Vanadium Complexes in a Lewis Basic Room-Temperature 1-Ethyl-3-methyl-1*H*-imidazolium Chloride/Aluminum Chloride Molten Salt

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Received February 21, 1997⊗

Complexes of VCl_3 and VCl_4 have been formed in a Lewis basic room-temperature molten salt consisting of 1-ethyl-3-methyl-1*H*-imidazolium chloride and aluminum chloride. Electrochemical and spectroscopic studies show that 3 equiv of chloride can be added to VCl_3 to form higher order chloride complexes. Each vanadium(III) complex can be reversibly oxidized to a corresponding vanadium(IV) complex. The potentials for the couples $VCl_4^- \leftrightarrow VCl_4 + e^-$, $VCl_5^{2-} \leftrightarrow VCl_5^- + e^-$, and $VCl_6^{3-} \leftrightarrow VCl_6^{2-} + e^-$ occur at 1.33, 1.23, and 1.00 V, respectively, measured versus a reference electrode consisting of an aluminum wire in a 0.6 mole fraction $AlCl_3$ melt. Although higher order chloride complexes of other transition metals have been reported in these melts, this is the first metal for which the stepwise addition of chloride accompanied by reversible electrochemistry for each species has been demonstrated. This also shows that molten salts are useful for stabilizing complexes which may be hydrolyzed by the residual water sometimes present in organic solvents.

Introduction

There has been much interest in the use of room-temperature molten salts as battery electrolytes in conjunction with alkali metal anodes.[1−3] One of the advantages of these melts is that they provide a very dry, nonaqueous environment so that sodium and lithium anodes do not spontaneously oxidize. This characteristic of the melts means that they may also be useful as solvents for studying non-oxygen-containing transition metal complexes which have a tendency to hydrolyze to oxo compounds. Such complexes may be important in the development of cathodes for use in molten salt cells. For this reason we have begun the study of vanadium complexes in 1-ethyl-3-methyl-1*H*-imidazolium chloride/aluminum chloride (EMIC/$AlCl_3$) molten salts.

Although most transition metal compounds studied in chloroaluminate molten salts have limited solubility in Lewis neutral and Lewis acidic melts, many have been reported to be soluble in basic (chloride-rich) melts. Hussey[4,5] has reviewed these, which include compounds of Ta,[6] Nb,[7] and Mo.[8,9] Compounds of the lanthanides Nb[10] and Eu[11] and the actinide U[12,13] have also been reported. Only recently have two reports of vanadium compounds in room-temperature molten salts appeared,[14,15] but no electrochemistry has been reported. We report here the electrochemistry of VCl_3 and VCl_4 complexes in Lewis basic EMIC/$AlCl_3$ molten salts.

Experimental Section

Instrumentation. All electrochemical experiments were carried out using a three-electrode cell set up in a Vacuum Atmospheres glovebox under a dry nitrogen atmosphere. The electrochemical measurements were made with an EG&G Princeton Applied Research (PAR) Model 263 potentiostat/galvanostat interfaced to a personal computer running PAR Model 250 software or with a Bioanalytical Systems (BAS) Model 100A electrochemical analyzer. A BAS glassy carbon working electrode (Model MF-2012, 7.07 mm^2) was used for voltammetry, while a Pt mesh electrode was used for coulometry. A Pt foil auxiliary electrode was isolated from the test solution by means of a fine-porosity fritted tube. The reference electrode consisted of an Al wire in an $N = 0.60$ EMIC/$AlCl_3$ melt ($N =$ the mole fraction of $AlCl_3$ in the melt), contained in a Pyrex tube with an asbestos tip to provide solution contact. UV−visible spectra were recorded using a Hewlett Packard Model 8452A diode array spectrometer and quartz cuvettes.

