

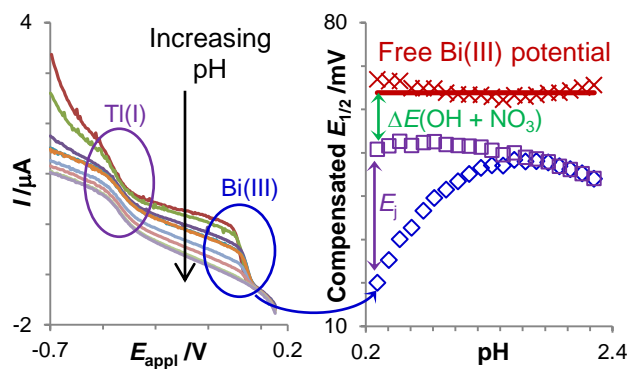
# Measurements and Modelling to Determine the Reduction Potential of Uncomplexed Bi(III) in Nitrate Solutions for Application in Bi(III)-Ligand Equilibria Studies by Voltammetry

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## ABSTRACT



The free metal ion potential,  $E(\text{M})$ , is a critical parameter in the calculation of formation constants when using voltammetry. When studying complex formation of Bi(III), however,  $E(\text{Bi})$  cannot be directly measured. In this work a nitrate background electrolyte was employed to obtain reversible reduction waves. In order to determine  $E(\text{Bi})$ , measurements have to be made below  $\text{pH} \sim 2$  before the bismuth-oxy-nitrate species precipitates and thus corrections for the diffusion junction potential (monitored using Tl(I) as an internal reference ion) must be made.

Additionally shifts in potential due to both Bi(III) hydrolysis and Bi(III) nitrate formation must also be compensated for before  $E(\text{Bi})$  can be evaluated. The value of  $E(\text{Bi})$  was determined relative to  $E(\text{Tl})$  so that in an experiments where ligand is added to determine formation constants,  $E(\text{Bi})$  can be determined as accurately as possible (since  $E(\text{Tl})$  can generally still be measured). The value of  $E(\text{Bi}) - E(\text{Tl})$  was found to be  $495.6 \pm 1.4$  mV for the conditions employed.

## 1. Introduction

Considering the myriads of studies conducted on metal-ligand equilibria, it may seem surprising at first that very little is known about the coordination chemistry of Bi(III), the most stable form of bismuth. This is despite bismuth having found applications in medicinal chemistry, in particular in treating peptic ulcers and more recently in cancer treatments.<sup>1-7</sup> This lack of information is due to the difficulty in studying complex formation caused by the extreme propensity of Bi(III) to undergo hydrolysis in aqueous environments.

Bi(III) hydrolysis, however, has been extensively studied and was instrumental in developing techniques to investigate hydrolysis of metal ions in general.<sup>8</sup> The formation of the  $\text{Bi}(\text{OH})^{2+}$  species was confirmed early on.<sup>9-11</sup> There was also indication of the formation of bismuth polynuclear species with much debate as to the exact stoichiometry of these species.<sup>12-14</sup> Evidence from various techniques supported the presence of the hexamer,  $\text{Bi}_6(\text{OH})_{12}^{6+}$ , as the dominant species under the specific experimental conditions.<sup>10,11,14-17</sup> This species could also be referred to as  $\text{Bi}_6\text{O}_6^{6+}$  because numerous techniques have difficulty in differentiating whether  $\text{O}^{2-}$  or  $\text{OH}^-$  is bound to the metal ion.<sup>8</sup> It was also recognised that the hexameric species was in

equilibrium with even larger complexes proposed to be  $\text{Bi}_9(\text{OH})_{20}^{7+}$ ,  $\text{Bi}_9(\text{OH})_{21}^{6+}$  and  $\text{Bi}_9(\text{OH})_{22}^{5+}$ .<sup>8,14,18</sup>

Other mononuclear species were also found in more dilute solutions and Bidleman<sup>19</sup> determined formation constants for  $\text{BiOH}^{2+}$ ,  $\text{Bi}(\text{OH})_3$  and  $\text{Bi}(\text{OH})_4^-$  (for  $\text{Bi}(\text{III}) < 10^{-4}$  M). The  $\text{Bi}(\text{OH})_2^+$  species was initially not detected and it was suggested that the stoichiometrically equivalent hexamer is much more stable than this species.<sup>11</sup> Only when Hataye *et al.*<sup>18</sup> analysed solutions at trace  $\text{Bi}(\text{III})$  concentrations ( $< 10^{-7}$  M) did they find  $\text{Bi}(\text{OH})_2^+$ , as well as  $\text{Bi}^{3+}$ ,  $\text{Bi}(\text{OH})^{2+}$  and  $\text{Bi}(\text{OH})_3$ , in solution between pH 0 and 5.7, with no evidence of polymeric species. It therefore appears that at very low  $\text{Bi}(\text{III})$  concentrations  $\text{Bi}(\text{OH})_2^+$  is formed, but at higher concentrations the hexameric species is more stable.

Table 1 summarises the critically assessed stability constants for the various  $\text{Bi}(\text{III})$  hydrolysis products included in the NIST database.<sup>20</sup> Log  $\beta$  values at 0.5 M ionic strength, calculated using experimental values and applying the Davies modification of the Debye-Hückel equation,<sup>21</sup> are also shown as these were used in the work presented here. Although these values were quoted to two decimal places, a single decimal place is a better indication of the actual precision. As will be seen, hydrolysis takes place from pH zero already in aqueous solutions.

**Table 1.** Log K values for Bi(III) hydrolysis products at 25 °C and given ionic strengths ( $\mu$ ).<sup>20</sup>

Species	Reactants	Log $K$	$\mu$ /M
Bi(OH) <sup>2+</sup>	Bi <sup>3+</sup> + OH <sup>-</sup>	12.3 <sup>a</sup>	0.5
		12.4	0.1
		12.3	1.0
		12.6	3.0
		12.9	0.0
		12.42 <sup>b*</sup>	0.5
Bi(OH) <sub>2</sub> <sup>+</sup>	Bi <sup>3+</sup> + 2OH <sup>-</sup>	23.5 <sup>*</sup>	1.0
Bi(OH) <sub>3</sub>	Bi <sup>3+</sup> + 3OH <sup>-</sup>	31.9	0.1
		31.3	1.0
		33.0	0.0
		31.88 <sup>b*</sup>	0.5
Bi(OH) <sub>4</sub> <sup>-</sup>	Bi <sup>3+</sup> + 4OH <sup>-</sup>	33.6	1.0
		34.8	0.0
		32.98 <sup>b*</sup>	0.5
Bi <sub>6</sub> (OH) <sub>12</sub> <sup>6+</sup>	6Bi <sup>3+</sup> + 12OH <sup>-</sup>	165.3	1.0
		170.3	3.0
		162.78 <sup>b*</sup>	0.5
Bi <sub>9</sub> (OH) <sub>20</sub> <sup>7+</sup>	Bi <sub>6</sub> (OH) <sub>12</sub> <sup>6+</sup> + 3Bi <sup>3+</sup> + 8OH <sup>-</sup>	23.9	0.1
		9Bi <sup>3+</sup> + 20OH <sup>-</sup>	266.92 <sup>b*</sup>
Bi <sub>9</sub> (OH) <sub>21</sub> <sup>6+</sup>	Bi <sub>9</sub> (OH) <sub>20</sub> <sup>7+</sup> + OH <sup>-</sup>	10.6	0.1
		9Bi <sup>3+</sup> + 21OH <sup>-</sup>	276.76 <sup>b*</sup>
Bi <sub>9</sub> (OH) <sub>22</sub> <sup>5+</sup>	Bi <sub>9</sub> (OH) <sub>21</sub> <sup>6+</sup> + OH <sup>-</sup>	11.1	0.1
		9Bi <sup>3+</sup> + 22OH <sup>-</sup>	287.30 <sup>b*</sup>

<sup>a</sup> at 20 °C<sup>b</sup> recalculated for 0.5 M ionic strength<sup>21</sup><sup>\*</sup> log  $\beta$  values used in this work

In all complex formation studies a high concentration of background electrolyte is added to keep the ionic strength of the solution constant during the titration experiment. These generally

consist of sodium or potassium salts of perchlorates or nitrates which are weakly complexing. Unfortunately, the presence of these anions result in the precipitation of Bi(III) oxy or hydroxy anion species. Kragten *et al.*<sup>22</sup> referred to this as BiOA, which could also be considered as Bi(OH)<sub>2</sub>A, where A refers to the anion. They showed that this species precipitated from solution at much lower pHs than Bi(OH)<sub>3</sub> and that the pH of precipitation decreased with increasing Bi(III) concentration. The precipitate was shown to be a polycondensation of Bi<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup> ions in solutions of basic Bi(III) salts to form the species [Bi<sub>6</sub>O<sub>x</sub>(OH)<sub>8-x</sub>]<sup>(10-x)+</sup>.<sup>17,23,24</sup> The structures of crystals grown from solutions below pH 1.2 and between pH 1.2-2.4 were found to be Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>A<sub>6</sub> and Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>A<sub>5</sub>, respectively.<sup>24-28</sup> For simplicity, the “empirical” formula BiOA will be used to refer to the insoluble product in general.

Usually chloride is used in background electrolytes for studies pertaining to biological applications, but due to the very limited solubility of BiOCl<sup>22</sup> it was avoided in this work. The use of perchlorate was initially considered here since BiOClO<sub>4</sub> is slightly more soluble than BiONO<sub>3</sub><sup>22</sup> and perchlorate is also less complexing than nitrate<sup>18,19</sup> (as would be required of an inert background electrolyte). Nitrate forms far stronger complexes with Bi(III) than with other metal ions and even exhibits some covalent character;<sup>29</sup> there is also evidence for negatively charged nitrate complexes of Bi(III) in solution.<sup>30</sup>

Voltammetry is ideally suited to studying Bi(III)-ligand equilibria because relatively low concentrations of Bi(III) can be used in order to postpone precipitation. Additionally, since mass balance equations (MBEs) for the metal ion concentration are solved when determining formation constants (rather than the MBEs for H<sup>+</sup> concentration as when using glass electrode potentiometry), measurements can be made in very acidic solutions (below pH 2).

