Redox Reactions of Bismuth Subhalides, Bil and Bi₆Cl₇, in Acidic Room-temperature Chloroaluminate Melt

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Electrochemical study on redox reactions of polybismuth cations has been carried out in the acidic 1-methyl-3-benzyl imidazolium chloride (MeBzImCl) + 67 mol % AlCl₃ melt, where MeBzImCl was synthesized from 1-methyl imidazole and benzyl chloride. The reduction of Bi₄⁺⁺⁺⁺ to Bi₆⁺⁺⁺⁺ (Bi₄⁺⁺⁺⁺ + 3e⁻ = 1/2 Bi₆⁺⁺⁺⁺) occurs at the cathodic peak around 0.6 V for Bil dissolved into this melt. The number of electron which took part into reduction at the cathodic peak around 0.6 V was determined as 2.8 ± 0.3 by polarography for Bil. For Bi₆Cl₇ dissolved into this melt, the reductions of Bi₃⁺⁺⁺⁺ to Bi⁺⁺⁺⁺, Bi₅⁺⁺⁺⁺ to Bi⁺⁺⁺⁺ and Bi⁺⁺⁺⁺⁺ to Bi metal occur at the cathodic peaks around 0.9, 0.7 and 0.2 V, respectively. The oxidations of Bi₅⁺⁺⁺⁺ to Bi⁺⁺⁺⁺ and Bi⁺⁺⁺⁺⁺ to Bi⁺⁺⁺⁺⁺ occur at the anodic peaks around 1.45 and 1.67 V for both Bil and Bi₆Cl₇.

Key Words: Polybismuth Cation, Cyclic Voltammetry, Polarography, Room-temperature Chloroaluminate Melt

1 Introduction

Solution of post-transition metals (Cd, Hg, In, Tl, Sb and Bi) and their halides is characterized by strong tendencies for formation of lower valence metal ions. For these many systems regions of liquid-liquid immiscibility tend to occur in metal-rich composition range. In BiₓBi systems (X = Cl⁻, Br⁻ and I⁻) their consolute temperatures were not so high and their own homogenous solutions can be prepared as a stable liquid-phase at their metal-rich side. The intermediate compounds, BiBr / Bi and Bi₂Cl₄, were stable in crystalline state: the structures of Bil and Bi₂Cl₄ are characteristic of mixed valence compound, [Bi(0);Bi(2+);I(1−)]⁻ (= [Bi₄I₆]), and discrete homopolymorphous ions Bi₄⁺⁺⁺⁺ surrounded by polymeric Bi(III)-Cl anions, respectively.

Here, the homopolymorphous cations, Bi₄⁺⁺⁺⁺ and Bi₆⁺⁺⁺⁺, are not expected to be stable in liquid state from the phase diagram of Bil (or BiCl₃) + Bi systems. However, the heat capacities of molten Bi + Bil mixtures showed the appreciable positive deviation from Dulong-Petit law between ca. 50 mol % Bi (40 at % Bil) and ca. 80 mol % Bi (62.5 at % Bil). The considerable deviation was explained by the contributions from the intramolecular vibration and rotation of homopolyatomic bismuth ions in the lower oxidation state. As the dc conductivities σ changed from 50 to 1500 Ω⁻¹ cm⁻¹ and their temperature coefficients -k_Bθ ln[σ / θ(1 / T)] from 0.3 to 0 eV, these molten mixtures between Bi₃I₁ and Bi₃I₂ are characteristic of semiconductor: the crystalline Bil is anisotropic semiconductor in a crystallographic b direction from their conductivity measurement and band structure calculations.

Since a couple of different homopolybismuth-ions have the different lower-valencies, the redox reactions and disproportionation take place among these ions and can be characterized using cyclic voltammetry. These polybismuth-ions are stable by being embedded by anions, such as BiCl₄⁻, AlCl₄⁻ and Al₂Cl₆⁻ in liquid state.

This work reports an electrochemical study on the redox reactions of bismuth monochloride Bil and subchloride compound Bi₆Cl₇ dissolved into the 1-methyl-3-benzyl imidazolium chloride (MeBzImCl) + 67 mol % AlCl₃ melt, which consists of AlCl₃ and Al₂Cl₆⁻ as major anions, using cyclic voltammetric and polarography techniques.

