CHEMISTRY AND ELECTROCHEMISTRY IN ALUMINUM CHLORIDE MOLTEN SALT SYSTEMS

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ABSTRACT

The 1:1 AlCl₃-NaCl system at 175°C may be considered as Na⁺AlCl₄⁻ with the dominant acid-base equilibrium given by

\[ 2 \text{AlCl}_4^{-} \rightleftharpoons \text{Al}_2\text{Cl}_7^{-} + \text{Cl}^{-} \quad K_m = 1.06 \times 10^{-7} \]

We have been interested in studying the chemistry of solute species, both organic and inorganic, which respond to the changes in acidity which can be achieved by varying the melt composition in the vicinity of the 1:1 system. A number of organic solutes, particularly amines, have been studied. We have found that the radical cations of triphenylamine and N,N-dimethyl-aniline (DMA) are stabilized in the melt, with the stability clearly depending on the acidity of the melt.

The oxidation of N,N,N',N'-tetramethylbenzidine (TMB) was studied; a chemical transformation of the dicomplexed amine to a monocomplexed amine precedes the oxidation of TMB.

Sulfur has been quantitatively reduced in both acid and basic melts at 175°C; the reaction appears to be a clean, two-electron process yielding sulfide. Copper(I) was generated coulometrically to titrate sulfide in the basic melts. In the acid system, cuprous sulfide possesses significant solubility. Thus, the solubility of metal sulfide in the system is dependent on the acidity of the melt. The sulfur electrode process appears to be:

\[ S_2 + 4e^{-} \rightleftharpoons 2 S^- \]

Measurements of the S/S⁻ potential as a function of melt acidity suggest that the solubility of the sulfides might best be explained by the acid-base equilibrium:

\[ S^- + \text{AlCl}_4^{-} \rightleftharpoons \text{AlSCl} + 3 \text{Cl}^- \]
For the past four years we have been engaged in an investigation of the solvent system NaCl-AlCl$_3$. Our interests have been to study the electrochemical behavior of a variety of solutes in these melts and to ascertain the most important properties of the melt which would reflect on the electrochemistry; that is, the interest has been to view the molten salt solvent system as a unique medium in which to study the electrochemistry and our interest in physical properties of the solvent has been secondary. A recent review discusses the physical properties of these melts, and several recent articles exist on various aspects of melt properties (1,2,3).

Most of the work in which we have been involved has employed the 1:1 NaCl-AlCl$_3$ system at about 175°C. The melt can be considered as an acid-base system in which the acid is defined as a chloride ion acceptor and a base as a chloride donor (4). The acid-base reaction

$$ \text{AlCl}_3 + \text{Cl}^- \rightleftharpoons \text{AlCl}_4^- $$

is essentially complete to the right, so the melt is substantially Na$^+$AlCl$_4^-$. The autosolvolyysis reaction is:

$$ \text{AlCl}_4^- + \text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^- $$

Since the Al/Al(III) system is electrochemically reversible, as determined by potentiometry, the electrode reaction at an aluminum indicator electrode in these melts can be considered to be:

$$ \text{AlCl}_4^- + 3\text{e}^- \rightleftharpoons \text{Al}^{3+} + 4\text{Cl}^- $$

The Nernst equation gives the chloride-ion activity response of the aluminum electrode:

$$ E = E_0 + \frac{RT}{3F} \log \frac{a_{\text{AlCl}_4^-}}{a_{\text{Cl}^-}^4} $$

In regions reasonably close to the 1:1 melt composition, the AlCl$_4^-$ activity is approximately constant, and the Al electrode potential responds to $p\text{Cl}^-$ - i.e., to $-2.3 \times 4/3 \times RT/F \log a_{\text{Cl}^-} - (3,4,5)$. Further, the acidity of the melt may be varied by coulometric addition (or subtraction) of Al(III) or by known weighed additions of NaCl or AlCl$_3$. Making use of the coulometric techniques, potentiometric measurements were made in melts over the range from NaCl-saturation (50.1 mole percent NaCl) to about 60 mole percent AlCl$_3$

Equilibrium constants for the reactions:
were determined, and, on the mole-fraction scale at 175°C, were 2.86 \times 10^7, 2.4 \times 10^{-1}, and 1.06 \times 10^{-7}, respectively (6).

