Electrochemistry and Spectroscopy of 1-Ethyl-3-methylimidazolium Chloride/VOCl₃ Room Temperature Molten Salts

David M. Ryan and Thomas L. Riechel
Department of Chemistry and Biochemistry
Miami University
Oxford, Ohio 45056

ABSTRACT

The electrochemistry and visible spectroscopy of VOCl₃ and VOF₃ in EMIC/AICI₃ solvents are reported. VOCl₃ and VOF₃ are both soluble in EMIC/AICI₃ room temperature molten salt liquids. Cyclic voltammograms of VOCl₃ have been obtained in five different melts: acidic, neutral, neutral melt buffered with NaCl, neutral buffered melt protonated by addition of triethanolamine-HCl, and basic melt. In all of the melts an irreversible reduction peak was observed at about 0.4V vs. a reference electrode composed of an Al wire immersed in acidic melt (60 mole % AICI₃) in a glass tube with a porous tip. In acidic melts, two additional reduction peaks were observed at more positive potentials. Controlled potential coulometry and spectroscopy demonstrated that the reduction at 0.4V was the reduction of V(V) to V(IV) and the more positive reduction peaks were caused by the reduction of some other V(V) species present in the acidic melts.

A new melt has been prepared by mixing acidic VOCl₃ with basic EMIC. The new melt is a dark red homogeneous liquid at room temperature. Its conductivity is similar to that of other EMIC melts but the voltage window is narrower.

INTRODUCTION

The electrochemistry and visible spectroscopy of several high oxidation state vanadium oxides in room temperature molten salts formed by mixing 1-ethyl-3-methylimidazolium chloride (EMIC) with AICI₃ have been previously reported [1]. For that project, six vanadium oxides (V₂O₅, V₂O₄, V₂O₃, NaVO₃, Na₃V₂O₇, and NH₄VO₃) were studied in five EMIC/AICI₃ molten salts. These solvents included acidic melts (EMIC:AICI₃ ratio < 1), neutral melts (EMIC:VOCl₃ ratio = 1), neutral melts buffered with NaCl, neutral melts buffered with NaCl and protonated with triethanolamine-HCl, and basic melts (EMIC:AICI₃ ratio > 1). It was noted that the presence of a V(V) species dissolved in any of these solvents resulted in a reduction peak at about 0.4V during cyclic voltammetry. It was also noted that when the melt was acidic an additional peak was
observed at about 1.6V. At that time no controlled potential coulometric data had been generated. While the observed reduction peaks were associated with the presence of V(V) in solution, no further data about their nature was known. Since then, two oxyhalide compounds, VOCl₃ and VOF₃, have been studied. Because the solubility of these two materials is so much greater than the solubility of the other oxides studied, it is now possible to answer some of the questions left unanswered by the earlier work.

Room temperature ionic liquids made by mixing Lewis basic EMIC with Lewis acidic AlCl₃ have been studied extensively as possible electrolytes for high energy density batteries [2,3]. The Lewis acid/base behavior of these melts influences their physical and chemical properties. It has been previously determined that the electrochemical window of a Lewis neutral melt is significantly wider than for a Lewis basic or Lewis acidic melt [4]. Several vanadium halides and oxides have been considered in these melts as possible cathode material for batteries [1,5]. Due to the Lewis acidic nature of VOCl₃ and VOF₃, an attempt was made to produce new room temperature melts by mixing stoichiometric amounts of EMIC with VOCl₃ and VOF₃. The results of these experiments are also be reported here.