2 Experimental

2.1 Synthesis

The bismuth subhalides, Bil and Bi₆Cl₇, were prepared by fusing mixture of bismuth (99.9999 %) and bismuth triiodide purified by sublimation or bismuth trichloride purified by distillation, respectively. MeBzImCl was synthesized from equimolar 1-methyl imidazole and benzyl chloride and recrystallized in acetonitrile + ethyl acetate (1 : 1, v/v) and assigned by ¹H NMR and elemental analysis: ¹H NMR (D₂O) 3.92 (N-C₃H₇), 5.43 (N-C₃H₇), 7.49 (benzene), 7.53 (imidazole),
8.78 (methylene). Anal. Found: C, 62.3; H, 7.1; N, 13.1; Cl, 16.6%. Calcd. for C_{11}H_{13}N_{2}Cl, C, 63.3; H, 6.2; N, 13.4; Cl, 17.0%. The introduction of mixture of MeBzImCl+AlCl_3 used as a solvent into reactor glassware was carried out in glove box filled with argon gas. The sealed reactor-glassware associated with the mixture was taken out from the glove box and the mixture was fused at 60-80°C to prepare the room temperature chloroaluminate melt. This melt is air-stable in comparison with 1-methyl-3-ethyl imidazolium chloride (MeEtImCl)+AlCl_3 melt\(^{13-15}\) and n-butyl pyridinium chloride (BuPyCl)+AlCl_3 melt\(^{13-15}\) from the view of liquidus-temperatur.

2. 2 DSC measurements

The phase diagram of chloroaluminate MeBzImCl+AlCl_3 was determined using differential scanning calorimeter. Sample cells for the measurements were prepared in glove box to prevent the samples from air and its moisture. Liquid nitrogen was used as cryogenic reagent under the flow of helium gas for the DSC measurements at lower than room temperature.

2. 3 Electrochemical measurements

Carried out were a few of electrochemical techniques, cyclic voltammetry (CV) and polarography using CV-50W (BAS) in glove box. A glassy carbon was used as the working electrode (WE), and platinum wire (diam. 0.5 mm) was used as the counter electrode (CE). The aluminum wire (diam. 1 mm) immersed into MeBzImCl+67 mol% AlCl_3 melt and separated from WE compartment by quartz wool was used as the reference electrode (RE).

3 Results

3. 1 Phase diagram for MeBzImCl+AlCl_3

The solid-liquid phase diagram for the MeBzImCl+AlCl_3 is shown in Fig. 1. The phase diagram shows the higher liquidus-temperatures above 40 mol% AlCl_3, compared with MeEtImCl+AlCl_3.\(^{10}\) The glass transitions were observed above 20 mol% AlCl_3 except for around equimolar compositions and there exists a stoichiometric compound at the equimolar composition.

3. 2 Electrochemical window of MeBzImCl+AlCl_3

Cyclic voltammograms of basic, neutral and acidic MeBzImCl+AlCl_3 melts at 45, 50 and 67 mol% AlCl_3 are shown in Fig. 2. The cathodic limits were observed around \(E = -2\) V vs. Al(III)/Al in the voltammograms of basic and neutral melts and around 0 V in acidic melt. The anodic limits were observed around 1 V for basic melt and around 2.3 V for neutral and acidic melts. Since the predominant ions are AlCl_2^- and MeBzIm^+, and the concentrations of Cl^- and Al_4Cl_7^- are quite low in neutral melt, the cathodic limit around \(-2\) V corresponds to reduction of MeBzIm^+ and the anodic limit around 2.3 V to oxidation of AlCl_2^- : \[
4\text{AlCl}_2^- \rightarrow 2\text{Al}_4\text{Cl}_7^- + \text{Cl}_2 + 2e^- \quad (1)
\]
Predominant Al_4Cl_7^- and AlCl_4^- suppressed Cl^- under the equilibrium reaction in acidic melts.
\[ 2\text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \]  

(2)

The cathodic limit around 0 V means the reduction of \( \text{Al}_2\text{Cl}_7^- \) to aluminum metal as follows,

\[ 4\text{AlCl}_7^- + 3e^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \]  

