

SUPERCOOLING PHENOMENA IN BINARY MIXTURES OF ACETAMIDE AND INORGANIC SALTS

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ABSTRACT

Liquid–solid equilibrium temperatures are measured in binary mixtures of acetamide and inorganic salts [NaClO₄, LiCNS, LiNO₃, CH₃COOLi, Ca(NO₃)₂, (CH₃)₄NCl, (C₂H₅)₄NBr]. In some ranges of concentration all these systems (with the exception of CH₃COOLi, R₄NX) exhibit supercooling phenomena and crystallization occurs only through vigorous agitation and in the presence of crystalline nuclei, or does not occur at all, according to the type of salt. A probable explanation is presented on the basis of the trend of $\Delta T/vmK$ vs. m .

INTRODUCTION

Acetamide in the molten state presents some features (e.g. dielectric constant, dissociation constant) [1,2] similar to water and is therefore widely employed as a solvent of electrolytes or nonelectrolytes [3–5]. In previous work [6,7] it was realized that the presence of ions in molten acetamide may cause some supercooling phenomenon. In these previous measurements [6,7] this phenomenon appeared to be dependent not only on the size of the cation but also on the type of anion. In fact, this phenomenon is evident with KCNS or NaCNS, but not with HCOOK or CH₃COOK, and between KCNS and NaCNS, NaCNS induces this phenomenon in a more manifest manner.

The eutectic mixture CH₃CONH₂–NaCNS does not crystallize spontaneously and easily reaches the glass transition temperature [8]. Its viscoelastic behaviour has been studied by ultrasonic method [8], showing a wide viscoelastic relaxation in the ultrasonic range and structural changes in the liquid phase. For these reasons in the present work we present the results of studies of liquid–solid equilibrium temperatures in other binary systems between acetamide and salts with the aim of explaining the causes of this phenomenon.

EXPERIMENTAL

The method employed has been described previously [9]. When the melting temperature was lower than room temperature the equipment described in the literature [10] was used and refrigerated by means of the circulation of thermostated liquid arising from an F3K Haake cryothermostat. The accuracy has been given previously [6,11] and is 0.03° when the melting temperature is obtained as a stop of the cooling (pure compounds or dilute solution) or 0.1° when the visual method is adopted. At low temperatures in order to prevent the condensation of humidity, a flow of dry nitrogen on the measurement vessel was employed. NaClO_4 and $\text{Ca}(\text{NO}_3)_2$ Erba RPE, $\text{C}_4\text{H}_{12}\text{NCl}$, $\text{C}_8\text{H}_{20}\text{NBr}$ and LiNO_3 Merck, LiCNS Alfa and CH_3CONH_2 Fluka were employed without further purification. They were hot-dried under dynamic vacuum. Acetamide was dried at room temperature as reported previously [6,7]. In the present paper 1 and 2 represent acetamide and the other component, respectively.

RESULTS AND DISCUSSION

The liquid–solid equilibrium temperatures as a function of the mole fraction of acetamide are given in Tables 1–7. The experimental measurements concerning the liquidus curve of acetamide are presented in the form $\Delta T/\nu mK$ vs. m , where ΔT is the temperature-lowering of the solutions, m is

TABLE 1

Cryoscopic data of the binary mixtures CH_3CONH_2 – LiNO_3

X_1	$T_{sl}(\text{K})$	X_1	$T_{sl}(\text{K})$
1.0000	352.9 ₄	0.7692	327.0
0.9212	339.2 ₄	0.7479	345.2
0.8763	327.1	0.7362	352.7
0.8738	326.3	0.7208	364.1
0.8500	318.2–318.6 ^a	0.7044	372.5
0.8198	305.1	0.6035	403.2
0.8100 ^b	298.1–290.8 ^c	0.5011	417.8
0.8001 ^b	292.8	0.4761	438.7
0.7945 ^b	293.2	0.4066	459.5
0.7898 ^b	290.3–302.7 ^a	0.2985	487.3
0.7878 ^b	295.5	0.1988	503.6
0.7797 ^b	313.6–319.9 ^a	0.0931	515.3
0.7779	295.5	0.0000	523.9 ₅

^a Dispersion due to the temperature from which the cooling starts.

^b Supercooling without agitation.

^c Explanation in the text.

TABLE 2

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2\text{-LiCNS}$

X_1	$T_{\text{st}}(\text{K})$
1.0000	352.9 ₄
0.9687	348.7 ₈
0.9501	345.0 ₄
0.9225	338.4
0.8784	324.1
0.8407	305.5
0.8346	300.8 ^a
0.8194	287.9 ^a
0.8103	303.4 ^a
0.7968	313.4 ^a
0.7828	322.1
0.7572	334.7
0.7381	342.8

^a These mixtures do not crystallize without agitation.

the molality of the salt, ν is the sum of the number of cations and anions in the salt formula, and K is the thermodynamic cryoscopic constant [6].

