Binary Molten Acetamide—Alkali Metal Iodide Eutectics – the Solution Chemistry of Seven First Row Transition Metal Compounds*

[a]D. H. KERRIDGE and [b]E. I. EWEKA

[a]Department of Engineering Materials, University of Southampton,
Highfield, Southampton, SO17 1BJ United Kingdom

[b]Department of Chemistry, University of Southampton,
Highfield, Southampton, SO17 1BJ United Kingdom

Partial binary phase diagrams with eutectic compositions and temperatures were determined for acetamide—potassium iodide, acetamide—sodium iodide, and acetamide—lithium iodide; together with the densities of these eutectics from their melting points to 100 °C.

The reactions of seven first row transition metal compounds were examined in acetamide—potassium iodide eutectic and one in acetamide—sodium iodide eutectic. Iodide was found to coordinate to the highly soluble cobalt(II) salts at 60 °C, giving electronic spectra typical of octahedral coordination with probably three oxygen-bonded acetamido ligands and three iodo ligands. With increasing temperature, up to 140 °C, the spectrum increasingly became that of four coordinate tetrahedral cobalt(II), probably with one acetamido and three iodo ligands. Cobalt(II) sulfate gave very similar spectra.

Chromium(III) chloride and nickel(II) chloride showed limited solubility and were principally coordinated by acetamide. Four other compounds were reduced, anhydrous copper(II) sulfate and iron(III) chloride forming brown triiodide (I_3^-) solutions containing copper(I) iodide precipitate and coordinated iron(II) cations, respectively. Potassium chromate and potassium dichromate were very slightly soluble, initially forming yellowish/pale orange solutions, which contained more chromium(III) as temperature and/or the time increased.

Acetamide is an excellent solvent for many inorganic salts and thus can be one component of many varied low melting eutectics, which potentially can have high ionic concentrations.

In the case of binary eutectics of acetamide with iodides, these melts may provide useful alternative routes for investigating ligand properties, since pure molten alkali metal iodides are thermally unstable and are prone to chemical oxidation by air as well as by other oxidants, but so far the acetamide—iodide melts have been little studied experimentally.

An investigation of the chemistry of these molten acetamide—alkali metal iodide eutectics, and in particular of their behaviour with a series of first row transition metal salts, was therefore undertaken for comparison with the limited amount of information available on the behaviour of these salts with pure alkali metal iodide melts, which was necessarily obtained at much higher temperatures.

Since the acetamide—iodide melts had not previously been studied and the eutectic compositions and temperatures were not known, the partial binary phase diagrams were determined for acetamide with the iodides of the three lightest alkali metals.

EXPERIMENTAL

Acetamide was recrystallized from methanol [1]. Potassium and sodium iodides (Analar, BDH) were dried at 180 °C for 8 h. Lithium iodide (Fluka, purum) was used as received. Appropriate proportions of the two components of the eutectics were weighed out and melted at 100 °C with stirring.

