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FINAL REPORT
ON
ELECTROCHEMICAL STUDIES IN
ALUMINUM CHLORIDE MELTS

AFOSR-75-2776

March 1, 1975 - May 31, 1976

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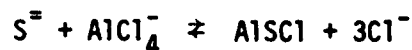
ELECTROCHEMICAL STUDIES IN ALUMINUM CHLORIDE MELTS

ABSTRACT

Work carried out under AFOSR-71-1995 was continued. The acid-dependent chemistry of sulfur was investigated. The Nernst behavior of the S/S^{\ominus} couple was in accord with

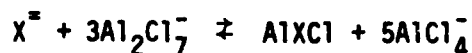


and the acid-base dependence can be expressed as



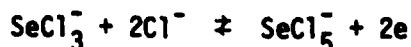
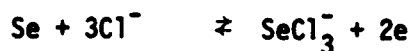
This explains the solubilization of metal sulfides in acid-chloroaluminate systems.

Oxides, selenides and tellurides show much the same behavior as sulfides. The stoichiometry indicates that the neutralization reaction for these bases may be written



where X is S, O, Se or Te.

A detailed electrochemical study of selenium has been undertaken. The following mechanism can be proposed:



Selenium also appears to exist, as determined potentiometrically, as a dimer.

The electrochemistry of various molybdenum species has been studied. Mo(V) reacts to form Mo(III) which is further reduced to Mo(II) and Mo(0). The last two steps involve considerable surface chemistry. An E.C.E. mechanism is postulated to explain the $Mo(V) + 2e \rightleftharpoons Mo(III)$ electrode process.

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The work reported here is a 15-month continuation of activity reported previously under the Final Report to AFOSR-71-1995. Frequent reference will therefore be made to that Report.(1)

The work on sulfur and sulfides reported in (1) was continued, and it was demonstrated that the S/S^{\equiv} potential equilibrium could best be described by the reaction

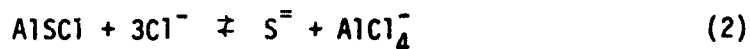


This was demonstrated by measuring the potential of an inert electrode in the $AlCl_3:NaCl$ melt at $175^\circ C$ and the S/S^{\equiv} ratio was changed by coulometric oxidation of S^{\equiv} (for reduction of S). A Nernst plot gave linear behavior for a plot of E vs $\log \frac{[S_2]}{[S^{\equiv}]^2}$ assuming

$$[S_2] = [S]_T/2$$

The slope was $\frac{2.3RT}{4F}$, as per equation (1).

Following this, the potential of the S_2/S^{\equiv} couple was measured as a function of melt acidity. The results indicated that the previously reported (1) solubility of metal sulfides in the acid melt could best be explained by an equilibrium

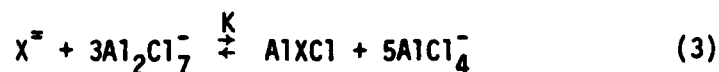


In the acid melt this equilibrium is displaced markedly to the left, markedly lowering S^{\equiv} activity. The results of this work were prepared for publication and are currently in press in the Journal of the American Chemical Society.

Further investigations have shown, as might be expected, that the solubilization shown by the metal sulfides is also observed for metal oxides, selenides and tellurides. These solubilities were determined from the height of the Cu^+ reduction cyclic voltammetry peak after equilibrating solid cuprous oxide, selenide or telluride with a 60:40 ($AlCl_3:NaCl$) mole % melt. The values were all found to be similar at $3.3 \pm 0.5 \times 10^{-1}$ mole liters⁻¹, in agreement with the value determined earlier for cuprous sulfide. (2) It was suggested in

our previous report that this solubilization is brought about by some form of acid-base reaction between the melt and the chalcogenide ion. The potentiometric studies described above confirmed the nature of that reaction.

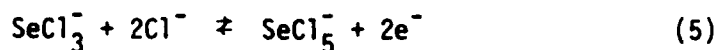
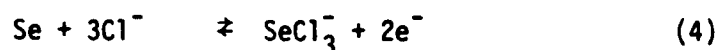
In order to investigate further the possible acid-base chemistry, it was decided to see if the chalcogenide ions could be titrated with $Al_2Cl_7^-$ (the principal acid species in the melt).⁽³⁾ A 50:50 melt was prepared by anodizing an Al wire in an NaCl saturated melt until the required composition was reached. A small sample of Na_2S , Na_2Se or Na_2Te was then added to the melt and the potential of an Al indicator electrode in the melt was observed to fall. The melt was then titrated with Al^{3+} (from the anodization of an Al wire) using an Al indicator electrode. We also wished to observe the behavior of the oxide ion but, as has been observed previously,⁽⁴⁾ Na_2O is not soluble in the melt. Instead we found that oxide ions could be introduced by adding $BaCO_3$ to the melt. Initially carbon dioxide was evolved and the residue, BaO , was found to be soluble. The titration curves all showed the behavior typical of a strong acid-strong base reaction and the stoichiometry showed one chalcogenide ion to be equivalent to three $Al_2Cl_7^-$ ions, indicating a reaction



where X is O, S, Se or Te. All the species $AlOCl$, $AlSCl$, $AlSeCl$ and $AlTeCl$ have been prepared (5,6,7,8) by reacting metal chalcogenides with $AlCl_3$ in sealed tubes at elevated temperatures. In the future it is hoped to determine if these, or any other, species can be extracted from the melt. It is also hoped to be able to determine the magnitude of the equilibrium constant K. An order-of-magnitude calculation for the equilibrium constant for Equation 2 has been made.⁽¹⁰⁾