(3)

The concentrations of \( \text{Cl}^- \) and \( \text{AlCl}_4^- \) are much more than that of \( \text{Al}_2\text{Cl}_7^- \) in basic melts. Thus, the anodic limit around 1 V means to production of \( \text{Cl}_2 \) from \( \text{Cl}^- \),

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \]  

(4)

### 3. 3 Cyclic voltammograms of \( \text{BiI}_6 \) and \( \text{Bi}_3\text{Cl}_7 \)

The cyclic voltammograms of \( \text{ca. 1.0 mM BiI}_6 \) in MeBzImCl+67 mol % \( \text{AlCl}_3 \) are shown in Fig. 3. The voltammogram exhibited a strong cathodic peak around 0.6 V. The voltamogram reversed at cut-off potential 0.1 V exhibited three strong anodic peaks around 1.15, 1.45, and 1.67 V. When Fig. 3(b) shows cyclic voltammogram reversed at 0.4 V for the same solution, the voltammogram exhibited no anodic peak around 1.15 V in Fig. 3(a). As the voltammograms reversed at 0.4 V exhibited no anodic peak around 1.15 V (Fig. 3(b)), the anodic peak means the stripping of Bi metal from glassy carbon used as WE. Therefore, the abrupt increase in cathodic current between 0.1 and 0.3 V means the electrodeposition of Bi metal.

The cyclic voltammogram of \( \text{ca. 1.0 mM BiI}_6 \) in MeBzImCl+67 mol % \( \text{AlCl}_3 \) melt was scanned to anodic way after potentiostatic electrolysis at 0.55 V for 20 s, as shown in Fig. 4. The anodic peak current, 4.8 \( \mu \text{A} \) around 1.67 V, became larger, compared with 0.8 \( \mu \text{A} \) around 1.45 V after the electrolysis at 0.55 V.

The cyclic voltammograms of \( \text{ca. 1.0 mM BiI}_6 \) in MeBzImCl+67 mol % \( \text{AlCl}_3 \) are shown in Fig. 5. The voltammogram exhibited three cathodic peaks around 0.9, 0.7, and 0.2 V. The voltammogram reversed at cut-off potential 0.1 V also exhibited three anodic peaks around 0.97, 1.45, and 1.67 V. Fig. 5(b) shows the cyclic voltammogram reversed at 0.4 V for the same solution. The voltammogram exhibited no anodic peak around 0.97 V in Fig. 5(a) and exhibited another anodic peaks around 0.77 and 1.03 V, which may have imperfectly their own reversible cathodic peaks around 0.7 and 0.9 V, respectively. Since the voltammogram reversed to anodic way before electrodeposition of Bi metal exhibited no anodic peak around 0.97 V, the anodic peak means the stripping of Bi metal from glassy carbon used as WE. The profile of these voltammograms was much similar that of \( \text{BiCl}_4^+ \) and \( \text{Bi}_4(\text{AlCl}_4)_3 \).  

The cyclic voltammograms of \( \text{ca. 1.0 mM BiI}_6 \) in chloroaluminate MeBzImCl+67 mol % \( \text{AlCl}_3 \) melt were scanned to anodic way after potentiostatic electrolysis at 0.55 V for 20 s.

**Fig. 3** Cyclic voltammograms for the reduction / oxidation of \( \text{ca. 1.0 mM BiI}_6 \) in MeBzImCl+67 mol % \( \text{AlCl}_3 \) melt at 28 °C. Scan rate is 0.02 V/s. The voltammograms were measured from 1.15 V into the cathodic direction and reversed at cut-off potentials (a) 0.1 and (b) 0.4 V, respectively.

