CORRELATIONS BETWEEN STRUCTURE, SPECTRA, AND THERMODYNAMICS IN SOLUTIONS OF COBALT CHLORIDE IN SODIUM TETRACHLOROALUMINATES.

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ABSTRACT

An EMF technique using the cell

\[ \text{Co/CoCl}_2-\text{NaAlCl}_4 // (\text{AgCl})_x-\text{NaAlCl}_4 (x \text{ fixed})/\text{Ag} \]

was used to measure the solubility of CoCl_2 in NaCl-AlCl_3 melts. The changes in EMF as a function of changes in melt composition were correlated with changes in the UV-Vis spectra of the dissolved cobalt species. From these data, the microscopic structural contributions to the macroscopic thermodynamic properties of the solutions were estimated.

INTRODUCTION

In recent years, organic and inorganic tetrachloroaluminates have become the focal points of a considerable amount of research. The solution chemistry of the chloroaluminates is theoretically interesting because the thermodynamic properties are highly dependent on composition. In addition, there is the potential to generate practical applications in the areas of energy storage batteries, coal liquefaction, and coal desulfurization.

Sodium tetrachloroaluminate (NaCl-AlCl_3) may be viewed as the prototype for these melts; the 50% - 50% mixture is best described as a highly ordered liquid, consisting of Na^+ and AlCl_4^- ions. It is well known that the tetrachloroaluminate system disproportionates only slightly. Values for the disproportionation constant:

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

vary from 1.06 x 10^{-7} at 175°C to 5.83 x 10^{-4} at 355°C.

An acid-base chemistry for these melts arises by considering the 50% - 50% mixture as neutral, a solution with more than 50% AlCl_3 as acidic and a solution with less...
than 50% AlCl₃ as basic. In the acidic melts, up to 66.6%
AlCl₃, the dominant anionic species are AlCl₄⁻ and Al₂Cl₇⁻
while in the basic melts they are Cl⁻ and AlCl₄⁻. In
addition, the liquid’s topological order decreases as the
composition varies in either the acidic or basic direction
from the neutral point.

Topological order may be defined as follows. Designating
Na⁺ as A, Al³⁺ as B, and Cl⁻ as C, a pure NaAlCl₄ melt can
be described topologically in one dimension as
...A - C - B - C - A - C - B - C ... and coulombically as
... + - + - + - ..., where Na⁺ = + and AlCl₄⁻ = -. When
some excess NaCl is added, for example, we have an excess
of A and C so that the coulombic order (...+ - + - ...) is
preserved, but not the topological order. A particular
sample of the liquid might be ...A - C - A - C - B - C - A
-C ... which is of lower topological order than ... A - C-
B - C - A - C - B - C where the A-C-B-C unit is repeated
classlessly. From this it can be deduced that the degree of
topological order at the 50 - 50 m% composition is larger
the smaller the value of the disproportionation constant
for Eq. [11. For NaAlCl₄ (and undoubtedly for almost all
other ordered liquids), topological ordering decreases with
an increase in temperature.

Since the rate of change in order is large at the
neutral point (because of the very small disproportionation
constant), a striking minimum in the solubility of metal
chlorides and maximum in solute activity coefficients occur
at, or near, this composition.(8) Both the chemical and
spectroscopic properties of an appropriate solute should
reflect this change in order as a function of composition.
Moreover, since the solubility is a thermodynamic property
which to a great extent reflects the magnitude of the
disproportionation constant and the ordering, there is the
possibility of an unambiguous correlation of topological
ordering with spectroscopic and thermodynamic properties.

Cobalt chloride was chosen as the probe molecule in
this preliminary study since its spectra in a similar salt,
KCl-AlCl₃, are well known (12) and its solubility in
NaAlCl₄ has recently been directly measured by an
analytical technique in which aliquots of the saturated
melts are removed and Na, Co, and Al contents measured by
inductively coupled plasma atomic emission spectroscopy
(ICP -AES).(8) These data, in effect, serve to calibrate
the simpler EMF measurements.

