METAL ELECTRODEPOSITION AND ELECTRON TRANSFER STUDIES OF URANIUM COMPOUNDS IN ROOM TEMPERATURE IONIC LIQUIDS

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ABSTRACT

The cyclic voltammetric and bulk coulometric behavior for several uranium complexes in room temperature ionic liquids is described. The ionic liquids are based on 1,3-dialkylimidazolium or quaternary ammonium cations and \( \text{N(SO}_2\text{CF}_3\text{)}_2 \) anions. For \([\text{UCl}_6]^2-\) both the \(\text{U(IV)/U(V)}\) and \(\text{U(IV)/U(III)}\) couples were studied and show full chemical reversibility at slow sweep rates. At faster sweep rates the \(\text{U(IV)/U(III)}\) reduction shows evidence for slower electron transfer. Anodic bulk coulometry allowed quantitative production of \([\text{U(V)Cl}_6]^2-\) in solution without decomposition. Details concerning the anodic and cathodic voltammetry of the organometallic complex \((\text{i-prCp})_3\text{UCl}\) are covered. The electrochemistry of the two uranyl complexes \([\text{UO}_2\text{Cl}_4]^2-\) and \(\text{UO}_2(\text{saldiene})\) have been studied in the \(\text{N(SO}_2\text{CF}_3\text{)}_2\) based ionic liquids and show chemically irreversible and chemically reversible behavior, respectively. Qualitative voltammetric data concerning the electrochemical plating and stripping of Na, K, Li and Al ions from the ionic liquid solutions are presented.

INTRODUCTION

Room temperature ionic liquids (RTIL's) comprised of 1,3-dialkylimidazolium or quaternary ammonium cations and one of several anions such as \(\text{PF}_6^-\), \(\text{BF}_4^-\), or \(\text{N(SO}_2\text{CF}_3)_2\), represent a class of solvents that possess great potential for use in applications employing electrochemical procedures (1). Part of the intrigue with RTIL’s stems from some of their inherent solvent properties including negligible vapor pressure, good conductivity, high chemical and thermal stability, and non-flammability. Additionally, a substantial number of RTIL’s can be envisioned simply by combining different cation and anion pairs, thereby making them attractive for specific application needs. We are interested in learning more about the possible use of RTIL’s within the nuclear industry. In this regard our research team has been exploring the electron transfer behavior of simple metal ions in addition to coordination and organometallic complexes in these novel solvents. We are concentrating our efforts on the interactions between electrogenerated odd-electron species and the anionic and cationic constituents of the RTIL’s. Due to the inherent ionic nature of these solvents they may have the ability to stabilize odd-electron compounds that are labile in conventional organic solvents and
chloroaluminate ionic liquids. Information in this regard would be pertinent to researchers looking for alternative electrochemical solvent systems in which to study interesting electrode reaction mechanisms. Although it will not be discussed in the current manuscript to any great extent, results from our research have already provided us with insight into the bonding interactions between our current anion of choice, bis(trifluoromethylsulfonyl)imide = NTf₂, and open coordination sites on actinide and transition metal fragments (2). Initial results from NTf₂ ligated metal fragments show measurable changes in the electronic environment about the metal center, which may help facilitate electrochemical reduction of metal ions from RTIL solutions.

EXPERIMENTAL

The room temperature ionic liquids used for these studies were prepared in our laboratory following previously published literature procedures (3). All experimental work was performed in an inert atmosphere (helium) Vacuum Atmospheres Company glovebox with continuous oxygen and moisture monitoring. Electrochemical experiments were conducted with a PAR 273A potentiostat controlled with a Windows PC running CorrWare from Scribner Associates Inc. A conventional three-electrode configuration consisting of a coiled platinum wire auxiliary, bare silver wire pseudo-reference, and various working electrodes was employed. The platinum (1 mm), glassy carbon (1.5 mm), and gold (1 mm) disk working electrodes were from Cypress Systems. The working electrodes were polished with 1 μm and 0.05 μm alumina slurries from Buehler LTD and rinsed with copious amounts of nanopure water before each experiment. During the electroplating experiments the reference electrode was placed in a separate compartment isolated from the bulk solution by a fine glass frit.