In using this technique, cognisance must be taken of factors affecting the electrochemical measurement. In this case it is that the reduction of metal ions of oxidation state three is not reversible in “non-complexing” media such as perchlorate at moderate ionic strengths (around 1 M) and this also pertains to Bi(III).<sup>30-33</sup> It was shown that the rate of electron transfer for Bi(III) reduction in highly acidic solutions increased with the addition of the following anions in solution:  $\text{ClO}_4^- < \text{NO}_3^- < \text{Cl}^-$ .<sup>31</sup> Interestingly, at very high  $\text{HClO}_4$  concentrations ( $\geq 8$  M) the reduction of Bi(III) becomes fully reversible,<sup>34</sup> as well as in solutions of 1 M  $\text{HClO}_4$  + 7 M  $\text{NaClO}_4$  when using DC polarography.<sup>35</sup> When solutions of 1 M  $\text{HClO}_4$  with varying concentrations of  $\text{NaClO}_4$  (1 to ~8 M) were studied it was clear that the half-wave potential was dependant on ionic strength.<sup>35,36</sup> At moderate ionic strengths, it was reported that the Bi(III) reduction was found to be fully reversible when chloride was added, but that it never reached full reversibility in a nitrate medium.<sup>30-33</sup> When determining formation constants by polarography, the relationship employed (Eq. 1) is only valid for reversible reduction potentials.<sup>37,38</sup> Since we wanted to work at moderate ionic strengths so that formation constants generated could have some application to the biological field, a nitrate background was chosen as the compromise between solubility of hydrolysis products and reversibility of the reduction process. The successful study of quasi-reversible systems had been previously been demonstrated,<sup>39,40</sup> however, as will be discussed, in this work it was found that the DC reduction waves could actually be considered as reversible when working in 0.25 - 0.5 M nitrate solutions.

To determine formation constants when employing polarographic-pH titrations, the relationship used is shown in Eq. 1 below,<sup>38,42</sup> where  $E(\text{M})$  and  $E(\text{M}_{\text{comp}})$  are the reduction potentials of the uncomplexed and complexed metal ion, respectively;  $I(\text{M})$  and  $I(\text{M}_{\text{comp}})$  are the reduction currents of the uncomplexed and complexed metal ion, respectively, and  $[\text{M}]$  and  $[\text{M}_\text{T}]$

are the concentrations of the free and total metal ion, respectively. The subscript pH indicates which parameters are functions of pH and in the case of  $I(M)$  and  $[M_T]$  this only applies to account for dilution when adjusting pH. The current and potential terms, as well as  $[M_T]$ , are determined experimentally. The value of  $[M]_{pH}$  is found by solving MBEs which include the formation constants for each solution species. For clarity, a summary of symbols used is presented in the Appendix.

$$\{E(M) - E(M_{comp})_{pH}\} - \frac{RT}{nF} \ln \frac{I(M_{comp})_{pH}}{I(M)_{pH}} = \frac{RT}{nF} \ln \frac{[M_T]_{pH}}{[M]_{pH}} \quad (1)$$

When refining formation constants the shift in potential,  $\Delta E = E(M) - E(M_{comp})_{pH}$ , is by far the most critical parameter measured when labile complexes are formed. All shifts are calculated relative to  $E(M)$ , thus it is essential that this parameter be determined as accurately as possible. Since  $\text{BiONO}_3$  precipitates under acidic conditions already (around pH 2 for the conditions used here),  $E(M)$  would have to be measured in very acidic solutions (well below pH 2) where the diffusion junction potential ( $E_j$ ) is significant and changes with pH. Procedures have already been developed to correct for  $E_j$  when employing Tl(I) as an in-situ witness ion to determine the magnitude of  $E_j$  as a function of pH in a non-linear fashion.<sup>39,41</sup> However, the process is far more complicated for Bi(III) studies because the measured reduction potential is not that of an uncomplexed (free) metal ion, but rather it represents the products of Bi(III) hydrolysis formed below pH 2 as well as the various Bi(III) nitrate species formed. This work describes how  $E(\text{Bi})$  can be determined, as this parameter must be used to accurately calculate formation constants of Bi(III)-ligand systems.

## 2. Experimental

### 2.1. Materials

All reagents were of analytical grade and deionized water of resistivity 18 M $\Omega$  cm was always used. A stock solution of 0.100 M Tl(I) was made by dissolving TlNO<sub>3</sub> (Merck) in 0.5 M HNO<sub>3</sub>. A 0.100 M Bi(III) stock solution was made by dissolving Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Fluka) in concentrated HNO<sub>3</sub> (65%, Merck) and then diluting with water such that a 1 M HNO<sub>3</sub> concentration was obtained.

### 2.2. Instrumentation

Polarographic experiments were carried out in a jacketed-cell maintained at 25.0  $\pm$  0.1°C which contained a dropping mercury electrode (set to the largest drop size on the Metrohm VA stand), a Ag/AgCl (3 M KCl) reference electrode in a 0.5 M KNO<sub>3</sub> salt bridge, a platinum counter electrode, a glass electrode (GE) and a thermocouple to monitor the solution temperature, all supplied by Metrohm. A BAS CV27 potentiostat was used as part of an automated setup as describe elsewhere.<sup>42</sup> Sampled DC polarography was employed with a step time of 1 s, current integration times of 60–100 ms and a step potential of 4 mV.

The GE (Metrohm cat. no. 6.0234.100) was calibrated by the titration of standardised solutions of 0.5 M HNO<sub>3</sub> with 0.5 M KOH (thus pH signifies  $-\log[\text{H}^+]$  in this work) and it functioned extremely well in the highly acidic medium. Since the accurate determination of pH is critical in this work, any slight deviation from linearity in the very acidic region on the calibration plot was accounted for as previously described.<sup>43</sup>



### 2.3. Procedure

Polarographic-pH titration experiments were performed starting with solutions of 0.5 M HNO<sub>3</sub> containing Bi(III) and Tl(I). Initially concentrations were  $5 \times 10^{-5}$  M Bi(III) and  $1 \times 10^{-4}$  M Tl(I), but later reduced to  $1 \times 10^{-5}$  M and  $2 \times 10^{-5}$  M, respectively. These solutions were then titrated with 0.5 M KOH using a pH step of about 0.1, where at each step a polarogram and the GE potential were recorded. As a consequence of attempting to work at a reasonable ionic strength ( $\mu$ ) of 0.5 M while employing very acidic conditions,  $\mu$  did vary somewhat (especially between pH 0.3-1) and this will be discussed later. Selected polarograms are shown in Fig. S1.

Because the DC reduction waves for Bi(III) and Tl(I) were well-separated, they were fitted individually using Eq 2 below<sup>44</sup> to determine half-wave potentials ( $E_{1/2}$ ) and diffusion limited currents ( $I_d$ ) at each pH step; where  $E_{\text{appl}}$  is the applied potential,  $n$  is the number of electrons transferred and  $\delta$  measures the steepness of the reduction wave (which should be unity for reversible electron transfer processes). The terms  $a + bE_{\text{appl}}$  described the capacitance current and  $c\{\exp(d \times E_{\text{appl}})\}$  accounted for the onset of mercury oxidation when fitting the Bi(III) wave or hydrogen evolution when fitting the Tl(I) wave. The reduction of Tl(I) was fully reversible across the pH range, as noted before.<sup>39,41</sup> Although it was expected that Bi(III) reduction would be quasi-reversible in a nitrate medium,<sup>30,45</sup> the  $\delta$  values obtained were very close to one (typically 0.95–1.00) provided data points at the onset of mercury oxidation were omitted when fitting the wave. Therefore, since  $I_d$  does not change with the extent of reversibility and  $E_{1/2}$  is dependent on the steepness of the wave, which in this case is Nernstian (since  $\delta \approx 1$  in Eq 2), the reduction of Bi(III) was considered as reversible for our purpose (see Section 2 of the Supporting Information for further discussion).

$$I = \frac{I_d}{\exp\{(n\delta F/RT)(E_{appl} - E_{1/2})\} + 1} + a + bE_{appl} + c\{\exp(d \times E_{appl})\} \quad (2)$$

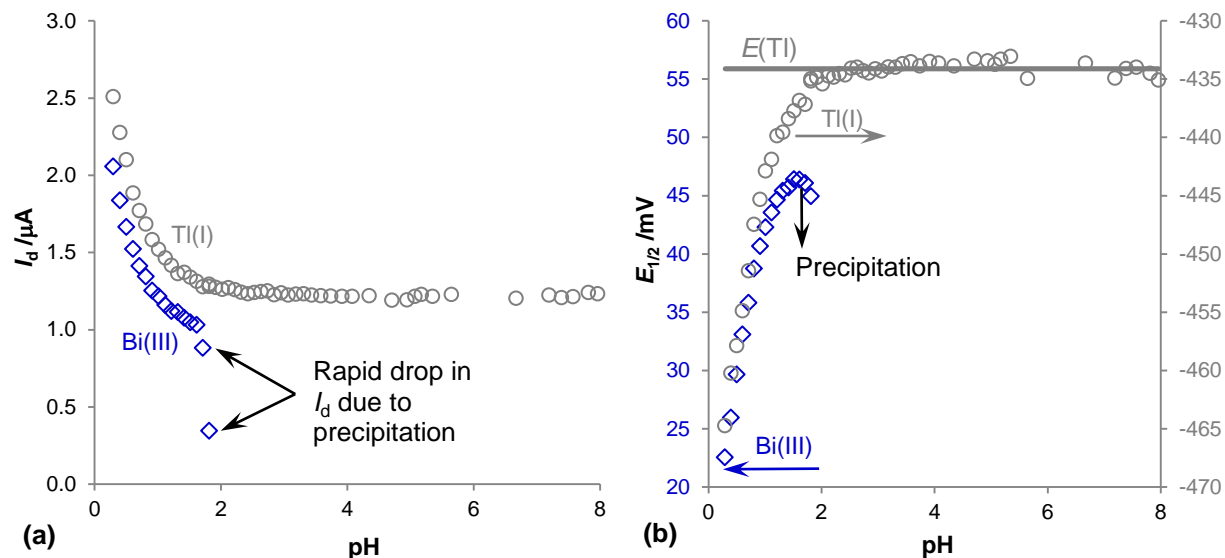
### 3. Results and Discussion

#### 3.1. Initial investigations at “higher” Bi(III) concentrations

Initial investigations were conducted in solutions containing the higher concentrations of Bi(III) and Tl(I), namely  $5 \times 10^{-5}$  M and  $1 \times 10^{-4}$  M, respectively. Precipitation of BiONO<sub>3</sub> was not visually seen, rather it was detected by the rapid drop in  $I_d$  above pH 1.5 as indicated in Fig. 1a. Powder X-ray diffraction analysis of a precipitate produced from 0.1 M Bi(III) solutions confirmed that both Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub> and Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>3</sub> were present (see section 3 of the Supporting Information for details). The initial decrease in  $I_d$  for both metal ions at the lowest pH range is due to dilution because large volumes of OH<sup>-</sup> solution are required to change the pH. Above pH ~2.5 only small volumes (~2 μL) were required between each pH step, resulting in very small changes in  $I_d$  for Tl(I).

