SPECTROCHEMICAL AND ELECTROCHEMICAL PROPERTIES OF SOME LANTHANIDES AND ACTINIDES IN ROOM-TEMPERATURE MELT

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Spectroscopic and electrochemical behavior of melts consisting of 1-methyl-3-ethylimidazolium chloride and AlCl₃ and solutions of Ce(III), Tb(III) and U(V) in 0.4 (basic) melt have been investigated. The predominant species in solution was found to be [MCl₃]⁺. The melt has been modified by treating it with gaseous HCl to increase the conductivity. NMR data shows the presence of a highly acidic proton, and a melt:HCl ratio of 1:1.

The family of ambient temperature melts resulting from 1,3-dialkylimidazolium chloride and AlCl₃ was discovered at the Frank J. Seiler Laboratories of the U.S. Air force Academy in Colorado Springs [1]. The most extensively investigated room temperature melts consist of a mixture of 1-methyl-3-ethylimidazolium chloride (MEIC) (I) and AlCl₃ in various mole ratios. These melts possess very interesting solvent properties. Some of the typical advantages and disadvantages are:

Typical Advantages
* Stable and relatively easy to prepare
* Low liquidus temperature
* Liquid over a wide temperature range (+80 to -70°C)
* Large variability of Lewis acid/base properties
* Anhydrous aprotic solvent
* Large electrochemical window (2.6 V)
* Good UV/VIS spectral transparency (down to 250 nm)
* Conductivities of the ambient temperature melts are comparable to that of the molten salts and aqueous electrolytes
* Miscibility with organic solvents

Disadvantages
* High sensitivity to air and moisture
* Corrosive
* High viscosity
1.1 Spectroscopic Properties of the Chloroaluminate Melt

The hydrated chloride ion \([\text{Cl}^-\text{(H}_2\text{O})_n]\) absorbs in the far UV region. In aqueous solution the first band appears around 194 nm possibly due to the charge transfer transition. The alkali metal ions that do not absorb in this range has virtually no effect on the position of this band. Aqueous solution of 1-methyl-3-ethylimidazolium chloride (MEIC) \((I)\) showed a broad band at 208 nm (Fig. 1) with molar absorptivity of \(4.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\) agreeing with previous measurements \([2]\). The high absorbance peak is due to the organic chromophore of the MEIC cation \((I)\).

The melts containing less than 0.5 mole fraction of AlCl\(^+\) (i.e. basic melts) exhibit an absorption edge cut off at 250 nm. The AlCl\(^+\) species present in these melts probably absorbs strongly around 246 nm and excludes the possibility of observing the peak due to MEIC cation moiety. However, as the mole fraction of Al\(_n\)Cl\(^-\) is increased, the acidic melts are found to absorb strongly around 280 nm (Fig. 2). The sample containing virtually 100% Al\(_n\)Cl\(^-\) \((N=0.6665)\) also showed a broad band at 335 nm beside the peak at 280 nm. The high wavenumber shoulder is probably due to other oligomeric forms of chloroaluminate, \([\text{AlCl}_x^y\text{Cl}_n]^-\).

We have examined a solution of LiAlCl\(^+\) in acetonitrile. The spectrum is shown in Fig. 3. The band at 240 nm in this spectrum is due to [AlCl\(^+\)] anion agreeing with the strong absorption edge observed for the basic melts containing the same species. On hydrolysis, the peak at 240 nm is displaced by a peak at 260 nm (Fig. 3) possibly due to the hydrolysis of the chloroaluminate anion to produce Al(III) aquo ion, \([\text{Al(OH})_3]^+\). It is found that Al(III) aquo ion at a pH 0.9 exhibits the same spectrum profile with a peak at 258 nm. Recent spectroscopic investigation of McIntyre et al. \([3]\) on the hexaaquo-Al(III) ion confirmed the presence of other equilibria involving the aquo ion, hydroxide ion and the counter anions.

The excitation and emission spectra of 1-methylimidazole (MIM), MEIC and 0.4 melt were investigated. Both MIM and MEIC show a strong and sharp excitation peak at 245 nm and a broad photoluminescence peak at 445 nm. This luminescence is due to \(\pi^* \rightarrow \pi\) transition of the imidazolium moiety. The excitation spectrum of the melt (0.4) consisted of three peaks at 270, 355 and 395 nm. On excitation with 270 and 355 nm radiation, we were able to observe a strong emission band at 445 nm similar to that observed for MIM and MEIC solutions (Fig. 4). However, excitation of the melt (0.4) with 395 nm radiation produced a new luminescence peak at 470 nm, which is tentatively assigned to the coexcited chloroaluminate species. Fluorescence studies on other melt compositions are in progress and will be reported elsewhere.