**Fig. 4** Cyclic voltammogram of \( \text{ca. 1.0 mM BiI}_6 \) in MeBzImCl+67 mol % \( \text{AlCl}_3 \) melt at 28 °C. Scan rate is 0.02 V/s. The voltammogram was measured from 0.55 V into the anodic direction after potentiostatic electrolysis at 0.55 V for 20 s.
Fig. 5 Cyclic voltammograms for the reduction/oxidation of ca. 1.0 mM Bi$_4$Cl$_7$ in MeBzImCl+67 mol % AlCl$_3$ melt at 28°C. Scan rate is 0.02 V/s. The voltammograms were measured from 1.15 V into the cathodic direction and reversed at cut-off potentials (a) 0.1 and (b) 0.4 V, respectively.

electrolyses at (a) 0.9 V and (b) 0.6 V for 20 s, as shown in Fig. 6. The anodic peak current 5.5 µA around 1.45 V was larger than 1.6 µA around 1.67 V after the electrolysis at 0.9 V. On the other hand, the anodic peak current 9.2 µA around 1.67 V was much larger than 1.8 µA around 1.45 V after the electrolysis at 0.6 V.

3.4 Polarogram of Bil

The polarogram of ca. 1.0 mM Bil in MeBzImCl+67 mol % AlCl$_3$ melt, as shown in Fig. 7, was constructed from current-time curve (pulse width is equal to 0.2 ms) obtained by stepping the potential from 1.2 V, at which no electrochemical reaction was taking place, to 0.5 V. The polarogram exhibited a shoulder around 0.85 V, a broad peak around 0.75 V and a step profile associated with a flatness between 0.6 and 0.5 V, which corresponded to the cathodic peaks around 0.85, 0.7 and 0.6 V, respectively, in the cyclic voltammogram (see Figs. 3 and 4).

Fig. 6 Cyclic voltammograms of ca. 1.0 mM Bi$_4$Cl$_7$ in MeBzImCl+67 mol % AlCl$_3$ melt at 28°C. Scan rate is 0.02 V/s. (a) Voltammogram was measured from 0.9 V into the anodic direction after potentiostatic electrolysis at 0.9 V for 20 s. (b) Voltammogram was measured from 0.6 V into the anodic direction after potentiostatic electrolysis at 0.6 V for 20 s.

Fig. 7 Polarogram of ca. 1.0 mM Bil in MeBzImCl+67 mol % AlCl$_3$ melt at 28°C: the solid circles and solid curve show data and calculation using equation (7). The polarogram was measured from 1.2 V into the cathodic direction. Scan rate is 0.01 V/s. Pulse width and pulse period are 0.2 and 0.4 ms, respectively.
4 Discussion

4.1 Voltammogram of Bi₆Cl₇

The profile of voltammograms of Bi₆Cl₇ was much similar to that of BiCl₃ and Bi₅(AlCl₄)₃. Since the solution of Bi₆Cl₇ dissolved into MeBzImCl + 67 mol % AlCl₃ melt became colorless from black in no time and the solution of BiCl₃ dissolved into MeBzImCl + 67 mol % AlCl₃ melt was colorless, Bi⁺⁺ ion should be unstable in liquid state. Thus, Bi⁺⁺⁺ will become Bi⁺⁺ in the melt and cathodic and anodic peaks related to Bi⁺⁺⁺ were not observed in voltammogram.

Torsi and Mamantov reported that the first cathodic peak around 1.0 V for the voltammogram of BiCl₃ in NaCl + 63 mol % AlCl₃ resulted from the reduction of Bi³⁺ to Bi⁺⁺.¹⁷

\[ \text{Bi}^{3+} + 2e^- \rightarrow \text{Bi}^+ \]  
(5)

Therefore, the first cathodic peak around 0.9 V for Bi₆Cl₇ in Fig. 6(a) resulted from the reduction of Bi⁺⁺⁺ to Bi⁺⁺ (equation (5)). Bjerrum et al characterized Bi⁺⁺⁺ as the products of the reaction between liquid bismuth metal and BiCl₃ in acidic chloroaluminate NaCl + 63 mol % AlCl₃ using electronic absorption spectroscopy. Herrman and D’Oliedlager proposed that coexistence between Bi⁺⁺ and Bi³⁺ produced low oxidation polybismuth ion Bi₅⁺⁺⁺⁺ through.

\[ 6\text{Bi}^+ = \text{Bi}^{3+} + \text{Bi}^{4+} \]  
(6)

Thus, Bi⁺⁺⁺ and / or Bi⁺⁺ are major species in the melt because of equilibrium constant \( K_{eq} \gg 1 \) for equation (6). As the anodic peak current around 1.45 V was larger than that around 1.67 V after the electrolysis at 0.9 V, the oxidation of Bi⁺⁺⁺ to Bi³⁺ occurs around 1.45 V.