Reagents and Synthesis. Components for the melts were synthesized and purified using published methods. 1-Ethyl-3-methyl-1*H*-imidazolium chloride (EMIC) was made from 1-methylimidazole and chloroethane (Aldrich) according to the method of Wilkes and co-workers.[16] Purification of $AlCl_3$ (Fluka) was carried out by recrystallization in a tube furnace.[17] Neutral melts were made in the glove box by mixing carefully weighed amounts of EMIC and $AlCl_3$. Traces of moisture arising from the synthesis of EMIC were reduced to a minimum by the addition of ethylaluminum dichloride (Aldrich).[18] Acidic melts were made by adding excess $AlCl_3$ to a neutral melt, while basic melts were made by adding excess EMIC. The vanadium compounds VCl_3 and VCl_4 were purchased from Aldrich and Alfa Aesar, respectively, and used as received.

Results and Discussion

The solubility of VCl_3 in Lewis neutral and acidic ($N = 0.55$) melts is negligible, and cyclic voltammograms recorded on such

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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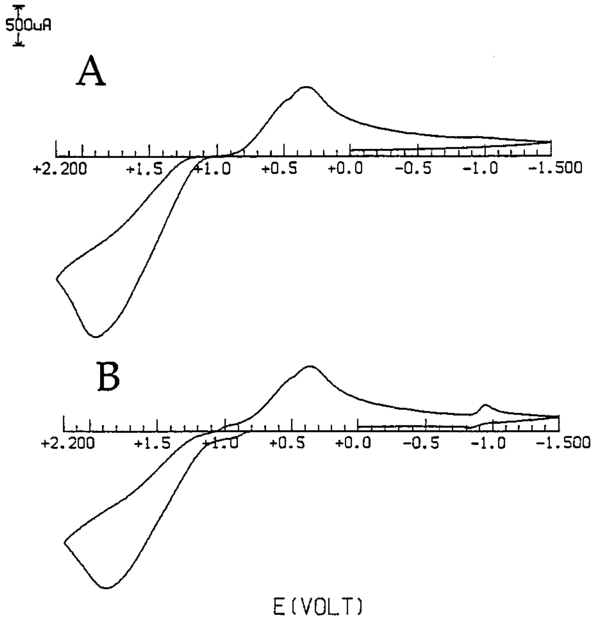

Figure 1. Anodic-scan cyclic voltammograms of a Lewis basic ($N = 0.45$) EMIC/$AlCl_3$ melt at a glassy carbon electrode: (A) melt without vanadium present; (B) melt as in (A) but with 30 mM VCl_3 added. Scan rate: 100 mV/s.

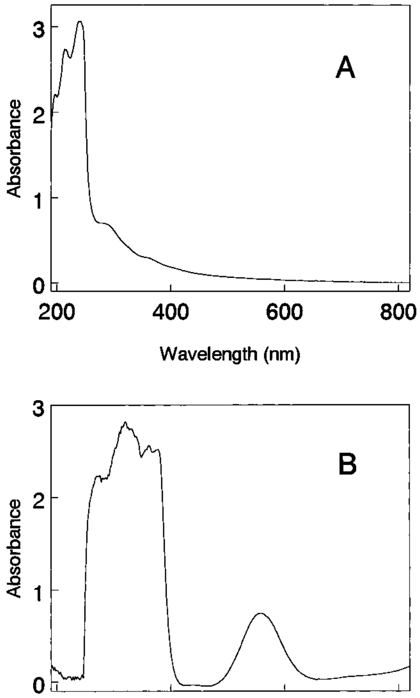

Figure 2. UV−visible spectra of a Lewis basic ($N = 0.45$) EMIC/$AlCl_3$ melt: (A) melt without vanadium present (reference is air); (B) melt as in (A) but with 30 mM VCl_3 added (reference is the blank melt from (A)).