An important part of this study was a procedure for melt purification; initial melt preparations are usually light straw colored, and prolonged pre-electrolysis between two aluminum electrodes results in removal of all color and a water-like, absolutely clear solution. Since all our experimental work is carried out in Vacuum Atmospheres dry boxes, the standard procedure followed is to prepare large batches of molten NaAlCl₄ and pipet aliquots into the cells used for detailed experimentation.

After reviewing organic reactions in molten tetrachloroaluminate solvents (7), it was apparent that organic electrode reactions had received little attention in these media.

Our first studies of amines in the AlCl₃-NaCl system indicated an unusually high stabilization of radical cations (8), as compared to that achieved in aprotic media at room or higher temperatures. One-electron reversible cyclic voltammograms were observed for triphenylamine. The blue oxidation product was generated by constant potential electrolysis and showed slow decomposition with time. The electrochemical behavior of N-N-dimethyl-aniline (DMA) was also studied in the AlCl₃-NaCl melts and, surprisingly, found to be acidity (pCl⁻) dependent (9). A complex electrode process (E.C.E.) was observed. A reduction wave for the radical cation formed on the oxidation of DMA could clearly be discerned as well as the waves for the coupled product, tetramethylbenzidine (TMB). The rate limiting step was deduced to be the base-assisted cleavage of C-H bonds. As the melt is made more acidic, the reduction peak for the radical cation formed in the oxidation of DMA increases markedly, relative to the reduction peak for the TMB dication. This behavior is accounted for by a slow acid-base reaction occurring prior to the electron transfer step:

\[
\text{AlCl}_3^+ + \text{DMA} \rightarrow \text{AlCl}_3 + \text{DMA}^+ + \text{e}^{-}
\]

Thus, it is the high acidity of the solvent that accounts for the increased stability of the radical cation when compared to observation in aprotic solvents at room temperature.
Since the oxidation of dimethylaniline was complicated by follow-up reactions, N,N-dimethyl-p-toluidine was studied since placing a methyl group in the para position of dimethylaniline stabilized the radical cation by electron donation and by blocking a reaction site. The cyclic voltammogram observed showed a single oxidation and reduction peak with no indication of additional peaks. The peak separation of 100 mV was somewhat larger than the theoretical value of 85 mV. When the pCl of the solvent was increased, the anodic peak shifted to more positive potentials for a given sweep rate. At the same time the peak gradually lost its shape, finally becoming an ill-defined wave as pCl increased. At the same time, the cathodic peak did not move or change shape significantly with increasing pCl. Similarly, as the sweep rate was increased at constant pCl, the anodic peak again lost its shape becoming a drawn-out wave at high sweep rates. This behavior can also be attributed to a slow preceding acid-base reaction as shown above for DMA.

These studies indicated that TMB should also exhibit an interesting acid-base chemistry, without the problems due to the coupling of radicals in DMA and based on these observations, the electrochemical oxidation of TMB in the AlCl₃-NaCl solvent at 175°C was investigated as a function of pCl⁻ (10). The predominant species in this medium was identified by ultraviolet spectroscopy and potentiometric techniques to be an (aluminum chloride)₂-TMB complex in the pCl⁻ range of one to four. A chemical transformation of the dicomplexed amine to a monocomplexed amine precedes the electron transfer. A $k_f k_1$ value of $5 \times 10^6$ M⁻¹ sec⁻¹ for the reaction

$$TMB (AlCl_3)_2 + Cl^− \xrightarrow{f} TMB (AlCl_3) + AlCl_4^−; K_1 = \frac{k_f}{k_b}$$

was found using normal pulse voltammetric and chronoanperometric techniques. The dicomplexed amine is electroactive at more positive potentials. The product of both electron transfers is the orange dication of TMB. Cyclic voltammetry and constant potential coulometric techniques were employed to obtain diagnostic criteria for the elucidation of the above pathways.

