ELECTROCHEMISTRY AND SPECTROSCOPY OF BISMUTH CLUSTERS
IN ACIDIC ROOM—TEMPERATURE CHLOROALUMINATES

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ABSTRACT

In 2:1 mole ratio \( \text{AlCl}_3—\text{BuPyCl} \) melts, the electrochemical reduction of \([\text{Bi}_5]^{3+}\) ion to the metal is the sum of two processes : 1) the reversible two—electron reduction of the closo—trigonal bipyramid with the formation of a closed shell nido—square pyramid and 2) the further reduction of this instable intermediate to the metal. On glassy carbon electrodes both processes give raise to separate waves because the deposition of the metal is retarded by nucleation phenomena. Anodisation of the metal or reaction of the metal with \( \text{BiCl}_3 \) produces \([\text{Bi}_3]^{3+}\) ion (or its solid salt \( \text{Bi}(\text{AlCl}_4)_3 \)) and minor traces of another low—valent species, probably "\( \text{BiAlCl}_4 \)".

INTRODUCTION

Bismuth possesses a number of unusual low oxidation states, i.e. lower than that of the familiar \( \text{Bi}(\text{III}) \), which include \( \text{Bi}^+ \) and a series of homopolyatomic ions ; in fact, bismuth has become the classical exemple of an element forming "naked" metallic polycations (1,2).

Early investigations were concerned mainly with solutions of bismuth metal in \( \text{BiCl}_3—\)melts. The results of emf studies and spectroscopic measurements are consistent with the presence of \( \text{Bi}^+ \) and \([\text{Bi}_3]^{+} \) (3—6). The solid phase \( \text{Bi}_{24}\text{Cl}_{28} \) (originall formulated as "\( \text{BiCl} \)" (7)) which can be separated from these melts has been shown by X—ray diffraction studies to be \( ([\text{Bi}_3]^{5+})_2([\text{BiCl}_5]^{2—})_4([\text{Bi}_2\text{Cl}_8]^{2—}) \) (8,9) (more recent work however suggests that the anionic part is better described as polymeric instead of the idealized \( ([\text{BiCl}_3]^{2—})([\text{Bi}_2\text{Cl}_8]^{2—}) \) structure (10)).

Several workers investigated the reaction between bismuth metal and dilute solutions of \( \text{BiCl}_3 \) in acidic (\( \text{AlCl}_3—\)rich) chloroaluminate melts which are particularly good solvents for the stabilisation of low oxidation states (11). Bjerrum et al. (12—15) characterized the products of this reaction in molten \( \text{AlCl}_3—\text{NaCl} \) eutectic (63 mole % \( \text{AlCl}_3 — 37 \) mole % \( \text{NaCl} \)) by UV—visible spectroscopy. These workers studied quantitatively the equilibria

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\begin{align*}
2 \text{Bi}_{\text{liq}} + \text{Bi}^{3+}_{\text{sol}} & \rightleftharpoons 3 \text{Bi}^{+}_{\text{sol}} \\
4 \text{Bi}_{\text{liq}} + \text{Bi}^{3+}_{\text{sol}} & \rightleftharpoons [\text{Bi}_3]^{3+}_{\text{sol}} \\
6 \text{Bi}^{+}_{\text{sol}} & \rightleftharpoons \text{Bi}^{3+}_{\text{sol}} + [\text{Bi}_3]^{3+}_{\text{sol}}
\end{align*}
\]
In addition to Bi\(^{+}\) and [Bi\(5\)\(^{3+}\)], the polycation [Bi\(g\)\(^{2+}\) was characterized in the presence of excess liquid metal (no information was obtained on the number of ligands, chloride or chloroaluminate ions, attached to these entities). Corbett (16,17) subsequently isolated the solid phases Bi\(5\)(AlCl\(3\))\(3\) and Bi\(8\)(AlCl\(4\))\(2\) from the pseudo-binary system Bi—(BiCl\(3\)— 3 AlCl\(3\)). In view of the absence of a salt of the [Bi\(5\)\(^{5+}\) cation in the chloroaluminate system, Corbett (18) also investigated the system Bi—(2 BiCl\(3\) + 3 HfCl\(4\)) to explore the effect of a large cation of relatively high stability and obtained a product with composition Bi\(_{10}\)Hf\(_3\)Cl\(_{18}\). An X-ray diffraction study showed that actual the composition of this compound is ([Bi\(g\)\(^{5+}\)(Bi\(^{+}\)([HfCl\(6\)]\(^2\)\(^-\))\(3\) and not ([Bi\(g\)\(^{3+}\)\(2\)([HfCl\(6\)]\(^2\)\(^-\). The structure of the [Bi\(5\)\(^{3+}\) ion was investigated by infrared and Raman spectroscopy (19). More recently, the preparation of single crystals and the full structural analysis of Bi\(5\)(AlCl\(4\))\(3\) (10) and Bi\(8\)(AlCl\(4\))\(2\) (20) was reported.

