CORRELATIONS BETWEEN UV-VISIBLE SPECTRA AND THERMODYNAMICS OF SOLUTIONS OF COBALT CHLORIDE DISSOLVED IN SODIUM CHLOROALUMINATE MELTS.

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ABSTRACT

The UV-vis spectra of CoCl₂ dissolved in molten NaCl-AlCl₃ solutions were obtained as a function of composition from slightly basic compositions to fairly acidic compositions. From these spectra it was concluded that in the basic melts the Co⁺⁺ ion is tetrahedrally coordinated whereas in the acidic melts the Co⁺⁺ ion is octahedrally coordinated. The solubility of CoCl₂ had been previously determined using an EMF technique. The cell used was Co/CoCl₂ - NaAlCl₄//(AgCl)ₓ/Ag, where the mole fraction, χ, is fixed. Saturation was detected when (δE/δχ(CoCl₂))ₓ = 0. A very sharp minimum in the solubility was found in the vicinity of the 50.00% NaCl-50.00% AlCl₃ composition. The solubilities in acidic melts indicate that the formation constant for the CoCl⁺ species is very large. The cobalt spectrum in the slightly acidic melt differed from the cobalt spectra in either the basic or the very acidic melts and occurred at a composition where
the CoCl$^+$ species should be abundant, suggesting that this spectrum is that of CoCl$^+$.
Adding a small quantity of AlCl$_3$ to the CoCl$_2$ saturated melt (at the 50.00%NaCl-
50.00%AlCl$_3$ composition) caused the measured EMF to jump and to abruptly change its
sign, which indicated that adding CoCl$_2$ to the 50.00%NaCl-50.00%AlCl$_3$ melt actually
caused a decrease in Co(AlCl$_4$)$_2$ activity. This unusual thermodynamic behavior is
correlated with changes in the UV-vis spectra and the abrupt sign reversal of the EMF is
associated with a specific structural change in the cobalt containing species and supports
the possibility that a large fraction of the cobalt containing species in a range of neutral to
acid melt compositions is CoCl$^+$.

INTRODUCTION

Molten sodium chloroaluminates are highly ordered ionic liquids with many
unusual properties (1). Among these properties are very steep minima in the solubilities
and maxima in the activity coefficients of the transition metal chlorides, CoCl$_2$ (2-5),
FeCl$_2$ (6), NiCl$_2$ (3) and CdCl$_2$ (3) in the most ordered composition region, which is the
50 m%NaCl-50 m%AlCl$_3$, or neutral, mixture. As an illustration of the kind of solubility
that is observed, the concentration of CoCl$_2$ as a function of composition at 255 °C is
shown in Fig. 1. The solvent species present at this composition are almost exclusively
Na$^+$ and AlCl$_4^-$ because the equilibrium constant for the reaction:

$$2\text{AlCl}_4^- = \text{Cl}^- + \text{Al}_2\text{Cl}_7^-$$  \[1\]

is small, ranging from $1.06 \times 10^{-7}$ at 175 °C to $5.8 \times 10^{-6}$ at 355 °C (7,8). A solution that
is more than 50 m%AlCl$_3$ is considered to be acidic and a solution with less than 50 m%
AlCl$_3$ is basic. In acidic melts up to 66 m%AlCl$_3$, the dominant anionic species are
AlCl$_4^-$ and Al$_2$Cl$_7^-$ while in basic melts the principal anions are Cl$^-$ and AlCl$_4^-$. The neutral melt is considered to be both coulombically ordered and topologically
ordered. Its topological order (TO) can be illustrated by designating Na$^+$ ions as A, Al$^{+++}$
ions as B and Cl$^-$ ions as C. A pure NaAlCl$_4$ melt is described topologically in one
dimension as ...A-C-B-C-A-C-B-C- ... and coulombically as ....+ - + - + - + - + - ...
where Na$^+$ is + and AlCl$_4^-$ is -. Adding excess NaCl or AlCl$_3$ to the equimolar mixture
maintains the coulombic order, but decreases the TO by reducing the range of repetition
of the A-C-B-C units. In general, TO tends to decrease with increasing temperature and
systems tend to maintain their TO, if possible. On either the basic side or acidic side of
the neutral melt composition, TO decreases sharply while transition metal chloride
solubility increases sharply and the two phenomena are clearly related to each other. The
basic composition range of the melt is severely restricted by the phase relationships extant
in the NaCl-AlCl$_3$ system (9) so that melt compositions more basic than about 46 m%
AlCl$_3$ cannot be obtained at useful temperatures. Never-the-less, the melt composition in
this range is different than either the composition at the neutral point or the composition
in the acid region. Therefore, both the thermodynamic and spectroscopic properties of a dissolved salt would be expected to reflect these composition changes in the solvent. The solubility is a particularly useful thermodynamic property because the solubility is especially dependent upon the disproportionation, Eq 1, and the topological ordering.

