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SUPERCOOLING PHENOMENA IN BINARY MIXTURES OF TRIFLUOROACETIC ACID SODIUM SALT AND AMIDES

G. GIOIA LOBBIA and G. BERCHIESI

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

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ABSTRACT

Liquid–solid equilibrium temperatures are measured in binary mixtures of trifluoroacetic acid sodium salt and amides (acetamide, propionamide, *n*-butyramide, stearamide).

In some ranges of concentration, all these systems (with the exception of $C_{17}H_{35}CONH_2 + CF_3COONa$) exhibit supercooling phenomena and the liquid becomes very viscous and does not crystallize.

INTRODUCTION

The importance of the supercooling phenomenon for the study of liquids [1] induced us to study this phenomenon in mixtures of amides and salts, continuing the observation [2] of the spontaneous supercooling occurring in the binary system CH_3CONH_2–NaCNS in the concentration range around the eutectic point.

Subsequently, we have pointed out that the appearance of this phenomenon depends on the nature of the anions and cations [3] as well as on the nature of the amide [4]. As the sodium ion is the cation that most markedly produces this phenomenon (when associated with an anion which behaves as a weak base), we present in this paper liquid–solid (LS) equilibrium curves for the binary systems CF_3COONa–$RCONH_2$ ($R = CH_3$, C_2H_5, C_3H_7, $C_{17}H_{35}$).

EXPERIMENTAL

The cryoscopic experimental method is described elsewhere [3,5]. The compounds employed were trifluoroacetic acid sodium salt, acetamide, propionamide and *n*-butyramide (Ega-Chemie), all used without further purification. Stearamide (Fluka) was recrystallized twice from C_2H_5OH. They were dried by a conventional method [3]. In this report 1 and 2 stand for amide and salt, respectively.

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TABLE 1

Liquid–solid equilibrium temperatures in the binary systems amide–CF_3COONa

CH_3CONH_2–CF_3COONa		$CH_3CH_2CONH_2$–CF_3COONa		$CH_3(CH_2)_2CONH_2$–CF_3COONa		$CH_3(CH_2)_{16}CONH_2$–CF_3COONa	
x_2	T (K)	x_2	T (K)	x_2	T (K)	x_2	T (K)
0.0000	353.1	0.0000	353.4	0.0000	387.7	0.0000	377.1
0.0121	352.0	0.0067	352.5	0.0214	384.9	0.0395	375.2
0.0424	348.4	0.0293	349.3	0.0672	380.0	0.0739	373.6
0.0875	342.6	0.0706	343.7	0.1234	373.3	0.1173	372.1
0.1422	334.9	0.1220	336.1	0.1915	364.8	0.1532	370.9
0.1997	324.7	0.1820	327.0	0.2595	356.5	0.2499	368.3
0.2269	318.7	0.2489	314.8	0.3046	349.6	0.2939	366.3
0.2566	310.3	0.3021	303.1	0.3298	345.7	0.3536	363.9
0.2781	302.0	0.3259	295.7	0.3964	335.6	0.4203	361.0
0.2985	290.6	0.3407	290.7	0.4578	322.2	0.4635	358.4
0.3038	287.5	0.3583		0.4788	316.0	0.5029	356.7
0.3197		0.3985		0.5020	310.7	0.5279	355.4
0.3611		0.4671		0.5252	303.4	0.5550	357.2
0.4140		0.5047		0.5358	296.2	0.5626	364.5
0.5321		0.5608		0.5513		0.5789	376.0
0.6602		0.6020		0.5675		0.6055	391.9
0.6888	299.7	0.6517		0.5764		0.6279	403.0
0.6959	325.3	0.6726	304.2	0.5852	304.7	0.6455	410.7
0.7088	345.9	0.6782	323.4	0.5994	316.6	0.6768	422.0
0.7186	362.0	0.6885	343.3	0.6194	328.5	0.6958	430.0
0.7378	385.0	0.7056	366.0	0.6488	345.7		
0.7724	413.4	0.7263	382.0	0.6820	364.7		
0.8142	432.3	0.7650	402.5	0.7069	378.2		
0.8968	457.9	0.8361	427.7	0.7398	395.1		
				0.7608	405.3		
				0.8018	424.9		

RESULTS AND DISCUSSION

The experimental values concerning the crystallization temperatures and the corresponding composition are given in Table 1 and shown in Fig. 1(a–d). It is evident that most of these binary systems show a concentration zone where the supercooling occurs spontaneously (while stirring); the supercooling range decreases with lengthening of the aliphatic chain. In fact, the difference $x_2 - x_2'$ (x_2 and x_2' being the mole fraction of component 2