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 [2] (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). Hydrated cobalt(II) sulfate (Aldrich) was heated at
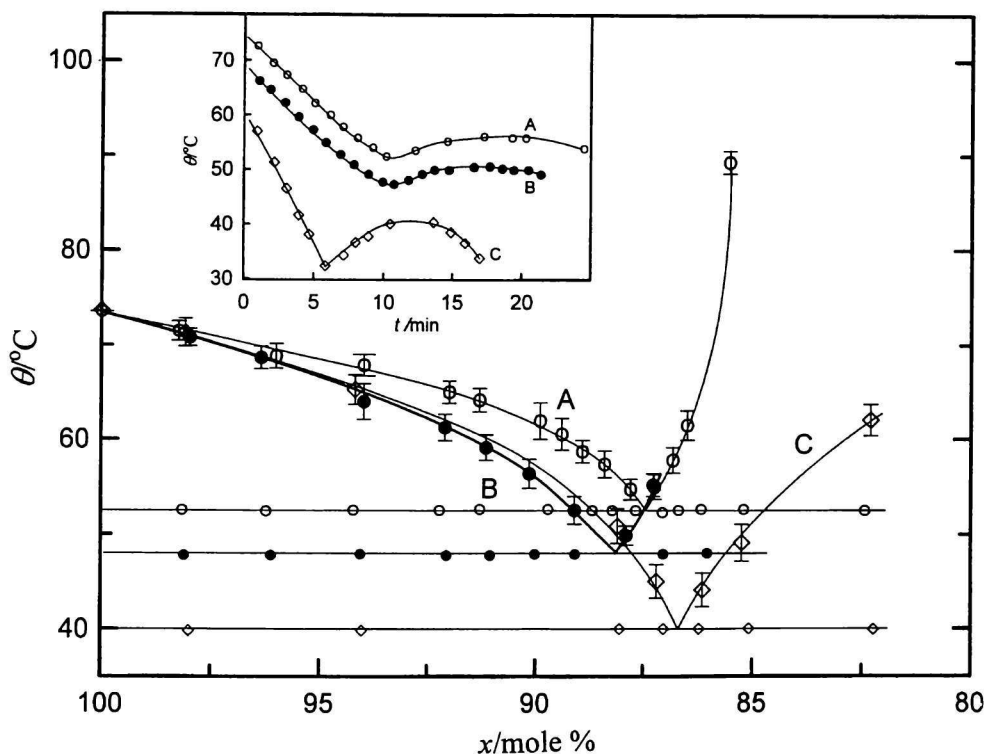
Fig. 1. Binary phase diagrams and cooling curves (inset) for acetamide—KI (○), acetamide—NaI (●), and acetamide—LiI (◊).

400 °C for 2.5 h (w_i(found): 37.9 % Co, 61.6 % SO_4; for $CoSO_4$ w_i(calc.): 38.0 % Co, 62.0 % SO_4), while 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 dichromate were dried at 120 °C for 24 h. Iron(III) chloride (Analar, BDH) was used as received.

Portions of the binary phase diagrams near the eutectic compositions and temperatures were 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 closed by fusion before measurement. 3—4 samples of each composition were measured and the average values and standard deviations plotted. The eutectic temperatures were checked on larger samples ($\gg$ 30 g) by recording cooling curves under well insulated conditions, with constant stirring, and supercooling minimized by seeding with acetamide crystals.

Densities were measured with a thermostated PAAR cell, model DMA55, calibrated with triply distilled water and aqueous lithium bromide solution (w_r = 0.35).

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 ($\tilde{\nu} = 4000$—13000 cm^{-1}) using RF-heated 1 cm quartz cells.

RESULTS AND DISCUSSION

The partial phase diagrams determined are shown in Fig. 1, together with the cooling curves for large samples of the eutectic composition, as an inset. The eutectic compositions and melting temperatures were 87 mole % acetamide—13 mole % KI, m.p. = 55 °C; 88 mole % acetamide—12 mole % NaI, m.p. = 50 °C; and 86.5 mole % acetamide—13.5 mole % LiI, m.p. = 41 °C.

Density (ρ) measurements on the eutectic compositions gave linear functions with temperature, following the equation

$$\rho = A - B\theta \qquad (1)$$

where A and B are constants and θ is the temperature in °C. The constants were found to be A (g cm^{-3}) = 1.425157, 1.388563, and 1.380602; with B (g cm^{-3} °C^{-1}) = 0.00119, 0.000107, and 0.000868, respectively for acetamide—KI, acetamide—NaI, and acetamide—LiI eutectics. These linear equations rep-

resented the densities to an accuracy of $\pm 9.5 \times 10^{-4}$ g cm^{-3}

On melting the eutectics were a faint yellow colour, due to very slight oxidation to the highly absorbing triiodide anion. Tiny additions of solid sodium thiosulfate produced colourless solutions. However, the yellow colour returned on heating to higher temperatures, or for longer times; and continued to do so, though at lower rates when a nitrogen atmosphere was substituted for air. The melt stability (m. s.) was found to decrease in the order m. s. (acetamide—KI) > m. s. (acetamide—NaI) ≫ m. s. (acetamide—LiI). Thus most of the chemical investigations were conducted using the acetamide—potassium iodide eutectic, with only limited measurements in acetamide—sodium iodide eutectic.

