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ADDITIVE TERNARY SYSTEM: ACETAMIDE–SUCCINAMIDE–SODIUM THIOCYANATE

G. GIOIA LOBBIA and A. AMICO

Dipartimento Scienze Chimiche, Università, via S. Agostino 1, 62032 Camerino (Italy)

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ABSTRACT

The liquid–solid equilibria in the ternary system acetamide–succinamide–sodium thiocyanate are determined in the thermal stability range, owing to our interest in supercooling phenomena in non-aqueous solutions.

INTRODUCTION

Sodium ions of salts of strong acids showed interesting behaviour when added to molten amides [1–4]. In fact, the phase diagrams indicate the existence of a concentration range where the mixture supercools, giving in certain cases a liquid system until the glass transition temperature.

Ultrasonic and viscoelastic relaxation spectra [5–7] suggest the presence of polymeric structures in these liquid systems below room temperature. The aim of this paper is to check the effect of the substitution of mono-amide with di-amide on these structures. The ternary system was studied in the thermal stability zone.

EXPERIMENTAL

The experimental cryoscopic method used is reported in a previous paper [8]. The chemicals: sodium thiocyanate (Baker, 99%), acetamide (Fluka, 98%), succinamide (Ega-Chemie, 98%) were used without further purification.

RESULTS AND DISCUSSION

The binary system CH_3CONH_2–NaCNS was reported previously [4]. The system CH_3CONH_2–$H_2NCO(CH_2)_2CONH_2$ is studied in the stability range

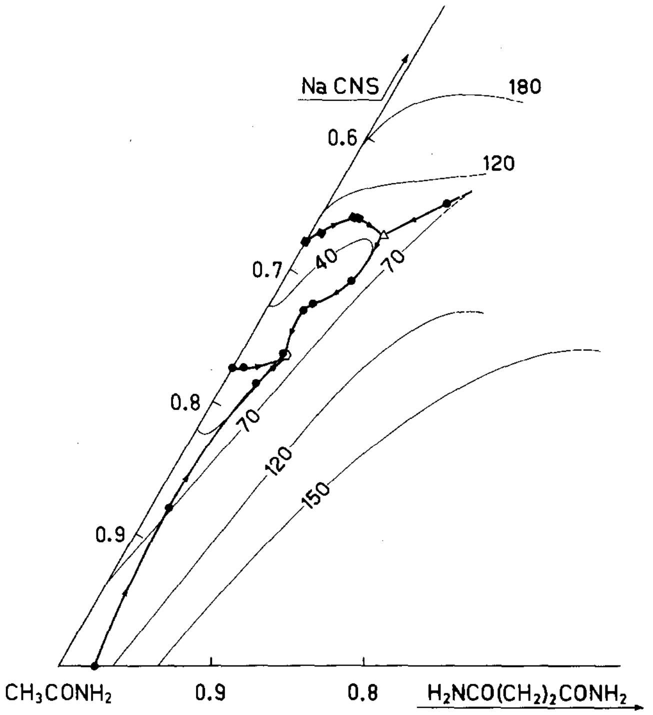

Fig. 1. Polythermal projections of the ternary system acetamide–succinamide–sodium thiocyanate.

and the solid–liquid equilibrium temperatures are reported in Table 1. In the range studied it exhibits a eutectic point whose coordinates are: $X_1 = 0.978$, $T_e = 78.8°C$.

The system succinamide + sodium thiocyanate was not studied owing to its instability over the entire concentration range. The composition triangle was studied in the stability region by means of nine internal cuts whose characteristic points are given in Table 2.

In Fig. 1 the isothermal lines, the eutectic and peritectic valleys and the crystallization area of the compounds are shown. An unusual behaviour is

TABLE 1

Liquid–solid equilibrium temperatures in the binary system acetamide + succinamide ($C_2H_5NO + C_4H_8N_2O_2$)

X_1	T (°C)	X_1	T (°C)
1.0000	79.9	0.9571	135.8
0.9904	79.4	0.9268	154.2
0.9832	79.0	0.8879	170.7
0.9756	96.1	0.8455	180.6
0.9662	115.0	0.8004	189.8
		0.7604	193.8