Fig. 1b shows  $E_{1/2}$  versus pH for the reduction of Tl(I) and Bi(III), where the range of the potential scale was set to 40 mV for both axes to enable more direct comparison. The value of  $E(M)$  is independent of pH (when  $E_j$  is negligible) and for Tl(I) it was calculated by averaging the data above pH ~2. The variation in potential below pH ~2 was due to  $E_j$ .  $E_j$  of the reference system in the cell was thus evaluated as follows:  $E_j = E(\text{Tl}) - E_{1/2}(\text{Tl})$  (described in detail elsewhere<sup>39,41</sup>).  $E_j$  was determined at each point for each experiment using the Tl(I) data to account for any slight changes in the setup and reference system. The  $E_{1/2}(\text{Bi})$  values were

influenced by both  $E_j$  and complex formation with hydroxide and/or nitrate. It is clear that there is no way to directly determine  $E(\text{Bi})$  from these data.



**Figure 1.** Data obtained from a polarographic pH-titration experiment where initial concentrations of  $\text{Bi(III)}$  and  $\text{Ti(I)}$  were  $5 \times 10^{-5} \text{ M}$  and  $1 \times 10^{-4} \text{ M}$ , respectively. (a) shows the change in  $I_d$  and (b) shows the change in  $E_{1/2}$  with pH.

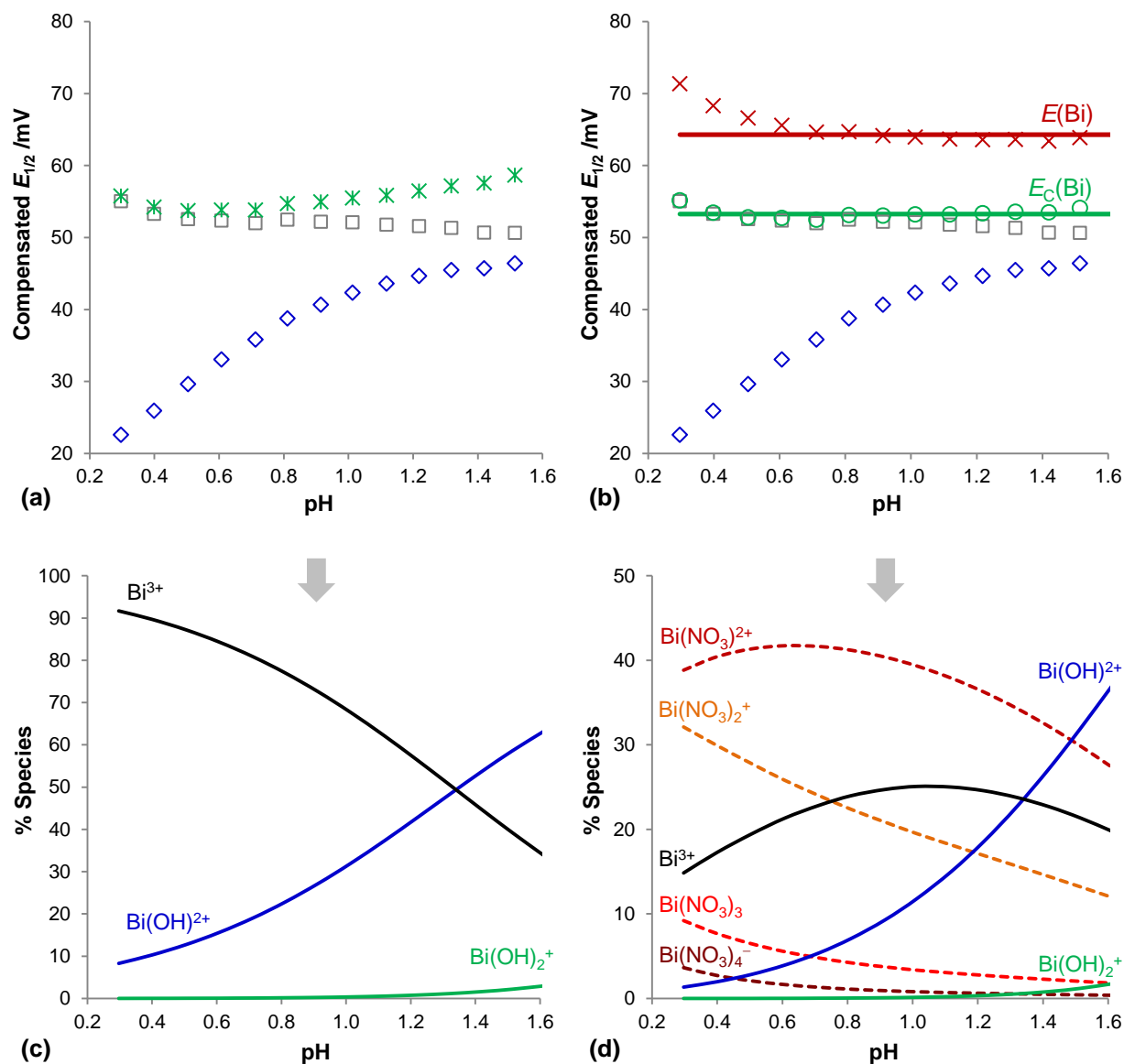
In order to determine  $E(\text{Bi})$ , the negative potential shifts due to both  $E_j$  and the formation of  $\text{Bi(III)}$  hydrolysis products (and possibly also  $\text{Bi(III)}$  nitrate species) had to be compensated. The magnitude of the shift in potential due to complex formation can be estimated by applying the Eq. 1 if the stability constants of the solution species are known.  $[\text{M}_T]_{\text{pH}}$  is calculated by accounting for dilution of the initial  $\text{Bi(III)}$  concentration and  $[\text{M}]_{\text{pH}}$  is calculated by solving MBEs which contain all the  $\text{Bi(III)}$ -ligand species that could form and their formation constants. In dealing with the current term, it was assumed that the rate of diffusion of  $\text{Bi}^{3+}$  (which would actually be the hydrated metal ion) and that of the  $\text{Bi(III)}$  complexes formed here were comparable and that all complex species were fully labile, thus  $I(\text{M})_{\text{pH}} = I(\text{M}_{\text{comp}})_{\text{pH}}$  giving:

$$\Delta E = (RT/nF) \ln ([M_T]_{pH}/[M]_{pH}) \quad (3)$$

To find the shift in potential due to Bi(III) hydrolysis ( $\Delta E_{OH}$ ) all the Bi(III)-hydroxide species were included in the MBEs.

Fig. 2a shows the experimental  $E_{1/2}$  values ( $\diamond$ ), these values corrected for  $E_j$  ( $\square$ ) and those also corrected for  $\Delta E_{OH}$  ( $*$ ). Only values up to the onset of precipitation were used. Fig. 2c gives the corresponding species distribution diagram (SDD) of the Bi(III) hydroxides as calculated for the solution conditions in that experiment. It was expected that after all these corrections, the resultant potentials would correspond to  $E(\text{Bi})$  which is pH independent and thus all values ( $*$ ) should be equal and produce a horizontal line. This was certainly not the case here. The accuracy of the  $\log \beta$  values used was initially questioned (especially that for  $\text{Bi}(\text{OH})^{2+}$  which appeared to be too large), however, modelling of the  $\log \beta$  values in section 3.2 gave confidence in the literature values. Instead it became evident that the formation of the Bi(III) nitrates could not be ignored and that this would suppress hydrolysis at low pHs significantly.

The potential shifts due to both Bi(III) hydrolysis and nitrate formation ( $\Delta E_T$ ) were calculated at each pH step using Eq. 1 by incorporating all known Bi(III) hydroxide and nitrate species when solving the MBEs and accounting for dilution of all species. Formation constants used for the Bi(III) nitrates are given in Table 2 (a  $\text{p}K_a$  value of  $-1.64$  was used for  $\text{HNO}_3$ <sup>46</sup>) and although these values are small, it is the high concentration of nitrate that drives complex formation. The  $\log \beta$  values for  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Bi}(\text{NO}_3)_4^-$  were used as presented in Table 2 since they had little effect on the overall  $\Delta E_T$  values, changing them by at most 0.6 mV as compared to when they were omitted. Fig. 2b shows the  $E_{1/2}$  values corrected for  $E_j$  ( $\square$ ) and  $\Delta E_T$  ( $\times$ ) and Fig. 2d shows the corresponding species distribution plot. Apart from approximately the first 3-4 points, these



**Figure 2.** Experimental  $E_{1/2}(\text{Bi})$  values ( $\diamond$ ) (initial  $[\text{Bi}(\text{III})] = 5 \times 10^{-5}$  M) and those corrected for  $E_j$  ( $\square$ ). Corrections were then made for potential shifts due to (a)  $\text{Bi}(\text{OH})_2^+$  and  $\text{Bi}(\text{OH})_2^+$  formation only (\*) and (b)  $\text{Bi}(\text{OH})_2^+$ ,  $\text{Bi}(\text{OH})_2^+$  and Bi(III) nitrate species ( $\times$ ) or just  $\text{Bi}(\text{OH})_2^+$  and  $\text{Bi}(\text{OH})_2^+$  in the presence of nitrate (○). The corresponding SDDs are given directly below the  $E_{1/2}$ -pH plots. (SDDs for the pH range 0-14 are modelled in Fig. S4a and b.)

values were relatively constant. These values were averaged (omitting the first points such that the standard deviation was  $<1$  mV) as indicated by the solid line and this represents the true

$E(\text{Bi})$ . Reasons for the first points being too high are due to (i) overcompensation of  $E_j$  by about 2–3 mV, as was noted in previous investigations,<sup>39,41</sup> and (ii) changes in ionic strength even though the variation in nitrate concentration was accounted for when calculating  $\Delta E_T$  (see Fig. S5 for a comparison of plots for compensated  $E_{1/2}(\text{Bi})$  and  $\mu$  against pH).

