

Solution Chemistry of Molten Amide-Nitrate Eutectics

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The partial binary phase diagram, eutectic composition, and temperature were determined for butyramide—sodium nitrate and acetamide—lithium iodide; together with the densities of the eutectics from their melting points to 100 °C.

The reactions of seven first-row transition metal compounds were examined in acetamide—potassium nitrate eutectic and four in butyramide—sodium nitrate eutectic. Cobalt(II) chloride was highly soluble at 90 °C and 140 °C, respectively, giving electronic spectra typical of octahedral coordination. In the acetamide eutectic increasing the temperature, up to 140 °C, gave more tetrahedral coordination.

Chromium(III) chloride, nickel(II) chloride, and copper(II) sulfate gave solution spectra indicating octahedral coordination by amide and nitrate, while the probably tetrahedral chloro complexes formed by iron(III) chloride were rapidly solvolyzed. Potassium chromate and potassium dichromate were only very slightly soluble, initially forming yellowish/pale orange solutions, due to the chromium(VI) charge-transfer transition, but with some reduction to chromium(III).

Acetamide is an excellent solvent for many inorganic salts [1] and thus can be one component of many varied low-melting eutectics, which potentially can have high concentrations of ions. Similar eutectics can be formed from inorganic salts with higher homologues of acetamide.

In the case of binary eutectics of acetamide and higher amides with alkali metal nitrates, these melts provide interesting new solvents for investigating ligand properties, and in particular for examining competition in coordination between ligands. Amides and nitrate are both oxygen ligands, as is water, but whereas nitrate is a much weaker ligand than water, to the extent that nitrate is always displaced from the coordination shell in aqueous solutions, in amide—nitrate melts the oxygens of nitrate and of amides are expected to be of more comparable ligand strength.

An investigation of the chemistry of two molten amide—alkali metal nitrate eutectics was therefore undertaken, and in particular of their behaviour with a series of first-row transition metal salts, for comparison with the information available on the behaviour of these salts with pure alkali metal nitrate melts, which was necessarily obtained at much higher temperatures and also with aqueous solutions.

While the eutectic compositions and temperatures of some acetamide—alkali metal nitrate melts have previously been published [2, 3], those between these salts and higher amides were not known, thus the par-

tial binary phase diagram of butyramide with sodium nitrate was first determined.

EXPERIMENTAL

Materials

Acetamide (Aldrich, 99 %) was recrystallized from methanol [1]. Butyramide (Fluka, 98 %) was recrystallized from hot ethanol giving white leaflets, melting point = 114–115 °C. Potassium and sodium nitrates (Analar, BDH) were dried at 180 °C for 24 h. Appropriate proportions of the two components of the eutectics were weighed out and melted at 100 °C with stirring. The eutectics were filtered under vacuum through a No. 4 porosity sintered glass disc in a thermostated oven.

Hydrated cobalt(II) chloride, nickel(II) chloride, and chromium(III) chloride (all Analar, from BDH, Koch-Light, and Aldrich, respectively) were dehydrated with thionyl chloride [4], w_i (found): 45.1 % Co, 55.0 % Cl; for CoCl_2 w_i (calc.): 45.4 % Co, 54.6 % Cl, w_i (found): 44.7 % Ni, 54.3 % Cl; for NiCl_2 w_i (calc.): 45.3 % Ni, 54.7 % Cl, w_i (found): 32.5 % Cr, 67.2 % Cl; for CrCl_3 w_i (calc.): 32.8 % Cr, 67.2 % Cl. Copper(II) sulfate pentahydrate (Analar, BDH) was heated at 200 °C under vacuum for 3.5 h, w_i (found): 39.5 % Cu, 59.8 % SO_4 ; for CuSO_4 w_i (calc.): 39.8 % Cu, 60.2 % SO_4 . Potassium chromate and potassium