**EXPERIMENTAL**

Cyclic voltammetry and controlled potential coulometry were performed using an EG&G Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat interfaced to a Gateway 2000 personal computer with PAR Model 270 software. Three-electrode electrochemical cells were used with a Pt foil auxiliary electrode, a Pt or glassy carbon (GC) disk working electrode and a molten salt reference electrode. The reference electrode consisted of an Al wire immersed in acidic EMIC/AlCl₃ melt (60 mole % AlCl₃) contained in a glass capillary equipped with a porous tip to provide solution contact. EMIC/VOCl₃ melts were prepared by mixing 1:1 stoichiometric amounts of VOCl₃ and EMIC in a small glass flask and stirring with a Teflon covered magnetic stir bar. The VOCl₃, a dark reddish-orange liquid, sealed in ampoules under nitrogen, was used as received from Aldrich. All melt preparations and handling were done under a dry nitrogen atmosphere in a Vacuum Atmospheres Corp. glove box. Conductivity measurements were made with an Extech Instruments, “Oyster”, conductivity meter kit. The instrument was calibrated with a KCl solution outside of the glove box in order to determine the cell constant. Then it was cleaned, dried, and taken into the glove box for the molten salt measurements. UV-visible spectra were recorded on a Hewlett Packard Model 8452A diode array spectrometer.
RESULTS AND DISCUSSION

VOCl₃ and VOF₃ in EMIC/AlCl₃ Melts

Figure 1 shows two cyclic voltammograms (CV) of VOCl₃ dissolved in EMIC/AlCl₃ melts of different Lewis acidities. The voltammogram with smaller currents was recorded for an acidic (ACID) melt and the voltammogram with larger currents is for a neutral, unbuffered (NUB) melt. These voltammograms are typical for VOCl₃ dissolved in EMIC/AlCl₃ melts of Lewis acidity ranging from N=0.45 to 0.55. The most important features are large, irreversible, reduction peaks located positive of 0.0V. The most positive and the least positive peaks are relatively tall and sharp and the center peak is relatively broad. While specific shapes and relative peak heights changed from melt to melt of different acidities, this general shape was observed for every solution of VOCl₃. The peaks at about 1.6V were not observed for basic (BASE) melts because the electrochemical window of these melts is not positive enough. This is in contrast to the earlier study of the less soluble vanadium oxides [1]. In the earlier study, only the reduction peak at 0.4V was consistently observed and the more positive reduction peaks were only observed for the most soluble materials and only in the acidic melts.

Controlled potential coulometry (CPC) was done to further understand what species were responsible for the observed reduction peaks. A 7mM VOCl₃/NUB solution was electrolyzed for 22 hours at 0.25V. At this potential all of the reduction peaks more positive than 0.25V should be electrolyzed. A voltammogram made before the electrolysis showed the usual characteristic reduction peak at 0.4V (Figure 2A) and two proton peaks at more negative potentials. After the electrolysis the peak was gone (Figure 2B) and the rest potential, as well as the proton peaks, had moved more negative. The color of the initial solution was dark brown but after electrolysis for nearly three hours it turned to a light green and after overnight electrolysis it was a light blue. These color changes corresponded to a total of 1.2 equivalents of electrons per vanadium. Before and after spectra are shown in Figure 3. The spectra in Figure 3 were taken with a 1 mm pathlength cell and demonstrate the loss of the 460 nm peak upon reduction. A spectrum recorded after reduction in a 1 cm cell (Figure 4) shows low intensity peaks consistent with the reduction of a V(V) species (d⁰) to a lower oxidation state V(IV) species (d¹) or a V(III) species (d²). This is similar to spectra reported by Dent [8] in basic melts. Therefore, it is believed that the reduction observed in various melts at 0.4V is the reduction of V(V) to V(IV).

Further work was done to try to identify the more positive reduction peaks observed particularly in acidic melts. A 7 mM VOCl₃/ACID solution was prepared (55 mole % AlCl₃). Figure 5A, shows a CV generated prior to CPC. Note the three
characteristic reduction peaks at 1.3, 0.75, and 0.4V. The solution was electrolyzed for 20 hours at 1.0V. Figure 5B shows a CV generated after the electrolysis. Note the absence of any remaining reduction peaks including the peak expected at 0.4V. This suggests that all of the V(V) had been reduced as a result of the electrolysis at 1.0V and there was no V(V) left to generate a reduction peak at 0.4V as would normally be expected. Furthermore, note that the open circuit potential has moved from 1.46 to 0.98V. Figure 6, curve A, shows a spectrum of the solution prior to the electrolysis (1 mm cell). This solution was originally dark brown. After electrolysis the solution was a dark purple (Figure 6, curve B). This demonstrates that there are at least two V(V) species present in Acidic melt and that V(V) can be reduced by two different paths.