**Table 2.** Log  $\beta$  values for Bi(III) nitrate species at 25 °C.<sup>20</sup>

Species	Log $\beta$	$\mu$ /M
$\text{Bi}(\text{NO}_3)^{2+}$	0.72	0.5
$\text{Bi}(\text{NO}_3)_2^+$	(0.94)	0.5
$\text{Bi}(\text{NO}_3)_3$	0.7	1.0
$\text{Bi}(\text{NO}_3)_4^-$	0.6	2.0

The  $\Delta E$  due to the formation of only the Bi(III) hydroxides in the nitrate supporting electrolyte (called  $\Delta E_{\text{OH,C}}$ ) was also considered, where the presence of nitrates suppresses Bi(III) hydroxide formation. This first required the conditional metal ion concentration ( $[\text{M}]_C$ ) at each pH be determined, which essentially includes the Bi(III) nitrate species, and is calculated as follows:

$$[\text{M}]_C = [\text{M}_T] - \{(\% \text{Bi}(\text{OH})^{2+} + \% \text{Bi}(\text{OH})_2^+)/100 \times [\text{M}_T]\} \quad (4)$$

and  $\% \text{Bi}(\text{OH})^{2+}$  and  $\% \text{Bi}(\text{OH})_2^+$  are shown in Fig. 2d.  $\Delta E_{\text{OH,C}}$  was then calculated using Eq. 1 (and substituting the value of  $[\text{M}]_C$  instead of  $[\text{M}]$ ). Corrections due only to  $E_j$  and  $\Delta E_{\text{OH,C}}$  are also indicated in Fig. 2b (○). These values were also relatively constant and the averaged value (omitting the first 2 points due to  $E_j$  overcompensation) is given as a solid line which was called the conditional  $E(\text{Bi})$  ( $E_C(\text{Bi})$ ) as this would only apply to nitrate solutions of these concentrations.

### 3.2. Justification of log $\beta$ values for mononuclear Bi(III) hydroxides

Barnum<sup>47</sup> established that for most metal ions, the standard free energy of formation of the  $M(OH)_y$  species (for the hydrolysis reaction  $M^{n+} + yH_2O \rightleftharpoons M(OH)_y + yH^+$  with formation constant  $\beta^*_{1y}$ ) plotted against the number of coordinated hydroxide ions ( $y$ ) yielded a smooth curve. Consequently he defined the function given in Eq. 5 below where the plot of  $U\{M(OH)_y\}$  versus  $y$  gives a straight line with slope  $C$  and intercept  $B$  (on the  $U$ -axis), and  $B$ ,  $C$  and  $D$  are empirical constants. Barnum<sup>47</sup> found the value of  $D$  to be  $8.37 \text{ kJ mol}^{-1}$  for di- and trivalent metal ions and zero for tetravalent metal ions (at  $\mu = 0 \text{ M}$  and  $25^\circ\text{C}$ ).

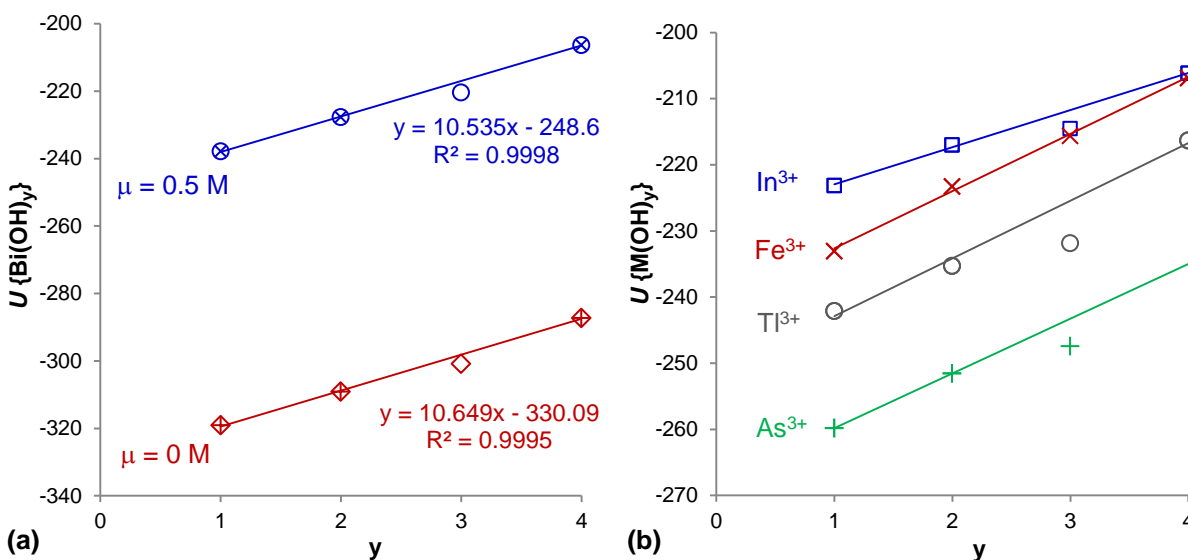
$$U\{M(OH)_y\} = B + Cy = [\Delta G_f^o\{M(OH)_y\} - \Delta G_f^o\{M^{n+}\} - D/y] / y \quad (5)$$

Alternatively,  $U\{M(OH)_y\}$  can also be calculated using the formation constants, as shown in Eq. 6.<sup>47</sup> The plot of  $U\{M(OH)_y\}$  versus  $y$  would allow unknown formation constants to be predicted or disparate values to be highlighted. Disparity may, however, not only signify experimental error in data, but may simply indicate failure of the empirical equations or something unusual about the structure or stability of the complex.<sup>47</sup>

$$U\{M(OH)_y\} = \Delta G_f^o\{H_2O\} - D/y^2 - (2.303 RT \log \beta^*_{1y})/y \quad (6)$$

The log  $\beta_{1y}$  values (for reactions written as  $M^{n+} + yOH^- \rightleftharpoons M(OH)_y$ ) in Table 1 at both  $\mu = 0$  and  $0.5 \text{ M}$  were converted to log  $\beta^*_{1y}$  values using  $\log \beta^*_{1y} = \log \beta_{1y} - y \log K_w$  where  $\log K_w$  is  $13.994$  for  $\mu = 0 \text{ M}$  and  $13.74$  for  $\mu = 0.5 \text{ M}$  at  $25^\circ\text{C}$ .<sup>20</sup> Log  $\beta_{12}$  values of  $24.5$  and  $23.5$  were used at  $\mu = 0$  and  $0.5 \text{ M}$ , respectively, where the former was roughly estimated using the Davies

equation.  $U\{M(OH)_y\}$  was then calculated using the Eq. 6 (setting  $\Delta G_f^\circ\{H_2O\} = -237.19 \text{ kJ mol}^{-1}$ )<sup>47</sup> and the results are presented in Fig. 3a. Although the values of the empirical constant  $D$  and  $\Delta G_f^\circ\{H_2O\}$  really apply to  $\mu = 0 \text{ M}$  at  $25^\circ\text{C}$ , both plots were given since the value of  $\log \beta_{11}$  at  $\mu = 0.5 \text{ M}$  was in question.



**Figure 3.** (a)  $U\{Bi(OH)_y\}$  plotted as a function of  $y$  for both  $\mu = 0$  and  $0.5 \text{ M}$ . The trendlines were fitted by omitting the values at  $y = 3$ . (b)  $U\{M(OH)_y\}$  plotted as a function of  $y$  for several trivalent metal ions at  $\mu = 0 \text{ M}$  and  $25^\circ\text{C}$ . Trendlines were fitted by omitting the value at  $y = 3$ , except for  $Fe^{3+}$  data.

Fig. 3a illustrates that the points were on a straight line except for  $U\{M(OH)_3\}$  which could imply that the  $\log \beta_{13}$  value was too high (it was predicted to be 30.1 for  $\mu = 0.5 \text{ M}$  when applying the trendline equation). However, this unusual stability may be due to the electroneutrality of this species. Similar plots are given in Fig. 3b for other trivalent metal ions (calculated at  $25^\circ\text{C}$  and  $\mu = 0 \text{ M}$ ) and with the exception of  $Fe(III)$ , all plots showed a lower than predicted  $\log \beta_{13}$  value. Thus confidence in the literature  $\log \beta_{1y}$  values was established and initial speculation that the  $\log \beta_{11}$  was too large was unfounded. This procedure suggested by



Barnum<sup>47</sup> certainly is a useful tool in assessing the validity of metal hydroxide formation constants.

### 3.3. Kinetics of precipitate formation

It was observed that the rate of the titration experiment affected the pH at which precipitation occurred. To test if this was merely due to kinetically slow precipitate formation, as suggested by Moussa and Sammour<sup>31</sup>, the time interval between addition of OH<sup>-</sup> to the test solution and the collection of polarographic data was set to range from 10–60 minutes for different titration experiments. The approximate pH at which precipitation commenced is given in Table 3,

**Table 3.** Approximate pHs for the onset of the precipitation of BiONO<sub>3</sub> for titration experiments with varying time intervals between OH<sup>-</sup> addition and polarogram collection (initial [Bi<sup>3+</sup>] = 5 × 10<sup>-5</sup> M). The values for ΔE(M) and ΔE<sub>C</sub>(M) are given, together with their difference.

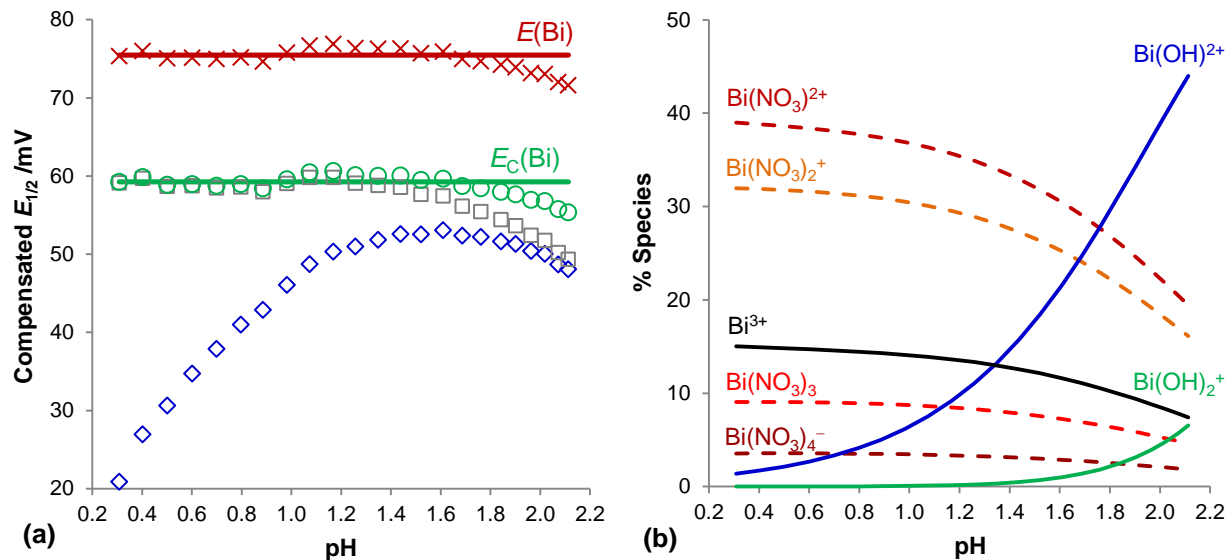
Time interval /min	~pH of precipitation	ΔE(M) /mV	ΔE <sub>C</sub> (M) /mV	ΔE(M) – ΔE <sub>C</sub> (M) /mV
0*	>2.1	508.1	491.9	16.2
10	1.7	502.8	491.9	10.9
20	1.5	501.4	490.1	11.3
30	1.3	496.2	485.5	10.7
45	1.3	495.9	484.8	11.1
60	1.0	493.6	481.9	11.7

\* The 0 min interval experiment is run differently to the rest (see text for details).

showing that precipitation could already start below pH 1 given enough time. The *I*<sub>d</sub> vs pH plots from which this data was derived (Fig. S6) reveal that the decrease in current after precipitation starts is also “slow” as *I*<sub>d</sub> does not drop to zero immediately.

