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ACETAMIDE-AMMONIUM SULFAMATE
A reactive binary system in molten state

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Molten mixtures of acetamide and ammonium sulfamate (indicated here AS) are reacted at mole fraction $X_{AS} < 0.35$ to produce $(NH_4)_2SO_4$ and CH_3CN. The experimental conditions and analytical methods adopted are given and a kinetic mechanism is proposed.

For several years we have been studying the particular properties of molten mixtures of amides and electrolytes [1-10]. In some cases they show polymeric structures which are reponsible for supercooling phenomena and for a very high dielectric constant [11-15]. With the aim of clarifying the chemical conditions where this type of phenomena occurs, we studied the liquid-solid equilibrium temperatures, in binary mixtures, amide + electrolytes; of these systems the acetamide + ammonium sulfamate mixture showed reactive properties.

Experimental

The cryoscopic method employed is reported elsewhere [16]: it consists of a potentiometric measurements of temperature (via a chromel-alumel thermocouple, calibrated against a Pt thermometer). NMR measurements were performed by means of a Varian XL-300. The chemicals employed were: acetamide Fluka AG, Buchs SG purum ammonium sulfamate Fisher Scientific Company certified. They were dried under dynamic vacuum for several days before use.

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Results and discussion

The melting points of acetamide and AS are 79.5° and 131.3° respectively, which agree with the literature data [1, 17]. In Fig. 1 we report the measured melting points to which a thermodynamic sense cannot be given, because this system is a reactive one. In fact, in Fig. 1, we have indicated the concentration zone where the molten mixture is limpid or opalescent and it may be seen that at mole fraction X_{AS} ~0.3 a sudden slope change occurs.

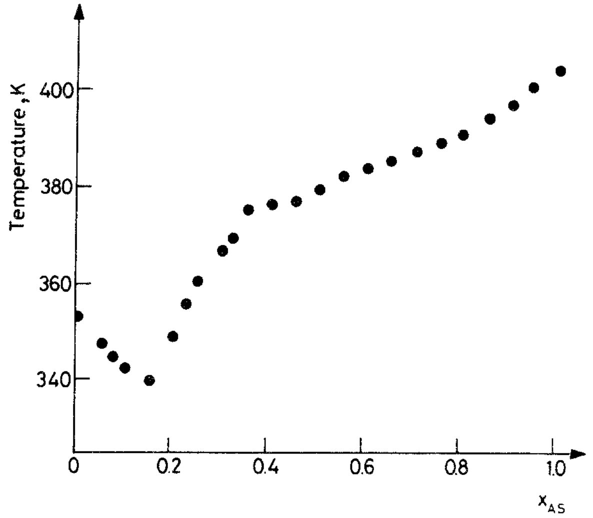

Fig. 1 Melting points of binary mixtures CH_3CONH_2-$NH_4SO_3NH_2$. At X_{AS} < 0.35 the liquid is opalescent; explanation in the text

At X_{AS} = 0.3499 a large quantity of a white precipitate is formed, whereas at X_{AS} <0.3499 the liquid is opalescent but no precipitate is observed and the fusion temperature is reproducible. This trend suggests that the mixture X_{AS} = 0.3499 is most reactive; for this reason we studied the reaction between acetamide and AS at this mole fraction. The mixture, contained in a caudate conical flask, was maintained in an oil bath at 140°. After both substances had melted the liquid obtained remained limpid for some minutes after which the product started to precipitate. Different essays were performed, keeping the molten mixture under air or under N_2 in order to exclude any reaction with oxygen. The white precipitate (obtained in the different essays) was separated by filtration with a filtering crucible and the compound was treated with different solvents, to choose the best solvent for purification by crystallization. The best solvents were H_2O and hot CH_2OH-CH_2OH. The compound was then treated by two different operations:

1) One part was dissolved in water, treated with charcoal and filtered; RPE C. Erba glacial acetic acid was added to the filtered liquid and the white precipitate was again obtained and dried under dynamic vacuum.

2) A second part was dissolved in hot ethylene glycol (Merck Pro Analysis), treated with charcoal and filtered; RPE C. Erba methylic alcohol was then added to the filtered liquid and the white precipitate was obtained and dried under dynamic vacuum.

The compound obtained by the operations 1 and 2 was analyzed in order to determine the costituent elements, their stoichiometric ratio and the molecular weight. The formula obtained was $(NH_4)_2SO_4$. The presence of N_2 or air over the molten mixture does not affect the reaction. Subsequently we turned our attention to probable gaseous products. Preliminary, classic essays excluded the presence of CO_2 and CO in the gas phase and confirmed the presence of NH_3 (also identified by its characteristic smell).

The reaction was then performed in a minidistillator (complete with thermometer and refrigereting unit). The vapours were collected in anhydrous ethyl alcohol (RPE C. Erba) and in acetone (Rudi Pont reagent free of acetic aldehyde); the functional group analysis was performed following indications in literature [18]. Several essays were carried out to find the functional groups of amine and nitrile (which we expected); we found evidence only of the nitrile functional group, which was confirmed in the following manner:

1) A part of the alcoholic solution used to collect the vapours produced during the reaction was treated with metallic Na [18] that reacts following the equation:

$$RCN \xrightarrow[ROH]{Na} RCH_2NH_2$$

The solution obtained was divided into two parts, which were tested separately as described below in points a and b:

a) CH_3Cl and KOH were added and warmed gently; a disagreeable smell of carbilamine confirmed the presence of a nitrile compound [18],

b) H_2O, CH_3COCH_3 (free of acetic aldehyde Rudi Pont Reagent) and one drop of aqueous solution of sodium nitroprussiate (1 %) were added to the solution. A red-violet colouring was obtained [18]. This is a selective essay for the presence of primary amines.

