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BINARY MIXTURES: $CH_3CH_2CONH_2$ + (Na, K)/(CNS, ClO_4)

G. GIOIA LOBBIA, G. BERCHIESI and G. POETI

Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Camerino 62032 (Italy)

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ABSTRACT

The enthalpy of fusion of propionamide is measured by the DSC method, and liquid–solid equilibrium temperatures are measured for the binary systems $CH_3CH_2CONH_2$ + (Na, K)/(CNS, ClO_4). The cryoscopic thermodynamic constant is compared with the experimental value. It was found that supercooling phenomena in these systems are very limited.

INTRODUCTION

In a previous paper we reported that acetamide, when mixed with electrolytes, can produce liquids that supercool until the temperature of glass transition is reached [1–3]. The dependence of this phenomenon on the nature of the anion and cation [2] and the visco-elastic nature of one of these liquids [3] have been studied previously. Owing to the importance of the supercooling phenomena in the study of the liquid state, our intention is to investigate the effect of the lengthening of the aliphatic chain of the amide.

EXPERIMENTAL

The experimental cryoscopic method employed has been described previously [4]. Calorimetric measurements were performed with a differential scanning calorimeter, Perkin–Elmer DSC-2C, calibrated against metal samples. The chemicals employed were: Propionamide 97% (Ega-Chemie); KCNS 99% (Merck); NaCNS 98% (Fluka); and $NaClO_4$ 99% (C. Erba), all used without further purification.

In the present paper 1 and 2 represent propionamide and the second component, respectively.

RESULTS AND DISCUSSION

The melting enthalpy of propionamide, measured calorimetrically, is 41.6 ± 0.1 cal g^{-1} and the fusion peak represents a diffusion of $\simeq 15$ K. The liquid–solid equilibrium temperatures are given in Table 1 and shown in Fig. 1. The melting enthalpy and temperature allow us to calculate the thermody-

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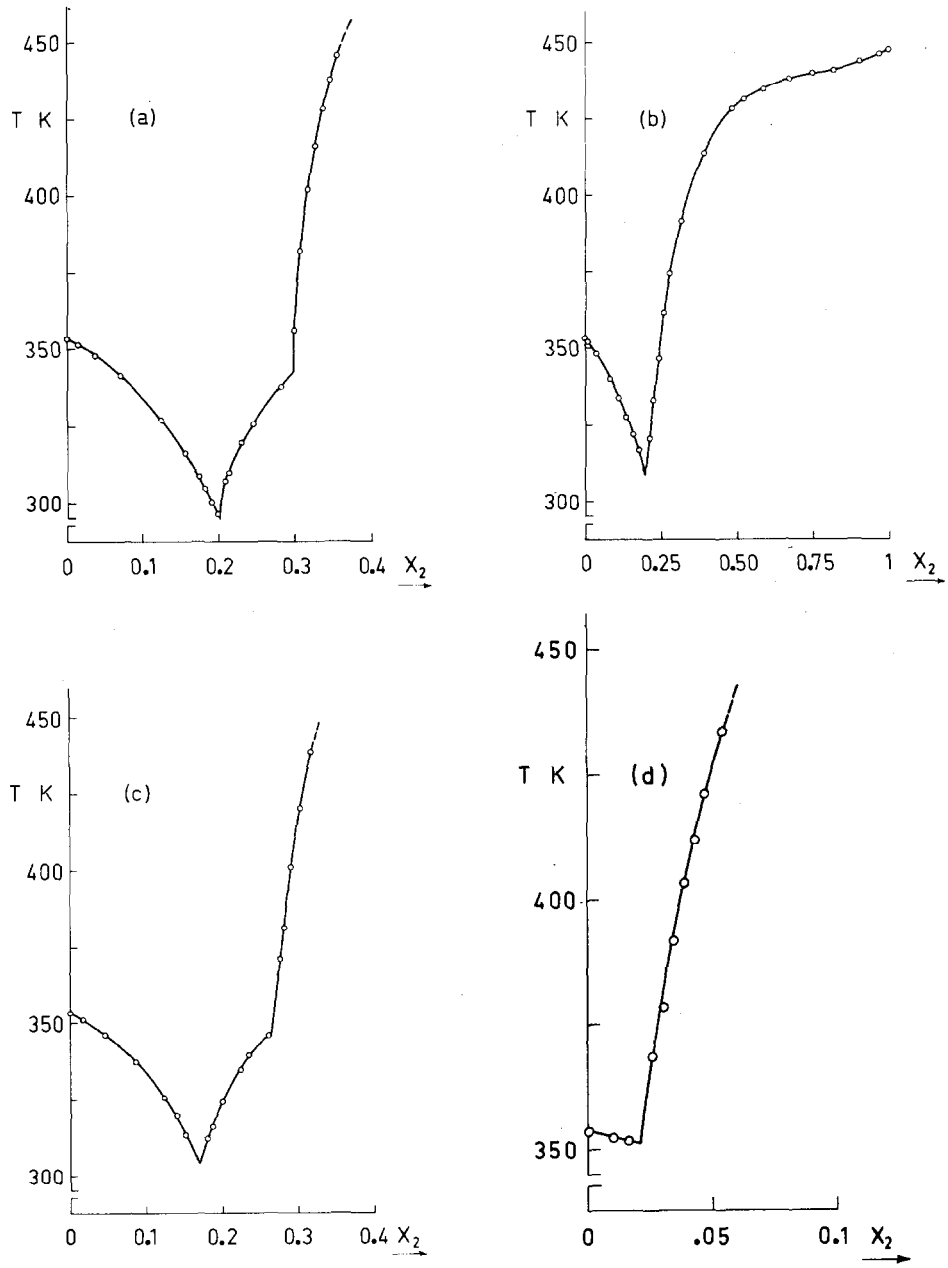