Cobalt chloride was selected as the probe solute and its solubility was measured by an EMF technique. This salt was chosen because its spectra in a similar solvent, KAICl₄, were known (10) and its solubility in sodium chloroaluminate melts had been measured by an analytical technique (4) that could be compared with the solubility obtained by the simpler and more informative EMF technique. Because the cobalt chloride's solubility is a thermodynamic property and its UV-vis spectrum a molecular property, the possibility of obtaining unambiguous correlations between spectra, structure, TO, and thermodynamics presented itself.

The solubility of CoCl₂ was measured using the cell: Co/CoCl₂ - NaAlCl₄//(AgCl)x/Ag, where the mole fraction, χ, is fixed (11). The cobalt electrode directly senses Co⁺⁺ ion only and none of the other associated species that might be present in the melt. Therefore, the EMF measured by the cobalt electrode reflects Co(AlCl₄)₂ activity only. What we observed was that the EMF of the cell increased positively upon addition of CoCl₂ to the stirred melt. Saturation was detected when

$$\delta E/\delta \chi(\text{CoCl}_2) = 0.$$  \[2\]

A striking sign reversal and large change in the magnitude of the EMF occurred immediately upon the addition of small quantities of AlCl₃ to the saturated 50.00 m%NaCl-50 m%AlCl₃ melt (3). Because adding AlCl₃ to the saturated melt increases the Co(AlCl₄)₂ activity, this sign reversal of the EMF meant that increasing Co(AlCl₄)₂ activity causes our cell voltage to become more negative. Therefore, the positive increase in EMF that initially accompanied the addition of CoCl₂ to the neutral melt prior to saturation must have been caused by a decrease in Co(AlCl₄)₂ activity, seemingly contradicting Le Chatelier's principle.

Formally, the increase in Co⁺⁺ concentration upon addition of AlCl₃ to the saturated melt occurs because, the AlCl₃ first reacts with a Cl⁻ to form NaAlCl₄ and with AlCl₄⁻ to form NaAl₂Cl₇ which lowers the Cl⁻ concentration and increases the Al₂Cl₇⁻ concentration:

$$\text{Cl}^- + \text{AlCl}_3 = \text{AlCl}_4^-$$  \[3a\]

$$\text{AlCl}_3 + \text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^-$$  \[3b\]
If the Cl' ion concentration is reduced, there must be an increase in the free Co^{++} concentration because the solubility product constant:

$$K_{sp} = \chi(Co^{++})\chi^2(Cl') \tag{4}$$

requires it to account for the marked rise in CoCl_2 solubility on the acid side of the neutral point. That is, if the Cl' concentration is decreasing and K_{sp} is getting larger, the Co^{++} ion concentration must increase.

A plausible explanation for the apparent anti-Le Chatelier behavior is that the dominant cobalt containing species near the neutral NaAlCl_4 composition is not Co^{++}, but CoCl_+, CoCl_2, CoCl_3, and CoCl_4^- with CoCl_+ dominating (3,5). The formation constant for CoCl_+ from Co^{++} and Cl' is very large (9.48 x 10^6 at 255 °C and has been calculated to be 1.25 x 10^8 at 175 °C). As CoCl_2 is added to the neutral melt, the activity of Co(AlCl_4)_2, which the electrode senses as Co^{++} with no complexing AlCl_4^- ions as nearest neighbors, decreases because of the reaction:

$$Co^{++} + CoCl_2 = 2CoCl^+ \tag{5}$$

where Co^{++} represents a cobalt ion surrounded only by AlCl_4^- ions and CoCl_+ represents a cobalt ion surrounded by one Cl' ion and the rest AlCl_4^- ion. The EMF increases as long as the average complex formed by the addition of CoCl_2 contains fewer than 2 Cl' ions. Upon addition of AlCl_3, the reaction

$$CoCl^+ + AlCl_7^- = Co(AlCl_4)_2 \tag{6}$$

causes an increase in the Co(AlCl_4)_2 activity resulting in the sharp jump in EMF and the sign reversal.

