquid–solid equilibrium temperatures in the binary system CH_3COCH_2-$CONH_2$–NaCNS.

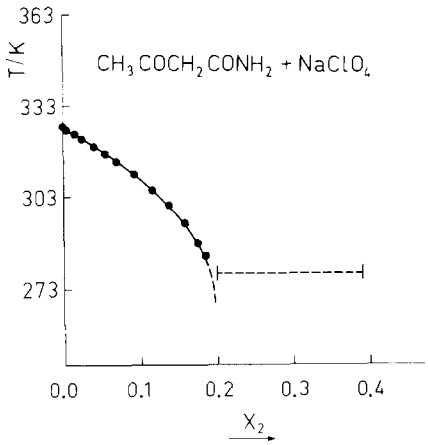

Fig. 2. Liquid–solid equilibrium temperatures in the binary system CH_3COCH_2-$CONH_2$–$LiNO_3$.

crystallization was not observed. At $X_2 > 0.4$, NaCNS does not dissolve. The eutectic point was not observed in this system. In fact, owing to supercooling phenomena, it was only possible to measure the crystallization curve of acetamide.

$LiNO_3$

The liquid–solid equilibrium curve in Fig. 2 shows that the amide crystallization curve is less spread out in comparison with that in the

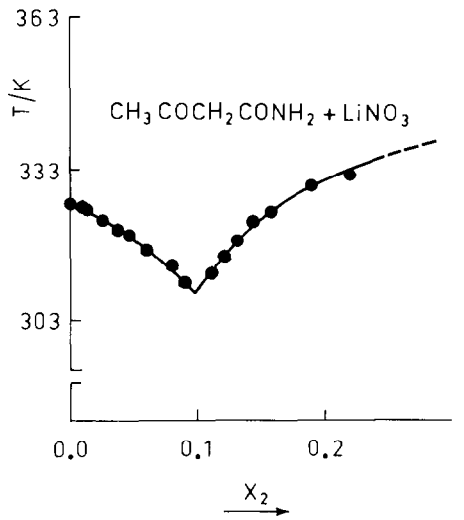

Fig. 3. Liquid–solid equilibrium temperatures in the binary system CH_3COCH_2-$CONH_2$–$NaClO_4$.

NaCNS system. Around the eutectic point supercooling phenomena (about 8°) may occur if the mixture is cooled without stirring.

$NaClO_4$

This system exhibits important supercooling phenomena at $X_2 > 0.16$, where the supercooled mixtures show a vitreous aspect (see Fig. 3).

$KClO_4$

This salt is only slightly soluble in acetoacetamide. In the range $0 \leqslant X_2 \leqslant 0.044$ where supercooling phenomena were not observed, it was difficult to study the system (Fig. 4). These measurements are not very reliable owing to the fact that, in order to solubilize the salt, the system was maintained at a high temperature for a long time.

All these systems show that $\Delta T/m$ (where ΔT is the cryoscopic lowering and m is the molality) is strongly dependent on molality (i.e. on temperature) as also noted previously in systems with acetamide [1].

For this reason and owing to the lack of thermodynamic data, the trend in $\Delta T/m$ cannot be discussed. The analogy with systems previously studied [1] may support the explanation given previously in ref. 1.

Density data in the acetoacetamide–$NaClO_4$ system (Table 3) show $\Delta d/\Delta X_2 = 0.83$ (where Δd is the variation in density and ΔX_2 the corresponding variation in X_2) at practically all the temperatures investigated, i.e. the system becomes more packed with increasing ion concentration.

Although this study should be continued, we can make the following observations:

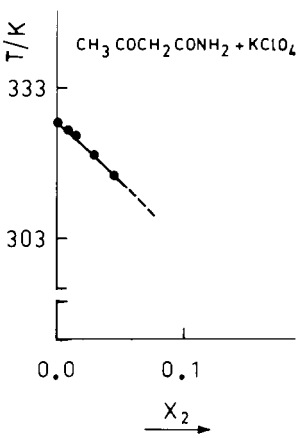

Fig. 4. Liquid–solid equilibrium temperatures in the binary system CH_3COCH_2-$CONH_2$–$KClO_4$.

TABLE 3

Density d data in the binary system $CH_3COCH_2CONH_2$–$NaClO_4$

X_2	T (K)	d (g cm^{-3})	X_2	T (K)	d (g cm^{-3})
0.270	303.3	1.38252	0.311	303.3	1.41686
	298.4	1.38668		298.4	1.42097
	293.4	1.39095		293.4	1.42524
	288.4	1.39512		288.4	1.42942
	283.4	1.39941		283.4	1.43374
	278.6	1.40347		278.6	1.43783
	273.6	1.40775		273.6	1.44217

(1) Supercooling phenomena are strongly affected by the presence of polar groups in the aliphatic chain. In fact, the butyramide [9] showed a very narrow concentration range where these phenomena occur and they are very limited; for comparison, in 2-ketobutyramide these phenomena are as widespread as in acetamide [1].

(2) The trend in $\Delta T/m$ and also that in $\Delta d/\Delta X_2$ seems to suggest the presence of packed structures that should be confirmed by other techniques.

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