Torsi and Mamantov (21) investigated the reduction of Bi\(3^{+}\) at solid electrodes in molten AlCl\(_3\)—NaCl eutectic at 175°C and reported a reversible reduction of Bi\(^{3+}\) to Bi\(^{+}\) (spectroelectrochemical experiments with a rather high concentration of BiCl\(_3\), ~0.3 M BiCl\(_3\), also indicated the formation of [Bi\(5\)\(^{3+}\] ; however, the further reduction of Bi\(^{+}\) is complex and involves an intermediate oxidation state which was not characterized electrochemically. Three reduction waves were observed for the electrochemical reduction of Bi\(^{3+}\) on glassy carbon electrodes in 2:1 mole ratio AlCl\(_3\)—BuPyCl melts (BuPyCl : N—(n—butyl)pyridinium chloride) : the first wave corresponds with the reduction of Bi\(^{3+}\) to [Bi\(5\)\(^{3+}\] but again the further reduction of the cluster ion to the metal was not well understood (22). The AlCl\(_3\)—BuPyCl molten salt system belongs to a class of chloroaluminates, including AlCl\(_3\)—MElI melts (MEIC : 1—methyl—3-ethylimidazolium chloride) which exist as ionic liquids at ambient temperatures (23,24). A comparison of available literature data indicates that these (AlCl\(_3\)—rich) room temperature chloroaluminate melts are by far more acidic solvents than systems such as (AlCl\(_3\)—rich) AlCl\(_3\)—NaCl melts (25,26). This probably explains why the reduction of Bi\(^{3+}\) in the room temperature molten salt results in the formation of [Bi\(5\)\(^{3+}\) and not Bi\(^{+}\) as was observed in AlCl\(_3\)—NaCl melts since acidic conditions and low temperatures generally enhance the stability of homopolyatomic ions. This paper reports some results on the electrochemistry and spectroscopy of bismuth in 2:1 mole ratio AlCl\(_3\)—BuPyCl melts and specifically on the reduction/oxidation of [Bi\(5\)\(^{3+}\] in these melts.

**EXPERIMENTAL**

The synthesis and purification of BuPyCl, the sublimation of AlCl\(_3\) (Fluka) and the preparation of the melts was described previously (27). Anhydrous BiCl\(_3\) (99.999 % ; Alfa Inorganics) was used as received ; a pure bismuth rod (99.999 % ; Goodfellow Metals) was used for anodisation experiments. Solid Bi\(_5\)(AlCl\(_4\))\(3\) was prepared by fusing the stoichiometric quantities of bismuth powder, AlCl\(_3\) and BiCl\(_3\) (19).

All experiments were carried out under a purified nitrogen atmosphere (VAC drybox ; HE—493 Dri Train). The temperature of the melts (25°C, unless indicated otherwise) was controlled by circulating oil, from a thermostat outside the dry box, through the jacket of the conventional Pyrex cell used for the electrochemical measurements.
A rotating disk electrode (Bruker ER—5; speed control E—RS—1) with interchangeable tips (glassy carbon/platinum; geometrical area: 0.282 cm²) was used for the voltammetric measurements; for cyclic voltammery, the electrode was used in the non—rotating mode. A glassy carbon crucible was used as the working electrode for controlled—potential electrolysis experiments. The reference and counter electrodes consisted of 1 mm diam. aluminum wire spirals, immersed in a melt of the same composition and separated from the working electrode compartment by fine porosity glass frits. A bismuth indicator electrode, prepared by electrodeposition of the metal on a gold wire from aqueous perchlorate solution, was used for emf measurements. The electrochemical instrumentation includes a PAR 173/179 potentiostat/digital coulometer, a PAR 175 function generator and a Houston 2000 XY—recorder. Potentials were measured with a Beckman 4500 digital pH meter.

UV—visible absorption spectra were obtained using 1—cm rectangular quartz cells and were recorded on a Beckmann Acta MIV instrument against a reference cell containing solvent. X—ray powder diffraction data were obtained from samples in thin—walled Pyrex capillaries using a Philips Debye—Scherrer camera (diameter: 5.73 cm) with Ni—filtered CuKα radiation.