EXPERIMENTAL DETAILS
Polarographic grade NaAlCl₄ and AlCl₃ were obtained from Anderson Physics Laboratory (Urbana II).

The electrochemical cell used in our experiments is a Co - Ag Galvanic cell which can be described schematically as:

\[
\text{Co/ CoCl}_2 \text{ - NaAlCl}_4 // (\text{AgCl})_x \text{ - NaAlCl}_4 (X \text{ fixed}) /\text{Ag asbestos diaphragm}
\]

The anodic and cathodic cell compartments were separated by an asbestos diaphragm sealed into pyrex glass as described previously. The fibers allow electrical contact, but minimal mass diffusion. Junction potentials were minimized by using dilute solutions of CoCl₂ and AgCl on either side of the diaphragm. The reference electrode composition was fixed at \( X = 1.252 \times 10^{-4} \). Fig. 1 represents data for the reference electrode. It should be noted that at 175°C the solution of AgCl in NaAlCl₄ is Nernstian up to approximately \( X = 1.0 \times 10^{-2} \). In addition, the solubility of AgCl in NaAlCl₄ is relatively high with \( X \) approximately equal to \( 1.87 \times 10^{-2} \).

Temperatures were measured with a sheathed K-type thermocouple directly immersed into the melt and the solutions were continuously stirred. All experiments were conducted in a controlled atmosphere glove box filled with anhydrous He and with a moisture content around 1 ppm. EMF measurements were made with a high impedance electrometer. Compositions were changed by adding CoCl₂, NaCl, or AlCl₃ to the electrode compartment. Cell voltages were stable to within \( \pm 2 \text{ mv} \) approximately 30 minutes after each addition. The measured cell potential is related to the activities of the solutes by the Nernst equation in the form:

\[
/\E = \left(\frac{RT}{2F}\right) \ln \left(\frac{a_{\text{CoCl}_2}}{a^2_{\text{AgCl}}}\right) [2]
\]

\[
= \E - \E^*_{\text{Co}} + \E^*_{\text{Ag}} [3]
\]

The UV-Vis spectra of the CoCl₂-NaCl-AlCl₃ solutions were obtained with a Carey 17 H spectrophotometer using a 1 mm quartz cell. A Carey 17 H has the optics reversed so that black body radiation does not interfere with the spectrum. Solutions of known CoCl₂ composition were made by dissolving carefully weighed amounts of the compound in NaCl-AlCl₃ in a furnace inside of the glovebox and filling the cell inside of the box.

RESULTS AND DISCUSSION
The UV-Vis spectra of six CoCl₂ - NaAlCl₃ - AlCl₃ solutions are shown in Figures 2 - 5. Two salient features of these spectra are immediately obvious. The first is that on the basic composition side of the melt, (Fig. 2), the spectra of saturated solutions of crystalline CoCl₂ are indicative of a tetrahedral structure, (12) and the second is that the height of the three peaks (absorption) increases with increasing temperature. This is consistent with the fact that NaCl's solubility increases with increasing temperature. The greater the Cl⁻ concentration, the more tetrahedral CoCl₄⁻ species and the more intense the spectrum.

In the 50.17 m% AlCl₃ melt (just barely acidic) the cobalt's spectrum (Fig. 3) is distinctly different than it is in the basic melts and is probably due to octahedrally coordinated Co⁺⁺⁺ ions having AlCl₄⁻ and/or Al₂Cl₇⁻ nearest neighbors. (12, 5, 14) At the 50.00% composition (Fig. 4, 5) the spectra seem to derive from a mixture containing some octahedral and some tetrahedral character, but with reduced intensity and with the tetrahedral species favored. However, since the extinction coefficient of a species with tetrahedral symmetry is generally much greater than the extinction coefficient of the same species with octahedral symmetry, the fact that the spectrum looks more tetrahedral than octahedral does not necessarily mean that the tetrahedrally coordinated species has a higher concentration than the octahedrally coordinated species. In fact, these spectra may represent neither symmetry, but represent species coordinated by different combinations of Cl⁻ and AlCl₄⁻.

