case 1–5 mbar of pure N_3F was mixed with excess reagent and allowed to stand at room temperature. No reaction occurred with H_2O, O_2, XeF_2, OF_2, and Me_3SiN_3. Reactions with NO, CO, and COS led to products that can be interpreted as arising from the formation of NF as an intermediate.

$$N_3F \rightarrow [NF] + N_2 \rightarrow N_2F_2 \text{ (cis/trans)}$$

$$[NF] + NO \rightarrow [?] \rightarrow FNO + N_2O$$

$$\begin{aligned}[NF] + CO \rightarrow [FNCO]^{18} &\xrightarrow{\text{dim.}} NF_2C(O)NCO \\ &\xrightarrow{F_2} NF_2C(O)F \\ &\xrightarrow{CO} FC(O)NCO\end{aligned}$$

$$[NF] + COS \rightarrow [FNS] + CO \rightarrow FSN$$

These few examples show clearly that the chemistry of N_3F is significantly different from the chemistry of other halogen azides.[19]

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. N_3F, 14986-60-8; HN_3, 7782-79-8; F_2, 7782-41-4; NaN_3, 26628-22-8; H_2SO_4, 7664-93-9; NO, 10102-43-9; CO, 630-08-0; COS, 463-58-1.

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Electrochemistry and Spectroelectrochemistry of the Hexachloroiridate(III) and -(IV) Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Room-Temperature Ionic Liquid

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In contrast to its behavior in aqueous solution, the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system exhibits classical reversible, uncomplicated electrochemical behavior at glassy-carbon electrodes in the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride room-temperature ionic liquid. The formal potential of this redox system in the 49.0/51.0 mol % melt was found to be 0.370 V vs. Al in the 66.7/33.3 mol % melt. Diffusion coefficients for $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ in the former melt were 4.3×10^{-7} and 3.0×10^{-7} cm^2 s^{-1}, respectively, at 40.0 °C. The Stokes–Einstein product for $[IrCl_6]^{2-}$ in the ionic liquid was remarkably close to its value in aqueous solution.

Introduction

Room-temperature chloroaluminate ionic liquids[1] are obtained when aluminum chloride is combined with certain organic chloride salts. Two examples of such mixtures are aluminum chloride–1-methyl-3-ethylimidazolium chloride ($AlCl_3$–MeEtimCl) and aluminum chloride–1-(1-butyl)pyridinium chloride ($AlCl_3$–BupyCl). Both ionic liquids can be made to exhibit a wide range of Lewis acidities and solvation characteristics at room temperature simply by varying the relative amounts of $AlCl_3$ and organic salt. The acid–base properties of these solvents have been reported;[2] mixtures that contain a molar excess of $AlCl_3$ are designated as "acidic", while those containing a molar excess of the organic salt are denoted as "basic".

Basic $AlCl_3$–BupyCl and $AlCl_3$–MeEtimCl are excellent solvents in which to study the solution chemistry of transition-metal chloride complexes at room temperature since the solvation and solvolysis reactions commonly associated with these complexes in aqueous solution are absent in the melts.[3] A number of first-row transition-metal chloride complexes have been investigated in room-temperature chloroaluminate melts, including cobalt(II),[4] copper(I) and copper(II),[5] iron(II) and iron(III),[6] nickel(II),[6a,7] and titanium(III) and titanium(IV),[8] while studies with second- and third-row transition-metal ions have been limited to silver(I),[9] molybdenum(III) and molybdenum(IV),[10] ruthenium(III) and ruthenium(IV),[11] and tungsten(III) through tungsten(V).[12]

The iridium(III) chloride complex, $[IrCl_6]^{3-}$, is known to undergo aquation readily in aqueous solution to form species of the type $[IrCl_{6-x}(OH_2)_x]^{x-3}$.[13] Moreover, a recent spectroscopic study of the iridium(IV) chloride complex, $[IrCl_6]^{2-}$, in the $AlCl_3$–MeEtimCl melt suggested that much of the classical spectroscopic data reported for this species in aqueous solution (even at high chloride ion activity) was actually obtained for a mixture of chloride and aquated chloride species.[3] In addition, $[IrCl_6]^{2-}$ is reported to undergo spontaneous reduction to $[IrCl_6]^{3-}$ in neutral or basic aqueous solutions with the evolution of oxygen.[14] The formal potential of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system has been determined by using potentiometry in aqueous solution, and diffi-