RESULTS AND DISCUSSION

A cyclic voltammogram of a ~1.0·10⁻³ M BiCl₃ solution at glassy carbon electrode (250°C) (fig.1a) exhibits three cathodic peaks at 0.95 V, 0.71 V and 0.2 V for the reduction of Bi³⁺ to the metal *. The cyclic voltammogram also exhibits three anodic peaks: a sharp peak at 0.92 V which evidently corresponds to the stripping of the metal with formation of a solute species and two peaks at 1.45 V and 1.65 V for the oxidation of this species to Bi³⁺ as is shown by the fact that successive scans are identical with the first. Cyclic voltammograms of the same solution but with different cut—off potentials (fig.1b,c) reveal the presence of other anodic peaks at 0.74 V and 1.05 V which are clearly associated with the first two reduction processes. Increase of the temperature (800°C) (fig.2) has no effect on the cyclic voltammograms beside the normal increase of the current except made on two points: the stripping peak is much more narrow and is shifted slightly to less positive potentials and the small anodic peak at 1.00 V is now observed directly.

The first cathodic peak corresponds to the reduction of Bi³⁺ to [Bi₅]³⁺ as was shown earlier (22) (the peak current of the first reduction process is rather large when compared with the peak currents of the subsequent reduction reactions: this immediately suggests the formation of a low—valent species). Thus, [Bi₅]³⁺ was prepared by exhaustive electrolysis (0.85 V): the solution, initially colorless, turned red—brown during the experiment and the spectrum of the solution, recorded after

* Controlled—potential electrolysis (0.2 V) results in the formation of a finely divided, powdery deposit of bismuth metal. However, the metal reacts slowly with an impurity in the melt with formation of [Bi₅]³⁺ ion. A similar observation was reported by Habboush and Osteryoung (28) who noted a slight oxidation of antimony metal in acidic melts and suggested that the metal reacts with a proton containing species which is present as an "hidden" impurity in these melts (29).
completion of the electrolysis, is in good agreement with the spectrum of \([\text{Bi}_5]^{3+}\) reported by Bjerrum et al. (12,13). Furthermore, the spectrum is identical with the spectrum of a solution prepared by dissolving a solid sample of \(\text{Bi}_5(\text{AlCl}_4)_3\) in the melt. However, the actual mechanism of the reduction of \(\text{Bi}^{3+}\) to \([\text{Bi}_5]^{3+}\) is no doubt more complex. This is shown by the presence of the small peak at 1.05 V which does not correspond to the reverse anodic reaction, i.e. oxidation of \([\text{Bi}_5]^{3+}\) to \(\text{Bi}^{3+}\) (vide infra) but which must be attributed to the oxidation of an intermediate species formed in the reduction reaction. Therefore, it seems logical to assume, in concordance with the work of Torsi and Mamantov (21), that \(\text{Bi}^{3+}\) is reduced in a first step to \(\text{Bi}^+\) (or another \(\text{Bi}(I)\) species) and that the oxidation peak at 1.05 V corresponds to the oxidation of this species: the cluster ion can then be formed by a follow-up chemical disproportionation step (reaction 3). The results obtained in this study did not provide any conclusive evidence for this mechanism: thus, a variation of the scan rate over the range 0.020–0.500 V/s has no effect on the general shape of the cyclic voltammograms, the relative heights of the peak currents or the position of the peak potentials (however, application of a 30–60 second potential hold at 0.85 V before scan reversal results in the disappearance of the small anodic peak). Therefore, the actual mechanism of the reduction of \(\text{Bi}^{3+}\) to \([\text{Bi}_5]^{3+}\) must be left open for further investigation.