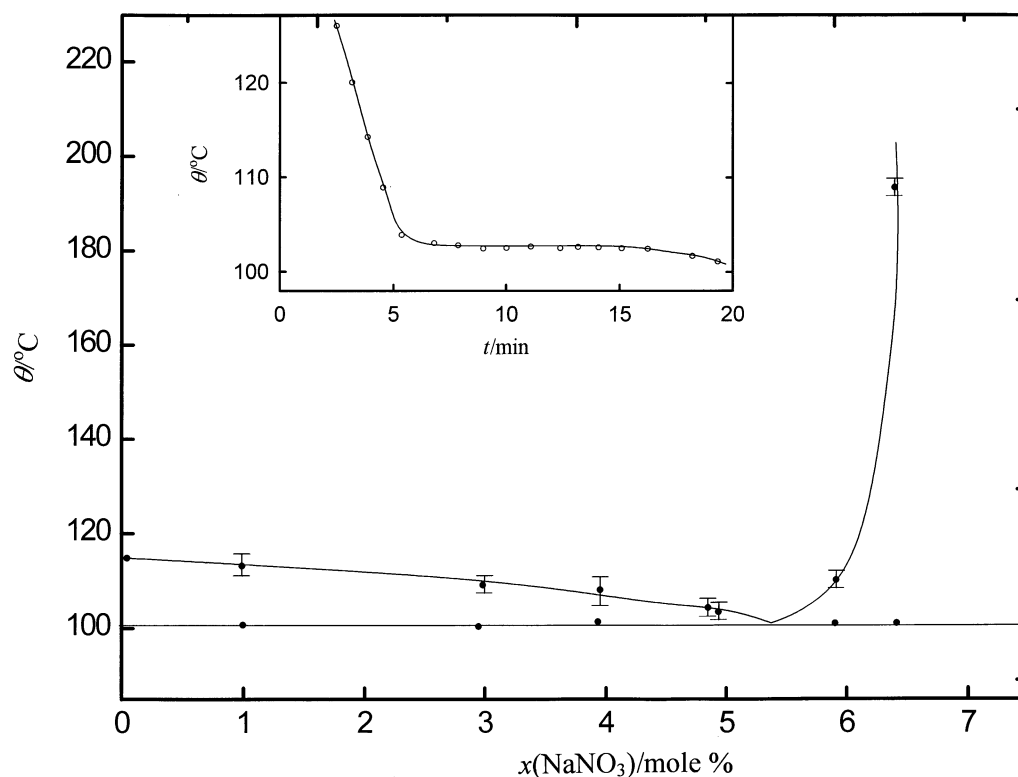


Fig. 1. Binary phase diagram and cooling curve (inset) for butyramide–sodium nitrate.

dichromate were dried at 120°C for 24 h. Iron(III) chloride (Analar, BDH) was used as received.

Methods

The binary phase diagram of butyramide with sodium nitrate near the eutectic composition was determined by visual observation of the beginning and ending of melting, using small samples in glass capillary tubes slowly heated in a Gallenkamp melting point apparatus. The samples were prepared under dry air in a glove box and the ends of the sample tubes sealed by fusion before measurement. 3–4 samples of each composition were measured and the average values and standard deviations plotted. The eutectic temperature was also determined on larger samples (≈ 30 g) by recording cooling curves under well insulated conditions, with constant stirring, and supercooling minimized by seeding with butyramide crystals. The melting point of the acetamide–potassium nitrate eutectic has been reported as 72°C [2] and 77.5°C [3], both investigators finding an eutectic composition of 6 mole % potassium nitrate. This was checked here by both the visual observation and cryoscopic methods and found to be $(76.5 \pm 1)^\circ\text{C}$.

Densities were measured by transferring 10 cm³ of melt from an oven thermostated at 90°C, or at 140°C, with a preheated pipette to a weighing bottle. A cor-

rection was made for the thermal expansion of the Pyrex pipette.

Reactions were carried out in Pyrex tubes under an air atmosphere, but closed with silica gel guard tubes, and heated in an electric furnace controlled with a RS CAL 9000 temperature controller and a step-down transformer.

Electronic absorption spectra were obtained with a Unicam SP-700 spectrophotometer, modified with reverse optics (from $\tilde{\nu} = 4000\text{--}13000\text{ cm}^{-1}$), using RF-heated 1 cm quartz cells.

RESULTS AND DISCUSSION

The partial phase diagram determined is shown in Fig. 1, together with the cooling curve for a large sample of the eutectic composition, as an inset. The eutectic composition and melting temperature was 94.5 mole % butyramide–5.5 mole % NaNO_3 , melting point = 102°C.

Density measurements on the eutectic compositions gave values of $(1.0617 \pm 0.004)\text{ g cm}^{-3}$ and $(0.9918 \pm 0.001)\text{ g cm}^{-3}$ at 90°C and 140°C, respectively for acetamide–potassium nitrate and $(0.9279 \pm 0.026)\text{ g cm}^{-3}$ at 140°C for butyramide–sodium nitrate.

