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SOLUBILITY DATA OF SOME SODIUM SALTS IN 2-HYDROXYACETAMIDE

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ABSTRACT

Liquid–solid equilibrium temperatures were measured, over a limited concentration range, in binary mixtures of 2-hydroxyacetamide with three inorganic sodium salts ($NaSCN$, $NaClO_4$, $NaNO_3$). The complete mole fraction range could not be studied because of the thermal instability of the amide.

INTRODUCTION

Research carried out in the last few years on binary mixtures of some molten amides and electrolytes [1–10] has shown the existence of supercooling phenomena, which can be promoted by the presence of cations of alkali or alkali earth metals in molten amide.

The information obtained from these previous measurements has led us to believe that, of the various cations, Na^+ is most effective in promoting supercooling phenomena, and in some cases the binary mixture may reach the glass transition temperature.

The existence of viscoelastic and dielectric relaxations [11–15] indicates that such phenomena may be due to the formation of polymeric structural equilibria by the association of amide molecules or solvated ions in the mixture.

In this paper we have turned our attention to binary systems of 2-hydroxyacetamide and $Na(SCN, ClO_4, NO_3)$ in order to determine the influence of polar substitutes in the aliphatic chain of the amide on the stability of the polymeric structures.

EXPERIMENTAL

The experimental cryoscopic method used here has been described in a previous paper [16]. In order to be able to follow the temperature decrease

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TABLE 1

Liquid–solid equilibrium temperatures in the binary system $(HO)CH_2CONH_2$–NaSCN

X_1	T (K)
1.0000	388.1
0.9876	386.2
0.9777	385.2
0.9492	381.2
0.8962	373.2
0.8671	370.2
0.8300	359.4
0.7925	352.9
0.7617	342.5
0.7484	338.1
0.7327	333.4
0.6971	319.6
0.6653	
0.6427	
0.5956	
0.5381	

below room temperature, the equipment described in ref. 17 was used, refrigerated by thermostatted liquid from an F 40 Julabo cryostat. The fusion enthalpy of the 2-hydroxyacetamide was measured using a Perkin Elmer DSC-1B differential calorimeter, whose calibration has been reported previously [17].

The chemicals employed were $(HO)CH_2CONH_2$ (α-hydroxyacetamide; ICN Biochemicals, Inc. K + K), $NaNO_3$ (99%), $NaClO_4$ (99%) and NaSCN (99%) (Carlo Erba RP), all used without further purification.

The sodium salts were hot dried under dynamic vacuum and the amide was dried for several days under dynamic vacuum at room temperature.

In this paper, 1 represents 2-hydroxyacetamide and 2 denotes the other components.

RESULTS AND DISCUSSION

Liquid–solid equilibrium temperatures are given in Tables 1–3. The crystallization curves are shown in Fig. 1, and in Fig. 2 it is possible to see the trend of $\Delta T/(\nu Km)$, where ΔT is the cryoscopic lowering, m is the molality, K is the thermodynamic cryoscopic constant of α-hydroxyacetamide and υ represents the sum of anions and cations in the salt formula.

The melting enthalpy of the 2-hydroxyacetamide, measured calorimetrically, is 75.9 ± 0.8 cal K^{-1}, and the fusion peak represents a spread of $\simeq$ 15

TABLE 2

Liquid–solid equilibrium temperatures in the binary system $(HO)CH_2CONH_2$–$NaClO_4$

X_1	T (K)
1.0000	388.1
0.9900	385.7
0.9798	384.2
0.9496	383.8
0.9378	383.6
0.8971	375.7
0.8500	371.5
0.7966	356.8
0.7492	339.5
0.7180	332.4
0.6998	318.9
0.6816	319.5
0.6519	308.4
0.6258	306.8
0.6147	334.2
0.5994	368.1

TABLE 3

Liquid–solid equilibrium temperatures in the binary system $(HO)CH_2CONH_2$–$NaNO_3$

X_1	T (K)
1.0000	388.1
0.9865	385.3
0.9770	384.1
0.9665	386.9
0.9373	389.2
0.9355	383.4
0.8997	375.8
0.8485	375.6
0.7963	369.3
0.7618	364.6

K. The thermodynamic cryoscopic constant was calculated from the enthalpy and temperature of fusion and the value obtained was 3.94 K mol^{-1} kg.