The cyclic voltammogram of a \([\text{Bi}_5]^{3+}\) solution, started from 1.0 V in the cathodic direction, exhibits cathodic peaks at 0.71 V and 0.2 V and, after scan reversal, the stripping peak at 0.92 V and the anodic peaks at 1.45 V and 1.65 V; a second scan, after a scan reversal at 1.80 V, exhibits again the large reduction peak at 0.95 V. A cyclic voltammogram started from 1.0 V in the cathodic direction but with the scan reversed at 0.5 V, i.e. after the first reduction peak, shows the corresponding anodic peak at 0.74 V, thus revealing the presence of a reversible oxidoreduction couple (which was shown already in fig.1c). Voltammograms for the reduction/oxidation of \([\text{Bi}_5]^{3+}\) at glassy carbon rotating disk electrodes (fig.4) exhibit two reduction and two oxidation waves as is expected on the basis of the results of cyclic voltammetry. The half-wave potential of the first reduction wave, 0.75 V, is in good agreement with the position of the corresponding peaks in the cyclic voltammogram. The deposition of the metal on carbon however requires a rather large nucleation overvoltage as is shown by a reverse scan, started after the deposition of the metal was initiated. The reverse scan shows that deposition of the metal is observed at potentials as positive as 0.83 V, i.e. slightly more positive than the half-wave potential of the first wave (but slightly negative with respect to the position of the first reduction peak in the cyclic voltammogram of \(\text{BiCl}_3\) solutions). This observation implies that the first wave is observed as a separate reduction step only because the deposition of the metal is retarded by nucleation phenomena (in fact, on platinum rotating disk electrodes both waves strongly overlap so that the reduction of \([\text{Bi}_5]^{3+}\) to the metal almost appears as a single wave). As a consequence, the product of the first wave is not a stable species; this is confirmed by the fact that controlled-potential electrolysis on the limiting current plateau of the first wave (on carbon electrodes) simply results in the deposition of the metal. Therefore, it was impossible to obtain any spectral information on this intermediate species.

The exact measurement of the ratio of the limiting currents of both reduction waves is obscured by the fact that the limiting current plateau for the deposition of the metal is not well-defined. The increase of the current in the limiting current region must be due to the predeposition of aluminum with formation of intermetallic
compounds and not to roughening of the electrode surface since the current decreases again during the reverse scan. Therefore, the ratio of the limiting currents was measured at 0.55 V, i.e. the limiting current of the first wave was obtained from the forward scan whereas the limiting current of the second wave was obtained from the reverse scan. The results obtained this way at different rotation rates (fig. 5) indicate a 2:1 ratio so that the reduction of \([\text{Bi}_{5}]^{3+}\) can be written as:

\[
\begin{align*}
[\text{Bi}_{5}]^{3+} + 2e^- & \rightleftharpoons [\text{Bi}_{5}]^+ \\
[\text{Bi}_{5}]^+ + e^- & \rightarrow 5 \text{Bi}
\end{align*}
\]

The conclusion that the first wave corresponds to a two-electron reduction is also supported by the separation of the cyclic voltammetric peaks, 0.030–0.035 V, in good agreement with the theoretical value (0.030 V). The \([\text{Bi}_{5}]^{3+}\) ion has a trigonal bipyramidal structure with 12 bonding electrons. However, for main group elements there exist no naked trigonal bipyramidal clusters with 12 + 2 bonding electrons: the two-electron reduction of a closo-trigonal bipyramid always results in the formation of a closed shell nido-square pyramid (31). The results of cyclic voltammetry indicate that the couple \([\text{Bi}_{5}]^{3+}/\text{Bi}\) is reversible so that the rate of the intramolecular rearrangement must be fast with respect to the time window of the measurements. At the same time, the observed reversibility virtually excludes any complicated stoichiometry of the reaction and thus indirectly supports the proposed mechanism.

Anodisation of a metallic bismuth rod at low current densities (typically < 100 μA, with an exposed electrode surface of 2–3 cm²) such that the potential of the electrode was less than 0.95 V results in the formation of red–brown solutions of \([\text{Bi}_{5}]^{3+}\) (although there is some other minor component in the solution; vide infra). In a series of experiments, the equilibrium potential of a bismuth indicator electrode was measured after each charge addition. A plot of E vs. log([\text{Bi}_{5}]^{3+}) has a slope close to 0.020 V/decade, in excellent agreement with the theoretical value for a 3-electron electrode reaction (fig. 6). The standard potential of the \([\text{Bi}_{5}]^{3+}/\text{Bi}\)-couple was estimated as \(E^0([\text{Bi}_{5}]^{3+}/\text{Bi}) = 0.925 \pm 0.015 V\) (this value roughly corresponds with the position of the stripping peak in the voltammetric experiments). Anodic dissolution of bismuth at higher current densities results in a red–brown solution with the concomitant formation of a peach–colored film on the electrode. This film was identified by X-ray diffraction as solid Bi₅(AlCl₄)₃ (excess melt adhering to the electrode was removed by repeated washings with dry toluene). The solution is a mixture of \([\text{Bi}_{5}]^{3+}\) (and the minor component) and rather high concentrations of \(\text{Bi}^{3+}\)-ion: this was evidenced by the presence of a reduction wave at 0.95 V in the rotating disk electrode voltammograms (besides the waves for the reduction of \([\text{Bi}_{5}]^{3+}\)). During the anodisation experiments at higher current densities strong potential oscillations were observed although apparently the potential never became more positive than 1.10 V: this seems to indicate that the standard potential of the \(\text{Bi}^{3+}/[\text{Bi}_{5}]^{3+}\)–redox couple is in the range 1.00–1.10 V and that the oxidation of