Anhydrous cobalt(II) chloride was very soluble in both eutectics, giving violet solutions. The visible-

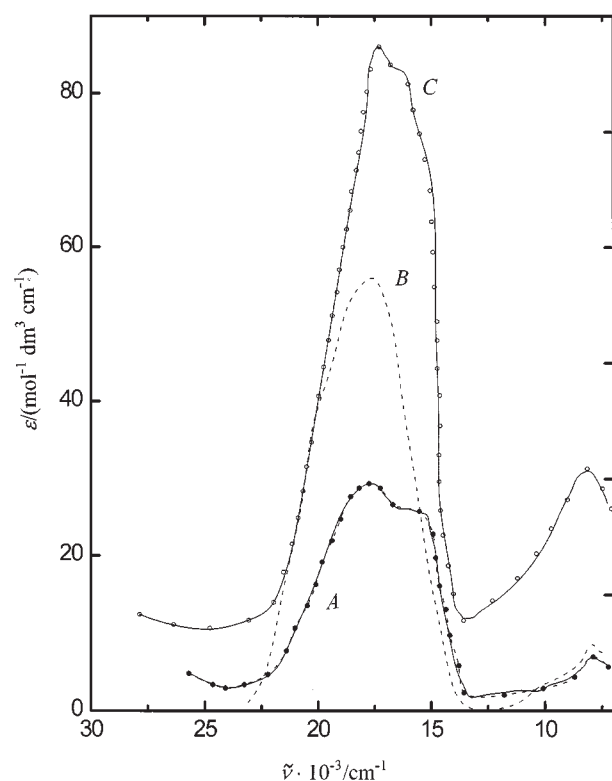


Fig. 2. Spectra of CoCl_2 ($0.019 \text{ mol dm}^{-3}$) in acetamide—KI eutectic at different temperatures, curve A – 90°C (\bullet), curve B – 140°C (— —), and of butyramide—sodium nitrate at 140°C , curve C (\circ).

ultraviolet spectrum of the acetamide solution (Fig. 2, curve A) showed two bands, with some splitting of the visible band, indicating octahedral coordination in each case. Calculations using Jorgensen's Rule of Average Environment suggest coordination by 4 acetamides and 2 chlorides in the acetamide—potassium nitrate eutectic. As the temperature of these solutions was gradually increased to 140°C , the absorption bands moved a little towards the red, while the band intensities increased considerably (Fig. 2, curve B). This change was in accord with a shift to a lower symmetry environment, possibly some nitrates replacing acetamide or perhaps a shift from octahedral to a more tetrahedral coordination, as has frequently been found for cobalt(II) salts in many melts with increased temperature [5, 6]. The larger red shifts and even higher extinction coefficients found with butyramide—sodium nitrate (Fig. 2, curve C) indicated an even lower symmetry coordination, possibly due at least in part to the steric strain imposed by the larger butyramide molecules.

Anhydrous chromium(III) chloride dissolved only slowly in either melt, forming pale green solutions after more than 15 h for $10^{-3} \text{ mol dm}^{-3}$ concentrations at 90°C for acetamide—potassium nitrate and 8 h at 140°C for butyramide—sodium nitrate. The spectrum

for the acetamide eutectic (Fig. 3, curve A) showed two absorption maxima, consistent with octahedral coordination. The band energies were close to those expected for 6 acetamide or 6 nitrate ligands, but the much higher extinction coefficients than those found in pure acetamide [6] suggested mixed, *i.e.* lower symmetry, complexes, though probably with little or no coordination by chloride ligands. The coordination in the butyramide—sodium nitrate eutectic, spectrum in Fig. 3, curve C, was probably rather similar.

Anhydrous nickel(II) chloride was soluble in both eutectics, giving yellow solutions. The spectra (Fig. 4, curves A and B) showed three absorption maxima indicating octahedral coordination of the nickel(II) cations. The bands are shifted to slightly lower energies than those found in pure molten acetamide [6, 7] suggesting some coordination by chloride, or less likely by nitrate. Jorgensen's Rule suggested 4 acetamides and 2 chlorides could give the observed bands and the less symmetrical complexes resulting would explain the higher extinction coefficients found. There are no data on the band positions of butyramide complexes, but if its ligand field is similar to that of acetamide, then the calculated coordination would also be 4 amide and 2 chloride ligands.

