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Fused Zinc Chloride.
Part 5: Spectroscopy of Nickel(II) and Cobalt(II) Ions in Melts containing Dissolved Anions

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The spectra of nickel(II) and cobalt(II) ions dissolved in zinc chloride–zinc sulphate melts at temperatures between 350°–610° C showed a tetrahedral–octahedral coordination equilibrium, the octahedral species being favored by increase in temperature and in zinc sulphate concentration. For nickel(II) ions in zinc chloride containing dissolved potassium iodate, perchlorate or cyanide no spectra were obtained, because of decomposition reactions, though in the former solution an absorption of dissolved iodine was observed. However, in zinc chloride–potassium cyanate melts which had been strongly heated, nickel(II) ions gave spectra attributed to an equilibrium between distorted tetrahedral and octahedral sites.

Introduction

In recent years, much valuable structural information on pure fused zinc chloride and on zinc chloride melts containing various solutes has been derived from studies of the electronic spectra of dissolved Ni(II) and Co(II) "probe" ions. For example, the spectra of Ni(II) in zinc chloride–alkali metal chloride melts have been interpreted in terms of one or more tetrahedral–octahedral coordination equilibria of the two species and continuous distortion types, the species present being dependent on melt composition and temperature.[1,2] For Co(II) in zinc chloride–aluminium chloride melts, the tetrahedral sites were progressively converted to octahedral sites as the zinc chloride mole fraction fell from 61.5 to 31.5%, while at a given composition, increasing temperature favored the tetrahedral sites.[3]

Such studies are here extended to chloride–sulphate melts, to determine not only the extent to which the zinc chloride structure was degraded by added sulphate, but also the ability of sulphate to displace chloride as coordinating species. The melt solution selected was zinc chloride–zinc sulphate, for which the liquidus on the zinc chloride side of the phase diagram is known;[4,5] the absence of alkali metal cations avoided any outer shell cation effect on the inner shell coordination geometry.[6] Spectroscopic information on this melt was not available earlier, although the Co(II) ion had been studied in KCl–$ZnCl_2$–$ZnSO_4$ and $ZnCl_2$–K_2SO_4 glasses.[7]

In addition the spectra of Ni(II) in zinc chloride melt solutions containing certain other solutes which were themselves potential ligands were investigated. The choice of systems was limited, because zinc chloride had been shown to react with most common anions at or below its melting point,[8,9,10] but limited studies were made with $ZnCl_2$–KIO_3, $ZnCl_2$–$KClO_4$ and $ZnCl_2$–KCN melts, and also $ZnCl_2$–KOCN melts after gas evolution.

Experimental Section

Materials

B.D.H. zinc chloride (sticks) was purified, dehydrated and analysed as previously described.[8] The preparation of anhydrous zinc sulphate, nickel chloride and cobalt chloride has also been described.[5] Analar KIO_3 and Reagent Grade $KClO_4$ were dried at 110° C and Reagent Grade KCN and KOCN at 200° C.

The Spectrometer

Spectra of the melt solutions were obtained on a Unicam SP 700 modified for use at temperatures up to 700° C. Silica cells of 1 mm pathlength were used unless otherwise stated, either evacuated or containing nitrogen under reduced pressure.

Procedure

As considerable heating was needed to prepare solutions of zinc sulphate in zinc chloride,[5] and very prolonged heating to dissolve even very small Ni(II) molarities in these melts, it proved essential to prepare the solutions in pyrex tubes under nitrogen rather than directly in the silica cells. The density of zinc chloride at temperatures in the range 350°–610° C were calculated from the expression given by Janz,[11] and used without modification for the dilute zinc sulphate solutions. For the solutions containing 15.2% zinc sulphate (13.1 molal), values of the melt density were obtained by interpolation between the densities of the pure components.

The curves were resolved into Gaussian components using a Dupont Instrument Co. Type 310 Curve Resolver. Corrosion of the optical cells became serious above 550° C, probably because of the presence of sulphate ion, resulting in displacements of the base line. Corrections were made for this, but it is considered that extinction coefficients are precise only to within ± 10%, and were thus quantitatively both less accurate and self-consistent than those obtained with the zinc chloride–alkali metal chloride systems.[1,2]

Results and Discussion

Nickel(II) Chloride in Zinc Chloride–Zinc Sulphate Melts

The results obtained are shown in Figure 1.