** The diffusion coefficient of \([\text{Bi}_{5}]^{3+}\) was estimated from the data of fig. 5 using Levich's equation (30) as \(D \approx 2.0 \times 10^{-7} \text{ cm}^2/\text{s}\).
[Bi₅]³⁺ on carbon (or platinum) electrodes is an irreversible process.

The absorption spectrum of [Bi₅]³⁺ solutions prepared by anodisation of the metal (or by reaction of bismuth metal with BiCl₃ solutions) always exhibits an absorption band at 730 nm (fig.7), indicating the presence of another species in the solution. Bi³⁺ — ion does not absorb in the spectral region of interest whereas Bi⁺ (in AlCl₃—NaCl melts) has its strongest absorption peaks at 585 nm and 663 nm (13). However, a species with a strong absorption band at 723 nm (ε = 5.4x10⁴ 1 mole⁻¹cm⁻¹) and identified as BiAlCl₄ was observed by Lynde and Corbett (32) in the gaseous ternary system Bi—BiCl₃—AlCl₃ (at temperatures above 400—450°C). Therefore it is suggested that small amounts of Bi(I) exist in these solutions as a chloroaluminate complex, "BiAlCl₄" (it is not clear whether the weak absorption in the region 610—660 nm can be attributed to Bi⁺— ion). As noted earlier, the occurrence of the small anodic peak at 1.05 V in the cyclic voltammograms at higher temperatures (fig.2) provides further, albeit indirect, evidence for the formation of a Bi(I) species during the anodisation of the metal.

Two anodic waves are observed in the voltammograms for the oxidation of [Bi₅]³⁺ to Bi³⁺ at carbon rotating disk electrodes (fig.4) but the actual electrode reactions no doubt are complicated. Thus, the total height of both anodic waves equals four times the sum of both reduction waves, as expected from the stoichiometry of the reactions. However, the ratio of the anodic wave heights varied from one experiment to another, almost at random (the height of the first wave is never less than about one half of the total wave height). A similar observation was made with platinum electrodes but the reason for this behavior is not understood at present. Apparently, the oxidation initially occurs only at preferred sites on the electrode surface: once these sites are saturated (or poisoned), the reaction can occur on the rest of the electrode surface but only at more positive potentials. It is not clear however what species is responsible for this saturation (or poisoning) or what is the reason for the observed non—reproducibility of the relative wave heights.

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Figure 1. Cyclic voltammogram for the reduction/oxidation on glassy carbon electrode of ~1 mM BiCl₃ solution in a 2:1 mole ratio AlCl₃:BuPyCl melt with different cut-off potentials (scan rate: 0.1 V/s; 25°C).

Figure 2. Cyclic voltammogram for the reduction/oxidation on glassy carbon electrode of ~1 mM BiCl₃ solution in a 2:1 mole ratio AlCl₃:BuPyCl melt (scan rate: 0.1 V/s; 80°C).
Figure 3. Electronic absorption spectrum of [Bis]$^{3+}$ in a 2:1 mole ratio AlCl$_3$:BuPyCl melt.

Figure 4. Voltammogram for the reduction/oxidation of [Bis]$^{3+}$ on glassy carbon rotating disk electrode in a 2:1 mole ratio AlCl$_3$:BuPyCl melt; also shown is the reverse scan started after the deposition of the metal was initiated.

Figure 5. Plot of $i_1$ vs. $\sqrt{\omega}$ for the reduction of [Bis]$^{3+}$ on glassy carbon rotating disk electrode in a 2:1 mole ratio AlCl$_3$:BuPyCl melt: 1) first reduction wave 2) sum of first and second reduction waves. Both limiting currents were measured at 0.55 V (see text).
Figure 6. Plot of $E ([\text{Bi}_3^{3+}/\text{Bi}])$ vs. $\log ([\text{Bi}_3^{3+}])$. Experimental points were obtained by measuring the potential of a bismuth indicator electrode after each charge addition during the anodisation of bismuth metal (filled circles are values measured when the experiment was continued the next day after standing overnight).

Figure 7. Absorption spectrum (part) of a solution prepared by anodisation of bismuth metal (see text).