Anhydrous cobalt(II) chloride was very soluble in the acetamide—potassium iodide eutectic, dissolving almost instantly to violet solutions, up to 0.1 mol dm^{-3} at 60 °C. The visible-ultraviolet spectra (Fig. 2, curve A) indicated octahedral coordination. The band positions, their broad nature and a shoulder ($\tilde{\nu} \approx$ 14500 cm^{-1}), suggested the presence of different numbers of halide ligands. Using Jorgensen's Rule of Average Environment and the approximation of 9/4 the ligand field for the tetrahedral complex ([CoI$_4$]$^{2-}$) [3] because values for an octahedral complex are not available, the lower energy band at $\tilde{\nu} = 7200$ cm^{-1} is best represented by an average coordination of 3 acetamido, 2 chloro, and one iodo ligands.

As the temperature of the solutions was gradually increased to 140 °C, the colour became bluer and the absorption bands moved progressively towards lower wavenumbers while the band intensities steadily increased (Fig. 2, curves B to F), all these features being typical of tetrahedral cobalt(II). This change from octahedral to tetrahedral coordination with increasing temperature, has frequently been found with other solvents containing cobalt(II) salts. The double maximum in curve E, Fig. 2, represents comparable absorption of octahedral and tetrahedral species. This preference for more tetrahedral coordination at higher temperatures was explained on the basis of increased ligand field stabilization energy in the classic paper by *Gruen et al.* [4], who first reported the phenomena for molten chloride solutions.

Cobalt(II) sulfate was only slightly soluble in the acetamide—potassium iodide eutectic at 60 °C, giving a pale pink/violet solution. Its spectrum was similar to that for the chloride solution, but with the higher energy band shifted some 700 cm^{-1} towards the blue, which suggests some coordination by sulfate in addition to iodide and acetamido ligands. The most likely coordination being either with bidentate sulfate, that is the complex [Coacet$_2$(OSO$_2$O)I$_2$]$^{2-}$, where "acet" represents acetamido, or with monodentate sulfate, *i.e.* [Coacet$_3$(OSO$_3$)I$_2$]$^{2-}$ As the temperature of these solutions was increased the absorption
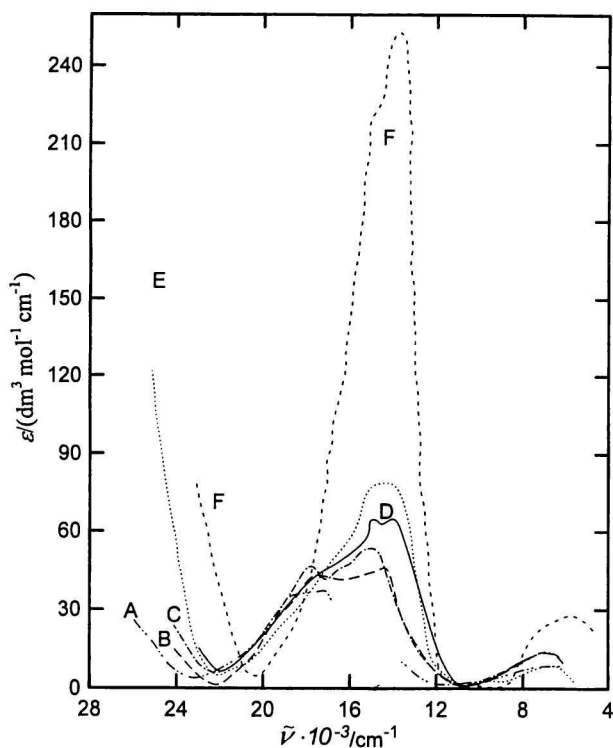

Fig. 2. Spectra of CoCl$_2$ ($c = 0.096$ mol dm^{-3}) in acetamide—KI eutectic at different temperatures. A 60 °C, B 70 °C, C 75 °C, D 85 °C, E 90 °C, F 140 °C.

bands again moved to higher intensities and to lower energies, the spectrum at 140 °C becoming closely similar to that of Fig. 2, curve F. Thus the sulfate ligand may well have been replaced at the higher temperature by iodo ligands (with the coordination perhaps being [CoacetI$_3$]$^-$), as the coordination changed to tetrahedral, because the difference in ligand field strength between sulfato and chloro ligands could not be seen in the higher temperature spectra.