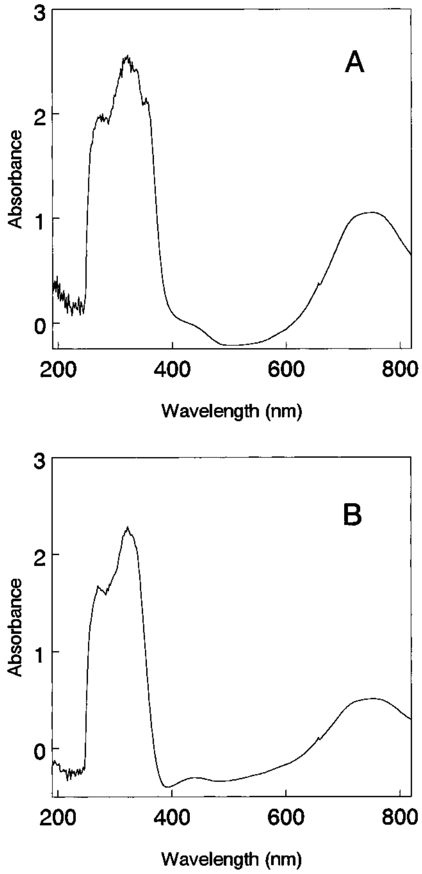

Figure 3. UV−visible spectra of Lewis basic ($N = 0.45$) EMIC/$AlCl_3$ melts: (A) melt with 30 mM VCl_3 added, after exhaustive electrolysis at 1.6 V; (B) melt with 30 mM VCl_4 added. (The reference in both cases was a blank melt as in Figure 2A.)

melts showed no peaks attributable to vanadium. In contrast, VCl_3 was found to be readily soluble in Lewis basic melts. Figure 1A is a voltammogram of an $N = 0.45$ melt with no vanadium present. The large oxidation peak at 1.8 V is due to Cl^- oxidation, and the reduction peak at 0.3 V is due to chlorine reduction on the reverse scan. These peaks are characteristic of all Lewis basic chloroaluminate melts. Figure 1B is a voltammogram of the same melt as in Figure 1A, but with 30 mM VCl_3 present. This composition corresponds to a Cl^-:VCl_3 mole ratio of 30:1. The small reduction peak near −1 V is due to moisture which entered the solution with the vanadium compound, but no redox peaks for the vanadium are observed. Nonetheless, the vanadium compound dissolved completely in the melt and gave a purple solution. Figure 2A shows the UV−visible spectrum of the basic melt without vanadium present, while Figure 2B shows the spectrum of the melt containing 30 mM VCl_3. (The spectrum in Figure 2B and all subsequent spectra (except that in Figure 7B) are displayed with the spectrum of the blank melt, Figure 2A, subtracted. Thus the peaks below 400 nm are not due to the melt components. Their origin is uncertain.) The spectrum of the melt without vanadium exhibits no peaks in the visible region, while the spectrum with vanadium present exhibits a peak at 555 nm. This is clear evidence of a vanadium complex, even though no electrochemistry is observed under these conditions.

The vanadium-containing melt described above was subjected to exhaustive electrolysis at 1.6 V. This was intended to oxidize the vanadium species known to be present. At this potential, though, chloride oxidation also occurred, leading to a very large number of coulombs and precluding the possibility of calculating the number of electrons in the vanadium oxidation. Nonetheless, the resulting spectrum is important. Figure 3A shows the spectrum of the melt following electrolysis. The absorbance peak at 555 nm has been replaced by a peak at 740 nm and a shoulder at 440 nm. Figure 3B is the spectrum of a similar basic melt ($N = 0.45$) with VCl_4 added. It is clear that the same two absorbance peaks are present. This means that the vanadium(III) complex is oxidized to a vanadium(IV) complex at a potential less than or equal to 1.6 V.

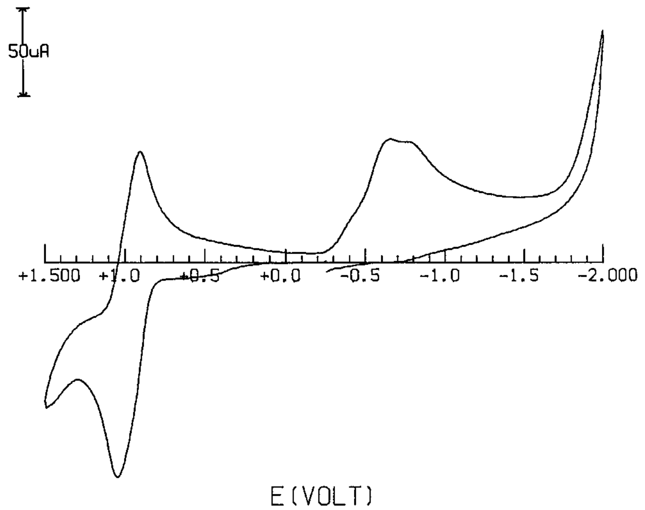

Figure 4. Anodic-scan cyclic voltammogram of a EMIC/$AlCl_3$ melt containing 30 mM VCl_3 and 120 mM chloride at a glassy carbon electrode. Scan rate: 100 mV/s.

