constant, though really a measure of the curvature near the potential well, bears a linear relationship with the dissociation energy, which is a measure of the depth of the potential energy well. Such a relationship has been confirmed for hexaamminemetal complexes, for which good thermochemical data exist.[12] Also, ligand field stabilization energy and formation constants decrease with a decrease in force constant, but the relationships are more complex.[18] Therefore, the decrease in the Cu–N force constant on dehydration suggests that the electrostatic field of the zeolite destabilizes the $Cu(NH_3)_4^{2+}$ complexes in its cavities in the absence of mediation from water. This is in contrast to complex formation in layer clays, where enhanced stabilization has been noted for formation of $Cu(en)_2^{2+}$ complexes.[19] The decrease in ligand field stabilization energy is also reflected in the electronic absorption spectrum; e.g., $Cu(NH_3)_4^{2+}$ in solution has d–d bands at 16 600 cm^{-1} compared to 15 600–16 300 cm^{-1} in zeolites X and Y.[7]

The electrostatic interaction between the zeolitic framework and the metal complex is considerably greater in the absence of water. This field must then polarize the Cu–N bond leading to a copper–ammine complex with a lower bond order. Richardson noted such field effects in the EPR spectra of Cu-faujasites.[20] These effects are very important for understanding the role of zeolite as an active support in the catalysis by transition-metal complexes within its cavities. This preliminary study indicates that Raman spectroscopy can play a role in elucidating such effects.

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Studies of Antimony(III) in Ambient-Temperature Ionic Liquids

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In previous work[1–4] we showed the advantage of using a neutral $AlCl_3$–RCl ionic liquid composed of equimolar amounts of $AlCl_3$ and RCl (R^+ = *N*-1-butylpyridinium ($BuPy^+$), 1-methyl-3-ethylimidazolium (Im^+)) to investigate a variety of chemical and electrochemical reactions.

In this note we study the behavior of Sb(III) under conditions where the unbuffered properties of this neutral melt play an important role.

Experimental Section

N-1-Butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride and the neutral $AlCl_3$–RCl melts were prepared as previously described.[1,5,6]

$SbCl_3$ (Alpha Products, anhydrous) was used without further purification.

The reference electrode was an Al wire (5N Alfa Inorganic) immersed in a 1.5:1 $AlCl_3$–RCl melt, and all potentials are given with respect to this electrode. The auxiliary electrode was also a coiled Al wire. The essential details of the experimental techniques, electrodes, and operations in the drybox (Vacuum Atmospheres Co.) have been presented previously.[7]

Working electrodes were glassy-carbon disk (area = 0.454, 0.196, and 0.071 cm^2), tungsten (0.078 cm^2), and platinum (0.049 and 0.12 cm^2). The electrodes surface preparation procedure has been described previously.[8]

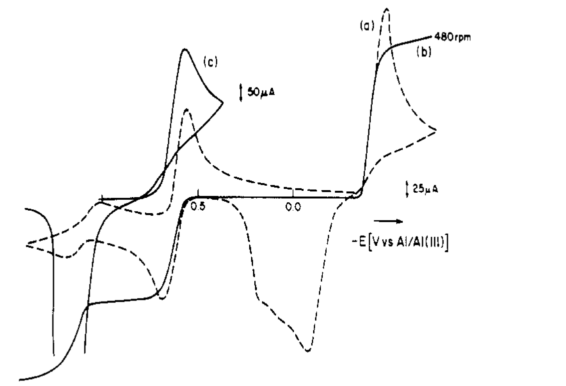

Figure 1. Comparison of electrochemical behavior of Sb(III) in slightly basic (a, b) and slightly acidic (c) $AlCl_3$–ImCl melts (tungsten electrode (area = 0.0784 cm^2); T = 305 K): (a) cyclic voltammogram for 33.1 mmol dm^{-3} Sb(III), v = 0.05 V s^{-1} (b) RDE voltammetric curve for 33.1 mmol dm^{-3} Sb(III) at 480 rpm; (c) cyclic voltammogram for 42 mmol dm^{-3} Sb(III) at v = 0.05 V s^{-1}.