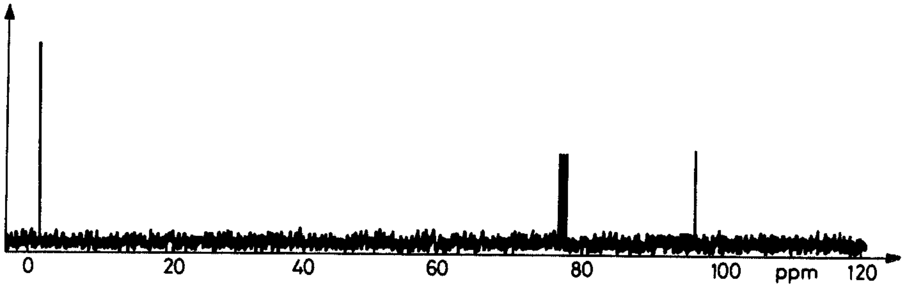

Fig. 2 ^{13}C NMR spectra performed in $CDCl_3$ with VARIAN XL-300. From the right it may be seen the peak corresponding to CH_3 of acetonitrile, three peaks of $CDCl_3$ then the peaks respectively of CCl_4 and CN group

2) A second part of the alcoholic solution was been treated as described in point b and the presence of primary amines was not noted. The same results were obtained with solution in acetone. It may be concluded that amines are not present in the reacting mixture, but a compound RCN is formed during the reaction, probably it is CH_3CN. Subsequently the reaction was performed again and the vapours were collected in CCl_4 (Baker analyzed reagent), because it is a good solvent for CH_3CN, but does not dissolve the acetamide.

The reacting melt was maintained at about 105° and the reaction was stopped when the presence of NH_3 in the vapour dropped in order to avoid decomposition of excess acetamide. The solution in CCl_4 was tested by NMR. The spectrum, reported in Fig. 2, clearly shows the presence of the nitrile of acetic acid [19].

Conclusion

The products ascertained were CH_3CN and $(NH_4)_2SO_4$ and they suggest a mechanism where the most important step which primes the process is an acid-base reaction between acetamide and ammonium sulfamate, as shown in Fig. 3. This proposed mechanism must be confirmed by further study, but the present research suggests that the presence of an acid as NH_4^+ in molten amides does not make the system thermally stable. A preliminary results for further research indicates that sulfamic acid also gives rise to the same reaction, with the formation of a white solid compound. For this reason molten amides cannot be employed as solvents for analytical or physicochemical purposes in the presence of this acid. Moreover, the mechanism proposed

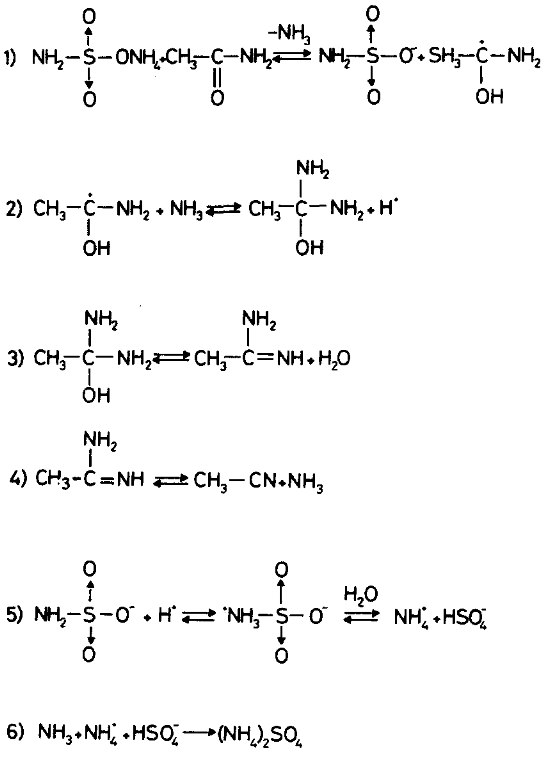

Fig. 3 Probable mechanism of the reaction involved in the melt

may explain the experimental evidence (Fig. 1) when the solid reaction product suddenly appears at $X_{AS} < 0.35$, whereas at $X_{AS} > 0.35$ the mixture is limpid. Probably step 1 at high AS concentration is shifted towards the undissociated ammonium salt, as shown by the salts examined [1] and consequently the reaction is blocked.

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Zusammenfassung — Acetamid und Ammoniumsulfamat (AS) wurden in Schmelzen mit dem Molenbruch X_{AS} umgesetzt, um $(NH_4)_2SO_4$ und CH_3CN zu erhalten. Es werden die angewendeten Reaktionsbedingungen und analytischen Verfahren sowie ein kinetischer Mechanismus gegeben.