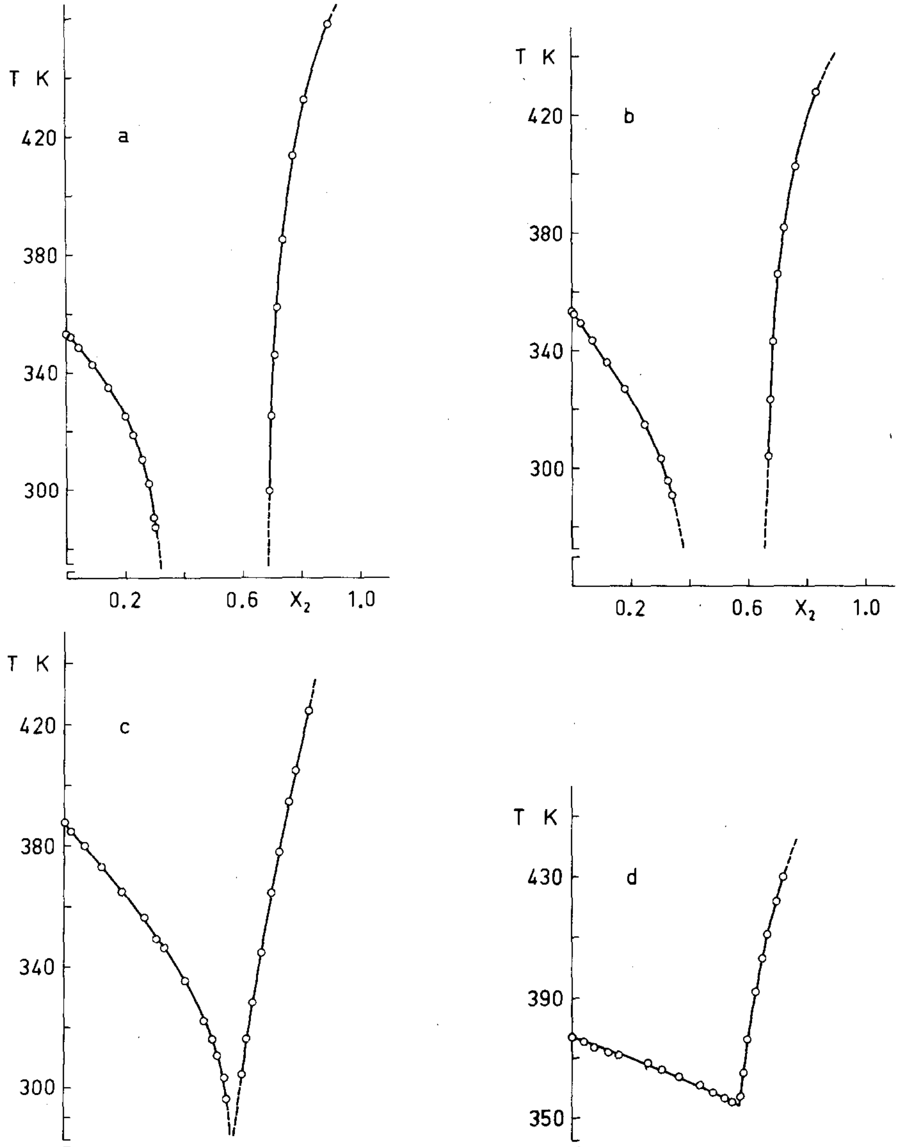

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems: a, acetamide + trifluoroacetic acid sodium salt; b, propionamide + trifluoroacetic acid sodium salt; c, *n*-butyramide + trifluoroacetic acid sodium salt; d, stearamide + trifluoroacetic acid sodium salt.

corresponding to the limits of the supercooling zone, for the side being more and less rich in CF_3COONa respectively) gives the following values; 0.38, 0.33 and 0.05 for the systems with acetamide, propionamide and butyramide respectively. Strong supercooling effects are not present in the system with stearamide; only mixtures with a composition near to that of the eutectic supercool 6–10°C if they are not stirred. In analogous systems previously studied [2–4] a monotectic point was in evidence, due to an intermediate compound with an incongruous melting point of probable formula 2 $RCONH_2 \cdot NaX$. The systems reported in this paper do not show this feature.

A comparison of the thermodynamic cryoscopic constant (K) of acetamide, propionamide and stearamide [2,4,6] with the experimental value (which may be calculated using data from Table 1) allows us to ascertain another difference between the systems with CF_3COONa and the systems previously studied [3,4]. Previously, we noted that the trend of $\Delta T/\nu mK$ vs. m presents a minimum, whereas the systems with CF_3COONa exhibit a decreasing trend in all the experimental concentration ranges with the exception of the system with acetamide. In fact, $\Delta T/\nu mK$ changes continuously from 0.96 to 0.40 in the range $0.14 \leqslant m \leqslant 3.94$ in the system with stearamide, and from 0.86 to 0.73 in the range $0.09 \leqslant m \leqslant 6.61$ in the system with propionamide. $\Delta T/m$ is also a decreasing function of m in the system with butyramide. However, with acetamide $\Delta T/\nu mK$ is an increasing function of m and increases from 0.55 to 0.87 in the range $0.20 \leqslant m \leqslant 7.20$.

The reason for this behaviour is not clear, but is probably due to the fact that the contact CF_3–CH_3 (or CH_2) increases free energy [7] and consequently the temperature of fusion. This effect is probably not evident with acetamide and increases with chain lengthening, and must be studied in more detail in order to ascertain the probable deviation from the random distribution of trifluoroacetate ion.

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