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Table I. Absorption Spectroscopic Data for $[IrCl_6]^{2-/3-}$ Complexes in Molten $AlCl_3$–MeEtimCl

species	mol % of $AlCl_3$	λ, nm (ε, L mol^{-1} cm^{-1})
$[IrCl_6]^{3-a}$	44.4	365 (80), 424 (90), ~580–590 (10)^b
$[IrCl_6]^{2-}$	44.4	300 (1.1 × 10^3), ~365,^{c} 436 (3.9 × 10^3),^{b} 494 (4.5 × 10^3), 581 (4.3 × 10^2)
$[IrCl_6]^{3-a}$	49.0	367 (80), 425 (90), ~580–590 (9)^b
$[IrCl_6]^{2-}$	49.0	302 (1.2 × 10^3), ~365,^{c} 436 (4.1 × 10^3),^{b} 495 (4.6 × 10^3), 582 (4.3 × 10^2)

^{a}Produced by electrolytic reduction of $[IrCl_6]^{2-}$. ^{b}Broad peak comprised of two or more bands. ^{c}Very weak.

culties associated with the conversion of the parent chloride complex to aquated complexes were noted here as well.[15] Several polarographic and voltammetric studies of $[IrCl_6]^{2-}$ and/or $[IrCl_6]^{3-}$ in aqueous solution have been reported,[16] but the extent to which the results of these investigations might have been influenced by the aforementioned aquation and reduction processes is indeterminable. The reduction of $[IrCl_6]^{2-}$ has also been studied in nonaqueous solvents.[16e,17] However, little detail was presented in these studies.

Investigations of iridium chloride complex solutes in chloride-based molten salts, where it should be possible to avoid solvolysis, are limited to those of Dickinson and Johnson,[18] who reported spectroscopic data for $[IrCl_6]^{3-}$ in molten LiCl–KCl at 450 °C, and Laitinen and Plambeck,[19] who measured the Ir(III)/Ir electrode potential in the same melt. The investigation described herein was undertaken in order to obtain electrochemical data for the $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ complexes in the $AlCl_3$–MeEtimCl ionic liquid. No previous electrochemical study of these complexes in chloroaluminate melts has been reported. Techniques that were used for this study include cyclic and rotating-disk voltammetry, chronoamperometry, controlled-potential electrolysis, and transmission spectroelectrochemistry.

Experimental Section

Apparatus. The glovebox system, electrochemical cell, glassy-carbon rotating disk electrode (GCRDE), and thermostated furnace employed during this study were identical with those used in a previous investigation.[12] Conventional cyclic and RDE voltammetry, chronoamperometry, and controlled-potential electrolysis were performed with an AMEL Model 551 potentiostat coupled to a PARC Model 175 universal programmer. Data were recorded on a Houston Instruments Model 100 X-Y/Y-t recorder. All potentials were referenced to an aluminum electrode immersed in the nominal 66.7/33.3 mol % $AlCl_3$–MeEtimCl melt and separated from the bulk melt by a fine-porosity frit.

Spectroelectrochemical experiments were performed in a 1 mm path length microcell containing a reticulated glassy-carbon optically transparent electrode (GVC-OTE) with a microprocessor-controlled, fiber optic spectrophotometry system,[20] an AMEL Model 552 high-voltage potentiostat, and an AMEL Model 566 function generator. Absorption spectra were also recorded in 1 mm path length fused silica cells fitted with airtight Teflon caps with the use of a Perkin-Elmer Hitachi 200 UV–vis spectrophotometer.

