

Some Effects obtained on "Diluting" Molten Salts with Dimethyl Sulphone

By T. R. GRIFFITHS

(Department of Inorganic and Structural Chemistry, The University, Leeds 2)

SINCE molten salts consist entirely of ions then, *ipso facto*, it is impossible to observe the effects of the ionic strength of the ions upon a reaction or an equilibrium within a melt. Various effects have

been achieved by employing, say, differing amounts of two salts containing a common anion or cation. The result has normally been that of altering the polarizing power of the melt and hence the species

formed or the position of the equilibrium set up.¹ The $d-d$ electronic absorption spectra of transition-metal ions are very sensitive to such changes and have consequently been much studied.^{2,3} Angell and Gruen⁴ have recently reported some interesting results using molten salt hydrates, such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as solvents and have drawn some analogies with results obtained in concentrated aqueous electrolytes and molten salts.

There are normally, however, marked differences in the types and the co-ordination of the complexes formed when these two media are employed as solvents for compounds of the transition metals. Molten salt hydrates do not appear to be satisfactory intermediates due to the very high co-ordinating power of water for small and/or highly charged ions. The possibility of finding a material that could be added to molten-salt solutions and which would not interact or co-ordinate strongly with the ions present, especially transition-metal ions, was therefore considered. Such a material would thus act as a diluent, like nitrogen, when studying rapid gaseous reactions, and would require the following characteristics: (a) it must not co-ordinate, or only very weakly, to the ions present in the melt; (b) it must be stable at reasonably high temperatures; (c) it must be transparent to ultraviolet, visible, and near-infrared radiation and, (d) it must be able to dissolve a wide variety of salts.

Dimethyl sulphone is the only material known at present that fulfills these criteria. Other sulphones are currently under investigation but do not seem so promising. This material, with m.p. 108° and b.p. 218° , is a very poor co-ordinator^{4,5} and is transparent, when purified, down to $190\text{ m}\mu$, and has two small overtone bands, in the near infrared region. It will dissolve, for example, large quantities of the lithium halides, calcium and magnesium chloride, quaternary ammonium and phosphonium halides, and reasonable amounts of sodium, potassium, and strontium chloride. Only very small amounts of many transition-metal compounds are soluble, but this demonstrates dimethyl sulphone's poor co-ordinating power to such materials. Greater concentrations of the latter may be obtained by adding them to dimethyl sulphone melts containing a halide, and consequently forming halogeno-complexes.

By this approach, the noted feature that the size of the cation within a melt influences the ease of formation of tetrahalogenonickelate(II) complexes, was studied.² The ease of formation of both NiCl_3^- and NiCl_4^{2-} with varying cation size is illustrated in the Figure. Using lithium chloride,

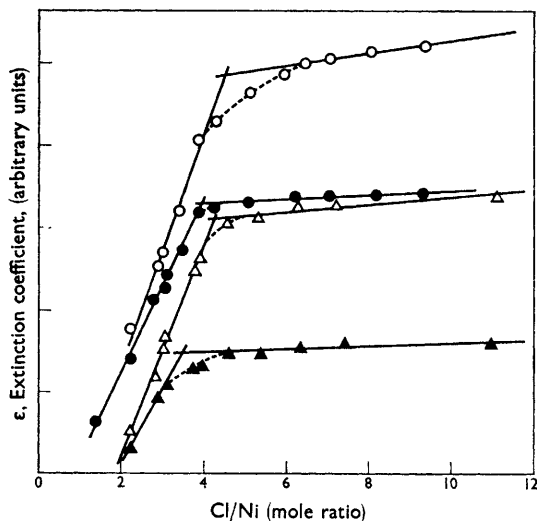


FIGURE. Mole ratio plots using a peak maximum of NiCl_4^{2-} ($650\text{ m}\mu$) for LiCl (\circ) and Hyamine 10X (\triangle), and a peak maximum of NiCl_3^- ($620\text{ m}\mu$), LiCl (\bullet) and Hyamine 10X (\blacktriangle).

the two species are first formed at Cl/Ni ratios of 4.0 and 4.6, respectively; but with the larger cation, Hyamine 10X (benzyltrimethyl-2-[2-(4-(1,3,3-tetramethylbutyl)-*m*-tolylloxy)ethoxy]ethylammonium chloride monohydrate), Cl/Ni ratios of only 3.6 and 4.35, respectively, are required. 90% conversion of all the nickel present into tetrahedral NiCl_4^{2-} occurred with all the chlorides studied at a Cl/Ni ratio of 5–10. Complete conversion occurred with lithium chloride at a ratio of around 40 and with Hyamine 10X at around 20.⁶

The provision of a Carey 14H Spectrophotometer by the S.R.C. is gratefully acknowledged.

(Received, August 25th, 1967; Com. 916.)

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