Anhydrous copper(II) sulfate dissolved readily in the acetamide—potassium nitrate eutectic to give blue-green solutions. Spectroscopy showed two bands at $\tilde{\nu} = 20700 \text{ cm}^{-1}$ ($\epsilon = 43 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and $\tilde{\nu} = 14000 \text{ cm}^{-1}$ ($\epsilon = 73 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at $\tilde{\nu} = 11000 \text{ cm}^{-1}$. The copper cations appear to be in an octahedral coordination, though with a higher extinction coefficient, and thus probably a lower symmetry (perhaps D_{4h}), than those found for the regular octahedral complexes in aqueous solution (band maxima at $\tilde{\nu} = 12600 \text{ cm}^{-1}$, $\epsilon = 12 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) [8], or in anhydrous alkali metal nitrate melts ($\tilde{\nu} = 13000 \text{ cm}^{-1}$, $\epsilon = 14 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) [9], because in this binary eutectic coordination is by both acetamide and nitrate. The higher energy band is anomalous for a D_{4h} complex and may be due to small amounts of a square pyramidal (C_{4v}) complex.

Iron(III) chloride was very soluble in the acetamide—potassium nitrate eutectic at 90°C giving initially a pale yellow solution which darkened rapidly to a strong brown colour within 15 min. The pale yellow solution gave one absorption band at $\tilde{\nu} = 16900 \text{ cm}^{-1}$ ($\epsilon = 35 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) close to an absorption edge at $\tilde{\nu} = 21000 \text{ cm}^{-1}$, while the dark brown solution showed only the absorption edge. The pale yellow solution may be due to a tetrahedral complex perhaps containing some chloride (FeCl_4^- in $\text{LiNO}_3\text{—KNO}_3$ eutectic at 160°C , band at $\tilde{\nu} = 16000 \text{ cm}^{-1}$, $\epsilon = 32 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) which was replaced over 15 min by more stable simple complexes containing acetamide and/or nitrate, or perhaps by more polymerized solvolyzed iron species.

Oxidation-reduction reactions were observed with

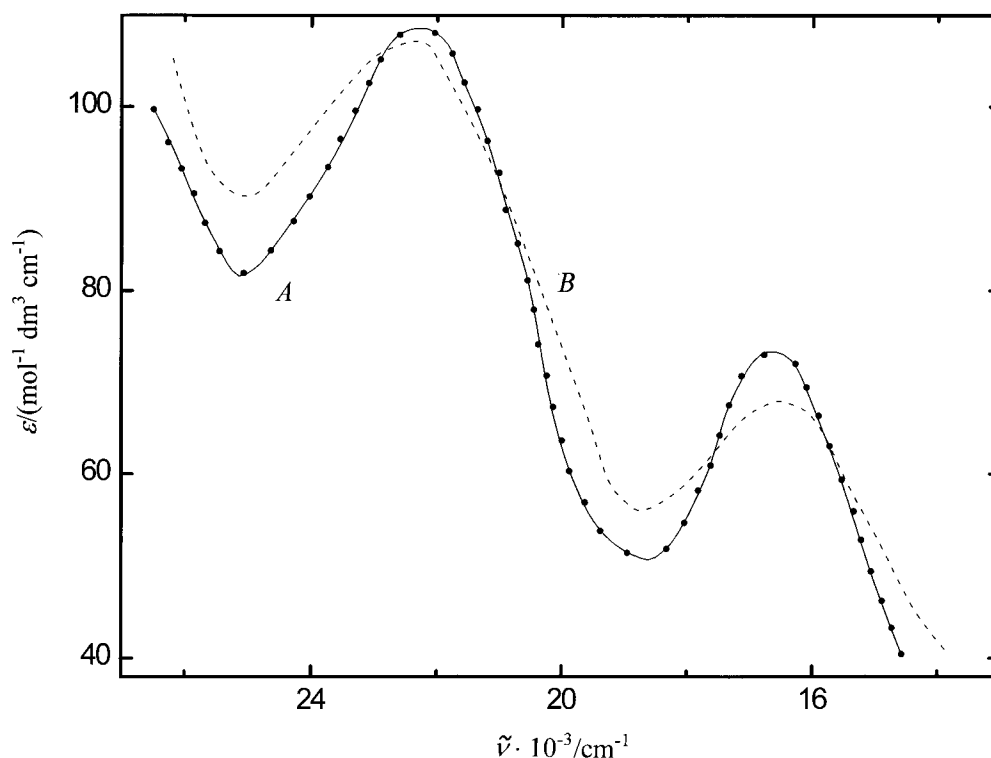


Fig. 3. Spectra of CrCl_3 , curve A – $c = 0.006 \text{ mol dm}^{-3}$ in acetamide–potassium nitrate at 90°C (●), curve B – $c = 0.003 \text{ mol dm}^{-3}$ in butyramide–sodium nitrate at 140°C (---).