Chemicals. Aluminum chloride (Fluka, A.G.) was purified by repeated sublimation directly in the glovebox. 1-Methyl-3-ethylimidazolium chloride was synthesized from chloroethane (Union Carbide Corp.) and 1-methylimidazole (Aldrich) and then purified according to the method described by Wilkes et al.[21] $K_2[IrCl_6]$ (Alfa, 99.9%) was used as received; $[MeEtim]_2[IrCl_6]$ (MeEtim = 1-methyl-3-ethylimidazolium ion) was synthesized by an exchange technique.[22]

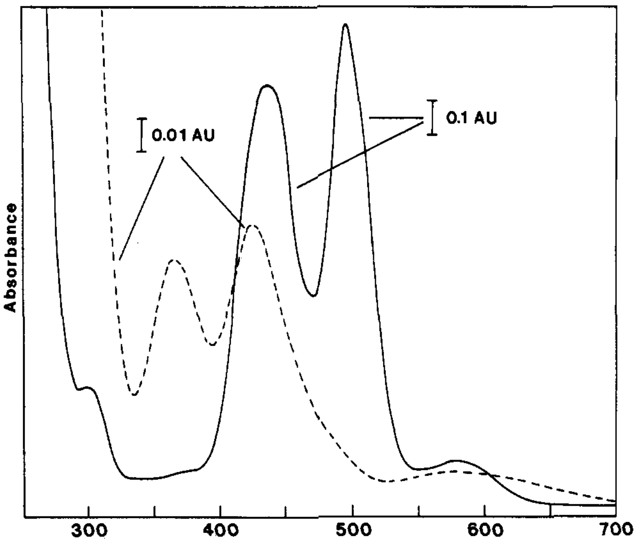

Figure 1. Absorption spectra of $[IrCl_6]^{2-/3-}$ complex ions in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt at approximately 25 °C: (—) 3.28 × 10^{-3} M $[IrCl_6]^{2-}$; (---) 9.09 × 10^{-3} M $[IrCl_6]^{3-}$ that was produced by exhaustive reduction of a 9.09 × 10^{-3} M $[IrCl_6]^{2-}$ solution at 0 V.

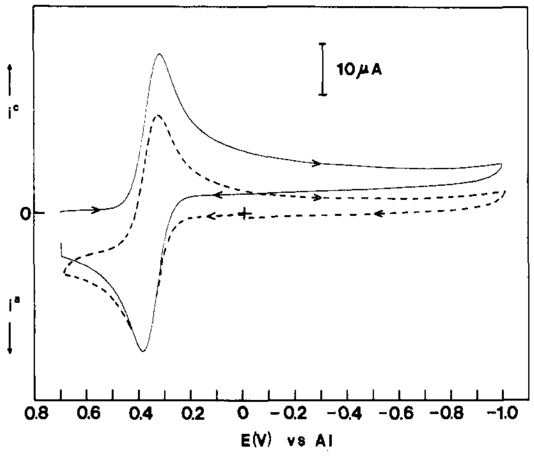

Figure 2. Cyclic voltammograms of $[IrCl_6]^{2-/3-}$ complex ions in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt at a glassy-carbon electrode at 40 °C: (—) 1.10 × 10^{-2} M in $[IrCl_6]^{2-}$ (---) 1.10 × 10^{-2} M in $[IrCl_6]^{3-}$ that was produced by exhaustive reduction of the $[IrCl_6]^{2-}$ solution at 0 V. The sweep rate was 50 mV s^{-1}.

Results and Discussion

Voltammetry. $K_2[IrCl_6]$ and $[MeEtim]_2[IrCl_6]$ each dissolved in the basic $AlCl_3$-MeEtimCl ionic liquid to produce red-brown solutions. The spectroscopic properties of these solutions were found to be independent of the source of $[IrCl_6]^{2-}$. An absorption spectrum of $[IrCl_6]^{2-}$ in the basic $AlCl_3$–MeEtimCl room-temperature ionic liquid is presented in Figure 1, and spectroscopic data for $[IrCl_6]^{2-}$ in the melt are given in Table I. A cyclic voltammogram for the reduction of $[IrCl_6]^{2-}$ in the 49.0/51.0 mol % melt at a glassy-carbon electrode is shown in Figure 2. The average voltammetric peak potential separation found during the reduction of $[IrCl_6]^{2-}$ was 0.062 V over a range of scan rates extending from 0.010 to 0.200 V s^{-1} at 40.0 °C. This value is in excellent agreement with the theoretical separation of 0.062 V for a one-electron, reversible charge transfer at this temperature. In addition, the peak current ratio, calculated by using Nicholson's method,[23] varied from 1.0 to 1.1 over this same range of scan rates. Cyclic voltammetric potential data for $[IrCl_6]^{2-}$ are collected in Table II.