It was also important to establish whether the value of  $E(\text{Bi})$  or  $E_{\text{C}}(\text{Bi})$  was affected by the rate of the experiment. Since the experimental  $E_{1/2}$  values varied slightly between experiments due to small variations in the reference system, the differences  $\Delta E(\text{M}) = E(\text{Bi}) - E(\text{Tl})$  and  $\Delta E_{\text{C}}(\text{M}) = E_{\text{C}}(\text{Bi}) - E(\text{Tl})$  were rather considered thus using Tl(I) as an internal reference. From the results in Table 3 it was noted that as the time interval between addition of  $\text{OH}^-$  and recording of the polarogram increased, both  $\Delta E(\text{M})$  and  $\Delta E_{\text{C}}(\text{M})$  decreased. This could point to some  $\text{BiONO}_3$  initially forming in solution before precipitation occurs and that formation of this product in both the solution and solid phase is slow. The slow kinetics probably signifies that the hexanuclear species also forms at the Bi(III) concentrations used here. Consequently, the higher the concentration of  $\text{BiONO}_3$  in solution, the greater the shift in  $E_{1/2}(\text{Bi})$  to less positive values and since this species was not accounted for when calculating  $\Delta E_{\text{T}}$  or  $\Delta E_{\text{OH}}$ , it would make the values regarded as  $E(\text{Bi})$  and  $E_{\text{C}}(\text{Bi})$  less positive and hence  $\Delta E(\text{M})$  and  $\Delta E_{\text{C}}(\text{M})$  smaller.

An experiment was also run as fast as possible by preparing solutions between pH 0.3–2.1 by mixing 0.5 M  $\text{HNO}_3$  and 0.5 M  $\text{KNO}_3$ , thus keeping the nitrate concentration relatively constant. The solutions were deoxygenated and just before pH was accurately measured and a polarogram was collected, the Bi(III) stock solution was added. No precipitation was initially evident up to pH 2.11, even with the concentration of Bi(III) kept constant at  $5 \times 10^{-5}$  M for all solutions in this case. The polarogram at pH 2.11 was remeasured after 2 min and a 28% drop in  $I_{\text{d}}$  was observed, and after another 2 min wait the  $I_{\text{d}}$  dropped a further 58%. A polarogram at pH 1.52 was also remeasured after 2 min and only a 11% drop in  $I_{\text{d}}$  was noted. Although this procedure is not feasible to run on a routine basis or to allow metal-ligand systems to reach equilibrium (unless the reaction is extremely fast) it did show that precipitate formation is slow.



**Figure 4.** For the experiment with time interval of 0 min the following data is shown: (a) Experimentally determined  $E_{1/2}(\text{Bi})$  values ( $\diamond$ ) (constantly at  $[\text{Bi(III)}] = 5 \times 10^{-5} \text{ M}$  and  $[\text{NO}_3^-] \approx 0.5 \text{ M}$ ) and that corrected for  $E_j$  ( $\square$ ). Corrections were then made for  $\Delta E_T$  ( $\times$ ) or  $\Delta E_{\text{OH}}$  ( $\circ$ ). (b) The corresponding SDD is given.

The compensated  $E_{1/2}(\text{Bi})$  values for this experiment are shown in Fig. 4, as before, together with the corresponding SDD. In this case the first few points at the lowest pH where  $E_{1/2}$  values were corrected for  $E_j$  and  $\Delta E_T$  ( $\times$ ) were not higher than the rest as previously seen in Fig. 2. This supports the suggestion that the variation is due to the change in ionic strength since in this case it is kept constant at 0.5 M. This also explains the high  $\Delta E(\text{M})$  value shown in Table 3. In Fig. 4a the data corrected for  $\Delta E_T$  ( $\times$ ) and  $\Delta E_{\text{OH}}$  ( $\circ$ ) show a decreasing trend above pH  $\sim 1.7$  and these points were omitted when determining  $\Delta E(\text{M})$  and  $\Delta E_C(\text{M})$ . This decreasing trend could be due to the formation of a solution species at the higher pHs that was not accounted for in the potential shift calculations and is probably the slightly soluble hexameric  $\text{BiONO}_3$  species. Given sufficient time this would form colloids which precipitate from solution as seen by the decreasing  $I_d$  discussed above. It is interesting to note how well this correlates to the pH of precipitation for the experiment with the 10 min interval (Table 3).

The  $\Delta E(M)$  and  $\Delta E_C(M)$  values for the interval times 10–20 min are within experimental error and therefore the timing for the usual titration experiments should not affect the values of  $E_C(\text{Bi})$  and  $E(\text{Bi})$  obtained. Even the  $\Delta E_C(M)$  value for the 0 min experiment was comparable to the values at 10–20 min intervals. The  $\Delta E(M)$  value for the 0 min experiment was significantly higher than the rest because of the higher nitrate concentration. Interestingly for the 10–60 min interval experiments, the difference between  $\Delta E(M)$  and  $\Delta E_C(M)$  is constant ( $11.4 \pm 0.4$  mV) irrespective of the time interval.

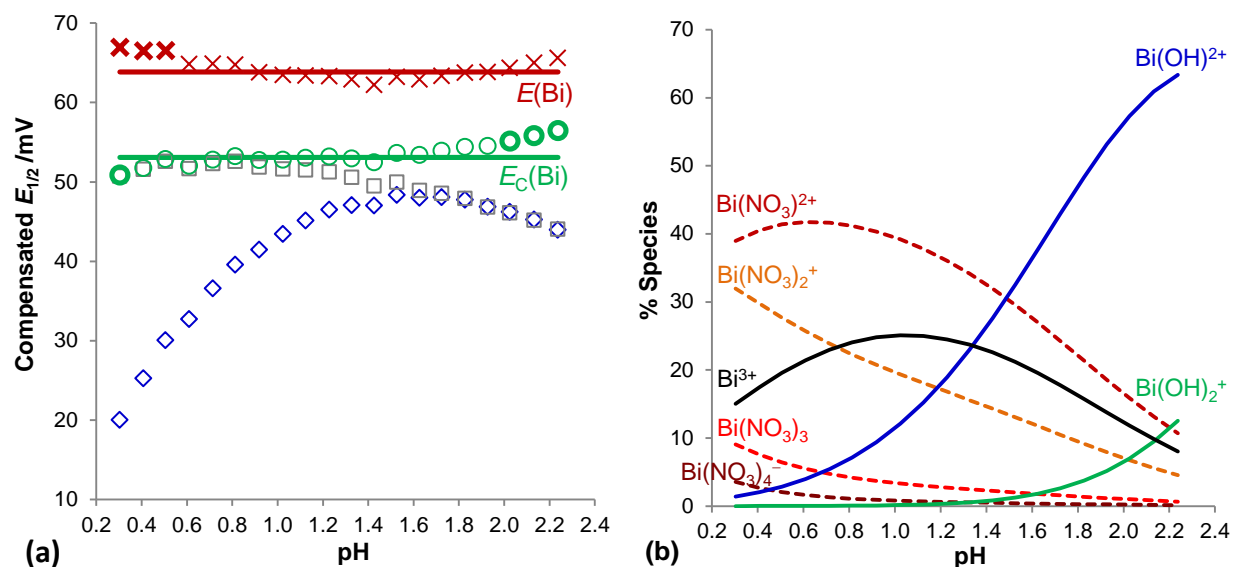
Berbel *et al.*<sup>48</sup> showed that polarographic data (considering both the negative shifts in potential and decreasing currents) can be used to determine the solubility product of a sparingly soluble salt. If this was to be done for this system, an out-of-cell approach would have to be used due to the slow formation of the insoluble product and thus allowing sufficient time for equilibrium to be established. This was not the aim here and experiments were run as quickly as possible to prevent precipitate formation as far as possible.

### 3.4. Investigations at “lower” Bi(III) concentrations

In order to postpone precipitation and increase the pH range in which data could be collected, the concentration of Bi(III) (and Tl(I)) was decreased five times and the current integration time was increased from 60 ms to 100 ms to still obtain reasonable polarograms. According to the pBi-pH diagram by Kragten *et al.*,<sup>22</sup> by changing the Bi(III) concentration from  $5 \times 10^{-5}$  M to  $1 \times 10^{-5}$  M, the pH of precipitation would be shifted by almost a pH unit. Two issues immediately came to the fore. Firstly, oxygen contamination introduced by  $\text{OH}^-$  addition became more evident and the test solution had to be purged for longer after pH adjustment (increased from 15 s to 5 min) yet still minimising  $\text{BiONO}_3$  formation. Secondly, in order to obtain  $\delta$  values close to

unity (indicating reversibility), data points at the most positive potentials that showed curvature due to mercury oxidation had to be removed when fitting the Bi(III) reduction waves because the parameters for fitting the background current are strongly correlated to  $I_d$  and  $\delta$ . The position of mercury oxidation wave also shifts to more negative potentials with increasing pH, so amending the initial potential of the polarogram slightly only solves the problem to a point.

Under these conditions a pH of 2.2 was attained before precipitation commenced (compared to pH 1.5 with the higher Bi(III) concentration).  $\Delta E_T$  and  $\Delta E_{OH}$  values were calculated as before and hence the  $E(\text{Bi})$  and  $E_C(\text{Bi})$  values determined as shown in Fig. 5a. Due to the increasing trend noticed for the last few points at the highest pH corrected for  $\Delta E_{OH}$ , it was initially thought that this was due to overestimation of  $\log \beta_{12}$  which was quoted for  $\mu = 1 \text{ M}$  and used as such. This value was roughly estimated to be 23.2 at  $\mu = 0.5 \text{ M}$  using the Davies equation and then tested by calculating  $U\{\text{M}(\text{OH})_2\}$  utilising the equation in Eq. 6. The plot of  $U\{\text{M}(\text{OH})_y\}$  vs  $y$  still gave a reasonable straight line ( $R^2 = 0.9997$ ). However, no significant changes occurred with recalculation of the  $\Delta E_{OH}$  values using this  $\log \beta_{12}$  value. Considering the corresponding SDD in Fig. 5b it is seen that as the pH increases the amount of Bi(III)-nitrates decrease and the extent of hydrolysis increases, thus the contribution to  $\Delta E_T$  from the nitrate species decreases and that from the hydroxide species increases. Above pH  $\sim 1.8$  more than 50% of Bi(III) is present as hydrolysis products, and it is approximately from this point that the increase was noted. It is expected that if it were possible to obtain data at higher pHs where Bi(III) nitrates no longer form in solution, the points demarcated (○) in Fig. 5a would eventually overlap with  $E(\text{Bi})$ . This highlights that  $E(\text{Bi})$  should be used instead of  $E_C(\text{Bi})$  where determining formation constants with another ligand and both the hydroxide and nitrates should be included in the species model as competing ligands.