The systems, except those with $\text{C}_4\text{H}_{12}\text{NCl}$, $\text{C}_8\text{H}_{20}\text{NBr}$ and CH_3COOLi , present supercooling phenomena in a concentration zone near the eutectic point.

LiCNS

Without agitation or at a low speed of agitation this system supercools easily in the concentration range $0.776 < X_1 < 0.835$, producing a paste which, if the concentration is near to the eutectic composition, crystallizes by means of vigorous agitation. On the other hand, if the concentration is in the limit of the range $0.776 < X_1 < 0.835$, the mixture supercools until approxi-

TABLE 3

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2\text{-CH}_3\text{COOLi}$

X_1	$T_{\text{st}}(\text{K})$
1.0000	352.9 ₄
0.9891	351.6 ₄
0.9789	350.7 ₄
0.9735	350.2 ₄
0.9655	358.7
0.9580	369.3
0.9493	380.5

TABLE 4

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2\text{-NaClO}_4$

X_1	$T_{sl}(\text{K})$
1.0000	352.9 ₄
0.9916	351.7 ₄
0.9588	346.8 ₄
0.9046	335.8 ₉
0.8543	321.2
0.8184	306.0
0.8037	300.0 ^a
0.7840	288.9 ^a
0.7602	b
0.7373	b
0.7221	b
0.7003	b
0.6934	b
0.6796	374.0
0.6687	395.2
0.6486	424.0
0.6279	442.4

^a These mixtures do not crystallize without agitation.^b These mixtures do not crystallize and supercool. When the liquid becomes very viscous the stirrer hauls little bubbles of air in the mixture, giving an opacity which disappears when the stirrer is stopped.

TABLE 5

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2\text{-Ca}(\text{NO}_3)_2$

X_1	$T_{sl}(\text{K})$
1.0000	352.9 ₄
0.9827	349.5 ₉
0.9510	342.3 ₉
0.9250	334.8 ₉
0.8982	323.7
0.8754	314.1
0.8587	333.3 ^a
0.8246	341.3 ^a
0.8000	345.1 ^a
0.7785	333.7 ^a
0.7596	336.5 ^a
0.7514	336.0 ^a
0.7290	b
0.6999	b
0.6953	b

^a The mixtures do not crystallize without agitation.^b The mixtures do not crystallize with agitation.

TABLE 6

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2 - (\text{C}_2\text{H}_5)_4\text{NBr}$

X_1	$T_{sl}(\text{K})$
1.0000	352.9 ₄
0.9915	351.1 ₄
0.9670	348.6 ₄
0.9523	346.4 ₉
0.9267	342.9 ₄
0.8957	337.9
0.8607	332.0
0.8199	323.4
0.8014	319.8
0.7863	323.3
0.7779	334.9
0.7554	352.9
0.7358	363.9
0.7015	378.2

mately 290 K. At this temperature spontaneous crystallization starts on the wall of the container and propagates slowly all over the mass following a round-topped ramification.

CH_3COOLi

This salt exhibits a low solubility in acetamide and the liquid–solid equilibrium does not depend (within the experimental accuracy) on the

TABLE 7

Cryoscopic data of the binary mixtures $\text{CH}_3\text{CONH}_2 - (\text{CH}_3)_4\text{NCl}$

X_1	$T_{sl}(\text{K})$
1.0000	352.9 ₄
0.9906	352.1 ₀
0.9743	351.1 ₀
0.9415	346.4 ₄
0.9208	343.0 ₄
0.8921	338.5
0.8757	335.2
0.8491	330.8
0.8398	328.0
0.8291	333.8
0.8229	341.3
0.8125	350.9
0.8035	359.1
0.7775	379.2

speed of agitation.

LiNO₃

In the concentration range $0.78 < X_1 < 0.81$ the liquid–solid temperature depends on the speed of agitation. At low agitation speed the liquid mixture supercools and gives a very viscous paste. In this concentration range the temperature of crystallization seems to depend on the thermal history. In fact, if the mixture ($X_1 = 0.85$) is cooled from 423 K or 323 K, little difference in the temperature of crystallization is obtained (317.7 and 318.1 K, respectively), but at $X_1 = 0.7898$, cooling started from 440 and 326 K produces crystallization temperatures of 290.3 and 302.7 K, respectively. Similar behaviour is observed in other mixtures. The mixture $X_1 = 0.81$ at 298.1 K gives a small number of needle-shaped crystals, but at 290.8 K produces a lactescence in all the liquid. The polarized light microscope shows that this lactescence is due to very small square crystals. This type of crystallization (lactescence) is characteristic of the concentration range $0.78 < X_1 < 0.81$.

Ca(NO₃)₂

In the concentration range $X_1 < 0.86$ supercooling phenomena occur, producing a very hard paste that can be stirred with difficulty. At concentration $X_1 < 0.8$ the stirring becomes so inefficient that the temperature of crystallization is not reliable. Some measurements were also performed in the region $0.695 < X_1 < 0.75$ where the mixtures do not crystallize even with stirring and with crystalline nuclei, but produce a paste that is practically vitrified at 336 K.