Similar experiments were performed with VOF3. VOF3 was much easier to work with because it was a stable solid. The solid was yellow-orange, very similar in appearance to V2O5, and was soluble in neutral and acidic EMIC/AICI3 melts. Figure 7A is a voltammogram of 7 mM VOF3/NUB and Figure 7B is a voltammogram of 7 mM VOF3/ACID. The most important feature in Figure 7A is the characteristic reduction peak at 0.4V. Notice the more positive reduction peaks at 1.6 and 1.2V that were present in the acidic solution, but not in the neutral solution. Note that the characteristic peak usually observed at 0.4V is at 0.6V here. Figure 8A is a spectrum of 7 mM VOF3 in NUB. Note the peak at ca. 480 nm that is also present in Figure 3, a VOCl3 solution. VOCl3 and VOF3 solutions appear quite similar to the eye.

CPC was also performed on VOF3 solutions and the results were similar to those observed for VOCl3. Figure 8B is a spectrum of VOF3 after overnight electrolysis at 0.0V. Note the new broad absorbance peaks at 560 nm and 720 nm. There was still a peak present at 480 nm indicating the electrolysis was not really complete. The peak at 720 has been previously reported as due to a V(IV) species [5]. The electrolyzed solution was deep purple.

EMIC/VOCl3 Melts

When an equimolar mixture of EMIC and VOCl3 was stirred in a small Erlenmeyer flask under a dry atmosphere, a homogeneous, dark red, almost black, liquid resulted. The low viscosity liquid clung tenaciously to the walls of the flask. It is believed that VOCl3 and EMIC reacted in a manner analogous to the reaction of EMIC and AlCl3:

\[
EMIC + VOCl_3 \leftrightarrow EMI^+ + VOCl_4^- \quad [6]
\]

It is also proposed that VOCl4- undergoes dissociation:

\[
VOCl_4^- \leftrightarrow Cl^- + VOCl_3
\]

This reaction is analogous to:
\[ \text{AlCl}_4^- \leftrightarrow \text{Cl}^- + \text{AlCl}_3 \]

in EMIC/AlCl₃ melts and

\[ \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+ \]

in aqueous solutions. This suggests that a new room temperature melt, EMIC/VOCl₃, is formed. Conductivity was measured and found to be 2 mS at 20°C. This value can be compared to 4 mS for a sample of neutral, unbuffered EMIC/AlCl₃ melt that was measured as a control sample. Figure 9 shows a cyclic voltammogram of a slightly basic (mole fraction of VOCl₃ = 0.49) EMIC/VOCl₃ melt. The main features observed during the negative scan were large reductions at 0.5 and -0.6V. The current then plateaus. During the positive scan, a large oxidation peak was observed at 1.6V, which may be due to the presence of chloride. The anodic limit is about 2.0V. After the experiment, when the Pt working and the Pt auxiliary electrodes were being washed, it was observed that both Pt surfaces were coated with a thick, dark film that turned brick red briefly before washing off with tap water. This film could account for the passivation of the electrodes during cyclic voltammetry.

There was also some undissolved EMIC still present. Additional VOCl₃ was added to make the melt acidic. The melt then became completely liquid without any undissolved solid. A CV for this melt is shown in Figure 10. In contrast to the original basic melt, the acidic melt showed more peaks. There were four apparently quasi-reversible couples noted. The oxidation at 0.4V was not present on anodic scans and must therefore represent the oxidation of some species created during the reduction processes. The anodic limit of this melt appeared to be at about 0.5V. The measured currents were very high (milliamps instead of the usual microamps) indicating that the melt itself was being reduced. Upon extending the CV cathodic scan limit out further for succeeding experiments, it was discovered that the Pt working electrode was being passivated and the passivation layer did not begin to break down until -5.0V was reached.

Figure 11 is a spectrum of a neutral EMIC/VOCl₃ melt diluted in CH₃CN. The neat EMIC/VOCl₃ melt is so intensely colored that it had to be diluted before a spectrum could be measured. The solution was prepared by dissolving 0.8 grams of melt in 100 grams of CH₃CN. The spectrum showed a strong absorption peak at 475nm and a smaller peak at about 660nm. Both Figure 11 and Figure 3 demonstrate the presence of VOCl₄⁺.