Table I lists the EMFs for the 50.00 m% mixture as CoCl₂ is added and also lists the EMF for the saturated solution after enough AlCl₃ is added to change the composition of the solvent to 50.17 m%. The temperature was 175 °C.

These data indicate that saturation occurs somewhere around XCoCl₂ = 3 x 10⁻⁴, which is consistent with the value of 2 x 10⁻⁴ obtained by Wai et al. (8), but the striking feature is the sign reversal and magnitude of the EMF that results from the addition of AlCl₃ to the neutral melt. The explanation for this unusual behavior is the following. Cobalt chloride solubilities reach a very low minimum near the 50%-50% NaCl-AlCl₃ composition and increase rapidly with increase in the concentration of either AlCl₃ or NaCl. (8) Such steeply rising solubilities are predicted by the coordination cluster theory (13) which has been shown to represent the concentration dependence of the solubilities of CoCl₂ at concentrations of AlCl₃ above 50 m%. However, these changes can be described more clearly
with a chemical description. On the acid side, the solubilities have been described in terms of the solubility product of CoCl₂ in NaAlCl₄:

\[ K_{sp} = X_{Co^{2+}}X_{Cl^-} \]  \[4\]

where \( \ln K_{sp} \) was found to be -33 at 175 °C, and where \( X_{Co^{2+}} \) and \( X_{Cl^-} \) are the cation and anion fractions in the reciprocal system Na⁺, Co⁺⁺/AlCl₄⁻, Al₃Cl₇⁻, Cl⁻. With an increase in the concentration of AlCl₃, the anion fraction of Al₃Cl₇⁻ increases (according to Eq.[1]), that of Cl⁻ decreases and \( X_{Co^{2+}} \) increases rapidly according to Eq.[4].

Adding NaCl to a 50%-50% solution increases the solubility of CoCl₂ for a very different reason. At the 50%-50% composition, with the dissolution of CoCl₂ and just enough AlCl₃ to form Co(AlCl₄)₂, a pseudobinary solution of Co(AlCl₄)₂ in NaAlCl₄ is formed. Additional NaCl will lead to association reactions of the Co⁺⁺ and the Cl⁻ ions to form a series of species:

\[
\begin{align*}
\text{Co}^{2+} + \text{Cl}^- & = \text{CoCl}^+ \quad [5] \\
\text{CoCl}^+ + \text{Cl}^- & = \text{CoCl}^- \quad [6] \\
\text{CoCl}_2 + \text{Cl}^- & = \text{CoCl}_3^- \quad [7] \\
\text{CoCl}_3^- + \text{Cl}^- & = \text{CoCl}_4^- \quad [8]
\end{align*}
\]

where the coordination of Co⁺⁺ ions with tetrachloroaluminate anions is not specified. The appropriate values for the formation constants of these species can be estimated. For example, the average bond free energy for forming a Co - Cl "bond" can be estimated from the negative of the standard free energy of the metathetical reaction:

\[
\text{CoCl}_2 + 2\text{NaAlCl}_4 = \text{Co}(\text{AlCl}_4)_2 + 2\text{NaCl} \quad [9]
\]