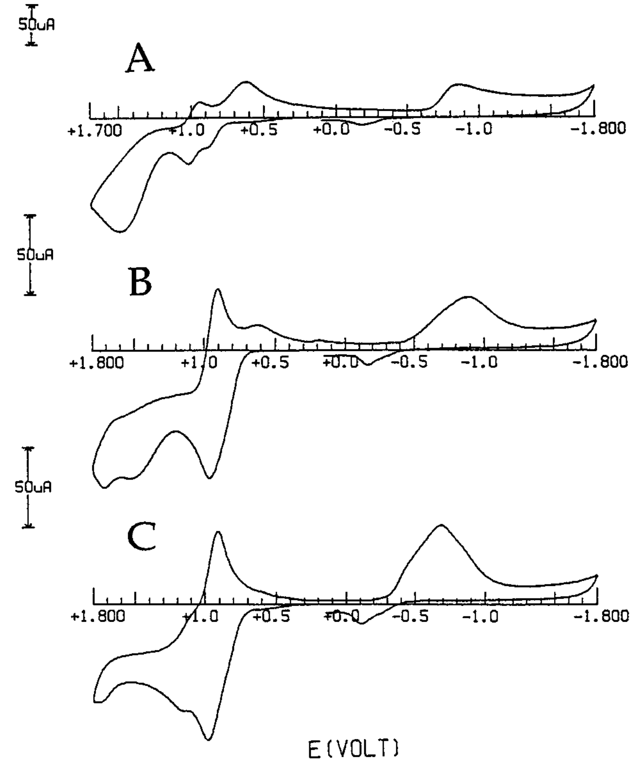

Figure 5. Anodic-scan cyclic voltammograms of a EMIC/$AlCl_3$ melt containing 120 mM chloride and (A) 10 mM VCl_3, (B) 20 mM VCl_3, and (C) 30 mM VCl_3 at a glassy carbon electrode. Scan rate: 100 mV/s.

Table 1. VCl_3 Complexation in a Basic Melt

amt of Cl^-(init), mol × 10^4	amt of VCl_3, mol × 10^4	amt of Cl^-(final), mol × 10^4	Cl^-:VCl_3 mole ratio
9.35	1.56	7.01	1.5
12.49	1.56	7.81	3.0
15.65	1.56	11.11	2.9
18.84	1.57	14.28	2.9
15.65	3.13	7.83	2.5
18.84	3.14	10.35	2.7

While the spectroscopic data indicate the presence of a vanadium(III) complex in the $N = 0.45$ melt, the electrochemistry of this complex is masked by the large chloride oxidation peak of the basic melt. By addition of $AlCl_3$ to the melt, the concentration of free chloride can be decreased, but as long as the mole fraction of $AlCl_3$ (N) remains below 0.5, the melt will remain basic and VCl_3 will still be soluble. Under such conditions, the electrochemistry of the vanadium(III) complex can be revealed. Figure 4 is the voltammogram of 30 mM VCl_3 in a melt containing only 120 mM chloride ($N = 0.49$, and the Cl^-:VCl_3 mole ratio is 4:1). The voltammogram exhibits a reversible couple at about 1.0 V. (The reduction peaks between −0.5 and −1.0 V probably correspond to protons in the form of HCl_2^- or $H_2Cl_3^-$, characteristic of melts containing small amounts of moisture,[19,20] or they may be due to oxychloride impurities.) Controlled-potential coulometry was carried out at