The very strong similarities in peak positions and relative peak intensities between these spectra and those of Ni(II) in $ZnCl_2$–KCl[1] and $ZnCl_2$–CsCl[2] melts indicated that the added zinc sulphate, like small additions of chloride ion, is able to break down the zinc chloride polymeric structure, increasing the ratio of octahedral to tetrahedral sites. The resemblance did not however extend quantitatively to the extinction coefficients, which were 20–25% lower in the dilute zinc sulphate solution. It is considered that these values were the results of zinc sulphate being able to produce more regular octahedral centres than the so-called O_N octahedral sites established in the $ZnCl_2$–CsCl melts.[2]

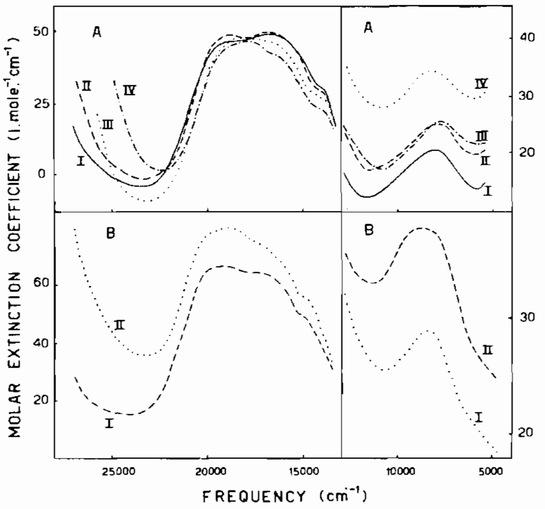

Figure 1. Absorption spectra of nickel(II) ions in zinc chloride–zinc sulphate melts. A: 96.5 mol % $ZnCl_2$–3.5 mol % $ZnSO_4$, *i.e.* 2.7 m $ZnSO_4$ with 0.012 m $NiCl_2$; Curve I 350°, II 420°, III 510°, IV 610° C. B: 84.8 mol % $ZnCl_2$–15.2 mol % $ZnSO_4$, *i.e.* 13.1 m $ZnSO_4$ with 0.013 m $NiCl_2$; Curve I 410°, II 500° C.

TABLE I.

Temp.	Octahedral absorption		Tetrahedral absorption	
°C	Wavenumber	E_{max}	Wavenumber	E_{max}
350	19,900	32	16,400	57
420	19,800	33	16,500	56
510	19,400	34	16,300	51
610	19,000	32	16,400	37

Increasing the temperature of the dilute zinc sulphate solution (3.5 mole %, 2.7 m) resulted in a fall in the extinction coefficient associated with tetrahedral absorption while that due to octahedral absorption remained almost constant (Table I), suggesting that the number of tetrahedral sites decreased with temperature while the regularity of the octahedral sites formed increased. However, a breakdown in the postulated simple two-centre behaviour of nickel(II)[2] could also account for these effects.

The spectroscopic results for the concentrated zinc sulphate melt were less conclusive, as satisfactory measurements were made only at the two intermediate temperatures (at 350° C, a homogeneous solution was not obtainable, while at 600° C etching was very rapid). In comparison with the dilute zinc sulphate solution the absorption maxima showed slight blue shifts (*ca.* 600 cm^{-1}), the ratio of octahedral sites to tetrahedral sites at a given temperature being larger and again increasing with increasing temperature.

The actual nature of the octahedral absorption species was not deduced conclusively, but it is considered possible that the absorbing species may be $NiCl_4(SO_4)_2^{6-}$ with unidentate sulphate.

Cobalt(II) Chloride in Zinc Chloride–Zinc Sulphate Melts

The results obtained are shown in Figure 2.