Further characterization of the melts may be carried out from the observed difference in the far IR spectra due to the presence of different chloroaluminate species \([\text{AlCl}_x^y\text{Al}_n\text{Cl}_m^+]\) (Fig. 5). The spectral difference in the 600-200 cm\(^{-1}\) region is due to the difference in symmetry of the two prominent chloroaluminate species described earlier. We were also able to observe characteristic difference in the hydrogen bonding region \((3300-2900 \text{ cm}^{-1})\) between a 0.4 and a 0.6 melt. This region is complicated by the presence of CH vibrations from the methyl and ethyl groups and definite conclusion have to wait further analysis. The present author, however, strongly
believes that a considerable amount of hydrogen bonding exists between the 2H of MEIC moiety and the chloride ion or the AlCl\textsubscript{4} anion in the basic melts.

1.2 Electrochemical Properties

The electrochemical window of the chloroaluminate melt is limited by the reduction of imidazolium cation and the oxidation of Cl\textsuperscript{-}, AlCl\textsubscript{4}\textsuperscript{-}, and Al\textsubscript{2}Cl\textsubscript{7}\textsuperscript{-} anions. Below 0.5 mole fraction the anodic potential is governed by the oxidation of Cl\textsuperscript{-} and is limited to about 1.0V. Our basic melt (0.4) exhibited an electrochemical window 1.4V with respect to a Al in 0.6 melt, at a scan rate of 50 mV/s agreeing well with that determined by Wilkes et al. [1]. The electrochemical windows are:

0.4 melt: 0.97 to -1.6 V
0.6 melt: 2.35 to -0.05 V

Other physical properties like the transport numbers [2], densities, phase transitions, conductivities, viscosities [4] have been measured. Comprehensive NMR studies [5] and theoretical molecular orbital calculations [6] have also been carried out.

2 Properties of Some Lanthanides and Actinides in Chloroaluminate Melt

Lanthanides and actinides are groups of very similar elements which exhibit a wide variation of oxidation states. The aqueous redox potentials of several of these ions are summarized below. In certain lanthanides these redox potentials show drastic change due to complexation and/or change in solvent polarity (cf. Ce(III)). Added advantages in working with the lanthanides and actinides are that UV/VIS and/or fluorescence spectra may be used for identification of the species present in melt solution.

2.1 Ce(III) Ion (4f\textsuperscript{1}):

The redox behavior of Ce(III)/Ce(IV) couple is strongly dependent on the nature of the counter ion present in aqueous solution. While the non-coordinating anion like perchlorate results in a E\textsuperscript{o} value of 1.70V, the strongly coordinating carbonate anion is found to produce a drastic change in the redox potential value (0.05V) [7]. The following anion dependence E\textsuperscript{o} values are observed: 1.70V (1M HClO\textsubscript{4}), 1.61V (1M HNO\textsubscript{3}), 1.44V (1M H\textsubscript{2}SO\textsubscript{4}), 1.28V (2M HCl) and 0.05V (5.5M K\textsubscript{2}CO\textsubscript{3}).
The redox behavior of Ce(III)/Ce(IV) couple in MEIC-AICI₃ melt (0.4) has been extensively studied by us [8] using a glassy carbon electrode. The redox process is found to be quasi-reversible with a $E_{1/2}$ value of 0.79V against a reference electrode consisting of Al in 0.6 MEIC-AICI₃ melt. Fig. 6 shows the variation of the cyclic voltammetric profile for Ce(III) in 0.4 melt with scan rate. The calculated rate constant($k^0$) for this one electron transfer redox process is $1.20 \times 10^{-5}$ cm/sec.

The species present in the melt was found to be the hexachloro complex of cerium from its charge transfer spectrum between 310 and 350 nm and the Ce-Cl stretching frequency at 280 cm⁻¹ in the infrared region (Fig. 5) [9]. The final confirmation of the tervalency of cerium in 0.4 melt, before the electrochemical oxidation, came from the observation of ionic fluorescence at 370 nm for the cerium containing melt (Fig. 7). The Ce(IV) solutions do not exhibit this type of ionic fluorescence. Combining the electrochemical and spectroscopic data we find the electroactive species to be hexachloro-cerium(III) ion, [CeCl₆]⁻.