NaClO₄

In the region $0.78 < X_1 < 0.80$ supercooling occurs if the mixtures are not stirred, but in the range $0.68 < X_1 < 0.78$ the mixtures do not crystallize even if the mixture is stirred and some nuclei are cast inside.

Tetralkyl ammonium salts

These salts do not exhibit supercooling phenomena.

Figure 1 shows the experimental trend $\Delta T/vmK$ vs. m , concerning the mixtures presented in this paper and in previous work [6,7]. It is clear that some salts (formates, acetates, and alkyl ammonium halides) have a cryoscopic lowering less than the thermodynamic one over the complete concentration range. On the contrary, thiocyanates, nitrates and perchlorates exhibit a particular trend, that is, at a certain concentration (which seems to

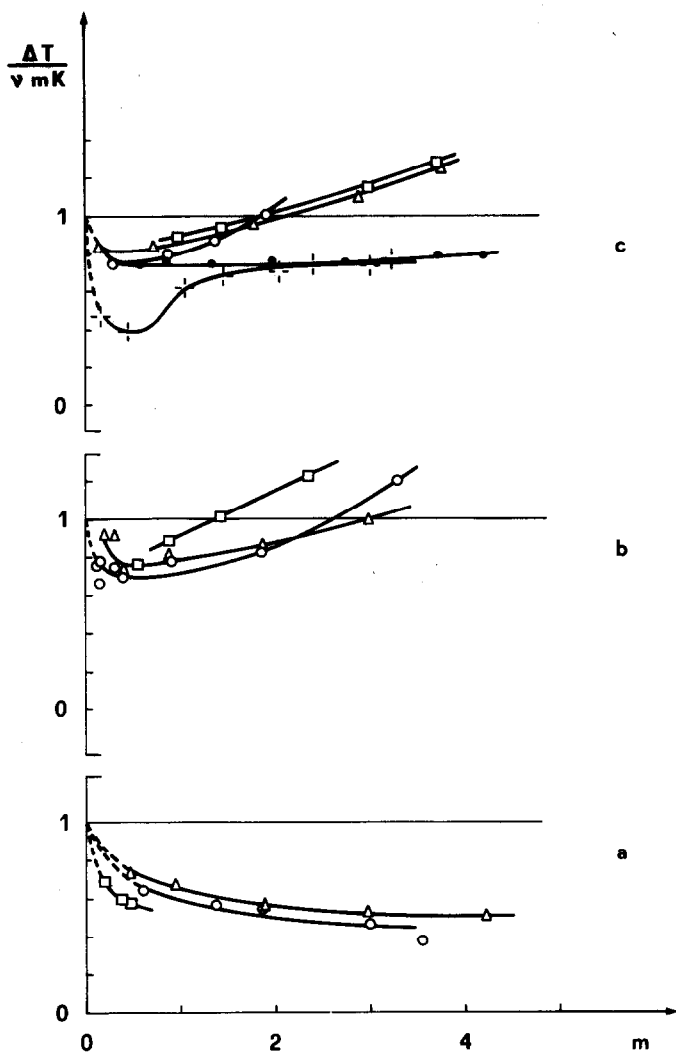


Fig. 1. Trend of $\Delta T/\nu mK$ vs. m (of the acetamide liquidus curve) in the binary systems. (a) With HCOOK (\circ); CH_3COOK (Δ); CH_3COOLi (\square). (b) With KCNS (\circ); NaCNS (Δ); LiCNS (\square). (c) With $\text{Ca}(\text{NO}_3)_2$ (\circ); NaClO_4 (Δ); LiNO_3 (\square); $\text{N}(\text{CH}_3)_4\text{Cl}$ ($+$); $\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$ (\bullet).

depend roughly on the density charge of the cation) the cryoscopic lowering becomes higher than the thermodynamic one. They are the systems which show the supercooling phenomena. A probable explanation of this behaviour is as follows: a salt M^+A^- is partially dissociated in molten acetamide [6]



When A^- is a strong base (formate, acetate) or M^+ is a weak acid (tetraalkyl ammonium ions) the equilibrium(I) is shifted towards the associated salt and $\Delta T/\nu mK$ is less than 1 over the entire concentration range. When M^+ is a strong acid and A^- is a weak base, the interaction of M^+ with CH_3CONH_2 becomes predominant at a certain temperature and the second reaction subtracts M^+ from the first equilibrium. The consequent complete dissociation of the salt and the diminution of the solvent owing to reactions (II) and (III) may cause the increase in $\Delta T/\nu mK$. An ultrasonic study [8,12] is in progress in order to ascertain the presence of these equilibria and the structure of the supercooled liquids. A difference in the behaviour of sodium and lithium salts is evident. Na salts give the same supercooling phenomenon as Li salts, but the supercooled mixtures containing Na salts are stable with respect to the agitation. On the contrary, mixtures containing Li salts tend to crystallize by stirring; this is due to the higher mobility of Li^+ ions.

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