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Table II. Summary of Electrochemical Data for $[IrCl_6]^{2-/3-}$ Complexes in Basic $AlCl_3$–MeEtimCl at 40 °C

solute	mol % of $AlCl_3$	E_p,[a] V	$E_{1/2}$,[b] V	$E_{1/2}$,[c] V	10^7D, $cm^2\ s^{-1}$ RDE	LSV	CA	$E°'$,[d] V	$10^8\eta D$,[e] g cm s^{-2}
$[IrCl_6]^{2-}$	44.4	0.306	0.340	0.338	2.6	2.5	2.8	0.344	5.6
$[IrCl_6]^{3-}$	44.4	0.368	0.337	0.337	1.9	1.8	2.0		3.9
$[IrCl_6]^{2-}$	49.0	0.324	0.355	0.354	4.2	4.1	4.6	0.361	5.5
$[IrCl_6]^{3-}$	49.0	0.390	0.358	0.355	2.9	2.8	3.2		4.0

[a] Average voltammetric peak potential over the range of sweep rates from 0.01 to 0.20 V s^{-1}. All potentials were referenced to Al in the 66.7/33.3 mol % melt. $E_{1/2}$ for the oxidation of ferrocene was observed at approximately 0.25 V vs. this reference electrode in 44.4/55.6 mol % melt. [b] Calculated from CV peak potentials by using $(E_{pa} + E_{pc})/2$. [c] Average GCRDE value over the range of angular velocities from 105 to 209 s^{-1}. [d] Estimated from the GCRDE values of $E_{1/2}$ and the average values of D_O and D_R with $E°' = E_{1/2} + 0.027 \ln (D_O/D_R)^{2/3}$. [e] Calculated from the average values of D_O and D_R.

A series of voltammograms for the reduction of $[IrCl_6]^{2-}$ obtained with use of glassy-carbon rotating disk electrode (GCRDE) were also recorded in the melt. The limiting current for the reduction of $[IrCl_6]^{2-}$ varied linearly with the square root of the electrode rotation rate. Similar linear behavior with the square root of electrode rotation rate was found for currents taken at potentials on the ascending portions of the GCRDE voltammetric waves. GCRDE $E_{1/2}$ values that were obtained during the reduction of $[IrCl_6]^{2-}$ are collected in Table I.

The voltammetric behavior of $[IrCl_6]^{2-}$ in the $AlCl_3$–MeEtimCl melt is strikingly different from that found in aqueous solution. For example, Wightman and co-workers[16f] reported very large pH-dependent cyclic voltammetric peak potential separations for the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system at a glassy-carbon electrode in aqueous sulfate solutions. A cyclic voltammogram of $[IrCl_6]^{2-}$ at a Pt electrode in aqueous 6 M HCl appears ill-defined with a reported peak potential separation of 0.38 V at a scan rate of 0.10 V s^{-1}.[24]

Chronocoulometry and Chronoabsorptometry. Exhaustive electrolytic reduction of $[IrCl_6]^{2-}$ was conducted in the RGC-OTE by stepping the applied potential from 0.60 to 0 V. Although the RGC-OTE cell is not actually a thin cell, its electrochemical behavior is nevertheless very similar to one.[25] Chronocoulometric charge–time and chronoabsorptometric absorbance–time plots that resulted from this experiment are shown in Figure 3. The latter plot was constructed from data obtained by monitoring the absorbance at 494 nm. This wavelength corresponds to an absorption maximum in the spectrum of $[IrCl_6]^{2-}$ (cf. Figure 1). It can be seen that the charge–time and absorbance–time plots become constant at approximately the same time, suggesting complete reduction of the electroactive species confined in the RGC-OTE.