UO₂(saldiene) was prepared according to the literature procedure by reacting N,N'-bis(salicylidene)-1,5-diamino-3-azapentane (H₂saldiene) with UO₂(CH₃CO₂)₂ in EtOH solvent and recrystallized from MeCN to give the solvent free complex (4). [UO₂Cl₂][EMI]₂ and [UCl₆][EMI]₂ were prepared from reactions of UO₂Cl₂(THF)₃(5) and UCl₄ in tetrahydrofuran (thf) solvent with two equivalents of [EMI]Cl, where EMI = 1,3-ethylmethylimidazolium. The organometallic complex (isopropylC₆)₃UCI was prepared by reacting UCl₄ with sodiumisopropylcyclopentadienide in THF solvent followed by subsequent isolation and purification.

Solutions of metal ions used for electrodeposition studies were prepared by reacting the appropriate metal hydride (NaH, KH, LiH), or in the case of aluminum (AlMe₃), with H[N(SO₂CF₃)₂] directly in the electrochemical cell containing the RTIL. The H[N(SO₂CF₃)₂] was sublimed under vacuum with minimal heating and stored in the drybox to eliminate the possibility of moisture contact as the material is very hygroscopic. An excess of the metal hydride or (AlMe₃)₂ was routinely employed to act as an internal drying agent for any trace moisture that may have entered the electrochemical cell and solution.
RESULTS AND DISCUSSION

The electrochemical behavior of uranium(IV) chlorides has been invested in various solvent systems including basic and acidic chloroaluminate ionic liquids (6), high-temperature molten salts (7) and conventional organic solvent/supporting electrolyte media (8). Many of these reports have focused on the electrodeposition of uranium metal and the associated U(III)/U(0) couple. Some reports contain information on the preceding U(IV)/U(III) process, with even less discussion focused on the U(IV)/U(V) couple. We are interested in the electron transfer behavior of U(IV) chloride complexes in RTIL’s to probe the influence of the solvent medium on the fate of the electrochemically generated species. Voltammetry (cyclic, square wave) and bulk electrolysis were employed to study [UCl₆][EMI]₂ in the RTIL [EMI][NTf₂] at several working electrode surfaces (Au, Pt, glassy carbon GC) and the preliminary results follow.

Figure 1 shows cyclic voltammograms (CV’s) obtained at slow (bottom) and moderate (top) scan rates for [UCl₆][EMI]₂ at a glassy carbon working electrode. The CV’s at 0.05 V/s show full chemical reversibility for the U(IV)/U(III) (E₁/₂ = -0.982 V vs Ag wire) and U(IV)/U(V) (E₁/₂ = 1.077 V vs Ag wire) couples as evidenced from i_{peak}/i_{fwd} values of unity. As the scan rate is increased the peak separation (ΔEₚ) for both couples increases, but that for the U(IV)/U(III) reduction process increases to a greater extent: 156 mV vs 93 mV for U(IV)/U(V) oxidation (9). There is also a difference in the magnitude of the peak currents for the U(IV)/U(III) couple compared to the U(IV)/U(V) couple due to an increase in the peak breadth, which is readily apparent in Figure 1. These observations are an indication of slower electron-transfer kinetics for the reduction process (quasi-reversibility) when compared to the oxidation, which may be indicative of a structural change during the reduction and/or a more substantial solvent reorganizational energy barrier. Results from an oxidative exhaustive bulk electrolysis confirm the one-electron nature of the process as the coulometry of the conversion was 94% efficient for one electron. The solution color changed from pale blue to yellow as the electrolysis progressed, which is consistent with previous reports concerning the color of [U(V)Cl₆]⁻ monoanion (10). The electrolysis results also indicate that the electrogenerated U(V) species is stable on the extended time scale of the experiment since a quantitative back electrolysis to the U(IV) starting material was accomplished. The identity of the U(V) in solution was confirmed from stirred-solution voltammograms displaying nearly full cathodic current. Future studies will focus on coupling visible spectroscopy with bulk electrolysis experiments and more extensive voltammetric analysis of the U(IV)/U(III) couple.
Continuing with the electron transfer chemistry of U(IV) complexes, (i-PrCp)$_3$UCl was studied as a model organometallic actinide compound. Several studies have appeared in the literature concerning the electrochemical behavior of (RCp)$_3$UCI complexes in thf solvent (11). The pertinent results from these previous studies include an uncomplicated U(IV)/U(III) reduction process to give [(RCp)$_3$UCI]$^-$ as a stable isolable species, and an oxidation process displaying limited chemical reversibility of the U(IV)/U(V) couple due to the instability of the electrogenerated [(RCp)$_3$UCI]$^+$ monocation. Studies in our laboratory with MeCN solvent and [(C$_4$H$_9$)$_4$N][PF$_6$] supporting electrolyte display the same general voltammetric behavior as reported for thf solvent studies. The voltammetric behavior of (i-PrCp)$_3$UCI in the RTIL [EMI][NTf$_2$] is shown in Figure 2.

