Room temperature ionic liquids (RTIL) are a relatively new class of solvents whose unique set of chemical and physical properties hold the promise of making revolutionary changes in many traditional chemical processes. We have previously reported on the redox behavior of uranyl chloride in room temperature acidic 1-ethyl-3-methyl imidazolium chloride by electrochemical and spectroscopic techniques.\(^1\)\(^2\) The uranyl moiety is unstable to oxygen loss in this melt with the concomitant growth of a uranium (V) chloride species. We proposed that an equilibrium is established between the Lewis acidic Al\(_2\)Cl\(_7\) and the uranium oxy-chloride species. Similar behavior may be expected for plutonium oxide species. We have demonstrated that a basic EMIC/AlCl\(_3\) solution of PuCl\(_3\) displays one reversible oxidation and an irreversible reduction. The reversible wave has been confirmed to be associated with the Pu (III)/Pu (IV) redox couple by comparison with the CV of an authentic sample of Cs\(_2\)PuCl\(_6\). The irreversible reduction wave is believed to come from the reduction of a plutonium oxide contaminant. In this talk we will focus on our work on the chemistry of plutonium complexes in room temperature ionic liquids (i.e. EMIC/AlCl\(_3\) and EMIBF\(_4\)).


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Actinide chemistry in RTIL systems (Why?)

Room temperature ionic liquids (RTIL) have potential throughout the nuclear industry in the recovery and purification of actinide elements, as reactor components, as waste disposal forms, and potentially as media for the storage and/or separation of spent nuclear fuels. Due to their unique dissolution properties, RTIL’s can be used as substitutes for solvents currently used in the extraction of uranium from native ores, and in the dissolution and reprocessing of spent nuclear fuels. Potential benefits include greater uranium and plutonium recovery efficiencies and the ability to recycle the solvent, leading to a decrease in waste generation and lower overall production costs. Another potential area of interest is in the use of RTIL’s as solvents for the recovery and purification of actinide elements. Many of the current recovery processes are redox based and are carried out in high temperature molten salt systems. These processes are inefficient, require extreme operating conditions and generate large quantities of contaminated residues. Substituting RTIL’s for the high temperature melts and performing these reactions at ambient temperature would allow for greater control over the reactions, leading to much higher yields and higher final product purity. The development of room temperature, low pressure processes would mitigate the safety concerns associated with high temperature operations. Also the ability to recycle these extremely low vapor pressure solvents would lead to significantly less waste generation. Finally, the unique ability to adjust the acid/base properties of some of the RTIL melts, coupled with the lack of interference from hydrolysis reactions, creates an opportunity to obtain much more detailed information on the fundamental chemical behavior of actinide compounds. This knowledge can be instrumental in the development of the next generation of actinide separation and purification processes.

Research efforts in our laboratory focus on determining the chemical properties (i.e. solubilities, complexation, redox properties, etc) of actinide species in RTIL systems. We are currently involved in RTIL projects ranging from the spectroscopic characterization of actinide complexes by O\textsuperscript{17}NMR, low temperature UV-Vis, and EXAFS, to the enhanced dissolution and separation of actinide oxides in room temperature ionic liquids. Further, we have experience in the electrochemical characterization of actinide complexes in ionic melts. Ultimately we would like to be able to compare the chemistries observed in the RTIL systems with the high temperature molten salt systems.
currently in use in the actinide recovery and purification processes. The results of our study will allow us to evaluate the potential of RTIL systems as alternative solvents in the nuclear industry.

II. Background

A. Actinides in RTILs

Published studies of actinide systems in room temperature ionic liquid (RTIL) solvent systems have been limited to neptunium (1) and uranium (2),(3). In basic melts the reduction of U (IV) to U (III) was found to be reversible and U (IV) and U (III) were determined to be present as the hexachloro anions over the entire basic range (4). In acidic AlCl3-BPC, U (IV) is stable over the entire acidic range, existing as UCl3+, UCl22+, and UCl32+, with increasing acidity (i.e., decreasing Cl- concentration). Similar studies have shown that U(V) is stable in all acidic compositions (4). The spectrum of U (V) in an acidic melt is similar to that recorded in SOC12(5) and nitromethane (6). Uranyl (VI) is stable in basic AlCl3-BPC and AlCl3-EMIC forming chloro-complexes of the type UO2Cl4+x(2+x)- which are irreversibly reduced to UCl62-. U (VI) introduced as UO3 to the acidic high temperature ionic liquid AlCl3-NaCl reacted to give U (V)(7).