The spectra in both solutions showed a band with the three maxima characteristic of the $CoCl_4^{2-}$ entity. While the positions of the maxima were very close to those of Co(II) in the LiCl–KCl eutectic,[6] their extinction coefficients were very much lower (*e.g.* 225 l mol^{-1} cm^{-1} at 410° C for 15,000 cm^{-1} (Figure 2A) instead of 360 l mol^{-1} cm^{-1} at 400° C in LiCl–KCl, quoting unresolved band maxima), and also decreased with increasing temperature and with an increase in zinc sulphate concentration. The very slight changes in half-width of the absorption band with temperature

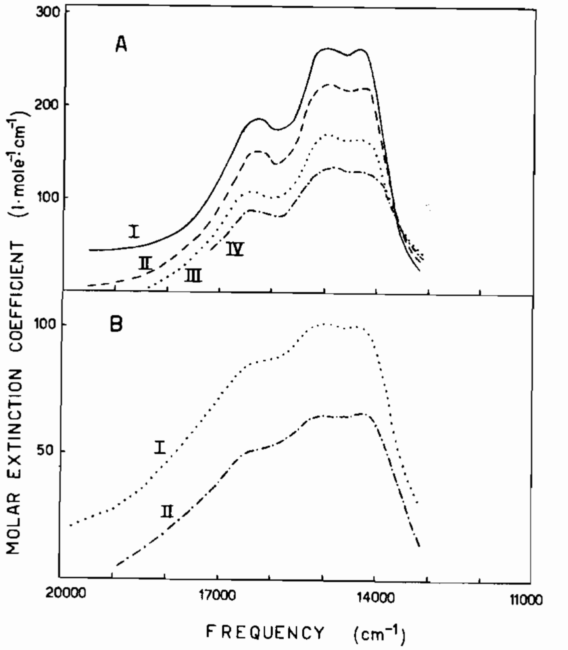

Figure 2. Absorption spectra of cobalt(II) ions in zinc chloride–zinc sulphate melts. A: 97.5 mol % $ZnCl_2$–2.5 mol % $ZnSO_4$, *i.e.* 1.9 m $ZnSO_4$ with 0.0027 m $CoCl_2$; Curve I 350°, II 410°, III 505°, IV 600° C. B: 84.8 mol % $ZnCl_2$–15.2 mol % $ZnSO_4$, *i.e.* 13.1 m $ZnSO_4$ with 0.0081 m $CoCl_2$; Curve I 500°, II 600° C.

were analogous to those observed for Co(II) ions in $ZnCl_2$–$AlCl_3$ melts but differed from those in LiCl–KCl melts, where the half-width was found to increase steadily with temperature.[6] In the $ZnCl_2$–$AlCl_3$ melt the spectroscopic changes were attributed to progressive replacement of tetrahedral by octahedral coordination, absorbing in the same spectra region but at lower intensities.[3] Results for Co(II) dissolved in various sulphate–chloride melts which had been frozen to glasses also gave octahedral absorptions at room temperature *e.g.* that at 17,800 cm^{-1} (ε_{max} = 20 l mol^{-1} cm^{-1}) observed in a 6:1 zinc chloride–potassium sulphate glass was attributed to a $[CoCl_4(SO_4)_2]^{6-}$ species with unidentate sulphate.[7]

These results from other melt systems suggest the cobalt(II) spectra in the zinc chloride–zinc sulphate melts are also due to the replacement of chloride ligands by sulphate, probably with a change from tetrahedral to octahedral coordination. The most likely supposition being the formation of a distinct octahedral species, possibly similar to that postulated in the zinc chloride–potassium sulphate glasses.[7] The decrease in the extinction coefficient with both temperature and zinc sulphate concentration would then indicate an increasing octahedral–tetrahedral ratio. The alternative explanations that the coordination of the Cobalt(II) varies continuously, or that the complex distorts continuously, with temperature and sulphate concentration seems less attractive in view of the low values of the extinction coefficients.

Nickel(II) Chloride in a Zinc Chloride–Potassium Iodate Melt

This melt was prepared by carefully remelting a quenched solution of nickel(II) chloride in zinc chloride ground with a small amount of potassium iodate. The melt became brown on fusion; its spectrum, run in sections because of the slow evolution of gas bubbles, showed an edge descending from 27,000–15,000 cm^{-1}, with a shoulder at 20,000 cm^{-1}. This was attributed to dissolved iodine, analogous to the absorption at 21,000 cm^{-1} of an aqueous solution of iodine rather than the 28,000 cm^{-1} absorption obtained in the presence of potassium iodide (in fact iodine has been found to be produced in the zinc chloride–potassium iodate reaction while the iodide ion was not[9]).