We have recently undertaken studies of sulfur, and various sulfur species, in AlCl₃-NaCl. It has been reported that sulfur and sulfides behave similarly to oxygen and oxides when reacted in sealed tubes at 350°C with AlCl₃ (11). Chlorination of sulfides was reported - i.e.,

$$AlCl_3 + Na_2S \rightarrow AlSCl + 2NaCl$$
$$AlCl_3 + ZnS \rightarrow AlCl + ZnCl_2.$$

A recent technical report and brief publication therefrom indicates a
cursory look at sulfur via cyclic voltammetry, in an approximately 2:1 
AlCl₃:NaCl melt. An oxidation wave and at least two reduction waves, 
which the authors felt "involved the reduction of sulfur to some poly-
sulfide", are reported (12). Sulfur chemistry has been studied in 
KCl - LiCl at some length (13-19). Reduction of S, to S² or polysul-
fides, gives rise to a blue solution. The electrochemical reduction 
of S appears to give rise to two waves in KCl - LiCl (17), with forma-
tion of the blue color at the surface.

The behavior of S in NaAlCl₄ at a vitreous carbon electrode gives 
rise to a single reduction wave at 0.5 V and oxidation waves at 1.3 V 
and beyond 1.8 volts. The wave at 1.3 V is associated with the oxida-
tion of the reduction product of the 0.5 V wave (S², see below). In 
an acid melt, one reduction wave for sulfur is also found, but the 
behavior at the very positive end is more complex.

To establish the stoichiometry involved, constant potential 
exhaustive coulometry was performed for the reduction and oxidation 
of sulfur and sulfide. Typical current-time behavior for the sulfur 
reduction in a tungsten crucible is shown in Fig. 1. Weighed amounts 
of sublimed sulfur were added to the crucible whose potential previ-
ously had been adjusted to a value 100 mV more negative than the 
sulfur reduction peak. In this way, loss of sulfur due to evaporation 
during the coulometric experiment was minimized. Reduction of 10-20 
mg sulfur in a 50-60 g melt could be completed in 3-4 hours. Both in 
acid and basic melt, the number of electrons per mole of sulfur (con-
sidered to be monomeric) was found to be 2.00 ± 0.01 from the coulombs 
passed. A coulometric experiment was carried out by holding the poten-
tial at the desired value for several hours before the sulfur was 
added. The average background current found was then calculated as 
coulombs/hour and subtracted from the total number of coulombs passed. 
Table I summarizes the data from several coulometric experiments.

**TABLE I**

| MELT          | THEORETICAL SULFIDE CONTENT μeqv | POTENTIOMETRIC Cu²⁺-TITRATION μeqv | POTENTIOMETRIC AQUEOUS TITRATION μeqv |
|---------------|---------------------------------|-----------------------------------|-------------------------------------|
| acid (54:46 - AlCl₃:NaCl) | 194                             | 197 ± 3                           |                                     |
| basic (NaCl Sat'd) | 198                             | 194 ± 3                           |                                     |
|                | 200                             | 190                               | 190                                 |

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The amount of sulfide produced was measured in two ways. In the first instance, the melt was dissolved in 1N sodium hydroxide and titrated with sodium plumbate solution using a sulfide sensitive indicator electrode (20). The amount of sulfide was also determined in situ by making the melt basic and carrying out a potentiometric titration with coulometrically generated Cu(I). The generation of Cu(I) in the melt has previously been studied and found to take place at 100% current efficiency (21). A typical titration curve is shown in Fig. 2. The solubility product for Cu₂S in the basic melt was calculated from the titration curve and by taking into account that Cu(I) is complexed by chloride ions in the basic melt (21). The solubility product was found to be \(6.8 \times 10^{-15} \pm 0.4 \times 10^{-15}\) M\(^3\) at 175°C. The calculation made use of the Nernst expression for the copper electrode potential, the solubility product expression, mass balance equations for copper and sulfide, and the complex equilibrium for copper (I) and chloride,

\[
\text{Cu}^+ + 2 \text{Cl}^- = \text{CuCl}_2^− \quad K = 6.5 \times 10^4 [\text{mole fraction}]^{-2}
\]

The expressions for pairs of points on both sides of the titration endpoint were compared and from that the solubility product and standard potential for the Cu⁺/Cu couple were calculated. The potential of the point prior to the endpoint is determined by \(K_{sp}\) and \(E_{Cu^+/Cu}^\circ\), while the potential of the endpoint is determined by \(E_{Cu^+/Cu}^\circ\). The average value of the standard potential was found to be 1240 ± 0.005 mV vs A1 reference in a NaCl saturated melt. Since A1 in a NaCl saturated melt is 170-175 mV more negative than A1 in a 50:50 melt, 1240 mV is in good agreement with 1073 mV reported earlier (21). The copper sulfide precipitate x-ray diffraction powder pattern showed that stoichiometric Cu₂S was formed.

