ELECTRODE POTENTIALS, ELECTRONIC SPECTRA AND OXIDATION STATE STABILITIES

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ABSTRACT

E.m.f. series and the electronic spectra of transition metal ions, particularly Co^{2+} and Ni^{2+}, permit one to draw conclusions concerning the structure of molten salt solvents and the oxidation state stabilities of metal compounds dissolved in them. A few electrode potential measurements, current-voltage scans and color comparisons enable one to characterize a new solvent well.

In order to carry out a variety of chemical experiments involving a new molten salt solvent it is advisable to collect together certain basic facts, either by extrapolation or interpolation from literature data or by actual measurements. We have found it useful to know the density of the solvent but not the conductivity, the surface tension, at least approximately, because capillary action can be useful in making salt bridges, the thermal properties only qualitatively, but the phase equilibria of the components in some detail.

The affinity of many molten salts for water is well known so that sundry attempts at removing the last traces of moisture from the components and then the mixture should be a matter of course for several types of measurement, particularly those of a voltammetric nature or involving reducing agents. In many cases water and its reaction products will show up in a voltammetric scan of the solvent using moderately inert cathode materials and it will also give rise to heavy metal hydroxide precipitates; especially of Fe^{3+}; however water may not interfere obviously with electrode potential measurements above the 10^{-4}# level or with the formation of clear solutions of many transition metal salts.

These last observations mean that voltammetry can be used to determine the purity of the solvent and, with the assistance of coulometry and surface and solution analysis, to determine the solvent oxidation and reduction products at a given purity level. E.m.f. measurements on the right systems—not those with potentials near the solvent limits—and electronic spectral studies of structure-sensitive ions such as Co^{2+} and Ni^{2+} should not be affected unduly by the solvent purity but should give some idea of the complexing ability and coordination preference of the solvent.
Table 1 lists the differences between the electrode potentials of certain couples in a variety of solvents. The number 0.210 in the second column is the e.m.f. in volts of the cell:

\[
\text{Co/Co(II) in NaCl-CaCl}_2 // \text{Ag(I) in NaCl-CaCl}_2/Ag
\]

with equal metal ion concentrations in mole fractions. The cell reaction is

\[
\text{Co} + 2\text{Ag(I)} \rightarrow 2\text{Ag} + \text{Co(II)}
\]

The number is forthcoming from a concentration cell experiment and the Nernst plots appear in Figure 1. Careful perusal of the Table shows that

(a) the cobalt potential is close or positive to the silver potential in thiocyanate and chloroaluminate;
(b) the cobalt potential is 0.2 to 0.3 v negative to the silver potential in alkali chlorides;
(c) the cobalt potential is very (0.7-1.1 v) negative to the silver potential in oxygenated solvents;
(d) the nickel and Cu(II)/Cu(0) potentials closely follow the cobalt potential;
(e) the Cu(II)/Cu(0) potential follows the silver potential except in thiocyanate, metaphosphate and hydroxide.

From these observations we conclude that Cu(I) is especially stable in CNS\(^-\), PO\(_3\)^- and OH\(^-\) melts, that Ag(I) and Cu(I) are moderately stable in Cl\(^-\) melts but not very stable in H\(_2\)O and CO\(_3\)^2- and SO\(_4\)^2- melts and that Co(II), Ni(II) and Cu(II) behave similarly in all the systems.

In Figure 2 we reproduce\(^{(3)}\) the electronic spectrum of Co(II) in A. water; D. a chloride melt; C. a nitrate melt and B. a sulfate melt. The colors of these solutions are pink, blue, purple and purple respectively, reflecting the spectral shapes. The intensities of the absorption bands also follow the colors: the blue being the strongest and the pink the weakest. These spectra have been associated with octahedral coordination of Co(II) in water (the pale pink case), tetrahedral coordination in chloride (the deep blue case) and dodecahedral coordination in sulfate and nitrate (the purple cases). When CoCl\(_2\) was dissolved in NaCl-CaCl\(_2\)\(^{(2)}\), the resulting solution was deep blue and almost identical in appearance to CoCl\(_2\) in LiCl-KCl; on the other hand a Co(II) solution generated coulometrically in Li\(_2\)Co\(_3\)-Na\(_2\)CO\(_3\) was purple\(^{(4)}\). It is safe to conclude that the symmetries about Co(II) in NaCl-CaCl\(_2\) and Li\(_2\)Co\(_3\)-Na\(_2\)CO\(_3\) are T\(_d\) and D\(_{2d}\) respectively.

In Figure 3 we reproduce\(^{(3)}\) the electronic spectrum of Ni(II) in D. CsCl C. LiCl B. LiCl-KCl and A. a sulfate melt. The first solvent gives rise to regular tetrahedral coordination of Ni(II); the second
and third to mixtures of distorted tetrahedral and distorted octahedral chromophores with the octahedral one more prevalent in B than C; the sulfate gives rise to a similarly distorted octahedral chromophore. The complex NiCl₄²⁻, made from LiCl or KCl and NiCl₂ in dimethyl sulfoxide is blue, the solution of NiCl₂ in LiCl-KCl is violet and the solution of NiSO₄ in the sulfate melt is red-brown. The ion Ni(H₂O)₆²⁺ is octahedral but imparts a green color to solutions, while many Ni(II) salts are yellow in the solid state and contain octahedral Ni(II). When NiCl₂ was dissolved in NaCl-CaCl₂(2) the resulting solution was purple, decidedly more red than the LiCl-KCl solution indicating that the Na⁺ and Ca²⁺ polarized the would-be NiCl₄²⁻ complex sufficiently to produce more distorted tetrahedral chromophores than Li⁺and K⁺in combination. A solution of Ni(II) in Li₂CO₃-K₂CO₃ was red-brown like the sulfate solution and presumably contained similar-shaped species.

Everyone is familiar with the pale blue Cu(H₂O)₆²⁺ ion and should not be surprised to learn that Cu(II) in a sulfate melt is pale green like the product of atmospheric copper corrosion. In chloride melts, however, a deep golden color arises from the charge transfer as well as ligand field bands of CuCl₄²⁻(6).

Thus, to get some idea of the coordination possibilities and hence the structure of a molten salt solvent, it may be sufficient to observe the colors of dilute solutions of Co(II), Ni(II) and Cu(II) in it. To get an impression of the e.m.f. series it is necessary to determine the Co-Ag standard potential difference and perhaps the Ag-Cu standard potential difference (in some systems, e.g. sulfate, the nickel potential is not available).

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Log Concentration

Potential in V. vs. Ag(I)-Ag(0) reference

Fig. 1 Nernst plots for A Co(II)-Co(0) and B Ag(I)-Ag(0) in NaCl-CaCl₂ at 524 °C.
Figure 2 Spectrum of Co²⁺
Figure 3: Spectrum of Ni$^{2+}$