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Note

SOLUBILITY IN BINARY MIXTURES $C_{17}H_{35}CONH_2$–(Na, K) (CNS, ClO_4, $C_{17}H_{35}COO$)

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In previous papers [1,2] we reported on the supercooling phenomena occurring in binary mixtures between acetamide and some alkali metal salts. The viscoelastic properties and the structural modifications were also investigated [3] in some cases. On the basis of these studies we concluded that the interaction between cations and the $-CONH_2$ group at a certain temperature (and, consequently, concentration) becomes so stable, compared with the anion–cation interaction, that precipitation of the salts does not occur.

In order to ascertain the influence of the temperature (and consequently of the concentration) zone and also of the chain length on this phenomenon we plan to continue this research on the higher amides and present in this note the results concerning liquid–solid and liquid–liquid equilibria in binary systems consisting of the amide of octadecanoic acid and alkali metal salts.

EXPERIMENTAL

The experimental method previously described [4] was adopted. The following chemicals were used: Fluka Stearamide (95%) and NaCNS (98%), Merck KCNS (99%), Erba $NaClO_4$ (99%). Stearamide was recrystallized twice from C_2H_5OH. Sodium and potassium stearates were obtained by reaction of a stoichiometric quantity of stearic acid (in alcoholic solution) with the corresponding carbonate. The soaps obtained were recrystallized from alcohol. All the products were dried under dynamic vacuum at increasing temperature up to 100°C (stearamide) and 140°C (other compounds). Throughout this paper 1 denotes stearamide, and 2 denotes the other compound.

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TABLE 1

Solid–liquid equilibrium temperatures (T_{sl}) and solid–liquid–liquid equilibrium temperatures (T_{sll}) in the binary systems: stearamide + alkali metals salts

System	x_2	T_{sl}(K)	$T_{(sll)}$(K)
$C_{17}H_{35}CONH_2$–$C_{17}H_{35}COONa$	0.0000	377.1_0	
	0.0185	375.7_5	
	0.0383	374.0_5	
	0.0501	376.3_0	
	0.0576	379.1_0	
	0.0641	382.4_5	
	0.0682	383.7_0	
	0.0860	389.9_5	
	0.1067	396.3_0	
$C_{17}H_{35}CONH_2$–$C_{17}H_{35}COOK$	0.0000	377.1_0	
	0.0188	376.7_0	
	0.0397	375.8_0	
	0.0519	375.2_5	
	0.0729	377.7_5	
	0.0786	379.5_5	
	0.0946	384.9_5	
	0.1085	389.2_0	
	0.1298	384.8_0	
$C_{17}H_{35}CONH_2$–KCNS	0.0000	377.1_0	
	0.0246	375.7_5	
	0.0432	374.9_0	
	0.0547	374.5_0	
	0.0874	373.1_0	
	0.1090	372.3_0	
	0.1212	371.8_0	
	0.1282	370.8_5	
	0.1479	370.2_0	
	0.1655	386.8_0	
	0.1705	398.3_0	
	0.1787	411.3_5	
	0.1837	424.7_0	
	0.2035	–	450.7_0
	0.2457	–	450.6_5
	0.9237	–	450.5_0
	0.9764	–	450.5_5
	1.0000	450.5_5	
$C_{17}H_{35}CONH_2$–NaCNS	0.0000	377.1_0	
	0.0238	375.7_0	
	0.0526	374.1_0	
	0.0862	372.0_0	
	0.1504	367.3_5	
	0.2238	362.3_5	
	0.2741		

TABLE I (continued)

System	x_2	T_{sl}(K)	$T_{(sll)}$(K)
$C_{17}H_{35}CONH_2$–$NaClO_4$	0.0000	377.1_0	
	0.0317	375.2_0	
	0.0665	372.6_5	
	0.0953	370.0_5	
	0.1572	365.0_0	
	0.2031	361.2_0	
	0.2218	360.0_5	
	0.3358	–	

RESULTS AND DISCUSSION

The equilibrium temperatures as a function of mole fraction of component 1 are given in Table 1 and are shown in Fig. 1.

It is evident that sodium and potassium stearates are less soluble than perchlorate or thiocyanate and the eutectic temperature is reached at $x_1 > 0.9$. In the system with sodium thiocyanate or perchlorate the crystallization curve of the amide extends until $x_1 \simeq 0.78$, but at $x_1 < 0.78$ the salts are practically insoluble and the system cannot be studied. The system with KCNS exhibits an eutectic point at $x_1 = 0.842$ and a liquid–liquid equilibrium in the region $0 \leqslant x_1 \leqslant 0.804$. The monotectic temperature corresponds to the melting temperature of KCNS; the liquid–liquid curve cannot be studied owing to the decomposition of stearamide. The fact that the monotectic temperature corresponds to the melting point of KCNS is evidence of the low solubility of stearamide in KCNS; in fact, the reproducibility of the temperature measurements $\simeq 1$ μV $= 0.03$ K, and 12.68 K mol^{-1} kg being the cryoscopic constant of KCNS [6], it can be deduced that a probable maximum molality of $C_{17}H_{35}CONH_2$ in KCNS is $m = 2 \times 10^{-3}$ mol kg^{-1}.

Previously, we gave the thermodynamic properties of stearamide [5]. A certain discrepancy exists between T_f given in this paper and that determined previously [5] and this fact may be ascribed to the purity of the chemical employed.