The U(IV)/U(III) couple exhibits reversible electrochemistry in basic AlCl3-EMIC melts. Potentiometric measurements for this couple as a function of Cl- concentration suggest that both species are present as the hexachloro anions (8). This behavior differs from that of the closely related element neptunium as, for solutions greater than 57 mol % AlCl3, Np(III) was found to be the only stable species (9). In basic melts U(V) is reduced by “free” chloride to U(IV)(10). Uranyl (UO22+) was found to be stable in basic AlCl3-BPC (11) and AlCl3-EMIC (12) forming chloro-complexes of the type UO2Cl4-x(2+x)- which were reduced irreversibly at the electrode to UCl62-.

The recent patent applications (13) (14) for the dissolution of UO3 as uranyl in RTIL systems, as an alternative to the Purex process, have heightened our interest into the chemistry of these systems. The limited data available on the stability of uranyl in acidic RTIL systems prompted our spectroscopic and electrochemical study of UO22+ in acidic AlCl3-EMIC (15) (16). In this work we demonstrated that in acidic AlCl3-EMIC ionic liquids the uranyl moiety is reduced over several days to a U(V) non-oxo species. We proposed a mechanism based on both acid-base and redox reactions between the melt components and the uranium species. This mechanism involves the formation and subsequent reaction of transitory uranium oxy-chloride complexes. In the present paper, we will present further evidence in support of our uranium mechanism and extend this work to include the spectroscopy of uranyl in low temperature glasses and our initial investigations into the electrochemistry of plutonium in the EMIC/AlCl3 RTILs.

B. Chemistry and Electrochemistry of Plutonium

i. Equilibria. A full review of this chemistry is well beyond the scope of this paper, but the interested reader is referred to the Plutonium Handbook (17) and references therein for further detail. The solution chemistry of plutonium is very complex and
unique among the elements. Due to the interplay between thermodynamic and kinetic drivers, plutonium can coexist in appreciable concentrations in each of its four oxidation states, Pu$^{3+}$, Pu$^{4+}$, PuO$^{2+}$, and PuO$_2^{2+}$, within a single solution.

Both Pu(IV) and Pu(V) complexes have a thermodynamic tendency to disproportionate and the kinetics of breaking the Pu-O bond are much slower than reactions involving electron transfers. The disproportionation reaction and associated equilibrium equations of Pu(IV) is shown below:

$$3\text{Pu}^{4+} + 2\text{H}_2\text{O} \leftrightarrow 2\text{Pu}^{3+} + \text{PuO}_2^{2+} + 4\text{H}^+$$

$$K = \frac{[\text{Pu(III)}]^2[\text{Pu(VI)}][\text{H}^+]^4}{[\text{Pu}^{4+}]^3}$$

The value of $K$ in both 1M perchloric and hydrochloric acid has been reported by Rabineau and Cowan (18) to be near 0.0089. In 0.002M HCl this equilibrium is established after 200 hr with the relative concentrations of Pu$^{3+}$, Pu$^{4+}$, PuO$^{2+}$, and PuO$_2^{2+}$ being 26.3%, 62.7%, 0.5%, and 10.5%, respectively. Although this equilibrium is effected by the stabilization of Pu (IV) through complexation, it generally holds that the more acidic the solution the less the extent of the disproportionation. Pu(V) has also been shown to disproportionate into Pu(VI) and Pu(III) with the overall rate being directly proportional to the hydrogen ion concentration. The dependence of both of these disproportionation mechanisms on [H$^+$] would seem to indicate that Pu(IV) and Pu(V) should be very stable in the aprotic RTIL systems.

ii. Redox Chemistry. All of the aqueous schemes currently in use for the purification of plutonium rely on the selective extraction of Pu in various oxidation states from solution. Methods for the control of both uranium and plutonium oxidation states have therefore received considerable attention (17 above). It is apparent, as expected, that the energy associated with the making and breaking of the metal-oxo bonds plays a very important role in the redox chemistry of these species. Thus, the reduction of Pu(VI) and Pu(V) to the non-oxo Pu(IV) and Pu(III) are slow while electron transfers between these pairs are expected to be facile.