The cathodic peak around 0.7 V for Bi₆Cl₇ in Fig. 6(b) was observed in the voltammograms of Bi₅Cl₃ and Bi₅(AlCl₄)₃. The fact that the cathodic peak around 0.7 V for the voltammogram of Bi₅(AlCl₄)₃ in MeBzImCl + 67 mol % AlCl₃ resulted from the reduction of Bi⁺⁺⁺ to Bi⁺⁺ was revealed by in situ electrochemical technique. The oxidation of Bi⁺⁺⁺ to Bi³⁺ can occur after the electrolysis at 0.6 V and Bi⁺⁺⁺ are major species in the melt. Thus, the oxidation of Bi⁺⁺⁺ to Bi⁺⁺ occurs around 1.67 V. Here, the anodic peak current around 1.67 V was much larger than that around 1.45 V after the electrolysis at 0.6 V (Fig. 6(b)). It is somewhat peculiar that the oxidation of Bi⁺⁺⁺ to Bi³⁺ occurs around 1.45 V and the oxidation of Bi⁺⁺⁺ to Bi⁺⁺ occurs around 1.67 V. It is worth while, however, to point out that, the anodic reactions of Bi⁺⁺⁺ to Bi⁺⁺ and Bi⁺⁺⁺ to Bi⁺⁺⁺ are regarded as irreversible reactions and the disproportionation of equation (6) takes place in the melt.

4.2 Voltammogram of BiI

The profile of the voltammograms of BiI was partially different from that of BiCl₃ and Bi₅(AlCl₄)₃. The new cathodic peak around 0.6 V was observed in the cyclic voltammogram (Fig. 3). As the anodic peak current around 1.67 V became large after the electrolysis at 0.55 V, Bi⁺⁺⁺ was formed at the cathodic peak around 0.6 V (Fig. 4). As the complex of BiI consists of \([\text{BiI}]_x^+(1-x)\) there exist Bi⁺⁺⁺ ions as major species for BiI dissolved into MeBzImCl + 67 mol % AlCl₃ melt and the reduction reaction of Bi⁺⁺⁺ to Bi⁺⁺ occurs at the cathodic peak around 0.6 V. The weak cathodic peaks around 0.85 and 0.7 V resulted from the reduction of Bi⁺⁺⁺ to Bi⁺⁺ and Bi⁺⁺⁺ to Bi⁺⁺⁺, respectively (Fig. 3). The anodic peaks around 1.45 and 1.67 V resulted from the oxidation of Bi⁺⁺⁺ to Bi⁺⁺⁺ and Bi⁺⁺⁺ to Bi⁺⁺⁺, respectively (Fig. 3). Here, these two anodic and two cathodic peaks were observed also in the voltammograms of Bi₅Cl₃ and Bi₅(AlCl₄)₃.

4.3 Polarogram of BiI

The reduction reaction of the step profile associated with a flatness between 0.6 and 0.5 V was controlled by diffusion rate-determining process, as shown in the polarogram of BiI (Fig. 7). When electrode reaction is diffusion rate-determining process, a relation among potential \( E \), current \( i \), half-wave potential \( E_{1/2} \), and diffuse limiting current \( i_d \) is expressed as

\[ E = E_{1/2} - (RT / nF) \ln [i / (i_d - i)], \]  
(7)

where \( n \) is the number of electron for electrode reaction, \( E_{1/2} \) half-wave potential and \( i_d \) diffuse limiting current. The simulation of the observed step-profile of Fig. 7 gave \( n = 2.8 \pm 0.3 \), \( E_{1/2} = 0.65 \) V and \( i_d = 4.1 \) \( \mu \text{A} \). The reduction of Bi⁺⁺⁺ to Bi⁺⁺⁺ for the cathodic peak around 0.6 V may be given by

\[ \text{Bi}^{4+} + 3e^- = 1 / 2 \text{Bi}^{2+}. \]  
(8)

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References
6) K. Ichikawa, *Supplement of the Progress of Theoretical Physics*, 72, 156 (1982).
19) N. Shimomura, A. Takamuku, and K. Ichikawa, unpublished work.