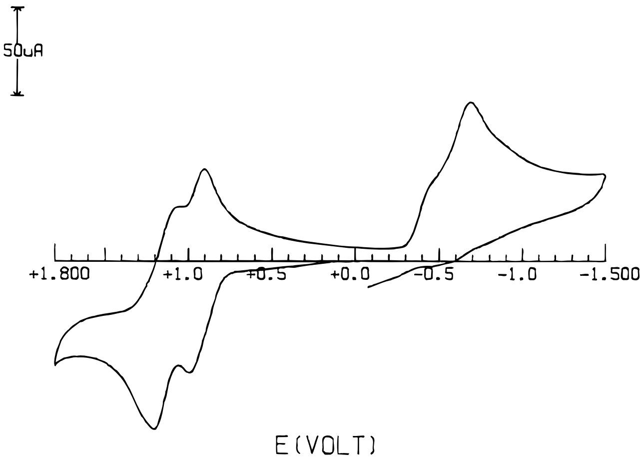

Figure 6. Anodic-scan cyclic voltammogram of a EMIC/$AlCl_3$ melt containing 30 mM VCl_3 and 100 mM chloride at a glassy carbon electrode. Scan rate: 100 mV/s.

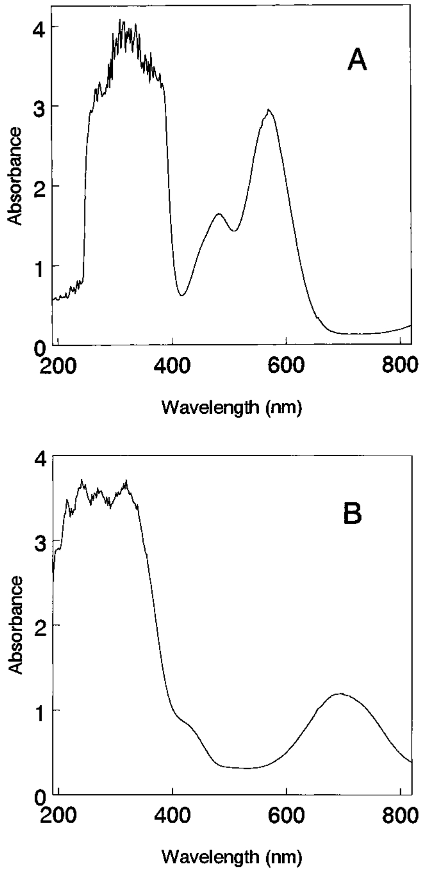

Figure 7. UV−visible spectra of a EMIC/$AlCl_3$ melt containing 30 mM VCl_3 and 100 mM chloride (A) before and (B) after exhaustive electrolysis at 1.6 V. (For spectrum A, the reference was a blank melt as in Figure 2A. For spectrum B, the reference was air.)

