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SUPERCOOLING PHENOMENA IN THE BINARY SYSTEMS: ACETAMIDE–ELECTROLYTES

G. Berchiesi, G. Gioia Lobbia, M. A. Berchiesi and *G. Vitali*

DIPARTIMENTO DI SCIENZE CHIMICHE DELL'UNIVERSITÀ, VIA S. AGOSTINO 1,
62032 CAMERINO, ITALY

This paper presents a final discussion on studies of solutions of electrolytes in molten acetamide. These studies deal with cryoscopic and ultrasonic (by shear waves) techniques and reveal the complexity of the behaviour of these systems due to strong ion-solvent interactions.

Acetamide is considered a good solvent for electrolytes and is often empolyed in electrochemistry as a non-aqueous solvent [1–5]. This fact and the similarity of some its physical properties (e.g. dielectric constant or ionization constant) with the corresponding values of water tend to induce the belief that solutions in acetamide are similar in structure to the corresponding solutions in water.

This paper and previous ones [6–9] may give a clearer idea of the complexity of these non-aqueous mixtures.

The methods employed were reported in previous papers [6, 10, 11], and are not given here.

Discussion

Cryoscopy

Liquid–solid equilibria in the binary systems acetamide + electrolytes [7–9] present differences in behaviour, depending on the types of the ions. Two classes may be distinguished:

1) The anion is ClO_4^-, NO_3^- or CNS^- (derived from strong acids) and the cation is an alkali metal or an alkaline earth metal.

2) The anion is CH_3COO^- or $HCOO^-$ (derived from weak acids) and the cation is an alkali metal.

In general, the temperature T_{eut} in the first class is lower than T_{eut} in the second class. That is, the solubility of a salt of the first class is higher in acetamide. Schematically, the two types of behaviour are shown in Fig. 1. Solutions of sodium or calcium salts with anions of the first class present a range of concentration in which the liquid does not crystallize and a very viscous system is produced. The composition range relating to this phenomenon was given in a previous paper [9]; it corresponds roughly to a range around the composition $X_2 = 0.2$ (2 = salt). Lithium salts of the first class exhibit complex behaviour: the solution crystallized in the eutectic range of concentration or does not, depending on whether it is stirred or not, respectively. The crystallization temperature around $X_2 = 0.2$ seems to depend on the temperature from which the cooling starts and also on the speed of agitation. Details of these results were given previously [9]; these results appear to be independent of the type of anion of this class (ClO_4^-, NO_3^- or CNS^-). The salts of the second class give solutions which crystallize regularly. Tetralkylammonium halides also display regular behaviour. If the cryoscopic results are plotted as $\Delta T/\nu mK$ (ΔT = cryoscopic lowering, ν = number of ions, K = thermodynamic cryoscopic constant), two different trends are obtained, as outlined schematically in Fig. 2. Systems *a* (second class) probably undergo incomplete dissociation at low molality, the association becoming complete with increasing molality.

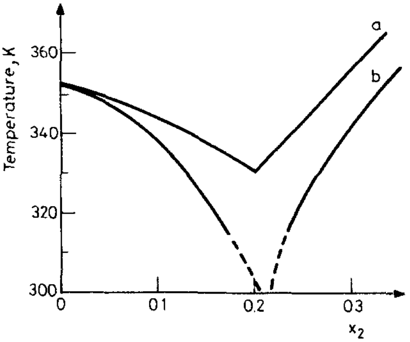

Fig. 1 Schematic trend of the crystallization curve concerning the binary systems: a) acetamide + MX (M = alkali ion, X = anion derived from a weak acid), b) acetamide + MX (M = alkali or alkali earth ion, X = anion derived from a strong acid)

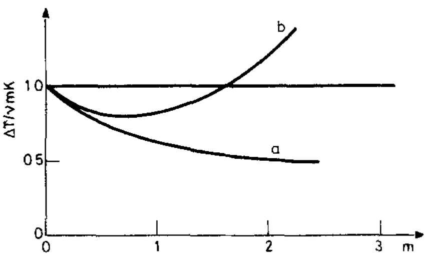

Fig. 2 Schematic trend of $\Delta T/\nu mK$ (where ΔT is the cryoscopic lowering, ν the number of ions derived from the dissociation, m the molality, K the thermodynamic cryoscopic constant) *vs.* the molality m of the salt

In contrast, systems *b* (first class) undergo incomplete dissociation at low molality, but with increasing molality (and consequently decreasing temperature) the dissociation increases. A competitive interaction of the solvent or of the anion with the cation may be an explanation of this behaviour, according to the following equilibria:

$$MX \rightleftharpoons M^+ + X^- \tag{1}$$

$$M^+ + xS \rightleftharpoons MS_x^+ \tag{2}$$

$$X^- + yS \rightleftharpoons XS_y^- \tag{3}$$

The acid-base equilibria (1), (2) and (3) may explain the existence of a temperature range in which the equilibrium constants of equilibria (2) and (3) are so high that equilibrium (1) is shifted towards complete dissociation of the salt.

Ultrasound

The viscoelastic relaxation has been studied [6] by means of a MATEC apparatus described previously [10]. The reduced mechanical impedance, $R/\sqrt{eG_\infty}$, as a function of the reduced frequency, $\omega\eta/G_\infty$, is shifted towards high frequencies of half-decade [6] in comparison to the Maxwell model: the experimental curve is interpreted by the B. E. L. model [12]:

$$\frac{1}{G^*} = \frac{1}{G_\infty} + \frac{1}{i\omega\eta} + \frac{2K}{G_\infty(i\omega\tau)^\beta}$$

and K and β values are given in the previous paper [6].

The shear modulus G' reaches the maximum value (= 0.8 GPa) in the ultrasonic range; the plot of mechanical impedance versus temperature provides evidence of probable structural changes [6]. The viscosity exhibits high values, ranging from 2.3 P (311 K) to 1627.8 P (264.4 K), and there is a change of slope in the Arrhenius plot. The fact that the viscoelastic relaxation relates to the ultrasonic range, the high viscosity values and the supercooling phenomena all indicate that the solution is complex from a structural point of view and may be regarded as a polymeric one. Other ultrasonic measurements are in progress to explain the shift in the curve of the reduced mechanical impedance and the structural changes. From this evidence the following idea may be suggested: the solvated ions MS_x^+ aggregate, producing species of high molecular weight.

This hypothesis is now under investigation.

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Zusammenfassung — Die über Lösungen von Elektrolyten in geschmolzenem Acetamid ausgeführten Untersuchungen werden diskutiert. Diese Untersuchungen erstrecken sich auf kryoskopische und Ultraschall-Methoden und vermitteln ein Bild von der durch starke Ionen-Lösungsmittel-Wechselwirkungen bedingten Komplexität des Verhaltens dieser Systeme.

Резюме — Представлено обсуждение исследований растворов электролитов в расплавленном ацетамиде. Исследования проводились криоскопическим и ультразвуковым методом, показавшие сложное поведение этих систем из-за сильных взаимодействий типа ион—растворитель.