Results and Discussion

Complexation of Sb(III) in $AlCl_3$–RCl Melts. Electrochemical studies of Sb, Sb(III), and Sb(V) carried out in molten mixtures of $AlCl_3$ and BuPyCl as a function of melt composition have been presented.[9] In melt compositions that are basic (mol of $AlCl_3$:mol of RCl < 1) both voltammetric and potentiometric studies indicate $SbCl_4^-$ formation. From potentiometric measurements, $SbCl_2^+$ was indicated as the dominant species in the acidic melts (mol of $AlCl_3$:mol of RCl > 1).

Implicit in the use of potentiometry to study the stoichiometry of complexation in $AlCl_3$–RCl melts is the assumption that complexation of the metal ion exclusively involves interaction with chloride ions whereas the interactions with other ligands, $AlCl_4^-$ and $Al_2Cl_7^-$, are neglected.[4]

To obtain additional information on the complexation of Sb(III) in acidic melts, we employed studies in "neutral" melts.[1,2,4] It is important, however, to emphasize two characteristic features of the Sb(III)/Sb system. The Stokes–Einstein parameter, $D\eta/T$, (where D, η, and T denote diffusion coefficient, viscosity, and temperature, respectively) for Sb(III) remains constant over the entire range of basic-melt composition.[9] However, it differs by 300% from the respective, but also constant, value characteristic of Sb(III) in the acidic melt. This indicates that there is only one species dominant in both basic and acidic melts and that they differ. Also, the entire change of the structure of the complex occurs in the proximity of a "neutral" melt.

Another feature of the Sb(III)/Sb system that changes drastically on going from basic to acidic melts is the reduction potential; Sb(III) reduction in basic melts occurs over 1 V more negative than in acidic melts. The comparison of these processes in basic and acidic melts is presented in Figure 1.

To study the behavior of the Sb(III) species in a neutral, unbuffered melt, the following procedure was employed. A solution of $SbCl_3$ in an exactly neutral $AlCl_3$–ImCl melt was prepared. The cyclic voltammetric and rotating disk electrode (RDE) voltammetric curves for this solution are presented in Figure 2. The heights of both RDE reduction waves are proportional to the $SbCl_3$ concentration; however, they do not follow the Levich equation dependence on $\omega^{1/2}$ for convective–diffusion-controlled

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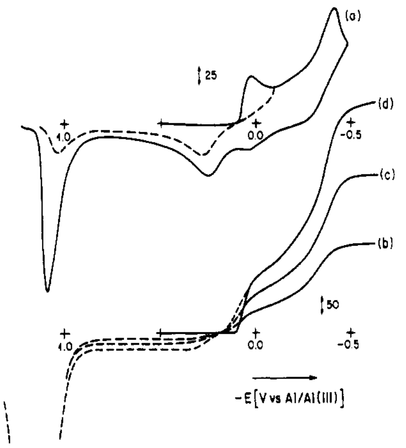

Figure 2. Cyclic voltammogram (a) and RDE voltammograms (b–d) for 17.4 mmol dm^{-3} Sb(III) in netural $AlCl_3$–ImCl melt (tungsten electrode (area = 0.0784 cm^2); T = 305 K): (a) v = 0.05 V s^{-1}; (b) ω (rotation rate) = 400 rpm; (c) ω = 1600 rpm; (d) ω = 3600 rpm. The dotted line corresponds to the reverse scan.

Table I. Electrochemical Parameters of the Sb(III)/Sb(0) System in a Neutral $AlCl_3$ImCl Melt[a]

rotation rate, rpm	half-wave potentials, V: I wave	half-wave potentials, V: II wave	limiting current, μA: I wave	limiting current, μA: II wave	$i_{II}:i_I$
150	0.09	−0.31	50	102	2.04
400	0.09	−0.31	70	160	2.29
1600	0.09	−0.30	118	292	2.47
3600	0.10	−0.30	165	435	2.64

[a] Rotating disk tungsten electrode (area = 0.0784 cm^2); T = 305 K; concentration of $SbCl_3$ = 17.4 mmol dm^{-3}.

processes. The ratios of limiting currents $i_{II}:i_I$ vary with rotation rates (see Figure 2 and Table I).

Upon scan reversal at the RDE, anodic current is observed regardless of whether the reversal potential is located at the plateau of the first or of the second wave. The charge under the anodic stripping peak equals that on the cathodic scan. This indicates that both processes correspond to antimony deposition, and no evidence for a low-valent oxidation state of antimony is found.