The calorimetric data of fusion of $(HO)CH_2CONH_2$ are given in Table 4.

TABLE 4

Calorimeter data of fusion of $(HO)CH_2CONH_2$

ΔH_{fus} (kcal mol^{-1})	ΔS_{fus} (cal K^{-1} mol^{-1})	T_{fus} (K)
$5.6_9 \pm 0.06$	$14.6_6 \pm 0.16$	388.1

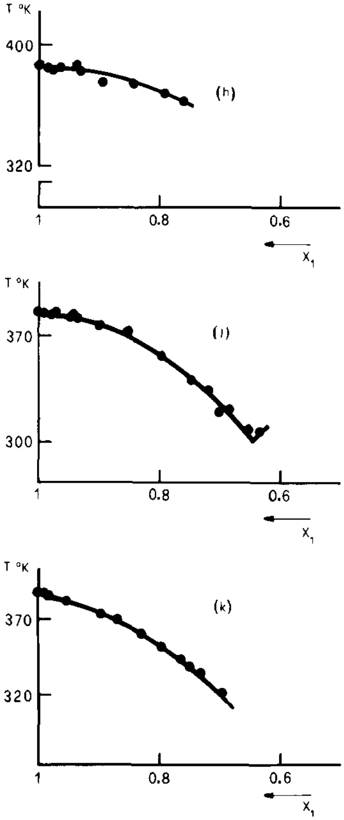

Fig. 1. Liquid–solid equilibrium temperatures in the binary systems 2-hydroxyacetamide–sodium nitrate (h), 2-hydroxyacetamide–sodium perchlorate (j) and 2-hydroxyacetamide–sodium thiocyanate (k).

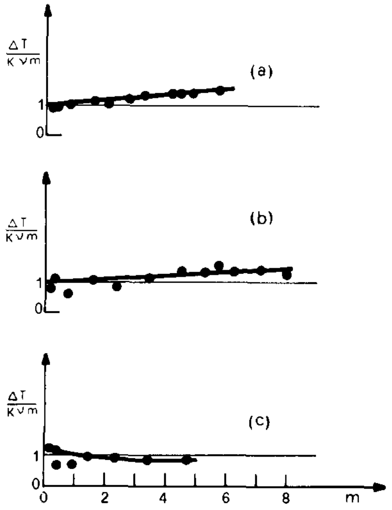

Fig. 2. Trend of $\Delta T/(\nu Km)$ vs. m for the binary systems of 2-hydroxyacetamide with (a) $NaNO_3$, (b) $NaClO_4$ and (c) NaSCN.

NaSCN

In this system supercooling phenomena occur in the mole fraction range $0.7 > X_1 > 0.54$. In this range the mixture becomes more and more dense and vitreous, making the stirring inefficient, and thus crystallization is not observed. At $X_1 < 0.5$ it is not possible to measure liquid–solid equilibrium temperatures because the amide decomposes.

$NaClO_4$

Supercooling phenomena occur in the mole fraction range $0.72 > X_1 > 0.61$, but in a different manner. In fact, if the liquid system is left alone, it crystallizes after a few hours. At $X_1 < 0.5994$ it is not possible to measure liquid–solid equilibrium temperatures owing to the thermal instability of the amide. In this system crystallization is observed as an opalescence occuring in the liquid mixture.

$NaNO_3$

In this system supercooling phenomena do not occur and the amide decomposes very quickly, making it possible to take measurements only until the mole fraction $X_1 = 0.7618$. The experimental values are subject to great uncertainty. In this system crystallization is observed as crystal formation.

The cryoscopic lowering ΔT in the NaSCN and $NaClO_4$ systems deviates from $K\nu m$ with increasing electrolyte concentration as a consequence of both the invalidity of the limited law ($K\nu m$) and of ion–amide interaction.

The introduction of an –OH group into the aliphatic chain modifies the behaviour of the electrolyte mixtures in comparison with CH_3CONH_3 mixtures. In fact, in acetamide solutions cation–anion interaction seems to prevail at low electrolyte concentration [3].

In the present mixtures the dissociation of the electrolyte seems to be complete over the entire concentration range investigated.

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