This free energy is -141.7 +/- (10.5) kJ/mol (8) which, when divided by 4, the assumed coordination number, gives a value of -35.4 kJ/mol, the negative of which is the average "bond energy", \( \langle \beta E \rangle \). Knowing this bond energy allows the corresponding formation constant for the CoCl⁺⁺ species to be calculated from the equation:

\[ K_i = Z[\exp(-\langle \beta E \rangle / RT) - 1] \quad [10] \]

where \( Z \) is a coordination number of Co⁺⁺ for Cl⁻ and here presumed to be 4. From this we estimate the value of \( K_i \) to be about 50,000. For silver halides this procedure...
underestimates values of Kj. With a value this high, or higher, there should be a significant amount of CoCl' even at the neutral composition; the disproportionation reaction of AlCl4- leads to a Cl- ion concentration (anion fraction) of about 3.3 x 10^-4. With Kj = 50,000, the ratio of the concentration of CoCl' to that of Co'' is about 17. With the addition of modest amounts of CoCl2, a major fraction of the cobalt is tied up in the four complex species and the apparent solubilities will be considerably higher than that predicted from the solubility product. If the bond energies of CoCl3- and CoCl4- are large enough, the solubility will increase with increasing Cl- concentration. Moreover, the unusual reversal in sign of the EMF shown in Table I is accounted for. As CoCl2 is added to the neutral melt, the activity of the Co(AlCl4)2 (free Co' no complexing Cl- as nearest neighbors) decreases because of complex formation, e.g.,

\[ \text{Co}'' + 2\text{CoCl}_2 \rightarrow 2\text{CoCl}' \quad [11] \]

and the EMF increases as long as the average complex formed by the addition of CoCl2 has less than two chlorides. Upon addition of AlCl3, the reaction:

\[ \text{CoCl}' + \text{Al}_2\text{Cl}_7^- \rightarrow \text{Co}'' + 2\text{AlCl}_4^- \quad [12] \]

causes the Co'' concentration and the activity of Co(AlCl4)2 (sensed by the cobalt electrode) to rise sharply, thus reversing the sign of the EMF. We plan to do more detailed measurements of EMF and solubilities in order to deduce the individual formation constants of the different chlorocobalt species present in the melt.

CONCLUSION

In very basic NaCl-AlCl3 melts, Co'' ions are tetrahedrally coordinated by Cl- ions with large UV-Vis absorption. In the 50.00% -50.00% melt, the spectra are indicative of a mixture of species which cannot be uniquely defined without independent information. In the slightly acidic 50.17% AlCl3 melt the Co'' environment is apparently octahedral. At this composition the Cl- ion concentration is so low that the species whose formation is described by Eq[5] - Eq[8] which have relatively small extinction coefficients are not present at a high enough concentration to be readily detected and distinguished from the octahedral species.

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Table 1. EMF as a Function of CoCl₂ Mole Fraction

| X_{CoCl₂} | X_{CoCl₂} / X_{AgCl} | EMF (mV) |
|-----------|-----------------------|----------|
| 8.17 x 10^{-5} | 5205 | 122.5 |
| 2.46 x 10^{-4} | 15703 | 138.1 |
| 3.65 x 10^{-4} | 23291 | 148.6 |
| 4.21 x 10^{-4} | 26810 | 149.9 |

50.17 m%

4.1 x 10^{-4} | 2500 | - 44.7 |

Figure 1. Reference Calibration

\[ X_{AgCl} = 1.252 \times 10^{-4} \]
\[ T = 175^\circ C \]
Figure 2. CoCl₂ in basic melt: $X\text{CoCl}_2 \approx 4.2 \times 10^{-4}$

$T = 190^\circ C$ Saturated with NaCl

Figure 3. CoCl₂ in NaAlCl₃, 50.17 m% AlCl₃ (slightly acid)

$T = 180^\circ C$ Saturated with NaCl

Figure 4. CoCl₂ in neutral melt: $X\text{CoCl}_2 \approx 4.2 \times 10^{-4}$

$T = 177^\circ C$ Saturated with NaCl

Figure 5. CoCl₂ in neutral melt: $X\text{CoCl}_2 \approx 1.33 \times 10^{-4}$

$T = 177^\circ C$ Saturated with NaCl

Absorption

Wavelength (nm)

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