$E_{1/2}$ of the first wave is located at about 0 V vs. 1.5:1 $AlCl_3$–ImCl, i.e. approximately in the middle between the values characteristic of the "acidic form" of Sb(III) ($E_{1/2}$ = 0.6 V) and "basic form" ($E_{1/2}$ = −0.5 V). The $E_{1/2}$ of the second wave is slightly positive with respect to the $E_{1/2}$ of the "basic form". These values suggest that the dominant species in a neutral melt differ from those in basic and acidic melts.

If small portions of $AlCl_3$ were added to a solution of $SbCl_3$ in a neutral melt, a new wave was observed at potentials characteristic of the reduction of the "acidic form" of Sb(III). As the ratio of concentrations, R ($=c_{AlCl_3}:c_{SbCl_3}$), was increased to about 3, the height of this wave increased at the expense of that characteristic of a neutral melt. This effect is presented in Figures 3 and 4. At R = 3 only one, "acidic", wave was observed, and further additions of $AlCl_3$ did not change the height of this wave.

This minimum value of R necessary to observe electrochemical behavior of the Sb(III)/Sb couple characteristic of the acidic melts is not surprising since all three chlorides incorporated into an $SbCl_3$ molecule must be neutralized either before and/or during electroreduction of Sb(III) to Sb(0). That is, the dissolution of $SbCl_3$ in the neutral or slightly acidic melt must generate three Cl^- ions on reduction of Sb(III), regardless of any preceding chemical reaction. If we assumed that $SbCl_3$ *did not* react directly with excess $AlCl_3$, then on reduction of $SbCl_3$, the liberated Cl^- must react. In order to determine how many chlorides are neutralized before the electrode process (i.e. what is the dominant Sb(III) species diffusing to the electrode and undergoing electroreduction) and how many chlorides are released during electroreduction, we analyzed the increase of the "acidic form" reduction current at

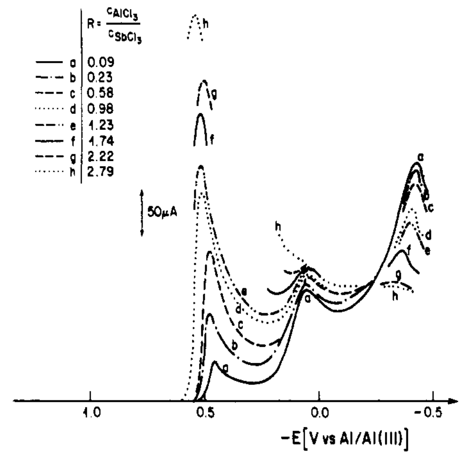

Figure 3. Voltammograms for 27.7 mmol dm^{-3} Sb(III) in neutral $AlCl_3$–ImCl melt at different $AlCl_3$:$SbCl_3$ concentration ratios R (platinum electrode (0.12 cm^2); T = 305 K; v = 0.05 V s^{-1}).

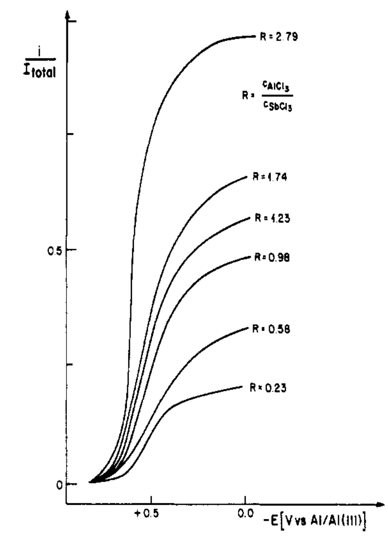

Figure 4. Rotating disk voltammograms for 27.7 mmol dm^{-3} Sb(III) in neutral $AlCl_3$–ImCl melt at different $AlCl_3$:$SbCl_3$ concentration ratios R (platinum electrode (0.12 cm^2); T = 305 K; rotation rate ω = 900 rpm).