![Cyclic voltammograms of [UCl$_6$][EMI]$_2$ in [EMI][NTf$_2$] at (bottom) 0.05 V/s and (top) 1.0 V/s. The working electrode was a 1.5 mm glassy carbon disk for all voltammograms and the potential scale is referenced to Ag wire.](image-url)
Potential (V)

Figure 2. Cyclic voltammogram of (i-prCp)₃UCl in [EMI][NTf₂] at 0.1 V/s and a 2 mm Pt disk working electrode versus Ag wire reference electrode.

The main difference between the CV's presented in [EMI][NTf₂] and those obtained in thf or MeCN solvent is the stability of the electrogenerated U(V) species [(RCp)₃UCl]⁺ in the RTIL, which is clearly identified from the chemically reversible U(IV)/U(V) couple. The E½ values for the two redox reactions of (i-PrCp)₃UCl are -1.682 V vs Fc/Fc⁺ for the reduction and 0.236 V vs Fc/Fc⁺ for the oxidation. These values are similar to those reported in thf for other (RCp)₃UCl compounds (11a). The only notable difference is a slightly more positive reduction potential in the RTIL by approximately 200 mV. At higher scan rates the appearance of the two electrode reactions remain electrochemically reversible with ΔEₚ values of ca. 75 mV and peak breadth values (Eₚ - Eₚ/2) of ca. 62 mV at 2 V/s. Chronoamperometry data and the Cottrell equation allowed the calculation of a diffusion coefficient for (i-PrCp)₃UCl of 2.25 x 10⁻⁷ cm²/s. This is almost two orders of magnitude lower than diffusion coefficients determined for (RCp)₃UCl complexes in organic solvents. Further electrochemical studies are planned to investigate the stability of the electrode products on longer time scales than that of the voltammetry experiments.

Coordination complexes containing the uranyl fragment, [U(VI)O₂]²⁺, have been the center of spectroscopic and electrochemical investigations for decades (12). We are interested in the redox properties of uranyl complexes in non-aqueous media to learn more about the consequence of electron transfer on the central [UO₂]²⁻ fragment in these molecules. We were hopeful that studies of uranyl complexes in RTIL's would help to stabilize the electrogenerated U(V) species, which are notorious for decomposition through disproportionation reactions. The lack of stability for [U(V)O₂]⁺ complexes has limited the number of detailed structural investigations. The first uranyl system studied in our work was [UO₂Cl₂][EMI]₂. Representative voltammograms obtained in [EMI][NTf₂] and [BMP][NTf₂], where BMP = N,N'-butylmethylpyrrolidinium, are shown in Figure 3. The BMP based RTIL allows more negative potentials to be reached before solvent
reduction. The first reduction process, Figure 3 (bottom), is chemically irreversible at low scan rates with $E_p = -0.648$ V vs Ag wire. As the scan rate is increased a small anodic return peak appears at ca. 3 V/s, but the couple is best classified as irreversible in both RTIL solvents. There are no additional electrode reactions observed at more negative potentials past the initial reduction process in the EMI based RTIL. With the BMP based RTIL, Figure 3 (top), a second reduction process is achieved at $E_p = -2.078$ V vs Ag wire. The peak current for this reduction process is six times larger than the first reduction at low sweep rates, but at the present time we are uncertain as to the origin of this second reduction. The voltammetric behavior of $[\text{UO}_2\text{Cl}_4]\text{[EMI]}_2$ in these NTf$_2$ RTIL’s is similar to behavior observed in other electrochemical solvent media. The nature of the first reduction, including the number of electrons transferred and the products formed, is currently under investigation.