When the coulometric reduction of sulfur had been carried out in an acid melt for the first time, an attempt was made to titrate the sulfide with coulometrically generated copper (I). The copper wire electrode was stirred continuously during anodization. The curve obtained is shown in Fig. 3 (O-A). It was observed that no precipitation of Cu₂S occurred. At point A sodium chloride was added to make the melt basic. Copper sulfide precipitated and the electrode potential moved to point B. A Nernst plot for Cu⁺ for the curve from 0 to A was made and was linear with the correct 2.3RT slope. Extrapolation of \(\log (Cu^+) = 0\) give \(E_{Cu^+/Cu}^\circ = 1240-1245\) mV in agreement with earlier results. These results show that the sulfide activity is markedly lower in acid melts, as a result of the sulfide species being complexed in the acid melt.

The potentiometric titration was also carried out by anodization of a silver wire to generate Ag(I). In an acid melt, behavior similar to that of copper was observed in that no precipitate formed. Upon addition of sodium chloride, black Ag₂S precipitated.
The sulfur-sulfide reaction was studied by measuring the electrode potential as a function of the ratio of sulfur and sulfide concentrations. Nernst plots obtained in acid melt are shown in Fig. 4. The solid straight lines drawn have a slope of RT/4F. These experiments were carried out in the tungsten crucible. A weighed amount of sublimed sulfur was added to a known amount of melt with the counter and reference electrodes isolated from the main body of the melt by glass frits. The sulfur was quantitatively reduced to sulfide by using the crucible as the working electrode as described previously. The sulfide of known concentration was then oxidized stepwise back to sulfur. After each step the sulfur-sulfide rest potential was measured with a vitreous carbon or tungsten indicator electrode. When plotting the experimental points, different sulfur and sulfide species were fitted to the expression for the electrode reaction, but only when S$_2$ and S$^-$ were used was a straight line obtained. The Nernst plots shown were calculated at fixed pCl$^-$ using the equations:

$$S_2 + 4e = 2 S^-$$  \hspace{1cm} (1)

$$[S_{total}] = 2 [S_2] + [S^-]$$  \hspace{1cm} (2)

The total amount of sulfur and sulfide was calculated from the coulombs passed during the reduction or oxidation. The initial reduction of added sulfur was quantitative, as was the oxidation of the sulfide back to sulfur. A summary of the Nernst plot data is given in Table II.

**TABLE II**

| NERNST EXPERIMENTS |
|---------------------|
| **Sulfur added:** 9.5 mg to basic melt | **LOSS** |
| Coulombs on first reduction correspond to: 9.5 mg sulfur | 0 |
| Coulombs on succeeding oxidation corresponds to: 9.33 mg | 0.17 mg = 1.8% |
| Coulombs on succeeding reduction corresponds to: 8.45 mg | 1.05 mg = 11% |
| n, Nernst plot | 4 \pm 0.05 |
| n, exhaustive coulometry | 2 \pm 0.01 |
| $E^\circ_{S_2/S^-}$ in basic melt (NaCl saturated)* | 1.32 \pm 0.010 |

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*Potential in volts vs A1 in NaCl saturated melt determined by extrapolation of the line in Figure 4 to $\ln (S_2/(S^-)^2) = 0$. 

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For low sulfur concentrations, the experimental points are above the line with slope $RT/4F$. A possible explanation for this might be that $S_2$ is in equilibrium with sulfur molecules containing more than two atoms. By postulating the reaction:

$$S_8 = 4S_2 \quad K_1 = [S_2]^4/[S_8]$$

line B in Fig. 4 is obtained for $K_1 = 2 \cdot 10^{-10}$ M$^3$.