CONCLUSIONS

The electrochemistry and visible spectroscopy of VOCl₃ and VOF₃ in EMIC/AlCl₃ room temperature molten salts have been investigated. Cyclic voltammograms of VOCl₃ have been obtained in five different melts: acidic, neutral, neutral melt buffered with NaCl, buffered neutral melt protonated by an addition of triethanolamine-HCl, and basic. In all of the melts an irreversible
reduction peak was observed at about 0.4V versus a reference electrode consisting of an Al wire immersed in acidic melt (60 mole % AlCl₃). In acidic melts, two additional reduction peaks were observed at more positive potentials at ca. 1.6V and 1.2V. Controlled potential coulometry and the resulting spectra demonstrated that the reduction at 0.4V was a one electron reduction of V(V) to V(IV). It was also demonstrated that the most positive peaks at ca.1.6 to 1.0V were reductions of some other V(V) species present in the acidic melts and it is suggested that V(V) can be reduced by either of two different paths in acidic melts. Similar results were obtained for VO₃ in neutral unbuffered and acidic melts.

A new melt has been prepared by mixing Lewis acidic VOCl₃ with Lewis basic EMIC. The dark red liquid that resulted was easily reduced and had a measured conductivity of 2 mS compared to a neutral EMIC/AlCl₃ melt with a conductivity of 4 mS.

Future work to be done to further characterize the EMIC/VOCl₃ room temperature molten salt will include electrochemical and EPR studies. The possibility of forming EMIC/VOF₃ melts will also be considered.

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Figure 1. Cyclic voltammograms of 7 mM VOCl$_3$ in Lewis neutral EMIC/AlCl$_3$ (NUB) and Lewis Acidic EMIC/AlCl$_3$ (ACID) melt. Pt disk working electrode and scan rate of 100 mV/sec.

Figure 2A. Cyclic voltammogram of 7 mM VOCl$_3$/NUB just prior to controlled potential coulometry (CPC) at 0.25 V for 22 hours. Pt disk working electrode and scan rate of 100 mV/sec.
Figure 2B. Cyclic voltammogram of 7 mM VOCl₃/NUB just after CPC at 0.25V for 22 hours. Pt disk working electrode and scan rate = 100 mV/sec.

Figure 3. Visible spectrum of 7 mM VOCl₃/NUB just prior to and just after CPC at 0.25V for 22 hours. The pathlength for these spectra was 1 mm.
Figure 4. Visible spectrum of 7 mM VOCl₃/NUB just after CPC at 0.25V for 22 hours. Similar to Figure 3B except the pathlength for this spectrum was 1 cm.

Figure 5A. Cyclic voltammogram of 7 mM VOCl₃/ACID just prior to CPC at 1.0V for 20 hours. Pt disk working electrode and scan rate = 100 mV/sec.
Figure 5B. Cyclic voltammogram of 7 mM VOCl\textsubscript{3}/ACID just after CPC at 1.0V for 20 hours. Pt disk working electrode and scan rate = 100 mV/sec.

Figure 6. Visible spectra of 7 mM VOCl\textsubscript{3}/ACID before and after CPC at 1.0V for 20 hours. The pathlength for these spectra was 1 mm.
Figure 7A. Voltammogram of VOF₃/NUB prior to CPC at 0.0V overnight. Pt disk working electrode and scan rate of 100 mV/sec.

Figure 7B. Cyclic voltammogram of 7 mM VOF₃/ACID. Pt working electrode and scan rate of 100 mV/sec.
Figure 8. Visible spectra of VOF$_3$/NUB. Spectrum A was measured prior to CPC and spectrum B is after CPC at 0.0V overnight. The pathlength for both spectra was 1 mm.

Figure 9. Cyclic voltammogram of EMIC/VOCl$_3$ (49 mole % VOCl$_3$). Pt working electrode and scan rate of 100 mV/sec.
Figure 10. Cyclic voltammogram of EMIC/VOCl₃, acidic melt. Pt disk working electrode and scan rate of 100 mV/sec.

Figure 11. Visible spectrum of EMIC/VOCl₃ in CH₃CN (0.8% by weight). The pathlength for this spectrum was 1 cm.