iii. Complexation. Complexation chemistry is more important in plutonium chemistry than in either uranium or neptunium chemistry due to its smaller ionic radius. The complex forming order for Pu is

$$\text{Pu}^{4+} > \text{Pu}^{3+} > \text{PuO}_2^{2+} > \text{PuO}_2^+$$

Spectroscopic techniques provide a valuable insight into the complexation chemistry of the actinides. For example, the absorption spectra of Pu(VI) shows a distinct absorbance at 830 nm in HNO$_3$ but no absorbance at this wavelength in nitromethane. The obvious differences in these spectra have been ascribed to the different symmetries of the ligand fields (see reference 17 above).
iv. High Temperature Molten Salt Chemistry. To data most of the work in high
temperature systems has focused on uranium. There have been several studies of Pu in
chloride based melts (ie. LiCl-CsCl, LiCl-KCl) and the absorption spectra recorded in
these melts are a good starting point for the determination of oxidation states (17 above).
Several studies have been performed to determine the phase equilibria of plutonium-
alkali/alkali earth salt systems. These studies have shown the presence of relatively low-
melting point eutectics in nearly all systems. The importance of selective extraction of
actinides from aqueous systems cannot be overestimated. Extraction schemes are limited
in high temperature melts due to the fragility of the organic extractants. One system of
note is the LiCl-KCl-AlCl3 ternary melt, which forms two phases from 350-775°C. The
upper phase consists mainly of KAlCl4 and has a 40 fold greater extraction coefficient for
U(IV) over Pu(III).

III. EXPERIMENTAL

EMIC was prepared by the method of Smith(19). AlCl3 (Aldrich) was purified by
sublimation. All uranium synthesis and electrochemical experiments were performed
inside a Vacuum Atmospheres Co. drybox under a He atmosphere. Pu experiments were
conducted under argon in specially designed negative pressure inert glove boxes.

Electrochemical experiments were performed on a BAS CV-50 and PAR 273A
electrochemical analyzers in a three-electrode cell. The current carrying electrodes in this
system consisted of a 3mm diameter glassy carbon working electrode (Bioanalytical
Systems), and a 0.5mm Pt wire spiral auxiliary electrode. The reference electrode was a
1mm diameter Al wire immersed in a 40/60 basic melt and separated from the working
electrode by a medium porosity glass frit. Absorption spectra were recorded on a Perkin
Elmer Lambda 19 spectrometer. Fluorescence measurements were taken on a Specs
Industries Fluorolog II with the cell maintained under a blanket of liquid nitrogen
throughout the experiment.

RESULTS AND DISCUSSION.

A. Validation of UO22+ reaction scheme.

In previous publications we have demonstrated that in an acidic AlCl3-EMIC ionic
liquid the uranyl moiety is reduced by the inorganic constituents of the RTIL over several
days, or through a combination of heterogeneous electrochemistry and melt chemistry in
several minutes, to a U(V) non-oxo species (15 above). In figure 2 we present
multicyclic voltammograms of uranyl chloride in an acidic EMIC/AlCl3 ionic liquid.
Note the rapid change that occurs in the uranium chemistry after several polarization
cycles. We proposed a mechanism (figure 3), based upon electrochemical and
spectroscopic investigations, to explain both the hetero- and homogeneous reactions. This
reaction scheme invokes both acid-base and redox reactions between the melt
components and the uranium species, and involves the formation and subsequent reaction
of transitory uranium oxy-chloride complexes. Examples of shifts in redox potentials of metal complexes with changes in the ligand environment are ubiquitous in organometallic chemistry. Addition of one dinegative oxygen to UO$_2^{2+}$ should result in a negative shift in the reduction potential; addition of a second oxygen is expected to result in a further negative shift. Analysis of the UO$_2^{2+}$ voltammetry in this light, and in comparison to that of pristine UCl$_4$, has led to the assignment of the redox potentials for the UO$_2$Cl$_2$ voltammogram. In this talk we will further develop this mechanism through the presentation of corroborating electrochemical and spectroscopic detail.

Several tests of our proposed scheme are readily apparent. We assume, from our previous work, that the final resting state for the product of the reaction between uranyl and the acidic melt is the non-oxo uranium (V), and that this outcome is not in question.

1. **Scan Rate and Switching potential.** Figures 4 & 5 present the effects of changes in switching potential and scan rate on the electrochemistry of this system. These experiments focus only on the potential window from 2.3V – 1.4V. Three redox couples are present in this region for uranium (UO$_2^{2+/1+}$, UO$_4^{+/3+}$, U$_4^{+/3+}$). Note that, as predicted, scans run under a faster scan rate show less electrochemical degradation of the uranium-oxo species to the non-oxo species than those run at slower scan rates. Further, if the direction of the scan is reversed prior to the second wave (UO$_2^{2+}$/UO$_2^{+}$) much less degradation is observed. These observations are in line with our scheme that calls for the rapid oxygen transfer from the di-oxo uranium (V) species to the melt.