Due to the instability of the electrode product from the reduction of $[\text{UO}_2\text{Cl}_4]\text{[EMI]}_2$, we turned our attention to a system that had a larger probability of yielding a stable $[\text{U(V)}\text{O}_2]^{2+}$ compound thus allowing a more detailed study. There have been several reports in the literature in recent years concerning the stabilization of uranyl compounds in non-aqueous media with uranium in the formal +5 oxidation state (13). The authors of these reports have found that the ligands surrounding the metal center can have a profound influence on the $E_{1/2}$ potential of the U(VI)/U(V) couple and the stability of the resulting U(V) uranyl compound. This is similar to the situation that develops in aqueous media (14). We chose to study a uranyl system coordinated by a pentadentate $N_3O_2$ ligand, $N,N'$-Bissalicylidene-1,5-diamino-3-azapentane (saldieneH$_2$), shown in Figure 4. This ligand can be complexed to the $[\text{UO}_2]^{2+}$ fragment to form a seven-coordinate molecule with the absence of any solvento coordination. Voltammetric studies for the reduction of $\text{UO}_2$(saldiene) in $\text{[EMI]}[\text{NTf}_2]$ show a chemically and electrochemically reversible U(VI)/U(V) couple, Figure 5. A bulk electrolysis study confirmed the one-electron nature of the reduction process and revealed that the electrogenerated $[\text{U(V)}\text{O}_2(\text{saldiene})]^{+}$ is stable over an extended time period (ca. 3 hours) in the RTIL. Additional voltammetric studies in MeCN solvent with a conventional supporting electrolyte [(C$_4$H$_9$)$_4$N][PF$_6$] and with the RTIL [EMI][NTf$_2$] as supporting electrolyte yield chemically reversible behavior for the U(VI)/U(V) couple. This indicates that the stability of the $[\text{U(V)}\text{O}_2(\text{saldiene})]^{+}$ compound arises from the saldiene ligand coordination, as we originally assumed, and not from a stabilizing influence of the RTIL medium. The long-term stability of the $[\text{U(V)}\text{O}_2(\text{saldiene})]^{+}$ compound will allow UV/Vis and IR spectroscopic studies aimed at comparing structural differences between the U(VI) and U(V) derivatives.
Figure 3. Cyclic voltammograms of [UO₂Cl₄][EMI]₂ in (bottom) [EMI][NTf₂] and (top) [BMP][NTf₂] both at 0.1 V/s, 1.5 mm glassy carbon disk versus Ag wire reference.

Figure 4. Structure of saldieneH₂ ligand.
One of the possible applications for RTIL solvents in the actinide field could be as an electrochemical medium for the separation of actinide elements by taking advantage of the difference in reduction potentials for each actinide species. The methodology here would be similar to research that has been conducted for processes in high-temperature molten salt solvents (15). While there is a large amount of work that needs to be accomplished before such a process can be envisioned with RTIL solvents, the basis of such a process demands that the fundamental electrodeposition behavior for the actinide elements from RTIL solutions be determined. Additionally we have learned that NTf\textsubscript{2} coordination to a metal center can lower the reduction potential (more positive) for certain metal fragments (2). Exploitation of this finding may allow “bare” metal atoms to be produced in RTIL solutions supported solely by the weakly coordinating NTf\textsubscript{2} anion. It is with these findings in mind that we began investigations into the feasibility of electrodepositing actinide metals, specifically uranium, from RTIL solutions with extended cathodic windows. Our RTIL of choice for these electrodeposition studies has been [([i-propyl](n-propyl)N(Me)\textsubscript{2})][NTf\textsubscript{2}] based on results from earlier studies (3).

![Figure 5](image-url)

**Figure 5.** Cyclic voltammogram of UO\textsubscript{2}(saldiene) in [EMI][NTf\textsubscript{2}] at 0.1 V/s and 1.5 mm glassy carbon working electrode.

The dissolution of uranium ions into RTIL solutions can be achieved by either of the following means: through oxidative electrodissolution of pure uranium metal directly in the RTIL or through metathesis reactions between UCl\textsubscript{4} and AgNTf\textsubscript{2} with subsequent filtration to remove AgCl. We have found that both methods produce emerald green solutions, presumably of U(IV) cations coordinated by NTf\textsubscript{2} anions. The coulometry for the electrochemical process consumes 4-electrons per equivalent of uranium dissolved and UV/Vis spectra of the solutions are diagnostic for U(IV) ions. Unfortunately voltammetry studies on the resulting solutions of U(IV) ions have not provided definitive data concerning the electroplating/stripping of uranium metal at Pt, Au, and glassy carbon...
Figure 6. Cyclic voltammograms of an ionic liquid solution, [(i-pr)(n-pr)N(Me)₂][NTf₂], containing uranium ions produced through a cathodic electrolysis of uranium metal. Both CV's obtained in same solution with different switching potentials at 0.1 V/s and a 1 mm Au disk working electrode.

working electrode surfaces. While we have identified what we believe to be the U(IV)/U(III) reversible couple, CV's out to more cathodic potentials have been inconclusive, Figure 6.