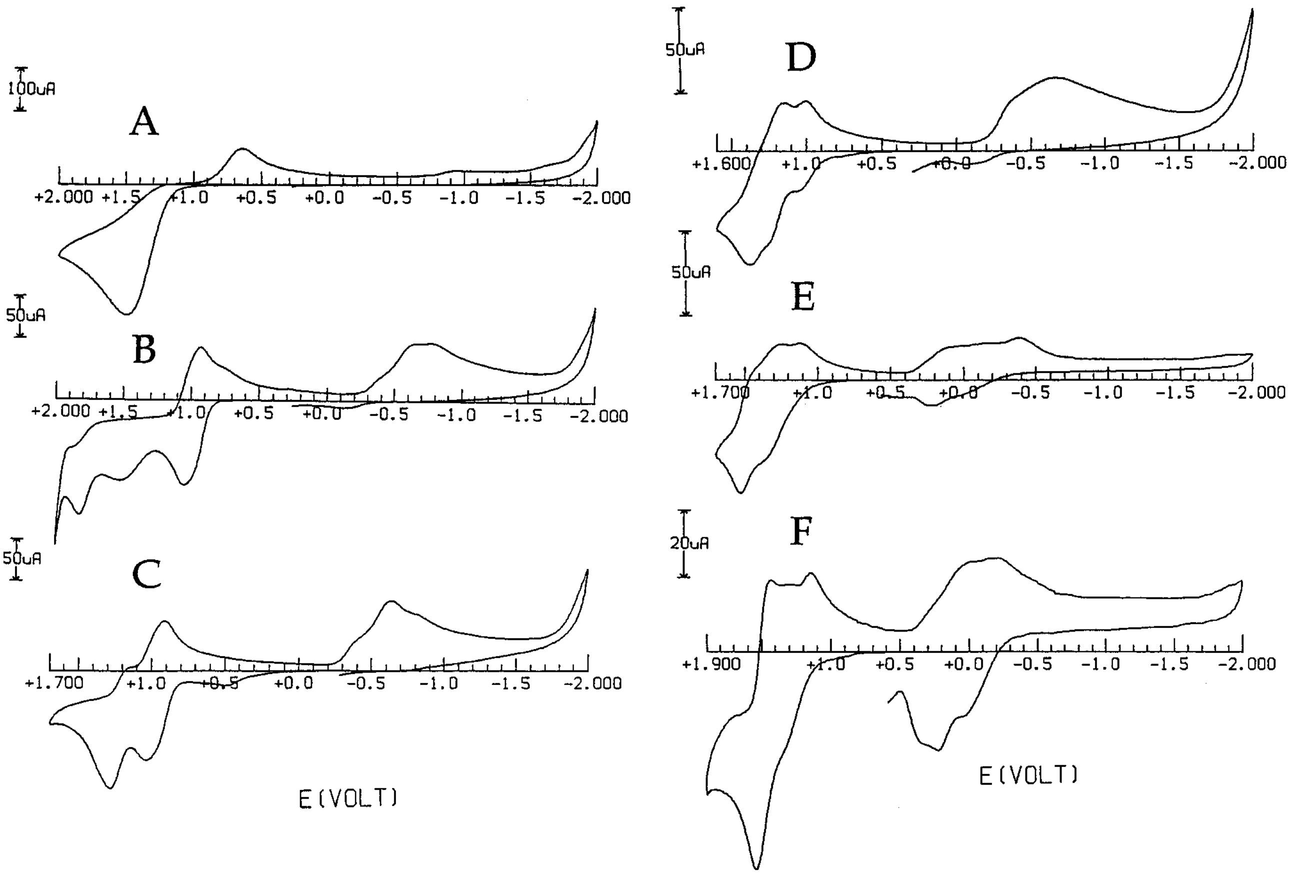

Figure 8. Anodic-scan cyclic voltammograms of a EMIC/AlCl$_3$ melt initially containing 120 mM chloride, titrated with AlCl$_3$, recorded at a glassy carbon electrode with a scan rate of 100 mV/s: (A) melt before the addition of vanadium or AlCl$_3$; (B) melt A after the addition of 30 mM VCl$_3$; (C) melt B after the addition of AlCl$_3$ resulting in a melt containing 110 mM Cl$^-$; (D) melt B after the addition of AlCl$_3$ resulting in a melt containing 60 mM Cl$^-$; (E) melt B after the addition of AlCl$_3$ resulting in a melt containing 40 mM Cl$^-$; (F) melt B after the addition of AlCl$_3$ resulting in a melt containing 30 mM Cl$^-$.

1.3 V on a melt containing 30 mM VCl$_3$ and only 100 mM Cl$^-$ ($N = 0.495$). This experiment gave a value of 0.89 electron, which agrees with the spectroscopic data indicating a one-electron oxidation of vanadium(III) to vanadium(IV).

Mole ratio studies were undertaken to determine the stoichiometry of the vanadium(III) complex. Figure 5 displays three voltammograms recorded after the incremental addition of VCl$_3$ to a 120 mM solution of free chloride. Parts A–C of Figure 5 correspond to VCl$_3$ total concentrations of 10, 20, and 30 mM, respectively. The addition of vanadium results in the subsequent decrease in both the chloride oxidation and the chlorine reduction currents. At the same time, the currents associated with the vanadium couple near 1.0 V increase. Figure 5C shows that the chloride oxidation peak is nearly gone, indicating that most of the free chloride is consumed when the VCl$_3$ concentration is 30 mM. These results suggest that the chloride to vanadium stoichiometry is 3:1.