**Figure 5.** (a) Experimental  $E_{1/2}(\text{Bi})$  values ( $\diamond$ ) (initial  $[\text{Bi(III)}] = 1 \times 10^{-5} \text{ M}$ ) and that corrected for  $E_j$  ( $\square$ ). Corrections were then made for potential shifts due to (i)  $\text{Bi}(\text{OH})_2^{2+}$ ,  $\text{Bi}(\text{OH})_2^+$  and Bi(III) nitrate species ( $\times$ ), or (ii)  $\text{Bi}(\text{OH})_2^{2+}$  and  $\text{Bi}(\text{OH})_2^+$  in the presence of nitrate ( $\circ$ ). Points that are bold were omitted when calculating  $E(\text{Bi})$  or  $E_C(\text{Bi})$  (such that the standard deviation was  $< \sim 1$ ). (b) The corresponding SDD is given. (The SDD for the pH range 0-14 is modelled in Figure S4c.)

For completeness, it was again tested if the interval time affected the  $E(\text{Bi})$  or  $E_C(\text{Bi})$  values by comparing  $\Delta E(\text{M})$  or  $\Delta E_C(\text{M})$  values, respectively, and the results are given in Table 4. For both  $\Delta E(\text{M})$  and  $\Delta E_C(\text{M})$  the values in the 5–20 min interval times were within experimental error and, for some unknown reason, corresponded to those given in Table 3 with 30 and 45 minute intervals. Using the lower Bi(III) concentration in these experiments provided more data points to calculate the  $E(\text{Bi})$  and  $E_C(\text{Bi})$  values in each experiment, thus giving more confidence to the results.

**Table 4.** Approximate pHs for the onset of the precipitation of BiONO<sub>3</sub> for titration experiments with varying time intervals between OH<sup>-</sup> addition and polarographic data collection (initial [Bi(III)] = 1 × 10<sup>-5</sup> M). The values for ΔE(M) and ΔE<sub>C</sub>(M) are given, together with their difference.

Time interval /min	~pH of precipitation	ΔE(M) /mV	ΔE <sub>C</sub> (M) /mV	ΔE(M) – ΔE <sub>C</sub> (M) /mV
5	2.2	495.3 ± 1.5 <sup>a</sup>	484.5 ± 1.7 <sup>a</sup>	10.8 ± 0.3 <sup>a</sup>
10	2.1	496.7	486.3	10.4
20	1.9	496.0	485.4	10.6

<sup>a</sup> Average of 5 determinations

For experiments used to determine formation constants for Bi(III)-ligand systems, where ligand is added to the solution containing Bi(III) and Tl(I) before the pH titration is commenced, it is proposed that the same experimental conditions employed to determine  $E(\text{Bi})$  (and  $E_{\text{C}}(\text{Bi})$ ) must be used. In this case experiments with the time intervals between 5-20 min are acceptable and an average  $\Delta E(\text{M})$  value of  $495.6 \pm 1.4$  mV (obtained for all 7 experiments) can be used. Having a reproducible  $\Delta E(\text{M})$  value allows  $E(\text{Bi})$  to be accurately calculated for experiments containing ligand in solution, where  $E(\text{Bi}) = \text{average } \Delta E(\text{M}) + E(\text{Tl})$ , and  $E(\text{Tl})$  can be determined for each experiment (since Tl(I) does not readily undergo complexation). The values of  $E_{\text{C}}(\text{Bi})$  can be determined in a similar fashion if required where an average  $\Delta E_{\text{C}}(\text{M})$  value of  $484.9 \pm 1.6$  mV was obtained for the 7 experiments. The  $E(\text{Bi})$  value can then be used in Eq. 1 to solve for stability constants for the Bi(III)-ligand system.

### 3.5. Comparison to other polarographic complex formation studies

Literature regarding the use of polarography to determine formation constants of Bi(III) with organic ligands is scant and most of these used either Lingane's method<sup>49-51</sup> or DeFord and

Hume's method<sup>52-54</sup> to calculate formation constants. Lingane's method is limited as it applies only to ligand titrations where there is a single predominant complex in solution at a time. DeFord and Hume's method also includes the reduction potential of the uncomplexed metal ion in the calculations,<sup>55</sup> but the actual value used was not mentioned in any of the publications.<sup>52-54</sup>

Bond and Waugh<sup>56</sup> also used DeFord and Hume's method to determine formation constants for the Bi(III)-chloride complexes using AC polarography by ligand titration in 2.0 M perchlorate solutions at pH 1. They assumed hydrolysis is negligible at pH 1 and according to Fig. S4a in a non-complexing background 30% Bi(OH)<sup>2-</sup> would be present, but since this would result in a very small shift in potential (around 1 mV) the assumption would hold. However, the reduction of Bi(III) is not reversible in 2.0 M perchlorate solutions and the reversible  $E(\text{Bi})$  could not be directly measured. On addition of low concentrations of chloride (~0.004 M – double the concentration of Bi(III) in solution) the reduction of Bi(III) becomes reversible and thus from the plot of the reduction peak potentials vs. chloride concentration, the reversible  $E(\text{Bi})$  value was determined by extrapolating to zero chloride concentration. As the authors state, this reduces the precision of the value of  $E(\text{Bi})$ . Additionally, this methodology would only apply to Bi(III)-ligand systems which form strong complexes at pH 1 already at low ligand-to-Bi(III) concentration ratios, which would not be the case for many organic ligands.

Cukrowski *et al.*<sup>57</sup> determined the  $E(\text{Bi})$  by collecting polarographic data in the absence of ligand (in 0.5 M nitrate background solution), correcting the measured  $E_{1/2}(\text{Bi})$  values for shifts in potential due to Bi(III) hydroxide formation and then fitted a third order polynomial to these corrected  $E_{1/2}(\text{Bi})$  values. The function was extrapolated to a constant value which was defined as  $E(\text{Bi})$ . The difference between this  $E(\text{Bi})$  and the corrected  $E_{1/2}(\text{Bi})$  values was ascribed to  $E_j$ , but this would mean they obtained an  $E_j$  of ~55 mV at pH 0.3, whereas the value should be



closer to 30 mV. It therefore appears that shifts due to Bi(III) nitrate formation were inadvertently largely accounted for in the acidic region.

For comparison, it was attempted to determine  $E(\text{Bi})$  using the same procedure as Cukrowski *et al.*<sup>57</sup> Experimental  $E_{1/2}(\text{Bi})$  values, as presented in Fig.'s 2 and 4, were firstly corrected for shifts in potential due to hydroxide formation, ignoring the formation of nitrate species (see Fig S7 in the Supporting Information). Extrapolating the third order polynomial was impossible as the function increased after the last data point, so instead the function  $y = a + b \exp(cx)$  was fitted to the data, with the value of  $a$  (i.e. the extrapolated value) corresponding to  $E(\text{Bi})$ . It should be noted that although  $\text{Bi}(\text{OH})_2^+$  was not incorporated in the species model used by Cukrowski *et al.*,<sup>57</sup> it was included here. The experimental  $E_{1/2}(\text{Bi})$  values were also correct for shifts in potential due to the formation of both Bi(III) hydroxide and Bi(III) nitrate species, and extrapolated in the same way. The results in Table 6 showed that  $E(\text{Bi})$  was slightly overestimated when extrapolating in each case and there was some agreement between the values determined from data corrected for just the Bi(III) hydroxide species and that corrected for Bi(III) hydroxide and nitrate species. Values at the higher pH's, where the extent of nitrate formation is minimal, has the greatest influence on the extrapolated value, so this was not surprising. In solutions with the lower Bi(III) concentration, data could be collected to higher pHs before precipitation occurred. Testing to what extent the extrapolated value was affected by having fewer data points (points only up to pH 1.6 were considered) showed there was a greater influence on the data where only the Bi(III) hydroxides were accounted for, probably due to the steeper curve at higher pHs. By correcting the experimental  $E_{1/2}(\text{Bi})$  values for shifts in potential due only to the Bi(III) hydroxides in the presence of nitrate, the extrapolated value was compared to the  $E_C(\text{Bi})$  and again the extrapolated values were overestimated.

**Table 6.** Comparison of  $E(\text{Bi})$  and  $E_C(\text{Bi})$  values determined in this work and by applying the extrapolation procedure suggested by Cukrowski *et al.*<sup>57</sup> for experiments where initial  $[\text{Bi(III)}] = 5 \times 10^{-5} \text{ M}$  or  $1 \times 10^{-5} \text{ M}$ .

	This work	Correct for $\text{Bi(OH)}_x$ only	Correct for $\text{Bi(OH)}_x + \text{Bi(NO}_3)_y$	This work	Correct for $\text{Bi(OH)}_x$ in presence of $\text{NO}_3^-$
	$E(\text{Bi}) / \text{mV}$			$E_C(\text{Bi}) / \text{mV}$	
$[\text{Bi}] = 5 \times 10^{-5} \text{ M}$ , pH 1.6*	64.3	68.9	67.8	53.3	57.3
$[\text{Bi}] = 1 \times 10^{-5} \text{ M}$ , pH 2.2*	66.5	70.7	68.2	55.4	58.8
$[\text{Bi}] = 1 \times 10^{-5} \text{ M}$ , pH 1.6•		67.9	67.7		58.1

\* last reading taken at this pH before precipitation

• last reading used at this pH, values at higher pH deleted

Extrapolation beyond the region where data is measured is generally not good practice, but may be required as an estimate when data cannot be obtained. Since the data points at the highest pHs are the least certain due to slow precipitate formation, as discussed in section 3.3, and these points also have the greatest effect on the extrapolated value, extrapolation is not recommended here. The manner in which  $E(\text{Bi})$  was calculated in this work allows discrepancies at higher pHs to be identified and it is really sufficient to calculate  $E(\text{Bi})$  by averaging the corrected values between about pH 0.5 – 1.5 if required (collecting a greater number of points in this region would statistically provide a better estimate). Thus by better understanding the overall solution chemistry, a more accurate representation of  $E(\text{Bi})$  can be achieved. The use of the  $\text{Tl(I)}$  reference ion also allows  $E(\text{Bi})$  to be accurately determined for experiments where the ligand is included, whereas Cukrowski *et al.*<sup>57</sup> ran two consecutive experiments (one without and one with the ligand). In our experience, there are slight fluctuations in the potential of the reference electrode between each multi-hour experiment and this would not be accounted for in the methodology proposed by Cukrowski *et al.*<sup>57</sup>.