TABLE 2

Sections in the ternary system

Section S	Composition of the starting mixtures (mol)	Added component (AC)	Characteristic points			
			X_{AC}	T (°C)	X_{AC}	T (°C)
I	$CH_3CONH_2 + NaCNS$ (7.33 : 1)	$H_2NCO(CH_2)_2CONH_2$	0.012	66.5		
II	$CH_3CONH_2 + NaCNS$ (2.33 : 1)	$H_2NCO(CH_2)_2CONH_2$	0.046	35.5		
III	$CH_3CONH_2 + NaCNS$ (3.55 : 1)	$H_2NCO(CH_2)_2CONH_2$	0.020	18.5		
IV	$CH_3CONH_2 + NaCNS$ (3.17 : 1)	$H_2NCO(CH_2)_2CONH_2$	0.030	9.0		
V	$CH_3CONH_2 + H_2NCO(CH_2)_2CONH_2$ (7.33 : 1)	NaCNS	0.348	58.5		
VI	$CH_3CONH_2 + H_2NCO(CH_2)_2CONH_2$ (13.3 : 1)	NaCNS	0.306 [a]	1.8 [a]		
VII	$CH_3CONH_2 + H_2NCO(CH_2)_2CONH_2$ (32.3 : 1)	NaCNS	0.262	14.0	0.337	51.5
VIII	$CH_3CONH_2 + H_2NCO(CH_2)_2CONH_2$ (124 : 1)	NaCNS	0.225	14.0	0.329	56.5
IX	$CH_3CONH_2 + H_2NCO(CH_2)_2CONH_2$ (24 : 1)	NaCNS	0.268	25.5	0.335	47.5

[a] Obtained by extrapolation.

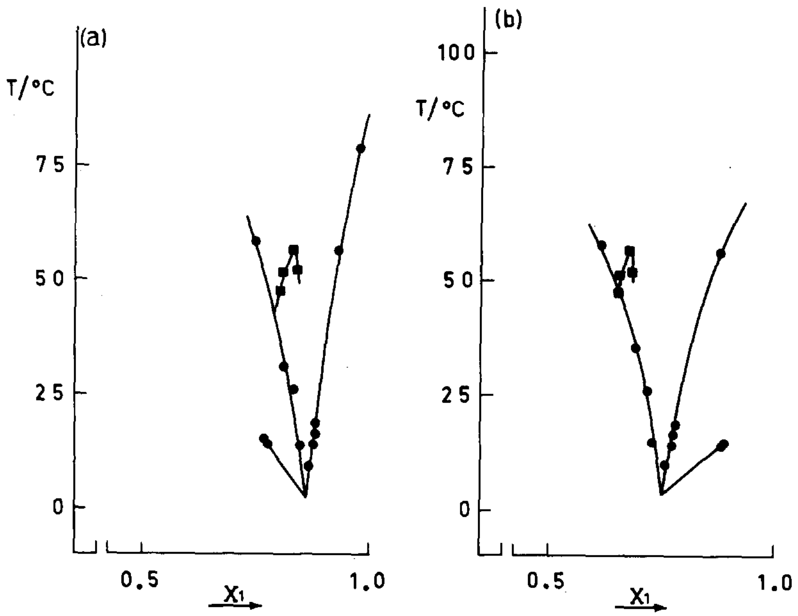

Fig. 2. (a) Projections on the side acetamide–succinamide. (b) Projections on the side acetamide–sodium thiocyanate. (●) Eutectic valleys, (■) peritectic valley.

exhibited by the peritectic valley (concerning the incongruent melting compound 2 $CH_3CONH_2 \cdot NaCNS$); in fact the temperature of the peritectic valley between the binary and the ternary peritectic point is not continuously decreasing, but is first increasing and then decreasing.

This experimental evidence can be seen in the polythermal projection shown in Fig. 2. The coordinates of the ternary eutectic and ternary peritectic are obtained from the polythermal projections on the base and on the left-hand side of the composition triangle. They are given in Table 3.

The ternary mixtures present supercooling phenomena in the crystallization region of the intermediate compound 2 $CH_3CONH_2 \cdot NaCNS$, but only when the agitation of the mixtures is stopped. It seems, therefore, that the substitution of acetamide molecules with succinamide allows a better crystallization of the system.

TABLE 3

Coordinates of the characteristic points

	Symbol	x_{NaCNS}	$x_{CH_3CONH_2}$	$x_{H_2NCO(CH_2)_2CONH_2}$
Ternary eutectic	○	0.234	0.737	0.029
Ternary peritectic	△	0.320	0.632	0.048

Recently [5–7], we have shown that polymeric structures are present in the supercooled binary mixtures acetamide + Na, K/CNS, probably produced by superaggregation of the solvated ions. The experimental observation that ternary mixtures crystallize more easily than binary mixtures means that the formation of polymeric structures is hampered by the presence of succinamide. The peculiar behaviour of the peritectic valley with a maximum (as shown in the polythermal projections), may be a consequence of this phenomenon. In fact, if succinamide destabilizes the formation of polymeric structures (which are the cause of the supercooling phenomenon) the temperature rises, (as observed experimentally, when the polymeric structures are not present the crystallization temperature is higher [9]) until the cryoscopic lowering law becomes the predominant factor.

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