2. **UO$_2^{2+}$ vs UOCl$_5$.** Based on our proposed scheme, the first intermediate formed would be the result of an acid/base reaction between the melt and the uranyl moiety resulting in the transfer of an oxygen from the uranium to the melt. This would result in a uranium mono-oxo intermediate. The conclusion is supported by figures 6 which shows a comparison between the electrochemistry of UO$_2^{2+}$ and an authentic sample of UOCl$_5$. The CV of the authentic mono-oxo uranium species appears to be growing in with time from the starting uranyl.

3. **UO$_2^{2+}$/U(IV) - ECE mechanism**
   The ECE mechanism is of great importance in the study of coupled chemical reactions. In general, these reactions can be represented as:
   \[
   A + e^- \leftrightarrow B \rightarrow C \rightarrow D
   \]
   If the product C is more easily reduced than A then the reaction will proceed spontaneously to D following the first reduction. The theory of ECE mechanism was first elaborated by Nicholson and Shain (20) (21). If a system is coupled in this way, then at short times the principle current observed is related to the reduction of A to B by $n_1$ electrons, while at longer times (ie. slower sweep rates) the current represents the reduction of A to D by $n_1 + n_2$ electrons. The Nicholson treatment has been applied to the first reduction wave seen in the cyclic voltammogram of uranyl. In figure 7 a plot of $I_{pc}/\sqrt{v}$ vs log $v$ is reported$^1$. The shape of this curve fits very well with that reported by

$^1$ Note: $I_{pc} = 2.69 \times 10^5 n^{3/2} AD^{1/2} C_v^{1/2}$
Nicholson for the theoretical shape for an ECE mechanism. Further, a plot of $I_{pc}$ vs $\sqrt{v}$ (figure 7) shows two linear regions indicating two distinct scan rate dependent processes. At fast scan rates this plot indicates that a one electron process is involved. At slow scan rates it appears that the slope of the curve doubles, indicating a process having two coupled 1 electron transfers.

B. Low Temperature Spectroscopy.
A report that EMIC/AlCl$_3$ forms low temperature glasses in both acidic and basic melts prompted our investigations into the possible use of this solvent system for luminescence studies (22). Our initial investigations focused on the much studied UO$_2$Cl$_2^-$ ion. We were able to prepare glasses of moderate optical clarity in 1 cm cuvettes at liquid nitrogen temperature. Under these conditions we observed highly resolved uranyl luminescence, remarkably similar to the emission reported from low temperature single crystals of various UO$_2$Cl$_4^-$ salts (23) or UO$_2$Cl$_2^-$ doped into cubic crystals (24). The electronic transition is electric dipole forbidden and is vibronically enabled through coupling to ungerade vibrations. We observed linewidths that are significantly wider than those reported for single crystals at 77K (24), indicating that inhomogeneous line broadening may be important in our solvent system. We deconvolved the emission spectrum (figure 8) to obtain ground state vibrational frequencies. The values that we obtained are in good agreement with the low temperature crystal data as shown in the Table below.

<table>
<thead>
<tr>
<th>VIBRATIONAL FREQUENCIES (cm$^{-1}$) DERIVED FROM EMISSION STUDIES</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>$\nu_{10}$</td>
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a) Unrestricted Gaussian fits, using unweighted averages for vibrational intervals  
b) Restricted Gaussian fits  
c) Room temperature Raman

We measured an emission lifetime of nearly 2 milliseconds, about the same as in low temperature crystals. This indicates that energy transfer processes involving the solvent are relatively inefficient and provides encouragement for further luminescence studies of other actinide species in this medium.

C. Plutonium Studies.
As mentioned in the introduction, one of the drivers for our work is the goal of developing new process schemes for the purification of actinides and actinide waste
forms. In figure 9 we present the cyclic voltammograms of PuCl$_3$ and Cs$_2$PuCl$_6$ in a basic AlCl$_3$/EMIC ionic liquid. Clearly, we are observing the pseudo-reversible Pu$^{4+/3+}$ couple ($E^0 = 0.37V$). In the PuCl$_3$ CV we also observe a second irreversible wave at $E_p = -0.35V$. We believed that this peak could be the result of an incipient Pu-oxo species in out PuCl$_3$.