Table II. Dependence of the Limiting Reduction RDE Current of Sb(III) "Acidic Form" on the $AlCl_3$:$SbCl_3$ Concentration Ratio R[a]

$R = c_{AlCl_3}:c_{SbCl_3}$	$i:i_{tot}$(exptl)	max $i:i_{tot}$ expected: eq 1	max $i:i_{tot}$ expected: eq 2	max $i:i_{tot}$ expected: eq 3
0.23	0.208	0.077	0.115	0.23
0.58	0.338	0.193	0.29	0.58
0.98	0.50	0.33	0.49	0.98
1.23	0.58	0.41	0.615	1.0
1.74	0.67	0.58	0.80	1.0
2.79	0.97	0.93	1.0	1.0
3.0	1.0	1.0	1.0	1.0

[a] Platinum electrode (0.12 cm^2); rotation rate ω = 900 rpm.

$0 < R \leqslant 3$ (see Figure 4). Table II shows the values of the ratio $i_{obsd}:i_{tot(R=3)}$ (experimental) as well as maximum values of this ratio calculated for three different mechanisms. The possibilities considered for the acid–base equilibria preceding the electrode reaction are

$$SbCl_3 + 3AlCl_3 \rightarrow Sb^{3+} + 3AlCl_4^- \quad (1)$$

$$SbCl_3 + 2AlCl_3 \rightarrow SbCl^{2+} + 2AlCl_4^- \quad (2)$$

$$SbCl_3 + AlCl_3 \rightarrow SbCl_2^+ + AlCl_4^- \quad (3)$$

and it is assumed that only the Sb(III) species on the rhs of eq 1–3 undergo reaction as the "acidic" species. The interaction of Sb(III) with other ligands, particularly $AlCl_4^-$, is neglected. We

Table III. Diffusion Coefficient of Sb(III) in $AlCl_3$–RCl Melts

melt	10^7D, $cm^2\ s^{-1}$	$10^{10}D\eta/T$, $g\ cm\ s^{-2}\ K^{-1}$
slightly basic $AlCl_3$–ImCl	2.65	1.3
slightly acidic $AlCl_3$–ImCl	8.39	4.1
basic $AlCl_3$–BuPyCl[a]		1.3
acidic $AlCl_3$–BuPyCl[a]		3.8

[a] Data taken from ref 11.

do not distinguish here between $SbCl_3$ and $SbCl_3\cdots AlCl_4^-$ or $SbCl_2^+$ and $SbCl_2^+\cdots AlCl_4^-$.

The calculated values of i:i_{tot} correspond to the case when chloride ions released during reduction of the Sb(III) complex do not influence the reduction current of Sb(III). However, all the possible reactions of Cl^- ions released at the electrode surface upon reduction of the Sb(III) will cause a *decrease* of this current; the calculated values are the maximum values for each mechanism. For example, if we consider reaction 1 as occurring in solution *prior* to the reduction of Sb(III), then, at $R = 1$, no more than one-third of the Sb(III) will be transformed into its "acidic form", because the stoichiometry of reaction 1 is 1:3 $SbCl_3$:$AlCl_3$. The experimental data indicates the current of the "acidic form" exceeds $^1/_3$ of i_{tot}, thus eliminating this possibility. By analogy, we can also eliminate the second possibility, i.e. $SbCl^{2+}$ formation.

We have treated the starting solute in a neutral melt as $SbCl_3$ (or $SbCl_3\cdots AlCl_4^-$). One can show that the possible partial autodissociation of $SbCl_3$ into $SbCl_2^+$ and $SbCl_4^-$ or even an equilibrium reaction of $SbCl_3$ with $AlCl_4^-$ to form $SbCl_4^-$ and $AlCl_3$, would not affect our analysis because the added $AlCl_3$ would react with $SbCl_4^-$ rather than with $SbCl_2^+$ or $SbCl_3$, since $SbCl_4^-$ is the strongest Lewis base among these three species.