2.2 Tb(III) (4f⁸) Ion:

It is tempting to assume that Tb(III) ion with one more electron than the half-filled configuration, 4f⁷, will easily lose an electron. Unfortunately, it has not been possible to oxidize Tb(III) to Tb(IV) in aqueous solution. The estimated $E^0$ value for Tb(III)/(IV) couple is above 2.8V, and Tb(IV), if present, in aqueous solution will tend to oxidize water.

Attempts to measure the Tb(III)/(IV) couple in 0.4 melt (MEIC-AICI₃) has also been unsuccessful. However, we were able to observe the characteristic green ionic fluorescence from Tb(III) in 0.4 melt. Excitation of the Tb(III) solution at the ligand (MEIC) absorption band (348 nm) resulted in a very broad fluorescence band of the organic moiety with a maxima at 450 nm. No sharp fluorescence due to Tb was noticeable. A time-resolved fluorescence study (Fig. 8) revealed a rise time of ~50μs for the ionic fluorescence. The sharp fluorescence from $^5D_4$ level of Tb(III) to the ground $^7F_j$ multiplets became evident.

We were interested in measuring the lifetime($\tau$) of the excited $^5D_4$ level by monitoring the time dependent decay of the green fluorescence at 550 nm due to the $^5D_4$ → $^7F_j$ transition of Tb(III). An average value of $\tau = 2.34$ ms was observed. A comparison of this data with that of the aquo ion and Tb(III) in other anhydrous solvents is presented below. The lifetime of the $^5D_4$ level in 0.4 melt is about five times that of the aquo ion and it is higher than that of TbCl₃ in AICI₃ vapor phase complex. The $\tau$ value is very close to that of the anhydrous laser liquid, POCl₃:SnCl₄. It is conceivable that 0.4 MEIC-AICI₃ melt may compete favorably with anhydrous POCl₃:SnCl₄ solvent as a laser liquid. From a series of spectroscopic measurements and a charge transfer band of Tb(III) in 0.4 melt, it is concluded that the active species present in solution is probably [TbCl₆²⁻] ion.

Comparison of the Lifetime (msec) Data:

| Levels | Aquo ion TbCl₃-(AlCl₃)x | TbPOCl₃:SnCl₄ | Tb-MEIC-AICI₃ |
|--------|------------------------|---------------|---------------|
| 5D3    | - 0.29(250°C)          | 0.29(25°C)    | 0.40(25°C)    |
| 5D4    | 0.43(25°C) 1.52(250°C) | 2.75(25°C)    | 2.34(25°C)    |

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2.3 Sm(III) 4f⁵, Eu(III) 4f⁶, Yb(III) 4f¹³ Ions:

Trivalent Sm, Eu and Yb could be easily reduced in aqueous solution. We have recently measured the M(III)/(II) redox couple in aqueous solution (1M KCl). The E\text{D/2} values(V) obtained from the cyclic voltammograms are -0.5 (Eu), -1.6 (Sm) and -1.2 (Yb). These values are in agreement with those predicted by Nugent et al. [10]. Recently, Schoebrechts et al. [11] have conducted cyclic voltammetric studies on these ions, but using 1-butylpyridinium chloride (BPC) and AlCl₃ melt. Electrochemical and spectroscopic studies were carried out in acidic BPC-AlCl₃ melt (0.6). These authors reported the following E\text{D/2} values(V): +1.86 (Eu) , +0.66 (Sm) and +1.23 (Yb). They proposed the presence of species like MCl₂⁺ (Sm, Yb), YbCl₂⁺, YbCl₃⁺ besides the free M³⁺ and M⁴⁺ ions. It is, however, difficult to see how the acidic melts have contributed to the formation of the lower chloro-species, unless these species have resulted from the dissociation of the lanthanide trichlorides used in these studies. We are at present systematically studying these systems in MEIC-AlCl₃ melts and the results will be reported in the near future.