The potential for the sulfur-sulfide couple depends on the acidity of the melt. Fig. 5 shows the sulfur-sulfide electrode potential in the chloroaluminate melt at 175°C as a function of log mole fraction $Cl^-$ in the melt. The experiment was carried out in the tungsten crucible which initially contained 60.55 g sodium chloride saturated melt. 5 mg sulfur was added and quantitatively reduced to sulfide. 2% of the sulfide was then re-oxidized to sulfur, giving a solution $4.4 \cdot 10^{-5}$ M $S_2$ and $4.3 \cdot 10^{-3}$ M $S^2$. Weighed amounts of acid melt (58 mole % $AlCl_3$- 42 mole % NaCl) were then added to this solution. For each addition, the total composition of the melt and the mole fraction of chloride ions were calculated.

From the Nernst plot for the sulfur-sulfide reaction (Fig. 4) showing a four-electron reaction and the $pCl^-$-plot showing a slope close to $3RT/2F$ (Fig. 5), the following electrode reaction is postulated:

$$S_2 + 2 AlCl^+_4 + 4e = 2 AlSCl + 6Cl^-$$

The Nernst expression for the electrode potential is:

$$E = E^o - \frac{RT}{4F} \ln \frac{[AlSCl]^2 \cdot [Cl^-]^6}{[S_2] \cdot [AlCl^+_4]^2}$$

where

$$E^o = E^o_1 - \frac{RT}{4F} \ln K_2^2$$

If it is assumed that except for a small dilution effect the concentrations of $S_2$, AlSCl and $AlCl^+_4$ are constant, which is reasonable for $pCl^- > 3$ (see below), equation 5 can be simplified to:

$$E = E^o_1 - \frac{RT}{4F} \ln [Cl^-]^6 = E^o_1 - \frac{3RT}{2F} \ln [Cl^-]$$

Formation of AlSCl from aluminum chloride and sodium sulfide in the dry state is reported to occur at 330°C with a 25% yield (11), as mentioned above.

Because of the observed change in solubility of copper sulfide and silver sulfide with acidity, the free sulfide ion concentration must be a function of the melt acidity. If the following equilibrium
is assumed:

$$\text{AlSCl} + 3\text{Cl}^- = \text{S}^= + \text{AlCl}_3$$

$$K_2 = \frac{[\text{S}^=][\text{AlCl}_3]}{[\text{AlSCl}][\text{Cl}^-]^3}$$

(7)

then equation 5 can be written:

$$E = E_0 - \frac{RT}{4F} \ln \frac{[\text{S}^=]_{\text{total}}^2}{\left[ \frac{1 + K_2[\text{Cl}^-]^3}{[\text{AlCl}_3]} \right]^2 \cdot [\text{AlCl}_3]^2}$$

(8)

Here $[\text{S}^=_{\text{total}}] = [\text{AlSCl}] + [\text{S}^=]$

By including constant terms in $E_0$, equation 8 at fixed total concentration of $\text{S}_2$ and $\text{S}^=$, is transformed to

$$E = E'' - \frac{RT}{4F} \ln \frac{[\text{Cl}^-]^6}{[\text{AlCl}_3]^2 + K_2[\text{Cl}^-]^3}$$

(9)

When $K_2[\text{Cl}^-]^3 \ll [\text{AlCl}_3]$, the slope of Fig. 5 will be $3RT/2F$, and when $[\text{AlCl}_3] \ll K_2[\text{Cl}^-]^3$, the slope will approach zero. In Fig. 5, the two points for the basic melt composition log, $[\text{Cl}^-] = -2$ and $-2.5$ are above the line with slope $3RT/2F$, which is as expected if the assumed equilibria are correct.

$K_2$ could be calculated from the deviation from the straight line, but due to the uncertainty in the calculated $\text{Cl}^-$ concentrations, a reliable value cannot be obtained by this method. However, from Fig. 5 $K_2$ can be estimated to be of the order of $10^7 - 10^9$ [mole fraction]$^{-2}$.