Anhydrous chromium(III) chloride had only a low solubility in the acetamide—potassium iodide eutectic and the violet solid dissolved only slowly to a clear green solution (> 10 h for 0.0025 mol dm^{-3} at 70 °C). The spectrum (Fig. 3, curve A) showed two absorption maxima, which were similar, but for small red shifts, to those found for hexakis acetamidochromium(III) in molten acetamide [5] and in nitromethane [6], indicating probable octahedral coordination largely by six acetamide ligands, but perhaps with smaller proportions of a pentakis acetamido complex with one iodo or chloro ligand. This less symmetrical coordination could explain the high extinction coefficients found.

Anhydrous nickel(II) chloride was also of low solubility in both the eutectics, but dissolved slowly giving yellow solutions, after 90 min, with three absorption maxima (Fig. 3, curves B and C). The spectrum in the potassium iodide eutectic was very similar to that of nickel(II) chloride in pure molten acetamide [5—7] and is probably also due to the formation of
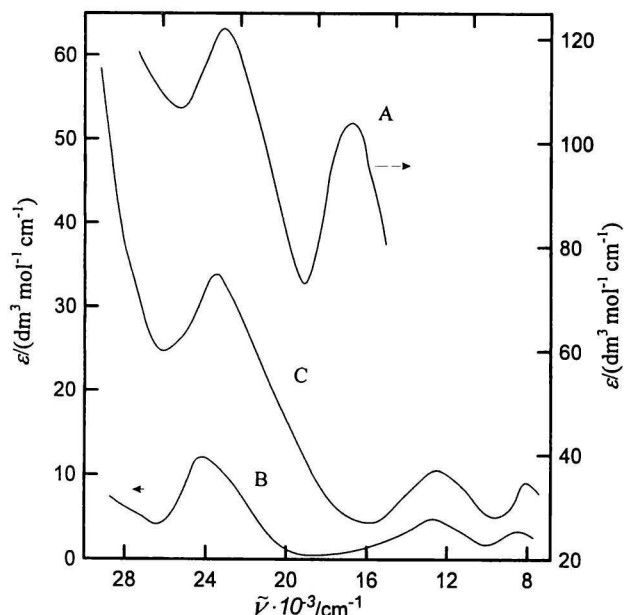
Fig. 3. Spectra of transition metal chlorides at 70 °C. A CrCl$_3$ ($c = 0.0025$ mol dm^{-3}) in acetamide—KI eutectic, B NiCl$_2$ ($c = 0.097$ mol dm^{-3}) in acetamide—NaI eutectic, C NiCl$_2$ ($c = 0.448$ mol dm^{-3}) in acetamide—KI eutectic.

the octahedral hexakis acetamido complex. However, in the acetamide—sodium iodide eutectic, the spectrum (curve C) showed that the ligand field strength was a little lower suggesting some coordination by iodide, or less likely in view of its low concentration by chloride, and the much higher extinction coefficient supported the suggestion of a less regular coordination. Using Jorgensen's Rule of Average Environment the observed ligand field is most likely to be due to 3 acetamido and 3 iodo, though if chloride is also coordinated 2 acetamido, 2 iodo, and 2 chloro ligands, or 2 acetamido, 3 iodo, and one chloro ligands give rather similar calculated ligand fields. In contrast nickel(II) in the lithium iodide—potassium iodide eutectic showed only tetrahedral coordination, by four iodides, though the temperature was 295 °C [8].

Anhydrous copper(II) sulfate dissolved in the acetamide—potassium iodide eutectic to give dark reddish-brown solutions and a whitish-brown precipitate. The solution had an absorption spectrum with only one, very strong, band at 28200 cm^{-1}. This intense band (optical density ≈ 1) was of the energy of the triiodide anion (e.g. $\tilde{\nu} = 28450$ cm^{-1} ($\varepsilon = 20400$ mol^{-1} dm^3 cm^{-1}) in LiNO$_3$—KNO$_3$ eutectic at 160 °C [9]) suggesting the oxidation-reduction reaction

$$2CuSO_4 + 5I^- \rightarrow 2CuI + I_3^- + 2SO_4^{2-} \qquad (2)$$
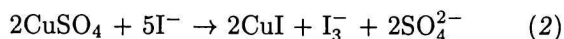
In support of this reaction, the whitish-brown precipitate, after washing and drying, gave the following X-ray diffraction lines ($d/10^{-10}$ m(I_r/%)) (3.503(100),

2.143(35), 1.827(21)), corresponding to the American Society for Testing Materials Index values for Marshite (CuI) (3.490(100), 2.139(55), 1.824(30)). This is a further illustration of the oxidizing power of copper(II) in nonaqueous solvents which has been found in many molten salt systems and was extensively investigated in molten chlorides [10, 11].