Due to the difficulties encountered with uranium electroplating we decided to study alternative electropositive metal ions that may help us better understand the specifics of electroplating metals from these RTIL solutions. Our preliminary results at this point show characteristic electroplating and stripping CV's for the monovalent ions Na, K, and Li, and for the trivalent Al ion. The data that we have collected thus far are limited to qualitative voltammetry studies on solutions containing the various metal ions just mentioned with more detailed analysis forthcoming. In order to limit the repetitiveness of CV's obtained at different working electrode surfaces, Figure 7 shows plating/stripping CV's for the four metal ions only at a 1 mm Pt disk working electrode surface. The four metal ions also show plating/stripping at a Au electrode surface while only Na and Al ions displayed this behavior at a glassy carbon working electrode surface. The metal ions were generated directly in the electrochemical cell by reacting an excess of metal hydride (NaH, KH, LiH) or (AlMe₃)₂ with HNTf₂. The excess metal hydride or trialkylaluminum acts as an internal drying agent to eliminate any trace water that may be in the electrochemical solution. We found that using freshly sublimed HNTf₂ was also important in eliminating trace moisture due to the highly hygroscopic nature of this compound. Consecutive CV's show the results at the different electrode surfaces to be repeatable. It is clear that more involved studies need to be performed in order to gain a better understanding of the electroplating/stripping process in these RTIL solvents. Our future studies will focus on more detailed electrochemical analyses and surface characterization of the deposits through microscopy.
Figure 7. Cyclic voltammograms of [(i-pr)(n-pr)N(Me)$_2$]$_2$[NTf$_2$] solutions containing metal ions. All voltammograms obtained at 0.1 V/s and a 1 mm Pt disk working electrode. (a) Na$^+$, (b) Li$^+$, (c) K$^+$, (d) Al$^{3+}$.

CONCLUSION

The electrochemical behavior for several coordination compounds and an organometallic compound of uranium have been described in $\text{N(SO}_2\text{CF}_3)_2$ based RTIL’s. For the organometallic system (i-prCp)$_3$UCl both the oxidation to the U(V) and reduction to the U(III) derivatives are chemically and electrochemically reversible on the voltammetric time scale from 0.1 to 2.0 V/s. The reversibility of the U(IV)/U(V) couple is in contrast to the observed behavior in conventional organic solvent/supporting electrolyte media. The chloride complex [UCI$_6$][EMI]$_2$ also shows chemically reversible behavior for the U(IV)/U(V) and U(IV)/U(III) couples, but slower electron transfer kinetics are evidenced for the reduction process at moderate scan rates. The chemical stability of the oxidation product in the RTIL solvent was confirmed through an exhaustive bulk electrolysis experiment. Studies on the reduction of [UO$_2$Cl$_4$][EMI]$_2$ in the $\text{N(SO}_2\text{CF}_3)_2$ RTIL’s shows a chemically irreversible process, which is similar to the behavior observed in organic solvents and chloroaluminate ionic liquids. A second high-current reduction process is observed for this uranyl compound when the [BMP][NTf$_2$] ionic liquid with its extended cathodic window is used. Changing the ligand architecture about the central uranyl fragment to the pentadentate saldien$^2$ ligand provides a
compound that undergoes a chemically reversible U(VI)/U(V) couple, which was confirmed through a bulk electrolysis experiment. Finally, our preliminary voltammetric data on the behavior of electropositive metals ions (Na, K, Li, Al) complexed by the \( \text{N}^+\text{(SO}_2\text{CF}_3)_2^- \) anion from the RTIL give definitive evidence for the electrochemical plating and subsequent stripping of metal from the working electrode surface.

ACKNOWLEDGEMENTS

For financial support we acknowledge the LANL Laboratory Directed Research and Development Program.

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