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ELECTROLYTIC SOLUTIONS IN SUCCINIMIDE: CRYOSCOPIC BEHAVIOUR

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ABSTRACT

The liquid–solid equilibria in the binary systems succinimide + (Na, K)/(CNS, ClO_4) are reported. The presence of intermediate compounds is shown. In some concentration ranges these systems (with the exception of $KClO_4$) present supercooling phenomena if the mixtures are cooled without agitation.

INTRODUCTION

In recent papers [1–3] it has been shown that monoamides (acetamide, propionamide,butyramide) exhibit strong supercooling phenomena. These phenomena depend on both the range of temperature and the composition. Ultrasonic studies [4,5] show viscoelastic and ultrasonic relaxation that suggest a highly structured liquid. In this paper the results of cryoscopic and calorimetric studies in solution of some salts in succinimide are presented in order to compare these results with those previously reported.

EXPERIMENTAL

Experimental details of the cryoscopic method are as previously reported [1,6]. The chemicals used were: $C_4H_5NO_2$ (Succinimide; Ega-Chemie; 99%); NaCNS (Fluka; 98%); $NaClO_4$ (99%); and $KClO_4$ (Erba; 99%); KCNS (Merck; 99%). They were conventionally dried, as previously described [1], and were used without further purification. The systems were studied in their thermal stability region. The index 1 stands for succinimide.

RESULTS AND DISCUSSION

The liquid–solid equilibrium temperatures, shown in Fig. 1, indicate the good solubility of the salts employed with the exception of $KClO_4$ which exhibits partial solubility. The experimental values are given in Table 1.

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TABLE 1

Liquid–solid equilibrium temperatures for the binary systems studied

X_1	T (K)	X_1	T (K)
$C_4H_5NO_2-NaCNS$		$C_4H_5NO_2-NaClO_4$	
1.0000	396.4_5	1.0000	396.4_5
0.9856	395.5_5	0.9919	395.9_3
0.9797	395.2_5	0.9825	395.4_5
0.9625	394.5_0	0.9705	386.0_0
0.9507	394.2	0.9573	394.4
0.9274	392.9	0.9344	392.8
0.8884	389.4	0.9172	391.4
0.8332	380.3	0.8901	388.4
0.8006	372.6	0.8568	385.0
0.7934	369.5	0.8385	390.3
0.7756	364.0	0.8125	401.1
0.7648	360.0	0.7913	409.1
0.7627	358.7	0.7666	415.7
0.7537	356.0	0.7395	420.8
0.7488	353.3	0.7024	425.3
0.7322	352.3	0.6669	426.1
0.7306	356.0	0.6432	425.2
0.7180	370.0	0.6185	423.3
0.7115	377.3	0.5857	419.0
0.6895	389.0	0.5703	424.8
0.6636	399.0	0.5596	438.4
0.6332	408.5	0.5487	451.2
0.5892	416.6	0.5444	453.3
0.5660	418.9	0.5125	479.8
0.5369	424.6		
0.5301	434.2		
0.5235	442.5		
0.4994	462.5		
$C_4H_5NO_2-KCNS$		$C_4H_5NO_2-KClO_4$	
1.0000	396.4_5	1.0000	396.4_5
0.9922	395.7_5	0.9893	396.2
0.9734	394.5_5	0.9852	396.0
0.9481	393.3_5	0.9704	404.9
0.9388	392.8_5	0.9534	419.6
0.9102	390.3	0.9411	430.6
0.8783	387.0	0.9055	451.5
0.8440	381.8		
0.8155	376.4		
0.7784	370.4		
0.7557	364.6		
0.7194	362.2		
0.7010	366.5		
0.6803	369.5		
0.6495	372.0		
0.6081	373.2		

TABLE 1 (continued)

X_1	T (K)	X_1	T (K)
0.5962	373.1		
0.5815	372.7		
0.5410	371.4		
0.5241	370.2		
0.4946	374.8		
0.4791	378.7		
0.4676	382.6		
0.4364	388.9		
0.3982	396.9		

$NaClO_4$

As shown in Fig. 1 an intermediate compound is produced with succinimide and $NaClO_4$ of the formula 2 $C_4H_5NO_2 \cdot NaClO_4$, m.p., 426.2 K. Two eutectic points present the following coordinates: $T = 383.4$ K, $X_1 = 0.847$; $T = 417.2$ K, $X_1 = 0.578$. The $\Delta T/m$ value exhibits the following trend: it decreases with increasing molarity between 0 and 0.45 mol kg^{-1}. The extrapolated value at $m = 0$ is 6.7 K kg mol^{-1}.

In the concentration range $0.84 < X_1 < 0.89$ a supercooling of ≈ 20 K is observed if the mixtures are cooled without agitation.

NaCNS

The corresponding binary system exhibits eutectic and peritectic points. The coordinates of the eutectic point are: $T = 346.5$ K, $X_1 = 0.736$; the coordinates of the peritectic point are: $T = 419.7$ K, $X_1 = 0.539$.

The composition of the incongruently melting compound has not been obtained by DSC measurements. In fact, mixtures of the composition $X_1 = 0.6$, $X_1 = 0.5$, $X_1 = 0.45$ exhibit eutectic transition; for this reason the composition of the intermediate compound is expected at $X_1 < 0.45$, where the mixtures are thermally unstable and as a consequence cannot be studied. The trend of $\Delta T/m$ vs. m is similar to that of $NaClO_4$ with a minimum at 0.6 mol kg^{-1}. The extrapolated value at $m = 0$ is 6.7 K kg mol^{-1}.