Nickel(II) Chloride in a Zinc Chloride–Potassium Perchlorate Melt

No spectroscopic results were obtained, as the system evolved gas rapidly on fusion.

Nickel(II) Chloride in a Zinc Chloride–Potassium Cyanide Melt

While it is possible to produce a colourless, almost completely clear zinc chloride–potassium cyanide melt,[9] it was observed that addition of nickel(II) chloride resulted in the immediate deposit of insoluble black particles, which analysed to contain 57.8% nickel, and were partly insoluble in dilute hydrochloric acid. This reaction seemed analogous to the thermal decomposition reported for nickel(II) cyanide: when heated in a closed container above 200° C, nitrogen and cyanogen were evolved leaving a residue of carbon-containing nickel.[12] Zinc chloride, unlike the alkali metal chlorides,[13, 14] is apparently unable to stabilise nickel(II) cyanide or cyano-nickel complexes.

Nickel(II) Chloride in a Zinc Chloride–Potassium Cyanate Melt after Gas Evolution

Addition of potassium cyanate to zinc chloride melts followed by strong heating in nitrogen gave a clear, almost colourless solution which dissolved nickel(II) chloride to produce clear blue solutions. Solutions, initially 0.2 m in potassium cyanate, could be heated to 340° C without decomposition and without insoluble black particles being formed. But more concentrated solutions (initially 1.5 m), decomposed with evolution of gas bubbles and formation of a black precipitate at rather lower temperatures. A semiquantitative spectrum of the 0.2 m solution run at 285° C in non-optical quartz cells (*ca.* 1 cm square and therefore giving spectra only approximately corrected for melt background) was resolved into absorptions of roughly equal intensities at 19,500, 15,800 and 13,700 cm^{-1} and a very broad absorption at 8,500 cm^{-1}.

These results, while incomplete, contrasted strongly with the spectroscopic results in zinc chloride–alkali metal chloride and zinc chloride–zinc sulphate melts described earlier. However, a two centred equilibrium between highly distorted octahedral sites (absorption at 19,500 cm^{-1}) and less distorted tetrahedral sites (absorption at 15,800 and 13,700 cm^{-1}), similar to the T_N sites in zinc chloride–caesium chloride at 350° C[2], would account for the experimental findings and is tentatively postulated.

Full explanations of the powerful stabilising effect on the nickel(II) ion and the drastically different spectrum are not at present available although the melt after gas evolution contained dissolved oxide in addition to cyanide ion[9] and possibly also small amounts of other reaction products which may have acted as stabilising ligands.

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References

1 C.A. Angell and D.M. Gruen, *J. Phys. Chem., 70,* 1601 (1966).

2 W.E. Smith, J. Brynestad and G.P. Smith, *J. Chem. Phys., 52,* 3890 (1970).

3 C.A. Angell and D.M. Gruen, *J. Inorg. Nucl. Chem., 29,* 2243 (1967).

4 N.N. Evseeva and A.G. Bergman, *Izv. Sov. Fiz. Khim. Akad., 21,* 208 (1952).

5 D.H. Kerridge and I.A. Sturton, Part 2 of this series, *Inorg. Chim. Acta, 8,* 27 (1974).

6 D.M. Gruen and R.L. McBeth, *Pure Appl. Chem., 6,* 23 (1963).

7 M. Ingram and J.A. Duffy, *J. Chem. Soc. (A),* 2575 (1968).

8 D.H. Kerridge and I.A. Sturton, Part 1, *Inorg. Chim. Acta, 7,* 701 (1973).

9 D.H. Kerridge and I.A. Sturton, Part 3, *Inorg. Chim. Acta, 8,* 31 (1974).

10 D.H. Kerridge and I.A. Sturton, Part 4, *Inorg. Chim. Acta, 8,* 37 (1974).

11 G.J. Janz, *Molten Salts Handbook,* Academic Press, New York, N.Y., 1967, p. 40.

12 L. Cambi, A. Cagnasso and E. Tremolada, *Gazz. Chim. Ital., 64,* 758 (1934).

13 D. Inman, B. Jones and S.H. White, *J. Inorg. Nucl. Chem., 32,* 927 (1970).

14 S. Von Winbush, E. Griswold and J. Kleinberg, *J. Am. Chem. Soc., 83,* 3197 (1961).