The charge–time plot was corrected for the background current that arises from the reduction of chlorine. Small amounts of Cl_2 were generated at the RGC electrode prior to the application of a negative-potential step because the 0.60-V initial potential needed to carry out the experiment is close to the positive-potential limit of the basic $AlCl_3$–MeEtimCl melt. Consideration of the number of moles of complex added to the RGC-OTE at the start of the experiment and the total charge passed, corrected for a small charge due to chlorine reduction, gave a value of $n = 0.994$ for the $[IrCl_6]^{2-}$ reduction process.

Bulk Controlled-Potential Electrolysis. Controlled-potential electrolysis experiments were also carried out in a glassy-carbon crucible with solutions of $[IrCl_6]^{2-}$ in order to obtain bulk solutions of the reduced species for further study. A UV–vis absorption spectrum of a solution of $[IrCl_6]^{2-}$ in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt after exhaustive electrolysis at 0 V is shown in Figure 1. The absorption spectrum of the reduced solution is similar to that of a solution containing $[IrCl_6]^{3-}$.[13b,26] Spectroscopic data for $[IrCl_6]^{3-}$, which was produced electrolytically, are collected in Table I. A cyclic voltammogram of an electrolytically reduced solution of $[IrCl_6]^{2-}$ in 49.0/51.0 mol % $AlCl_3$–MeEtimCl (Figure 2) also indicates that $[IrCl_6]^{3-}$ is the only electroactive species produced during the reduction process.

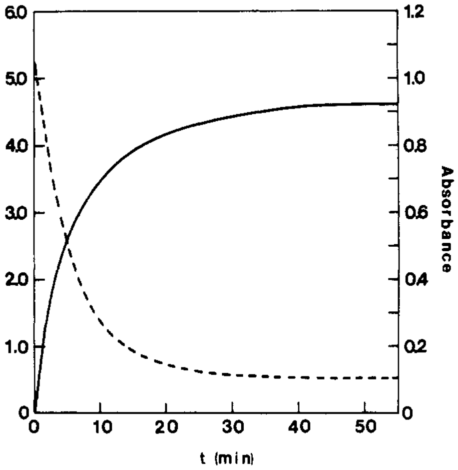

Figure 3. Chronocoulometric (—) and chronoabsorptometric (---) curves for the reduction of $[IrCl_6]^{2-}$ in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt at 40 °C in the RGC-OTE cell. The potential was stepped from 0.60 to 0 V. The absorbance was monitored at 494 nm, and the $[IrCl_6]^{2-}$ concentration was 2.09×10^{-3} M.

Taken together, the results presented above provide convincing evidence that $[IrCl_6]^{2-}$ can be reduced to $[IrCl_6]^{3-}$ in the $AlCl_3$–MeEtimCl melt in a one-electron, reversible electrode reaction that is free from both coupled homogeneous chemistry and the formation of adventitious side products.

$$[IrCl_6]^{2-} + e^- \rightleftharpoons [IrCl_6]^{3-} \qquad (1)$$

The electrochemical and spectroscopic properties of the $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ solutions did not change over several weeks provided that the solutions were maintained in an inert atmosphere.

A small shift in $E°$ for the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system with melt composition is evident in Table II. Similar negative shifts in $E°'$ or $E_{1/2}$ for transition-metal complex ions, which do not exhibit a change in halide coordination upon oxidation or reduction, with increasing chloride ion concentration have been noted before in the $AlCl_3$–MeEtimCl and related ionic liquids.[5b,6b,10-12] The factors leading to this shift are not clearly understood. However, in the apparent absence of a significant composition-dependent liquid-junction potential,[27] this shift may be related to Coulombic interactions in the melt that involve the constituent ions and the solute chlorometalate anions. For example, the 50.0 mol % melt consists principally of melt cations, $MeEtim^+$, and tetrachloroaluminate anions, $AlCl_4^-$. NMR studies suggest that these ion–ion interactions are weak compared to those between $MeEtim^+$ and Cl^-.[28] As the melt is made more basic, the relative fraction of $MeEtim^+$ that is ion paired with Cl^- becomes greater. Thus,