2.4 U(V) 5f¹ Ion:

Uranium presents an interesting challenge to the electrochemists. The oxidation state may vary between 3 and 6. In aqueous solution "naked" U(V) and U(VI) are rare. We were interested in preparing a solution of U(IV) by dissolving UC₁₄ in 0.4 MEIC-AlCl₃ melt. The resulting solution was green in color, showing the presence of U(IV) ion in solution. However, within a few hours the green solution bleached to a clear yellow color. Spectroscopic examination of this yellow liquid showed no absorption bands due to U(IV) nor did it exhibit the characteristic peaks of the UO₂⁺ ion in the visible region. The spectrum profile (Fig. 9) [11], however, corresponded closely to the reported [12] U(V)-chloro complex, UC₁, in nitromethane solution. The species responsible for causing oxidation of U(IV) to U(V) is believed to be the proton (H⁺) generated from the minute amount of water present as water of crystallization in MEIC and acting as a strong oxidizing agent in almost-anhydrous chloroaluminate melt.

Cyclic voltammetric studies were performed on this unusual solution of UC₁₄ by scanning the glassy carbon electrode between 0.6 and -1.2V. In dilute solution a cathodic peak (U(IV)→U(IV)) was observed around -0.7V but no anodic peak was found. It was apparent that reoxidation of the reduced U(IV) species is taking place before the anodic potential is reached. In a more concentrated solution (0.04 M) strong hysteresis (Fig. 10) was observed and the cathodic peak occurred at -0.55V. This system is being further investigated.

3 Modification of Chloroaluminate Melts:

Arising from the previous work that a proton (H⁺) may coexist in chloroaluminate melts, the author has conducted preliminary experiments to increase the conductivity of these melts by treating the melts with dry HCl gas. Fig. 11 shows the measured specific conductivities of a 0.36 melt at 27°, -23° and -64° C. Treatment of this melt with dry HCl gas noticeably increased
(3-fold) the conductivity of the melt both at 27° and -23° C. The conductivity of the HCl-treated melt at -23° (melt remains fluid, although slightly more viscous) is comparable to that of the untreated melt at 27° C. The very low conductivity of the melt and the HCl-treated melt at -64° is due to the glassy transition of the melt at this temperature with significant increase in internal resistivity.

To gain further insight and have some idea of the nature of the species present in the HCl-treated melt, we have examined the HCl-treated melt by H-nuclear magnetic resonance (NMR) spectroscopy. The presence of a highly acidic proton at 0.6 ppm downfield from 2H of the imidazolium ring (2H is the most acidic proton in MEIC) is detected (Fig. 12). A semi-quantitative analysis of the intensities revealed the composition to be 1:1 MEIC:HCl. This composition did not seem to alter over a period of at least two weeks at room temperature. Further investigation on the composition, conductivities and electrochemical properties of the HCl-treated melt is under progress.

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Fig. 1. Ultraviolet absorption spectrum of aqueous 1-methyl-3-ethylimidazolium chloride (1 cm pathlength).

Fig. 2. Ultraviolet absorption profile of MEIC-AICl₃ melts containing varied amount of AICl₃ mole fractions(N) (3mm pathlength).

Fig. 3. Ultraviolet absorption spectra of (a) said LiAlCl₄ in acetonitrile, (b) hydrolyzed solution of (a), and (c) Al(III) aquo ion of pH 0.9.
Fig. 4. Fluorescence/excitation spectrum of 0.4 (basic) MEIC-\text{AlCl}_3\ melt.

Fig. 5. Far IR spectra of (a) 0.4, (b) 0.6 melts and (c) Ce(III) in 0.4 melt.

Fig. 6. Variation of cyclic voltammograms of Ce(III) solution (0.08 M) in 0.4 (basic) melt at a glassy carbon electrode at 25°.
Fig. 7. Excitation and emission spectra of Ce(III) in 0.4 (basic) melt.

Fig. 8. Time resolved fluorescence spectra showing (a) rise time (exc. 348) and (b) fluorescence decay (exc. 384) of 5D4→7F5 band of Tb(III).
Fig. 9. Ultraviolet absorption spectrum of the yellow solution resulted after oxidation of a UCl$_4$ solution in 0.4 melt and exhibiting charge transfer bands of UCl$_6$ species.

Fig. 10. Cyclic voltammogram of the yellow UCl$_6$ solution in 0.4 MEIC-AICI$_3$ melt (0.04 M) at glassy carbon electrode and showing strong hysteresis.
Fig. 11. Variation of electrical conductivity of a 0.36 MEIC-AlCl₃ melt and the same melt after treatment with HCl(g) as a function of temperature.

Fig. 12. H-NMR spectrum of the HCl-treated melt showing the presence of an acidic proton at ~0.6 ppm upfield of 2-proton in MEIC (melt).