PuO$_2$Cl$_x$ was synthesized by the bulk electrolysis of PuCl$_3$ in 1M HCl and have confirmed its characterization through UV-Vis spectroscopy in both HCl and HNO$_3$. The cyclic voltammogram of this species in basic AlCl$_3$/EMIC is shown in figure 10. Notice that this voltammogram looks very much like that shown for the PuCl$_3$ in the basic melt. On repeated scans the irreversible wave disappears (Figure 11) and there is a growth in the first wave. The growth in the first wave does not appear to be concommitant with the loss of the more anodic wave and is attributed to a kinetically slow ECE mechanism.

We have also examined the electrochemistry of PuO$_2$Cl$_2$ in an acidic AlCl$_3$/EMIC RTIL. The cyclic voltammetry of this system is shown in figure 12. This result is similar to that obtained for uranyl in this melt. The plutonyl quickly looses its oxygens to the melt and forms an insoluble precipitate, presumably Pu (IV).

In figure 13 we show all of the possible pathways for the chemical and electrochemical reactions of PuO$_2$Cl$_2$ in the basic melt. Although our data to date is rather scant we have been able to rule out several of the available pathways, as shown in the figure. Admittedly, this scheme must be approached as speculative given out current data set. However, we can make a few statements in support. Our current understanding of the chemistry of Pu in the AlCl$_3$/EMIC system and the basis for our proposed mechanism are summarized below:

1) The scheme presents all of the possible pathways for the reaction of PuO$_2^{2+}$ in the melt.
2) We have confirmed by UV-Vis that that starting product, at least in aqueous media, is PuO$_2^{2+}$
3) From our voltammetry on the non-oxo Pu$_{3+/4+}$ couple, we can rule out any stable non-oxo products above the +4 oxidation state
4) We have shown experimentally that PuO$_2$ has negligible solubility in this melt.
5) Both IpV$^{1/2}$ and Chronocoulometry suggests that there are at least two processes underway at $E = .35V$, suggesting the presence of multiple species at this potential.
6) Neither Pu$_3+$ or Pu$_4+$ have any solubility in acidic AlCl$_3$/EMIC
7) PuO$_2$Cl$_2$ has an irreversible redox couple in the acidic system and all activity dissappears within several minutes with the formation of an insoluble precipitate.

Figure 2. Multicyclic and single scan voltammograms of uranyl chloride ($\text{UO}_2\text{Cl}_x$) in a 55/45 acidic aluminium chloride/1-ethyl-3-methyl imidazolium chloride RTIL.
Figure 3. Overall scheme for the reaction of uranyl chloride in acidic RTIL.
Figure 4. Effect of scan rate on the voltammogram of $\text{UO}_2^{2+}$
The scan rates shown are 5, 10 and 50 mV/s.
Figure 5. Effect of changes in switching potential on the UO$_{3+}$/$4^+$ & U$_{4+}$/$5^+$ couples. (A) $\nu_2 = 1350$ mV; (B) $\nu_2 = 1100$ mV. I = UO$_{3+} \rightarrow$ UO$_{4+}$; II = U$_{4+} \rightarrow$ U$_{3+}$. 
Figure 6. UO$_2^{2+}$ vs. UOCl$_5^-$ in Acidic EMIC-AlCl$_3$

A = UO$_2^{2+}$; B = Pristine UOCl$_5^-$
\[ I_{pc} = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \]

Figure 7. Nicholson treatment of ECE mechanism
Figure 8. $\text{UO}_2\text{Cl}_4^{2-}$ Emission Spectrum in EMIC/AlCl$_3$ Glass at 77K

- Experimental Data
- Gaussian Fits to the Data

$v_1$ progression on $0-0$
$v_1$ progression on $v_{10}$
$v_1$ progression on $v_3$
$v_1$ progression on $v_2$
Figure 9. Pu(III) and Pu(IV) in a 45/55 basic AlCl₃/EMIC RTIL
Figure 10. Cyclic Voltammogram of PuO$_2$Cl$_x$ in 45/55 Basic EMIC/AlCl$_3$
Figure 11. Cyclic voltammetry of PuO$_2^{2+}$ in basic ALCl$_3$/EMIC RTIL. (A) Full scan (B) Highlight 1st wave.
Figure 12. Cyclic voltammetry of PuO$_2^{2+}$ in 55/45 acidic AlCl$_3$/EMIC RTIL.
(A) $t=0$ min. (B) $t=5$min.
Figure 13. Possible reaction pathways for PuO$_2^{2+}$ in AlCl$_3$/EMIC RTIL
PuO$_2$ in 4555 melt