In the eutectic region the mixture supercools by ≈ 40 K if cooled without agitation.

KCNS

An intermediate compound is exhibited by this binary system. The formula of this compound is 3 $C_4H_5NO_2 \cdot 2$ KCNS, m.p., 373.2 K.

The coordinates of two eutectic points are: $T = 357.2$ K, $X_1 = 0.732$;

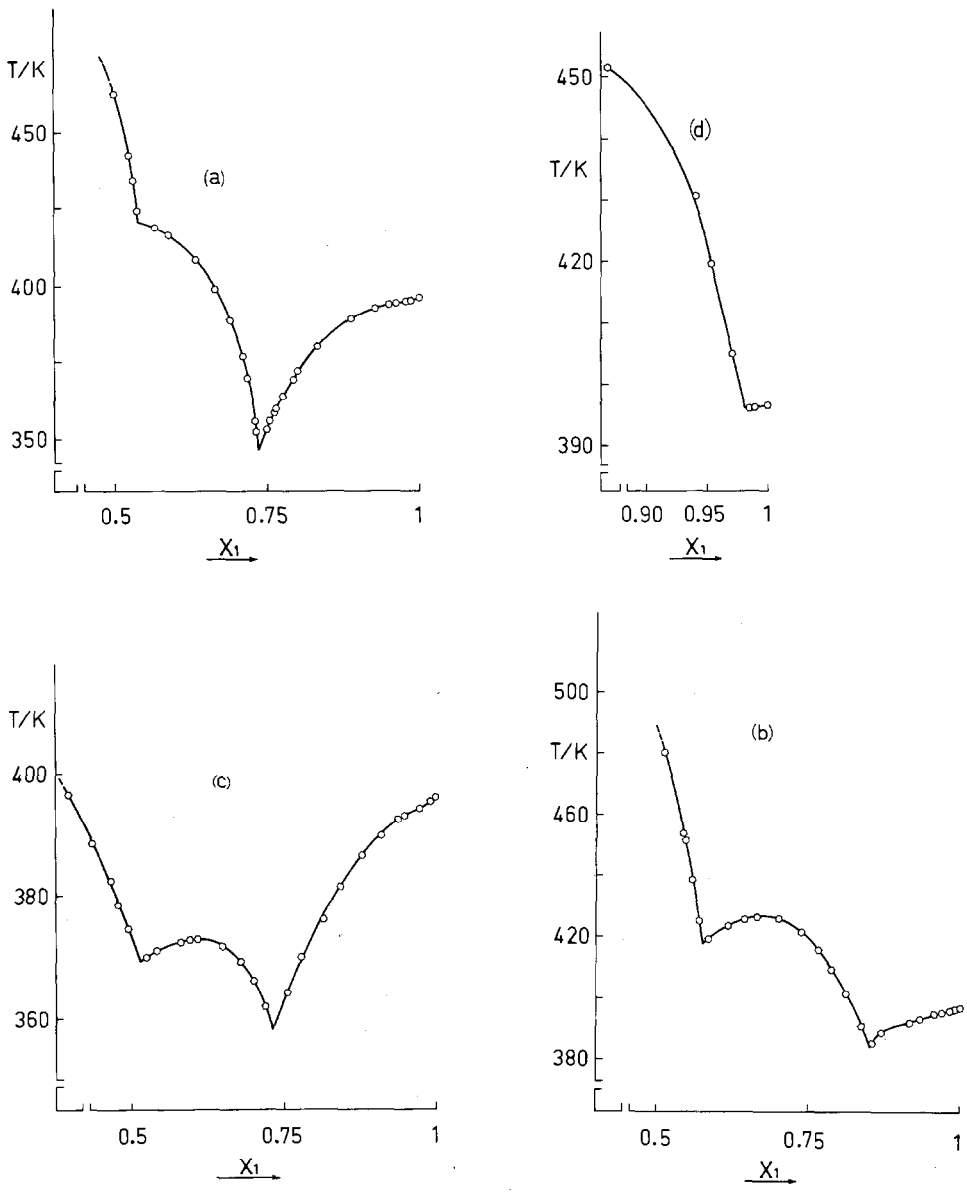

Fig. 1. Liquid–solid equilibrium temperature in the binary systems: (a) succinimide + NaCNS; (b) succinimide + $NaClO_4$; (c) succinimide + KCNS; (d) succinimide + $KClO_4$.

$T = 368.7$ K, $X_1 = 0.512$. The trend of $\Delta T/m$ is similar to the preceeding cases, with a minimum at 0.6 mol kg^{-1}. The extrapolated value at $m = 0$ is ≈ 9.4 K kg mol^{-1}.

In the range $0.75 < X_1 < 0.85$, supercooling phenomena are evident ($\simeq 35$ K) if cooled without agitation.

$KClO_4$

The crystallization region of succinimide is very limited and the eutectic coordinates are: $T = 395.5$ K, $X_1 = 0.98$.

CONCLUSIONS

With the exception of $KClO_4$, all these salts in mixtures with succinimide exhibit a concentration range where supercooling phenomena occur, but, unlike the systems with acetamide [1,2], these phenomena occur only if the agitation of the mixture is stopped.

A high incidence of intermediate compounds is observed, and unlike previously studied systems [1,7] potassium salts also give intermediate compounds.

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