Iron(III) chloride also dissolved in the acetamide—potassium iodide eutectic at 70 °C giving initially a light brown solution which showed an absorption edge at $\tilde{\nu} = 30000$ cm^{-1} with no distinguishable maxima at lower frequencies. The solution darkened steadily over 1 h and then showed another very intense absorption maximum at $\tilde{\nu} = 27500$ cm^{-1}, which again suggested oxidation of iodide to triiodide as well as possibly some dissolved iodine, i.e.

$$2Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^- \qquad (3)$$
$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \qquad (4)$$
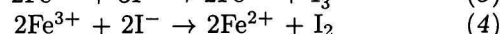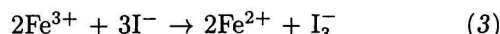
The light brown colour was restored when thiosulfate solution was added to the dark brown solution. However, the resulting solution was too dilute in iron ($c \approx 10^{-3}$ mol dm^{-3}) to give any absorption maxima attributable to iron(II) complexes. Assuming the original iron(III) had been entirely reduced by iodide, the extinction coefficient of the $\tilde{\nu} = 27500$ cm^{-1} band in the dark brown solution would be $\varepsilon \approx 8500$ mol^{-1} dm^3 cm^{-1}. Rather similar bands with optical densities of ≈ 2.5 have been reported for the triiodide anion at $\tilde{\nu} = 26400$ cm^{-1} in lithium iodide—potassium iodide eutectic and at $\tilde{\nu} = 28000$ cm^{-1} in aqueous potassium iodide [12].

Further oxidation-reduction reactions were observed with chromium(VI) compounds in the acetamide—potassium iodide eutectic. Potassium chromate was only very slightly soluble ($c \approx 4.6 \times 10^{-4}$ mol dm^{-3} after 15 h at 70 °C) giving a faintly yellow solution with an absorption maximum at $\tilde{\nu} = 27150$ cm^{-1} ($\varepsilon \approx 1900$ mol^{-1} dm^3 cm^{-1}) and a shoulder at $\tilde{\nu} = 27000$ cm^{-1} ($\varepsilon = 450$ mol^{-1} dm^3 cm^{-1}), similar to that found for chromate in many other molten salt solvents (e.g. LiNO$_3$—KNO$_3$ and LiCl—KCl [13]) and also to that of chromate in pure acetamide [5], evidently due to the same charge-transfer transition. However, the presence of the shoulder and the lower extinction coefficient suggest some reduction to chromium(III) as was found to occur over longer times in pure acetamide [5].

Potassium dichromate was a little more soluble at 70 °C ($c = 8.3 \times 10^{-3}$ mol dm^{-3}) forming a clear orange solution with a single absorption maximum at $\tilde{\nu} = 26800$ cm^{-1} ($\varepsilon \approx 860$ mol^{-1} dm^3 cm^{-1}) and again a shoulder at $\tilde{\nu} = 23000$ cm^{-1} ($\varepsilon = 300$ mol^{-1} dm^3 cm^{-1}). Once again the main absorption corresponded to that of the well-known charge-transfer transition, as has been found in many molten salts [13], while the shoulder again probably indi-

cated some reduction to chromium(III), since pure acetamide has been reported to reduce dichromate to chromium(III) [14], with a similar reduction in acetamide—calcium nitrate hexahydrate melts [15]. In acetamide—potassium iodide melt the concentration of chromium(III) was too low to give the characteristic d—d absorption at $\bar{\nu} \approx 16000$ cm^{-1}, which has a relatively low extinction coefficient.

In conclusion, it appears that these oxidation-reduction reactions, which may be attributed to the reducing power of iodide and of acetamide, are in accord with analogous studies in pure alkali metal iodide and pure acetamide. However, in the iodide—acetamide eutectics the coordinating power of iodide is only comparable with, and in some cases smaller than, that of acetamide, which frequently resulted in the formation of mixed ligand complexes.

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