Scatter plot with delta E on the y-axis and Scan Rate on the x-axis.
Square wave voltammetry of PuO\textsuperscript{2+}

- Voltage range: -5.00 to 75.00 mV
- Current range: -5.00 to 35.00 μA
- E (mV) values: 750.0, 650.0, 550.0, 450.0, 350.0, 250.0, 150.0, 50.0

Graph showing the relationship between voltage (E) and current (I) for PuO\textsuperscript{2+}.
Normal pulse voltammetry of PuO22+

- I (µA)
- E (mV)

150.00
130.00
110.00
90.00
70.00
50.00
30.00
10.00
-10.00
1000.0 600.0 200.0 -200.0 -600.0 -1000.0 -1400.0
Note to reviewer:
The following overheads may be included in the talk along with those figures specifically included in the paper.

-DC
Time Evolved Absorption Spectra of $\text{UO}_2\text{Cl}_2$ in Acidic EMIC/$\text{AlCl}_3$
Relative Uranium Potentials

Acidic EMIC/AICl₃ RTIL

1M HClO₄

LiCl/KCl at 450°C

1M HClO₄

Potential vs. U⁴⁺/U³⁺

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Vibrational Modes of $\text{UO}_2\text{Cl}_4^{2-}$ ($D_{4h}$)

- $v_1 A_{1u}$
  - 831 cm$^{-1}$

- $v_2 A_{2u}$
  - 916 cm$^{-1}$

- $v_3 E_u$
  - 252 cm$^{-1}$

- $v_4 A_{1g}$
  - 264 cm$^{-1}$

- $v_5 B_{2g}$
  - 230 cm$^{-1}$

- $v_6 E_u$
  - 238 cm$^{-1}$

- $v_7 B_{1g}$
  - 131 cm$^{-1}$

- $v_8 E_u$
  - 112 cm$^{-1}$

- $v_9 A_{2u}$
  - 112 cm$^{-1}$

- $v_{10} B_{1u}$
  - 91 cm$^{-1}$

- $v_{11} E_g$
  - 200 cm$^{-1}$

One - vs Two-Photon Absorption: complementary techniques

- Electronic transitions are electric-dipole forbidden in OPA
- In OPA, the vibrational structure arises from both ungerade and gerade modes

- Electronic transitions are electric-dipole allowed in TPA
- In TPA, the vibrational structure arises from gerade modes
Two Photon Spectroscopy of UO$_2$Cl$_2$ at 77K

UO$_2$Cl$_4^{2-}$ in AlCl$_3$/EMIC (77K)

- One Photon Excitation
- Two Photon Excitation
Fit of Uranium EXAFS Scattering for EMIC Melts

U(IV): Single chlorine shell at 2.60 Å, n=7.05

U(VI): Uranyl oxygens at 1.75 Å, n=2
Chlorine shell at 2.66 Å, n=2.66

- U(IV) data were obtained from both acidic and basic melts. There was no difference between the structural parameters from acidic and basic melts.
- An Al shell was not seen in the EXAFS data, however the data could not rule out complexation by AlCl₄⁻. The small scattering cross section of Al combined with the large distance for an Al shell results in a weak contribution to the EXAFS from Al. Data with higher S/N ratio extending to higher k would detect an Al shell.

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Oxidation States Determined from Xanes Edge

Desired XANES Edge Positions of the Series of Uranium Oxidation States Available in Room Temperature Ionic Liquids, Especially the V Oxidation State without the Uranyl Oxygens

- Seven samples sent to SSRL for XAS studies: 2 U(III), 3 U(V), and 2 U(VI)
- XANES edge energies and the distance of chlorine shells from the EXAFS suggest that the U(III) samples were oxidized to U(IV) and the U(V) samples were reduced to U(IV). Absorption spectroscopy verified these observations.
- Need to modify existing XAS sample holders to be inert to this media.

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Cyclic Voltammogram of $\text{UO}_2^{2+}$ in an Acidic Melt

Potential (Volts vs. Al$^0$)

Current (Amps)

$\text{UO}_2^{2+}/\text{UO}_2^{1+}$

$\text{UO}_3^{3+}/\text{UO}_2^{2+}$

$\text{U}_4^{4+}/\text{U}_3^{3+}$

$\text{U}_5^{5+}/\text{U}_4^{4+}$

$\text{U}_6^{6+}/\text{U}_5^{5+}$

First scan

Final scan