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems: (a) propionamide–sodium thiocyanate; (b) propionamide–potassium thiocyanate; (c) propionamide–sodium perchlorate; (d) propionamide–potassium perchlorate.

TABLE 1

Liquid–solid equilibrium temperatures for the binary systems studied

$C_2H_5CONH_2$–NaCNS		$C_2H_5CONH_2$–KCNS		$C_2H_5CONH_2$–$NaClO_4$		$C_2H_5CONH_2$–$KClO_4$	
x_2	T (K)	x_2	T (K)	x_2	T (K)	x_2	T (K)
0.0000	353.4	0.0000	353.4	0.0000	353.4	0.0000	353.4
0.0149	351.3	0.0107	352.2	0.0163	351.1	0.0103	352.2
0.0376	347.7	0.0364	348.3	0.0460	346.2	0.0165	351.5
0.0698	341.5	0.0803	339.9	0.0860	337.5	0.0260	368.5
0.1246	327.3	0.1113	333.9	0.1231	325.7	0.0311	382.0
0.1547	316.4	0.1344	327.7	0.1399	319.7	0.0348	391.7
0.1741	308.8	0.1569	322.0	0.1525	313.9	0.0390	403.1
0.1815	304.8	0.1748	317.2	0.1800	312.4	0.0431	411.8
0.1897	300.2	0.2106	320.9	0.1870	316.2	0.0470	421.0
0.1971	296.2	0.2250	333.2	0.1995	324.3	0.0543	442.7
0.2087	306.7	0.2401	346.7	0.2234	334.9		
0.2135	309.9	0.2616	361.6	0.2345	339.9		
0.2294	319.8	0.2799	374.6	0.2603	345.7		
0.2445	325.9	0.3145	391.9	0.2752	371.2		
0.2811	337.8	0.3917	413.6	0.2812	381.5		
0.2985	356.3	0.4848	428.4	0.2899	401.0		
0.3063	382.4	0.5244	431.5	0.3021	420.3		
0.3166	402.1	0.5858	434.4	0.3176	438.7		
0.3266	416.3	0.6721	438.0				
0.3371	428.2	0.7496	440.3				
0.3452	437.9	0.8201	441.1				
0.3551	446.0	0.9081	443.9				
		0.9709	446.4				
		1.0000	447.8				