### 3. Conclusion

This work clearly illustrates the complexities involved in studying Bi(III) complex formation. Precipitation of the hexameric  $\text{BiONO}_3$  species occurred around pH 2, thus it was thus necessary to commence the study at pH <2 where Bi(III) is still in solution and resulting in  $E_j$  having to be evaluated and compensated. Also, the formation of soluble hydrolysis products occurs from pH 0.3 already and nitrate complexes are formed at low pH, which suppresses the extent of hydrolysis somewhat but also results in only about 15% of Bi(III) being uncomplexed at pH 0.3 (see Fig. S4b and c). Therefore all these factors had to be considered when determining  $E(\text{Bi})$ .

In order to best predict  $E(\text{Bi})$  as accurately as possible for an experiment used to study Bi(III)-ligand equilibria, the average difference between  $E(\text{Bi})$  and  $E(\text{Tl})$  (i.e.  $\Delta E(\text{M})$ , where Tl(I) was the in-situ reference ion since it is not readily complexed) was first determined for several experiments in the absence of ligand. For experiments including ligand,  $E(\text{Tl})$  for that experiment was measured and  $E(\text{Bi})$  can be determined using the average  $\Delta E(\text{M})$ . Also, when refining stability constants, both nitrate and hydroxide must be incorporated in the species model as competing ligands. This process will be applied to the study of Bi(III)-ligand equilibria, thus enabling a knowledge-base for Bi(III) coordination chemistry to be built.

### 4. Appendix: Description of selected symbols

$E_j$             Diffusion junction potential

$E_{1/2}(\text{M})$     Half-wave potential of the metal ion

$E(\text{M})$         reduction potential of the free or uncomplexed metal ion (true free metal ion potential)

$E(M_{\text{comp}})$	Reduction potential of the complexed metal ion
$E_C(M)$	Conditional free metal ion potential
$\Delta E$	Shift in potential due to complex formation: $\Delta E = E(M) - E(M_{\text{comp}})$
$\Delta E_{\text{OH}}$	Shift in potential due to the formation of Bi(III) hydroxide species
$\Delta E_{\text{OH,C}}$	Shift in potential due to the formation of Bi(III) hydroxide species in the nitrate supporting electrolyte, taking into account the suppression of hydroxide formation in the presence of nitrates.
$\Delta E_T$	Shift in potential due to the formation of Bi(III) hydroxide and nitrate species combined
$\Delta E(M)$	Difference in the free metal ion potentials for Bi(III) and Tl(I): $\Delta E(M) = E(\text{Bi}) - E(\text{Tl})$
$\Delta E_C(M)$	Difference in the conditional and true free metal ion potentials for Bi(III) and Tl(I) respectively: $\Delta E_C(M) = E_C(\text{Bi}) - E(\text{Tl})$
$I(M)$	Reduction current of the uncomplexed metal ion
$I(M_{\text{comp}})$	Reduction current of the complexed metal ion
$[M]$	Concentration of the free metal ion
$[M_T]$	Concentration of the total metal ion

[M]<sub>c</sub> Conditional concentration of the free metal ion which includes the Bi(III) nitrate species

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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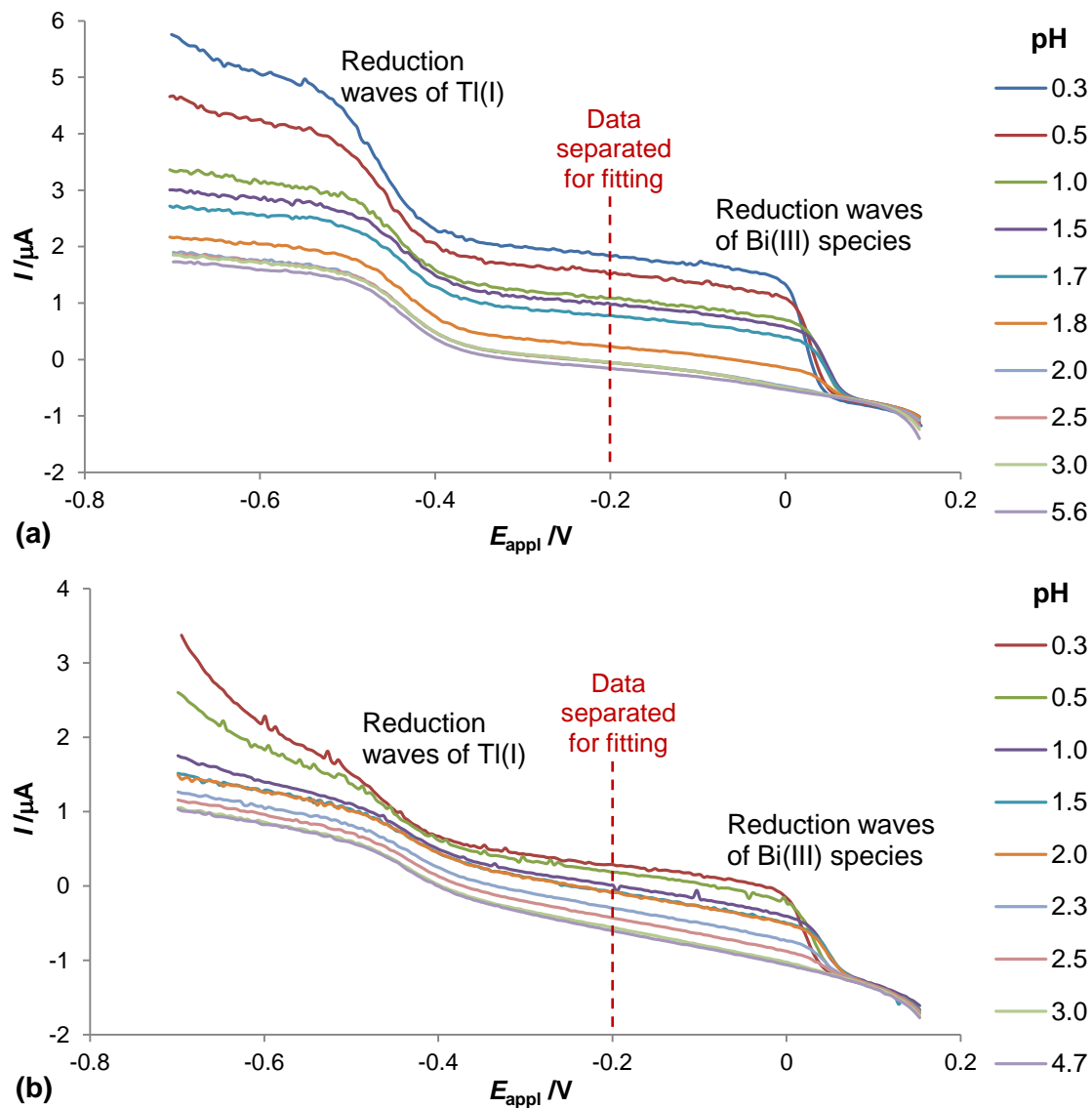
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## Supporting Information

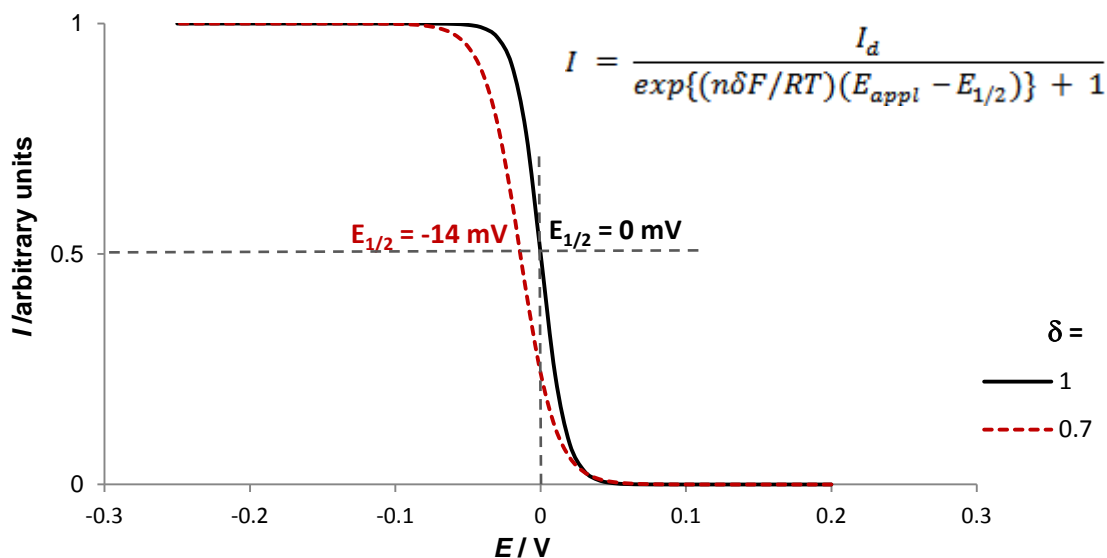
### 1. Polarographic data



**Figure S1:** Selected polarograms from polarographic-pH titrations with initial concentrations as follows: (a)  $[\text{Bi(III)}] = 4.99 \times 10^{-5} \text{ M}$  and  $[\text{Tl(I)}] = 9.99 \times 10^{-5} \text{ M}$ , or (b)  $[\text{Bi(III)}] = 9.97 \times 10^{-6} \text{ M}$  and  $[\text{Tl(I)}] = 1.99 \times 10^{-5} \text{ M}$ .

## 2. Reversibility of DC reduction waves

Although it was expected that Bi(III) reduction would be quasi-reversible in a nitrate medium,<sup>1,2</sup> the  $\delta$  values obtained when fitting Eq 2 to the Bi(III) reduction waves were very close to one. In DC polarography, the steepness of the reduction wave is related to the term  $\delta nF/RT$  in Eq. 2. If  $\delta = 1$ , the reduction wave displays a reversible electron transfer process, but for  $\delta < 1$  it is quasi-reversible (it has been suggested that it is irreversible for  $\delta < 0.5$ ) and the steepness of the wave is then lower than for the reversible process. The onset of reduction for a quasi-reversible process generally occurs at the same potential as that for a reversible wave and theoretical illustrations are given in Fig. S2. Here it can be seen that a decrease in the value of  $\delta$  changes the slope of the wave and results in a more negative  $E_{1/2}$  value.