Apart from one very cursory study (9) (one cyclic voltammogram), the electrochemical behavior of selenium in these melts does not appear to have

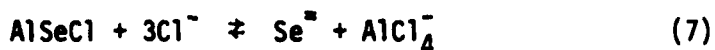
been investigated. The lower oxidation states of selenium have, however, been the subject of a detailed spectroscopic study (10) and a number of polynuclear species with formal oxidation state less than unity have been identified in the eutectic melt as stable. We have recently commenced a detailed electrochemical study of selenium and various selenium species. In basic melts, pCl less than 3.5 (mole fraction scale), selenium shows a two-electron quasi-reversible reduction to selenide and two quasi-reversible two-electron oxidations (the number of electrons being determined coulometrically by exhaustive controlled potential electrolysis). From the pCl dependence of the cyclic voltammetry peak potentials for the oxidations, the following mechanism for the oxidation of selenium in basic melts can be proposed



When the pCl of the melt is increased to greater than about 3.5 selenium still shows a two-electron reduction but the oxidation now becomes a single four-electron process, again quasi-reversible. The potential of this oxidation now shows no acidity dependence, implying that the Se^{4+} species is not solvated by any acidic or basic species (Cl^- , Al_2Cl_7^- or AlCl_3). Support for these proposed oxidation mechanisms is at present being sought from spectroscopic studies.

Equilibrium potential measurements of the selenium-selenide couple have been made in both acidic and basic melts and also for fused selenium and selenide concentration as a function of acidity. The measurements for variable selenium and selenide concentrations indicate that in both acid and basic melts, selenium is present as a dimer, while a plot of equilibrium potential against pCl for fixed selenium and selenide concentrations has a slope of $\frac{3RT}{2F}$ (120 mV). From these observations the following electrode reaction for the reduction of selenium can be postulated

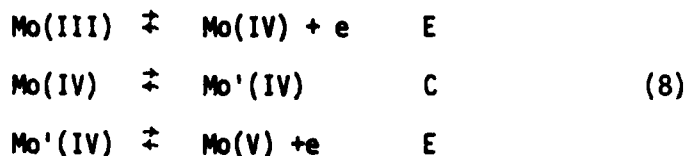




with the latter equilibrium lying well to the left hand side. This is the same mechanism as was proposed for the reduction of sulfur (see above and 10) and is in agreement with our earlier postulates concerning the acid-base chemistry of metal chalcogenides in these melts. The kinetics of the selenium reduction also show marked acidity dependence and are being studied further.

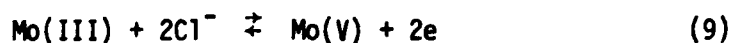
The electrochemical work on the chemistry of molybdenum was continued utilizing the rotating ring-disc glassy carbon electrode.(1) The electrochemistry of Mo(V) and Mo(VI) was found to be identical; however, it was discovered that Mo(VI), introduced as MoO₃, oxidized the melt to yield Cl₂, being itself reduced to Mo(V). The Mo(V) reduces to Mo(III) in a diffusion controlled, first-order process. Further reduction, to the Mo(II) and Mo(0) state is very complex and involves considerable surface chemistry. Mo(V) could be quantitatively reduced to Mo(III); however, the ring-disc collection efficiency for this process was rotation rate dependent, increasing with decreasing rotation rate. This indicates that a chemical step, perhaps the generation of an initially electrochemically inactive species, of Mo(V), occurs or an ECE mechanism exists.

A possible scheme to explain the Mo(III)-Mo(V) electrochemistry is

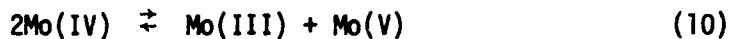


The cyclic voltammetric and ring-disc work tends to support this scheme, since values of $\frac{i_p}{\nu^{1/2}}$ and $\frac{i_d}{\omega^{1/2}}$ are close to 2:1 for low:high sweep rates or rotation rates.

The Mo(III)-Mo(V) chemistry exhibited marked acidity dependence. The overall scheme, involving the measurement of the Mo(III)-Mo(V) potential as the melt acidity was varied, is consistent with



The detailed mechanism, however, is complex and is incomplete at this time. Clearly, Cl^- must be involved in the E.C.E. scheme. The chemical step, given above as $\text{Mo(IV)} \rightleftharpoons \text{Mo'(IV)}$, may be a second order disproportionation - i.e.,



Some experimental data appears to support this conclusion.

The very complex nature of Mo-chemistry is clear. Earlier work indicating that MoO_3 yields either MoO_2Cl_2 appears incorrect(11), although the oxidation of the melt by MoO_3 is slow and may be acid dependent.

It is hoped that the problem of Mo-electrochemistry may be completed in the near future.

During the period of this report several meetings were held with personnel at the Seiler Research Laboratory at the United States Air Force Academy. Discussions were held relating to both the sodium tetrachloroaluminate system and the room temperature ethylpyridinium bromide-aluminum chloride melt. In addition, Lieutenant Charles Hussey spent a week or so working in the laboratory at Colorado State. Numerous telephone contacts were maintained with both Hussey and Colonel Lowell King of the Seiler Laboratory.

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J. Robinson and R. A. Osteryoung, "Acid-Base Chemistry of Chalcogenides in Sodium Tetrachloroaluminate Melts", to be prepared for J. Am. Chem. Soc.

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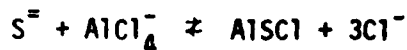
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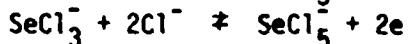
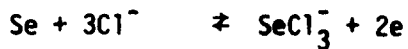
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