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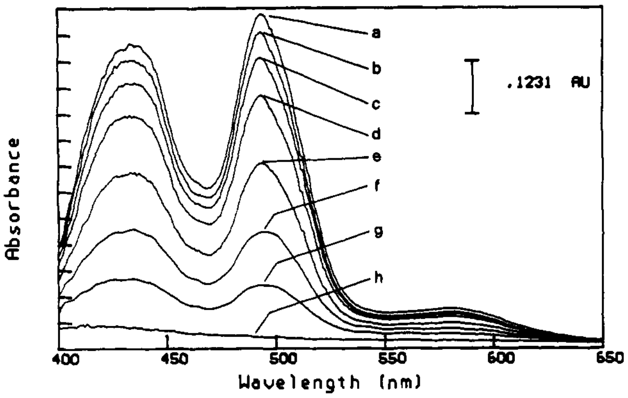

Figure 4. Absorption spectra for a 2.09×10^{-3} M solution of $[IrCl_6]^{2-}$ in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt in the RGC-OTE cell at 40 °C at various applied potentials (V): (a) 0.600; (b) 0.450; (c) 0.425; (d) 0.400; (e) 0.375; (f) 0.350; (g) 0.325; (h) 0.

Coulombic attraction between transition-metal complex anions and the cationic environment is expected to become stronger as the melt is made less basic because proportionally fewer cations are involved in ion-pair formation with Cl^-. These interactions may render anionic complexes slightly easier to reduce or slightly more difficult to oxidize.

Diffusion Coefficients. Diffusion coefficients were estimated for both $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ in the room-temperature ionic liquid from GCRDE limiting-current data, linear-sweep-voltammetric data (LSV), and chronoamperometric data (CA). The average values that resulted from several determinations with each technique are summarized in Table II. The Stokes–Einstein products, $D\eta$, for these two species, which are inversely proportional to the radii of the diffusing entities through the Stokes–Einstein equation, are included in this table also. The values of $D\eta$, and hence the solvodynamic radii for both $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$, do not appear to vary significantly with melt composition. The larger $D\eta$ value for $[IrCl_6]^{3-}$, which suggests that the solvodynamic radius of $[IrCl_6]^{3-}$ is larger than that for $[IrCl_6]^{2-}$, is expected since the metal atom in this complex is in a lower oxidation state than that in $[IrCl_6]^{2-}$.

The diffusion coefficient for $[IrCl_6]^{2-}$ in aqueous solution, 6.4×10^{-6} cm^2 s^{-1},[16f] is considerably larger than that found in the melt. However, when the different solvent viscosities and temperatures are taken into account, a surprisingly close agreement is found between $D\eta/T$ in the melt, 1.8×10^{-10} g cm s^{-2} K^{-1}, and $D\eta/T$ estimated from the diffusion coefficient in aqueous solution, 1.9×10^{-10} g cm s^{-2} K^{-1}. This close agreement suggests that the diffusing species in these two very different solvents may have similar radii.

Spectropotentiostatic Experiments. Spectropotentiostatic experiments were undertaken in order to obtain an independent estimate of the formal potential of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ redox couple, $E°$, in the 49.0/51.0 mol % melt under conditions where current flow was negligible and potential shifts due to uncompensated cell resistance could be expected to be minimal. Absorption spectra were recorded for solutions of $[IrCl_6]^{2-}$ in the RGC-OTE cell after equilibrium was established following the application of selected potential steps. (It should be noted that when equilibrium was established, the steady-state current was very small, since the design of this cell essentially eliminates edge current.[20]) The applied potential, E_a, controls the ratio [Red]/[Ox] through the Nernst equation, and this ratio is in turn reflected by the absorption spectrum[29]

$$E_a = E°' + 2.3(RT/nF)\log\,[(A_R - A)/(A - A_0)] \quad (2)$$

where A_0, A, and A_R represent the absorbances of solutions in the cell containing only $[IrCl_6]^{2-}$, a mixture of $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$, and only $[IrCl_6]^{3-}$, respectively, at 494 nm. Absorption spectra recorded for the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system at different E_a values are shown in Figure 4. A plot of E_a vs. log $[(A_R - A)/(A - A_0)]$ was linear with a slope of 0.064 V (a 0.062-V slope is expected for $n = 1$) and exhibited an intercept of 0.370 V. This value compares favorably with the value of $E°' = 0.361$ V that was calculated from the GCRDE $E_{1/2}$ value and the diffusion coefficients for $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$.

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