This stoichiometric ratio was confirmed by an amperometric titration. First, a calibration curve was constructed by plotting chloride oxidation current vs chloride concentration for basic melts with various N values but no vanadium present. Then the decrease in chloride oxidation current was monitored as a function of the amount of VCl$_3$ added to a melt. By a comparison of the chloride oxidation currents before and after an addition of vanadium, the number of moles of chloride from EMIC consumed was determined. Dividing by the number of moles of vanadium present yields the mole ratio of the complex. Data for several experiments are given in Table 1, clearly indicating a 3:1 stoichiometry.

Numerous higher order chloride complexes of transition metals in Lewis basic chloroaluminate melts have been reported, such as TaCl$_6^-$ and TaCl$_6^{2-}$,[6] NbCl$_6^-$, NbCl$_6^{2-}$, and NbCl$_6^{3-}$,[7] and MoCl$_6^{2-}$ and MoCl$_6^{3-}$.[8] Complexes of lanthanide and actinide elements include NdCl$_6^{3-}$,[10] EuCl$_6^{3-}$,[11] and UCl$_6^{2-}$ and UCl$_6^{3-}$.[12,13] These are formed by the addition of chloride to the corresponding neutral salt or by oxidation or reduction of a related complex. EuCl$_6^{3-}$, for example, can be formed directly by the addition of 3 equiv of chloride to the trichloride salt:

$$\mathrm{EuCl_3 + 3Cl^- \leftrightarrow EuCl_6^{\ 3-}}$$

NdCl$_6^{3-}$ can be formed by an analogous process. The data presented here suggest that a similar reaction occurs for vanadium chloride:

$$\mathrm{VCl_3 + 3Cl^- \leftrightarrow VCl_6^{\ 3-}}$$

During the course of the mole ratio studies, it was noticed that more than one vanadium(III) complex may exist. For example, the voltammogram of 30 mM VCl$_3$ in a melt of 100 mM chloride (Figure 6) shows the redox couple at 1.0 V (as before) and a second couple at about 1.2 V. Both couples appear to represent reversible processes. The absorption spectrum of this melt (Figure 7A) exhibits a peak at 570 nm, near the 555 nm peak observed earlier, and a new peak at 480 nm. This peak may correspond to the second redox couple and a second vanadium(III) complex. Figure 7B is a spectrum of

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Table 2. Dependence of Vanadium Peak Currents on Chloride Concentration[a]

		current, μA			
Cl^- concn, mM	Cl^-:VCl_3 mole ratio	Cl^- Ox/Red 1.5 V/0.7 V	couple A Ox/Red 1.05 V/0.95 V	couple B Ox/Red 1.3 V/1.15 V	couple C Ox/Red 1.4 V/1.25 V
120 (no VCl_3)		292/83	0/0	0/0	0/0
120	4:1	71/38	92/75	0/0	0/0
110	3.7:1	50/33	92/88	108/67	0/0
100	3.3:1	25/16	67/63	96/63	0/0
90	3:1	0/0	71/63	−	0/0
80	2.7:1	0/0	56/52	38/40	0/0
70	2.3:1	0/0	42/40	54/52	44/−
60	2:1	0/0	18/17	48/46	54/−
50	1.7:1	0/0	0/0	33/30	56/34
40	1.3:1	0/0	0/0	33/29	56/38
30	1:1	0/0	0/0	25/22	58/56

[a] Addition of $AlCl_3$ to 30 mM VCl_3 in a basic melt.

this solution recorded after exhaustive oxidation at 1.6 V. Only the single peak at 740 nm is present, suggesting that there is only one stable vanadium(IV) product.