From the fusion enthalpy the cryoscopic constant of stearamide may be calculated as 7.4 K mol^{-1} kg. This value is a little higher than the cryoscopic value (6.8 K mol^{-1} kg) [5]. The thermodynamic value (7.4 K mol^{-1} kg) may be employed in order to calculate $\Delta T/\nu m\ K_{cr}$ ($\nu = 2$); with K salts $\Delta T/\nu m\ K_{cr} \leqslant 1$ and with Na salts $\Delta T/\nu m\ K_{cr} \geqslant 1$, showing complete dissociation in the case of Na salts and a higher interaction of Na^+ with amide. This fact is emphasized with stearate anion. The trend of $\Delta T/\nu m\ K_{cr}$ vs. m is different from that observed in acetamide [2]: $\Delta T/\nu m\ K_{cr}$ does not change slope. This fact is probably a consequence of the higher temperature in the present case;

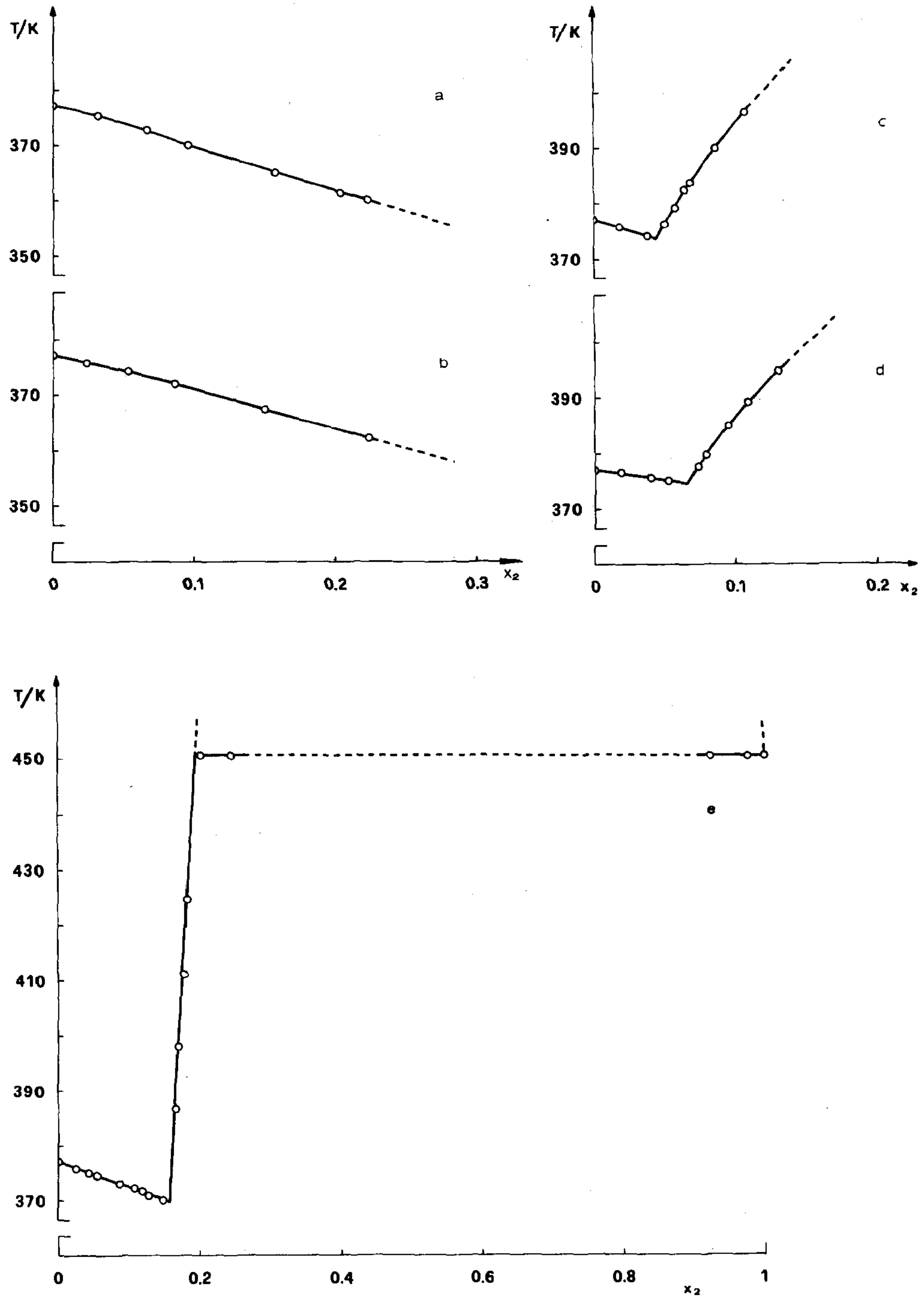

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems: (a), stearamide–sodium perchlorate; (b), stearamide–sodium thiocyanate; (c), stearamide–sodium stearate; (d), steramide–potassium stearate; (e), stearamide–potassium thiocyanate.

that is the saturation concentration is reached at a temperature (in this case higher than the corresponding temperature with acetamide) where the equilibria ("S" standing for stearamide)

$$M^+ + xS \rightleftarrows MS_x^+$$

$$A^- + yS \rightleftarrows AS_y^-$$

practically do not withdraw ions from the equilibrium

$$M^+ + A^- \rightleftarrows MA$$

Further research will allow us to ascertain the existence of these equilibria.

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