chromium(VI) compounds in the acetamide–potassium nitrate eutectic. Potassium chromate was only slightly soluble ($c \approx 10^{-3} \text{ mol dm}^{-3}$ after 5 h at 90°C) giving clear faintly yellow solutions. Spectroscopy showed one absorption band with an absorption maximum at $\tilde{\nu} = 26600 \text{ cm}^{-1}$ ($\varepsilon = 1.430 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at $\tilde{\nu} = 23000 \text{ cm}^{-1}$. The main band is undoubtedly due to the usual charge-transfer transition ($e \leftarrow t_1$). However, the lower extinction coefficient than found for aqueous solutions [10] and for anhydrous nitrate melt solutions [11, 12] may well be due to some reduction of chromium(VI) by acetamide, as has been found in pure acetamide [6] and in acetamide–calcium nitrate tetrahydrate [9]. The shoulder could then be attributed to the first $d-d$ transition of chromium(III) with some borrowed intensity from the nearby charge-transfer band, the characteristic low-energy band at $\tilde{\nu} = 16000 \text{ cm}^{-1}$ not being observed because of its low intensity, the low concentration of chromium(III), and intensity borrowing not being possible for such a distant absorption.

Potassium dichromate dissolved only slowly in either eutectic, but eventually gave clear orange solutions with two absorption bands at $\tilde{\nu} = 26400 \text{ cm}^{-1}$ ($\varepsilon = 3795 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at $\tilde{\nu} = 22500 \text{ cm}^{-1}$ and at $\tilde{\nu} = 27000 \text{ cm}^{-1}$ ($\varepsilon = 1050 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at $\tilde{\nu} = 23200 \text{ cm}^{-1}$ for acetamide–potassium nitrate and butyramide–sodium nitrate, respectively. Once again the main ab-

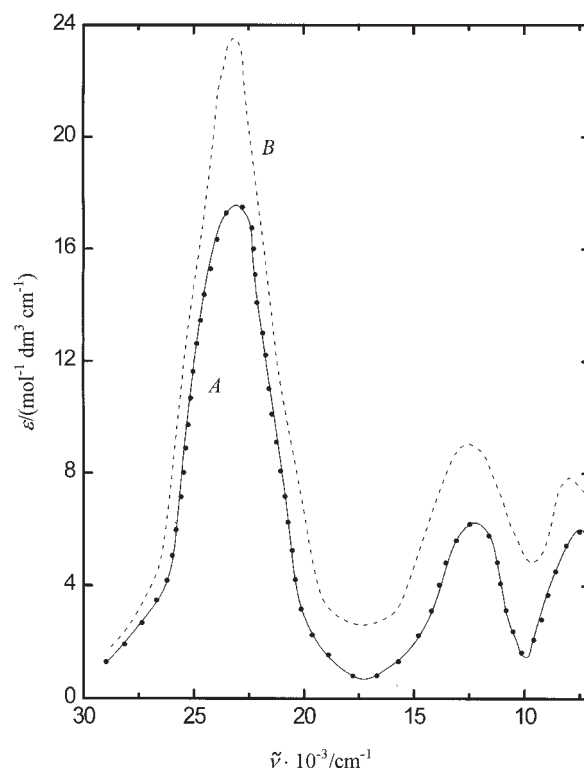


Fig. 4. Spectra of NiCl_2 , curve A – $c = 0.046 \text{ mol dm}^{-3}$ in acetamide–potassium nitrate at 90°C (●), curve B – $c = 0.012 \text{ mol dm}^{-3}$ in butyramide–sodium nitrate at 140°C (---).

sorption band corresponded to that of the well-known charge-transfer transition, as has been found in many molten salts [11], while the shoulder again probably indicated some reduction to chromium(III), since pure acetamide has been reported to reduce dichromate to chromium(III) [13], with perhaps more reduction in the butyramide eutectic.

CONCLUSION

Because of the similar ligand fields exercised by acetamide and nitrate, also probably by butyramide for which no other evidence exists, the absorption band maxima are relatively poor indicators of the coordination geometry of the transition metal cations studied. However, the generally higher extinction coefficients measured here, when compared with melts containing only one ligand, strongly suggested mixed coordination in every case, most usually with amide and nitrate as well as sometimes with chloride.

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