On the highly acidic composition side of the chloroaluminate melt, the Co^{++} ion probably dominates with the structure of the Co^{++} containing species being very different than on the basic side, or at the neutral point. However, spectral data were lacking to confirm or reject this conjecture. Therefore, the UV-vis spectra of the cobalt chloride solutions were obtained as a function of composition from slightly basic (χ(AlCl_3) = 0.4988) to fairly acidic (χ(AlCl_3) = 0.5494).

**EXPERIMENTAL**

Polarographic grade NaAlCl_4, AlCl_3 and CoCl_2 were obtained from Anderson Physics Laboratory, Urbana Illinois.
The absorption measurements were obtained with a Hitachi U-3000 UV-vis spectrophotometer equipped with a home-made high temperature optical furnace. The samples were contained in a quartz cell with a 2 mm path-length. Because stirring inside the cell was not feasible, the samples were allowed to equilibrate at temperature in the optical furnace. This process often took as long as 20 hours before no change in absorptivity was recorded.

All transfer operations and sample handling were done in a controlled atmosphere glove box to prevent contact with water since the melt is extremely hygroscopic.

RESULTS AND DISCUSSION

The spectra, obtained at 175 °C, are shown in Fig. 2, Fig. 3, and Fig.4. Fig. 2 shows the increase in absorbance as a function of time for the dissolution of CoCl₂ in the slightly basic, $x_{NaCl} = 0.5012$ melt for the first six hours of the dissolution process. The dissolution and concomitant reactions took approximately 20 hours to completely equilibrate in the 2 mm cell. This sort of equilibration time was typical for all of the solutions that were allowed to equilibrate at temperature inside the quartz cell without stirring and indicates that the kinetics inside of the flat 2mm quartz cell used to measure the UV-vis spectra were probably different than the kinetics occurring in the well stirred EMF cell (11) used to measure the solubilities. The EMF measurements took approximately one hour to equilibrate and spectra of melt samples taken directly from the reaction vessel were already equilibrated. The thermodynamics, of course, had to be the same in both vessels.

Figure 3 shows the spectra of five different NaCl-AlCl₃ melts initially saturated with CoCl₂. From these spectra several conclusions can be drawn. The spectra obtained from the slightly basic ($\chi(AlCl_3) = 0.4988$) and neutral melts ($\chi(AlCl_3) = 0.5000$) are similar and are indicative of a tetrahedral cobalt species (2,3,10). The spectra obtained from the more acidic melts, d and e in the figure, are clearly different from a and b in the figure and are indicative of an octahedral species, CoCl₆⁴⁻ (10). The most striking feature of these spectra is that the minimum absorption occurs not at $\chi(AlCl_3) = 0.5000$, but at $\chi(AlCl_3) = 0.5015$, either indicating that the minimum in solubility and maximum in topological order might not occur at the exact neutral point, but just inside the acidic region, or that the spectrum of c of Fig. 3 (or a of Fig. 4) is that of a species of much lower symmetry than that in b of Fig.3. Having lower symmetry causes this species to absorb much less light than the more symmetric species in (b) would absorb and therefore, it is possibly the asymmetric CoCl⁺ species. Lending further support to this conjecture is the fact that the precisely neutral melts were still light greenish blue, whereas the 0.5015 melt was colorless. Fig. 4 shows the spectra of four saturated acidic melts. From spectra (b), (c) and (d), it is clear that the intensity increases with increasing acidity and a decreasing concentration of Cl⁻ ions, indicating the probability of a higher
concentration of octahedrally coordinated free Co\(^{++}\) ions, because of the higher solubility and smaller CoCl\(^+\)/Co\(^{++}\) ratio.

From these spectra, and the earlier work by Oye and Gruen (10), it is virtually certain that at least two distinct configurations exist about the cobalt ion. On the basic side of the neutral composition and probably at the exact neutral point, the tetrahedrally coordinated Co\(^{++}\) ion is very likely the dominant species. The tetrahedral geometry can arise in three different ways. A Co\(^{++}\) ion can coordinate with four Cl\(^-\) ions, with one Cl\(^-\) ion and the face of a tetrachloroaluminate tetrahedron, or with the edge of two different AlCl\(_4^-\) tetrahedra. In all likelihood, as the melts become more basic, or as temperature of a basic melt increases (1), coordination by four Cl\(^-\) ions seems more likely. On the other hand, not observing spectral evidence for the presence of CoCl\(_2\), and CoCl\(_3^-\) in the melts does not necessarily mean that these species do not exist. It may be that their symmetry is too low to be observed. The presence of CoCl\(^+\) was deduced from the solubility measurements to be a major component of acid melts certainly down to \(\chi(\text{AlCl}_3) = 0.5346\) and probably down to, at least \(\chi(\text{AlCl}_3) = 0.5000\).