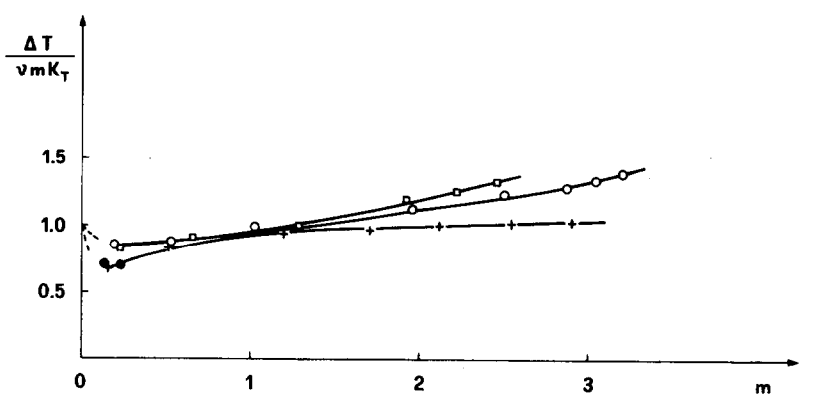

Fig. 2. Trend of $\Delta T/\nu mK_T$ vs. m for the binary systems of propionamide with: ○, NaCNS; +, KCNS; □, $NaClO_4$; ●, $KClO_4$.

TABLE 2

Characteristic points of binary systems

System	$T_{eut.}$	$x_{2eut.}$	$T_{per.}$	$x_{2per.}$
$C_2H_5CONH_2$–NaCNS	295.00	0.200	342.50	0.287
$C_2H_5CONH_2$–KCNS	306.50	0.195		
$C_2H_5CONH_2$–$NaClO_4$	304.00	0.170	346.25	0.264
$C_2H_5CONH_2$–$KClO_4$	351.25	0.021		

namic cryoscopic constant of propionamide (K_T), 5.97 K mol^{-1} Kg. The trend of $\Delta T/\nu m K_T$ ($\nu = 2$ in the present systems) as a function of m is shown in Fig. 2; the theoretical value of $\Delta T/\nu m$ is reached and exceeded at $m > 1$ mol Kg^{-1}. The probable explanation of this behaviour (as suggested for a solution of acetamide [2]) must be present of the following equilibria

$$MX \leftrightarrows M^+ + X^- \quad (1)$$

$$M^+ + xS \leftrightarrows MS_x^+ \quad (2)$$

$$X^- + yS \leftrightarrows XS_y^- \quad (3)$$

where S stands for solvent. Due to equilibria (2) and (3), lowering of the temperature may cause a complete dissociation of the salts. The systems with potassium salts exhibit phase diagrams with simple eutectic behaviour, while the systems with sodium salts also exhibit a peritectic transition point (whose coordinates are given in Table 2). The thermograms obtained by DSC measurements in systems (with sodium salts) with compositions in the range $0.6 < x_1 < 1$ show that the eutectic transition disappears when $x_1 < 0.66$; this fact demonstrates that the peritectic transition may be ascribed to an incongruently melting compound of the following formula $NaX \cdot 2\ CH_3CH_2CONH_2$.

The behaviour regarding the crystallization of propionamide is different in comparison with the behaviour of acetamide [2]; in fact, important supercooling phenomena are not observed. Only without stirring compositions near the eutectic point give a supercooling of $\simeq 10$ K.

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REFERENCES

1 F. Castellani, G. Berchiesi, F. Pucciarelli and V. Bartocci, J. Chem. Eng. Data, 26 (1981) 150.
2 G. Berchiesi, G. Gioia Lobbia, V. Bartocci and G. Vitali, Thermochim. Acta, 70 (1983) 317.
3 G. Berchiesi, P. Passamonti, G. Vitali and R. Plowiec, J. Chem. Soc., Faraday Trans. 2, 79 (1983) 1257.
4 M. Braghetti, D. Leonesi and P. Franzosini, Ric. Sci., 38 (1968) 116.