The analysis of the data on the changes of the wave height with the amount of $AlCl_3$ added does not eliminate the existence of $SbCl_3$ in solution. It does indicate that at least some $SbCl_2^+$ must be present in the solution and that it is the species reducing at +0.6—i.e., the first wave that grows in as $AlCl_3$ is added (Figure 3). If one examines the morphology shown in Figure 1 for the reduction of Sb(III) in basic and acidic melts, then the first wave seen in the reduction in the "neutral" melt (Figure 2) at ca. 0 V is absent. We thus conclude that this wave involves a species not present in the basic or acidic melt and that it is most probably $SbCl_3$, perhaps solvated by tetrachloroaluminate. The second wave in Figure 2 involves the reduction of $SbCl_4^-$, the dominant species of Sb(III) in the basic melt, which forms as a result of the increased basic character in the vicinity of the electrode as the $SbCl_3$ is reduced in this unbuffered, neutral melt. (Table III compares $D\eta/T$ values for Sb(III) in acidic and basic melts.) Thus, we conclude that the addition of $AlCl_3$ to Sb(III) in the neutral melt in fact is as per eq 3.

The presence of $SbCl_2^+$ in molten mixtures of $SbCl_3$ with alkali-metal chlorides and/or $AlCl_3$ has been postulated in the literature.[10-12] Raman studies however did not give support for the above species and instead indictaed some interactions between $SbCl_3$ and $AlCl_3$ in their molten equimolar mixtures.[13] However $SbCl_2^+$ has recently been postulated as the species responsible for the chemical oxidation of perylene in molten $SbCl_3$ containing $AlCl_3$.[14]

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Registry No. ImCl, 65039-09-0; $SbCl_3$, 10025-91-9; $AlCl_3$, 7446-70-0; W, 7440-33-7; Pt, 7440-06-4; Sb, 7440-36-0.

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Photosubstitution Quantum Yields for Hexacyanorhodate(III), $Rh(CN)_6^{3-}$, and Hexacyanoiridate(III), $Ir(CN)_6^{3-}$

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It has been shown that the photochemical properties of the $M(CN)_6^{3-}$ (M = Co(III), Rh(III), Ir(III)) complexes are parallel, each giving the pentacyanoaquo complex as the only photoproduct when photolysis is conducted in acidic aqueous media (eq 1).[1]

$$M(CN)_6^{3-} \xrightarrow[H_3O^+]{h\nu} M(CN)_5H_2O^{2-} + HCN \qquad (1)$$

However, of these, only $Co(CN)_6^{3-}$, which displays a wavelength-independent quantum yield for photoaquation of 0.31 ± 0.02 mol/einstein, has had its solution photosubstitution properties quantitatively characterized.[2-8] Reported here are quantitative investigations of the photosubstitutions displayed by the $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$ ions in acidic aqueous solution at 25 °C. Also reported are the low-temperature (77 K) luminescence spectra and emission lifetimes of these species and of the photoproducts $M(CN)_5H_2O^{2-}$.

Experimental Section

Materials and Synthesis. Reagent grade compounds were used for all preparations described in this work. Water used for syntheses and experimental determinations was deionized and then distilled in an all-glass apparatus.

Potassium hexacyanorhodate(III), $K_3[Rh(CN)_6]$, and potassium hexacyanoiridate(III), $K_3[Ir(CN)_6]$, were prepared from $RhCl_3\cdot xH_2O$ and $IrCl_3\cdot xH_2O$, respectively, according to previously published procedures.[9,10] (*Caution* must be exercised in these syntheses since HCN gas is generated!) Purification of the Rh(III) salt by recrystallization proved insufficient, so the method described by Geoffroy employing alumina and silica gel column chromatography was used.[1] A constant electronic absorption spectrum was obtained after several chromatography runs. The electronic absorption band maxima were in agreement with the literature values; however, the extinction coefficient of the longest wavelength band (260 nm) was found to be significantly lower than reported[1,9] (see below). The infrared spectrum of purified samples agreed with published values.[1,11] The Ir(III) complex was purified by repeated recrystallizations. In agreement with reported results, the spectrum of $Ir(CN)_6^{3-}$ in aqueous solution showed no measurable absorption bands between 700 and 270 nm.[1,10] Below 270 nm the absorption increases (without structure) and goes off scale at ~230 nm. The infrared spectrum was in close agreement with published results.[1,11]

Electronic absorption spectra were recorded on a Cary 118 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. A Radiometer PHM 84 pH meter was used for all pH measurements. A specific-ion electrode (Gam Rad PHI 93100), sensitive to 1×10^{-6} M, was used to detect free CN^- in solution via millivolt readings on the pH meter.

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