From the copper deposition peak of a cyclic voltammogram of a saturated solution of cuprous sulfide in an acid melt, the copper concentration in solution can be calculated to be in the order of 0.1M. In order to fit the solubility product of $10^{-17}$, the concentration of free sulfide cannot be higher than $10^{-12}$, which should give an $[\text{AlSCl}]/[\text{S}^=]$ ratio of $10^{11}$. If this is introduced into equation 7 together with $[\text{Cl}^-] = 10^{-6.7}$ and $[\text{AlCl}_3] = 10^{0.5}$, $K_2$ is calculated to be $10^{8.6}$ [mole fraction]$^{-2}$, roughly the same order of magnitude as estimated from Fig. 5.

The oxidation of sulfur has been briefly investigated in the basic melt. Cyclic voltammograms of $\text{S}_2\text{Cl}_2$ are shown in Fig. 6. (The cyclic voltammogram is identical to that obtained upon addition of sulfur, after cycling to a steady state.) $\text{S}_2\text{Cl}_2$ boils at 135.6°C and after a few hours disappears from the melt. Coulometric oxidation of sulfur was attempted by holding the electrode potential for oxidation at 2.01 volt vs Al.
An n-value of 1.15 was obtained without correcting for background. Since the oxidation takes place close to the chlorine evolution potential, the background was high and very sensitive to small changes in acidity. The cyclic voltammograms obtained after the oxidation resembled those in Fig. 6. Because of the volatility of $S_2Cl_2$, most of what was produced probably evaporated from the solution during the oxidation.

The experimental results obtained for the sulfur-sulfide system show that sulfide ion acts as a strong base in the AlCl$_3$-NaCl melt. The change of solubility of metal sulfides show that sulfide ion activity is several orders of magnitude smaller in acid than in basic melt, and experimental evidence indicates the formation of AlSCl. The reduction of sulfur showed no evidence of formation of polysulfide ions. Sulfur can be oxidized to $S_2^{2+}$ and perhaps higher oxidation states. Thus, a number of organic and inorganic systems show pronounced dependence on melt acid-base chemistry.
ACKNOWLEDGMENTS

The work reported here was carried out by Drs. Larry Boxall, H. Lloyd Jones, Duane Bartak and Knut Paulsen; support from the Air Force Office of Scientific Research and the American Chemical Society Petroleum Research Fund is gratefully acknowledged.

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Figure 1. Reduction of sulfur in a tungsten crucible at 175°C. Melt: 34 ml AlCl₃ – NaCl (54-66 mole %)
(a) 9 mg sulfur added
(b) 75.3 mg sulfur added
(Total added sulfur = 2.139 mmol for a two-electron reaction. Total coulombs passed = 2.146 mmol)

Figure 2. Potentiometric titration of 0.0107 M Na₂S in NaAlCl₄, with coulometrically generated Cu⁺ at 175°C. Amount melt: 8.665 g.
Theoretical titration curve calculated from the experimental points. Arrow indicates theoretical equivalence point based on added sulfur.

Figure 3. Potentiometric titration of sulfide formed from coulometric reduction of S, 31.6 mM, with coulometrically generated Cu⁺
A: Acid melt (54-66 mole % AlCl₃ - NaCl)
B-C: Basic melt (NaCl saturated)
5.175 g melt with theoretical endpoint 194 μeq

Figure 4. Nernst plot for sulfur-sulfide in AlCl₃ - NaCl (53.5 - 66.5 mole %)
Curve A: Reduction of 1.172 mm sulfur to sulfide in the tungsten crucible.
Curve B: Same as A, but the equilibrium S₂ = 4S with K = 2.10⁻¹⁰ (M⁻²) was included when [S₂] was calculated.
Figure 5  Sulfur-sulfide electrode potential in the chloroaluminate melt at 175°C was a function of log mole fraction Cl⁻.
Sulfur concentration: 4.4 \times 10^{-5} \text{ M} S_2
Sulfide concentration: 4.3 \times 10^{-3} \text{ M} Na S_2

Figure 6  S_2Cl_2 in basic melt. Tungsten electrode (0.07 cm²) Concentration approximately 0.05 ml S_2Cl_2 in 10 ml melt (50-60 mM)