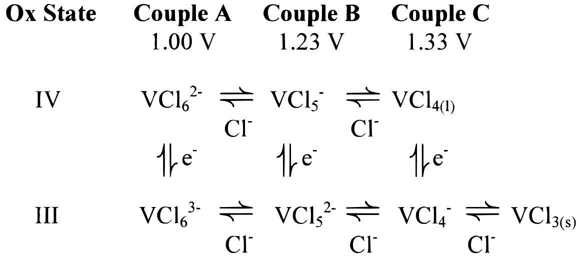
Because the number of couples present in the voltammograms is dependent on the concentration of free chloride, a titration was carried out in which small incremental additions of $AlCl_3$ (a Lewis acid) were made to a basic melt containing VCl_3. This caused the melt to become less basic as the chloride was neutralized. (Due to the limited solubility of VCl_3 in the neutral melt, this experiment could not be done in the forward direction, that is, by adding chloride to a neutral melt.) Figure 8A is the voltammogram of a 120 mM chloride melt before the addition of vanadium. Only the chloride peaks are observed. Figure 8B shows the voltammogram of the melt after the addition of 30 mM VCl_3. Only one vanadium couple is evident, and the chloride peak is decreased. Parts C−F of Figure 8 show the results of four additions of $AlCl_3$, which decrease the concentration of free chloride to 110, 60, 40, and 30 mM, respectively. It can be seen that as the chloride concentration decreases, multiple, overlapping vanadium couples appear at potentials more positive of the first couple. The resulting data are given in Table 2. Three couples have been identified. Couple A dominates at high chloride concentration. At intermediate concentrations of chloride, both couples A and B are evident, or all three couples may be seen. At low chloride concentrations, couples B and C are dominant.

Conclusion

The electrochemical and spectroscopic data suggest the stepwise addition of 3 equiv of chloride to VCl_3 resulting in the formation of VCl_4^-, VCl_5^{2-}, and VCl_6^{3-}. As indicated in Scheme 1, each of these vanadium(III) complexes can undergo a one-electron oxidation, resulting in VCl_4, VCl_5^-, and VCl_6^{2-}, respectively. These processes occur at 1.33, 1.23, and 1.00 V, versus a reference electrode consisting of an aluminum wire in an $N = 0.6$ melt. The order of these potentials is reasonable, as VCl_6^{3-} has the highest negative charge and thus is the easiest to oxidize.

In a recent paper, Dent and co-workers[14] reported the isolation of $(EMI)_2VCl_6$, a salt of VCl_6^{2-}. This vanadium(IV) species was made by treating $(EMI)_2VOCl_4$ with $SOCl_2$ in order to remove the oxygen. It was found that VCl_6^{2-} was spontaneously reduced to VCl_6^{3-} in basic melts, perhaps by excess chloride. These workers also suggested that VCl_6^{3-} was formed when VCl_3 was dissolved in a basic melt. Our work agrees with these results. The addition of 3 equiv of chloride to VCl_3 to form VCl_6^{3-} was verified by our mole ratio study. Both groups report a visible absorption band for this species at 555 nm. We have used controlled-potential coulometry to show that VCl_6^{3-} undergoes a one-electron oxidation without a loss of chloride, giving VCl_6^{2-}. Just as Dent found that this species was unstable, we found that after bulk electrolysis the rest potential of the cell solution quickly shifted back to its value before oxidation, and the resulting voltammogram resembled that of the vanadium(III) species VCl_6^{3-}, rather than showing a reduction peak for VCl_6^{2-}. This process may be catalyzed at the surface of the electrode, as the spectrum of the bulk solution remained that of the vanadium(IV) species.

Scheme 1



Neither the results of Dent and co-workers nor those of Gau and Sun,[11] who studied the formation of $EuCl_6^{3-}$ by the addition of chloride to $EuCl_3$, nor those of Lipsztajn and Osteryoung,[10] who studied $NdCl_6^{3-}$, gave any indication that stable intermediate chloride complexes were formed. Also, Dent did not report any electrochemical results. Our results demonstrate the stepwise addition of chloride to VCl_3 and the reversible electrochemistry of each species. These properties suggest that vanadium compounds may be useful as cathodes in rechargeable cells using room-temperature chloroaluminate molten salt electrolytes.

Acknowledgment. This work was supported by the Undergraduate Summer Scholars Program and an Undergraduate Research Program grant awarded to K.R.H. by Miami University.

IC970201C