On the highly acidic side of the neutral composition, the free Co\(^{++}\) ions are probably octahedrally coordinated, sharing the triangular face of each of two different tetrachloroaluminate (or heptachloroaluminate) tetrahedra.

These spectra afford strong evidence that the abrupt sign reversal of the EMF upon addition of the AlCl\(_3\) to the neutral saturated melt is associated with a specific structural change in the cobalt containing species. When the AlCl\(_3\) is added, the Co\(^{++}\) containing species changes from being tetrahedrally coordinated, or of mixed symmetry, to being distinctly octahedrally coordinated and is therefore the likely microscopic cause of the macroscopic sign reversal of the EMF. In addition, the spectrum at \(\chi(\text{AlCl}_3) = 0.5015\) ( (c) in Fig.3 and (a) in Fig.4) does not appear to be the same as the octahedral or tetrahedral spectra. Because this spectrum is in the range of compositions where the stable CoCl\(^+\) species seems to be dominant, this spectrum could be that of CoCl\(^+\). Further work is needed to test this speculatio. The low symmetry of CoCl\(^+\) should lead to absorption intensities that are low and would lead to the low (relative to that at \(\chi(\text{AlCl}_3) = 0.5000\)) absorption seen in spectrum (a) in Fig 4, despite a relatively large total cobalt concentration. In Fig.4, we see that the third peak on the r.h.s. of the (a) spectrum is also present, at reduced intensity, as a small shoulder in the octahedral (b) spectrum. Because the (d) spectrum has an arbitrary height scale, we cannot determine if this shoulder is also present in the (c) spectrum.

**CONCLUSION**

In basic NaCl - AlCl\(_3\) melts, complexes of cobalt chloride exhibit tetrahedral symmetry (probably due to the CoCl\(_4^-\) species) while in the very acidic melts they...
exhibit octahedral symmetry (probably due to the free Co\(^{++}\) species). No spectral evidence exists to corroborate the presence of cobalt complexes with different symmetry such as CoCl\(_2\) and CoCl\(_3\) in basic melts. Solubility measurements indicate that CoCl\(^{+}\) is a strongly bound dominant species in a range of acidic melts. One spectrum (a) of Fig. 4) could be that of CoCl\(^{+}\) at a composition where this ion is predominant and there is very little free Co\(^{++}\), which probably has a much larger absorption intensity than CoCl\(^{+}\) and might have masked its spectrum, even if it had a lower concentration than the CoCl\(^{-}\)

REFERENCES

1. M. Blander, P.J. Tumidajski, I. Bloom and D.S. Newman; Proceedings of the Seventh International Symposium on Molten Salts, C. Hussey, S.N. Flengas, J. S. Wilkes, Y. Ito, Editors PV 90-17, p. 30, The Electrochemical Proceedings Series, Pennington, NJ 1990

2. D.S. Newman, P.J. Tumidajski and M. Blander; Proceedings of the Seventh International Symposium on Molten Salts, C. Hussey, S.N. Flengas, J. S. Wilkes, Y. Ito, Editors PV 90-17, p. 264, The Electrochemical Proceedings Series, Pennington, NJ 1990

3. D.S. Newman, P.J. Tumidajski and M. Blander, Materials Science Forum, 73-75, p.159 (1991)

4. C. Wai, I. Bloom, D. Caveny and M. Blander, J. Phys. Chem. 94, 1666 (1990)

5. P.J. Tumidajski and M. Blander, J. Phys. Chem. 99, 9992 (1995)

6. P.J. Tumidajski and M. Blander, Materials Science Forum, 73-75, 251 (1991)

7. G. Torsi, and G. Mamantov, Inorg. Chem. 10, 1900(1971)

8. L.G. Boxall, H.L. Jones and R.A. Osteryoung, J. Electrochem. Soc. 120, 233 (1973)

9. J. Kendall, E.D. Crittenden and H. K. Miller, J. Am. Chem. Soc. 45, 976 (1923)

10. H.A. Oye and D.M. Gruen, Inorg. Chem. 4, 1173 (1965)

11. P.J. Tumidajski, M. Blander and D. S. Newman, J. Electrochem. Soc. 141 895(1994)
Fig. 1 CoCl₂ Dissolved in NaAlCl₄

Fig. 2 Dissolution of CoCl₂ in NaAlCl₄

Fig. 3 NaAlCl₄ Saturated with CoCl₂

Fig. 4 Acidic Melts saturated with CoCl₂