**Figure S2:** Simulated DC reduction waves for a reversible ( $\delta = 1$ ) and a quasi-reversible ( $\delta = 0.7$ ) electron transfer process where  $n = 3$ .

As reported, the criteria for reversibility do not only depend on the system being studied, but also on the technique and the specific conditions used.<sup>3</sup> It was shown that the log plots used to determine reversibility for DC polarographic data were not sufficiently sensitive to changes in reversibility, whereas parameters determined by AC polarography changed more significantly as the reversibility changed.<sup>3</sup> It was thus assumed that the reversible  $E_{1/2}$  value is determined when  $\delta$  is unity, even if parameters determined by another techniques indicate that the process is not fully reversible. In complex formation studies, the shift in  $E_{1/2}$  from the value of the free metal ion to that of the complexed metal ion ( $\Delta E = E(M) - E(M_{comp})_{pH}$ ) is used to evaluate formation

constants. Therefore, as long as all reduction waves give  $\delta = 1$ , the  $\Delta E$  value calculated does not include an additional shift due to the change in steepness of the DC wave (due to changes in reversibility as measured by  $\delta$ ) and the assumption that this is reversible is adequate for our purpose.

(58) Bond, A. M. The AC and DC Polarographic Reduction of Bismuth(III) in Acidic Halide and Other Media. *Electrochim. Acta* **1972**, *17*, 769-785.

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### 3. Analysis of the precipitate

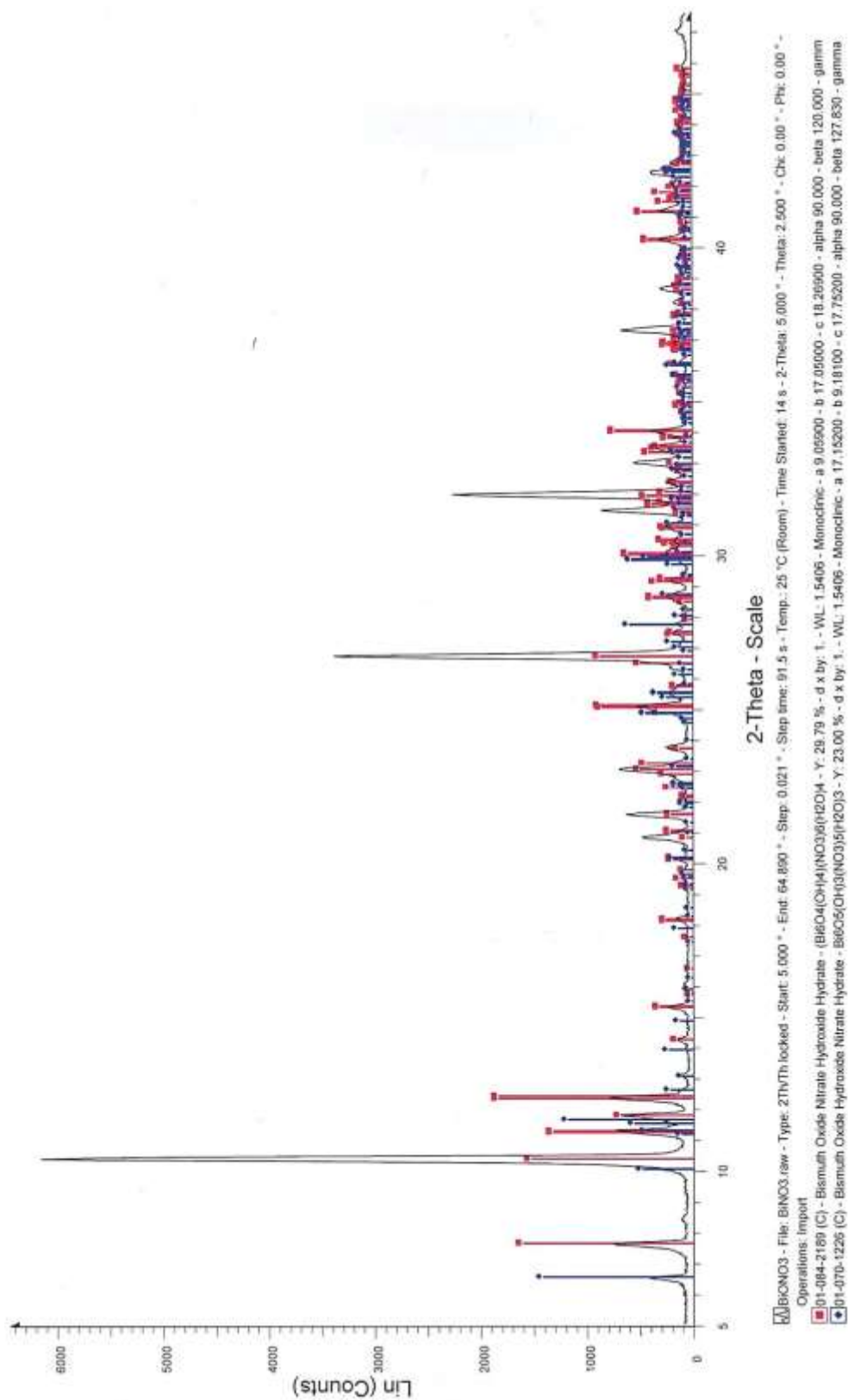
Since the amount of precipitate produced was negligible in the dilute solutions used in polarographic experiments, a 0.1 M Bi(III) solution in 0.5 M HNO<sub>3</sub> was made up and 0.5 M NaOH was slowly added until precipitation occurred below pH 2. The solution was then filtered and allowed to dry and yielded white shiny platelets as noted by Swinehart and Garrett.<sup>4</sup>

The precipitate was analysed using a Bruker D2 Phaser powder X-ray diffractometer with a Co X-ray source (1.78897 Å) and a Bruker Lynxeye PSD detector. The sample was prepared on a zero background holder. Analysis showed that both Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub> and Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>3</sub> were present as shown by the superimposed powder patterns in Figure S2 that were calculated from single crystal data by Lazarini<sup>5,6</sup> (as given in the Inorganic Crystal Structure Database<sup>7</sup>). This precipitate was formed using Bi(III) concentrations about 10<sup>4</sup> times greater than in the polarographic cell, so the question remains whether the hexamers are still formed under significantly more dilute conditions.

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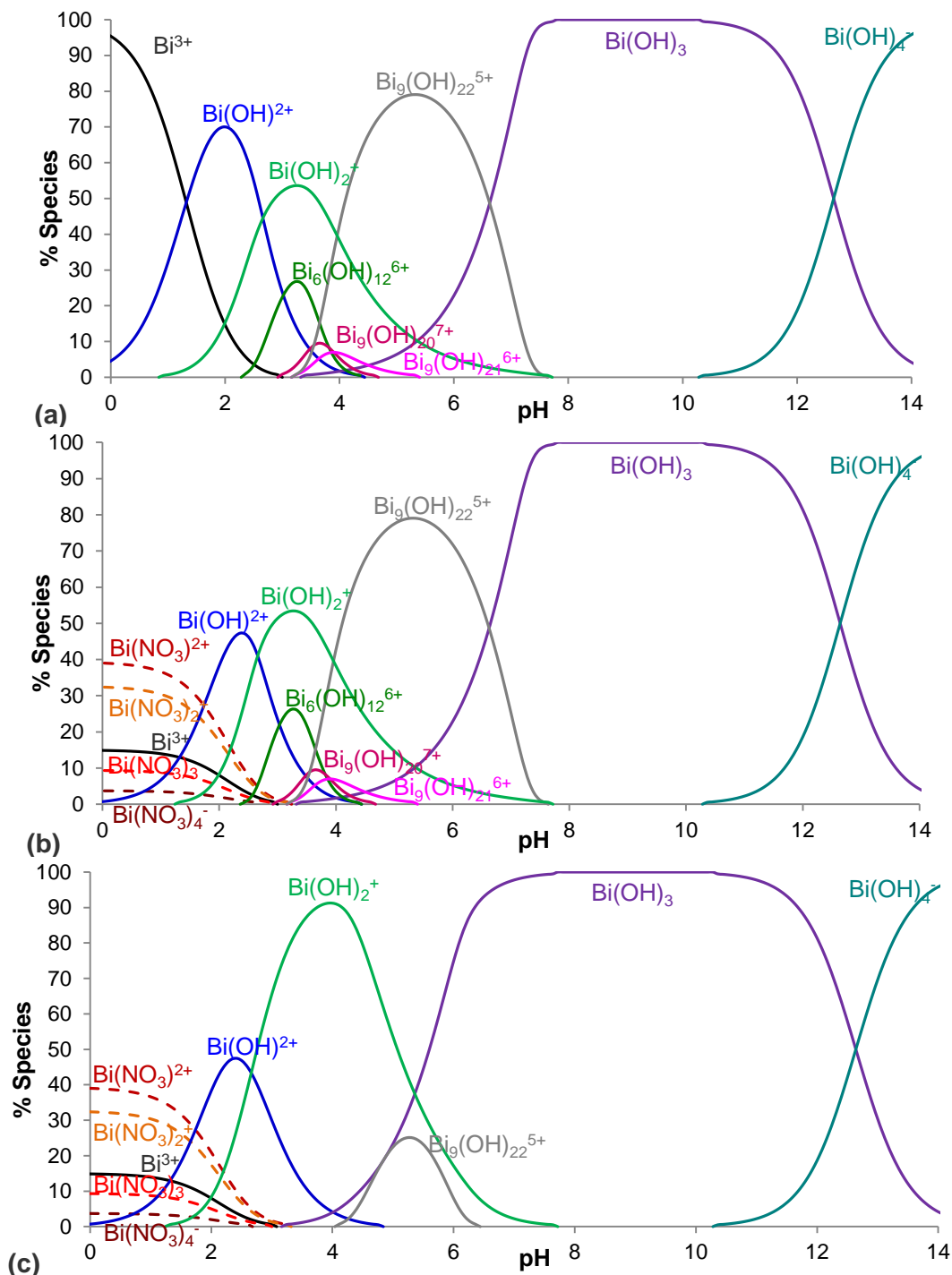
- (63) Lazarini, F. Basic Bismuth Nitrate  $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)\text{O}_4(\text{OH})_4](\text{NO}_3)_5$ . *Acta Cryst.* **1979**, *B35*, 448-450.
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**Figure S3:** PXRD scan of the “BiONO<sub>3</sub>” precipitate. Superimposed lines correspond to the calculated structures as follows: (Red) Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub> and (Blue) Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>3</sub>.

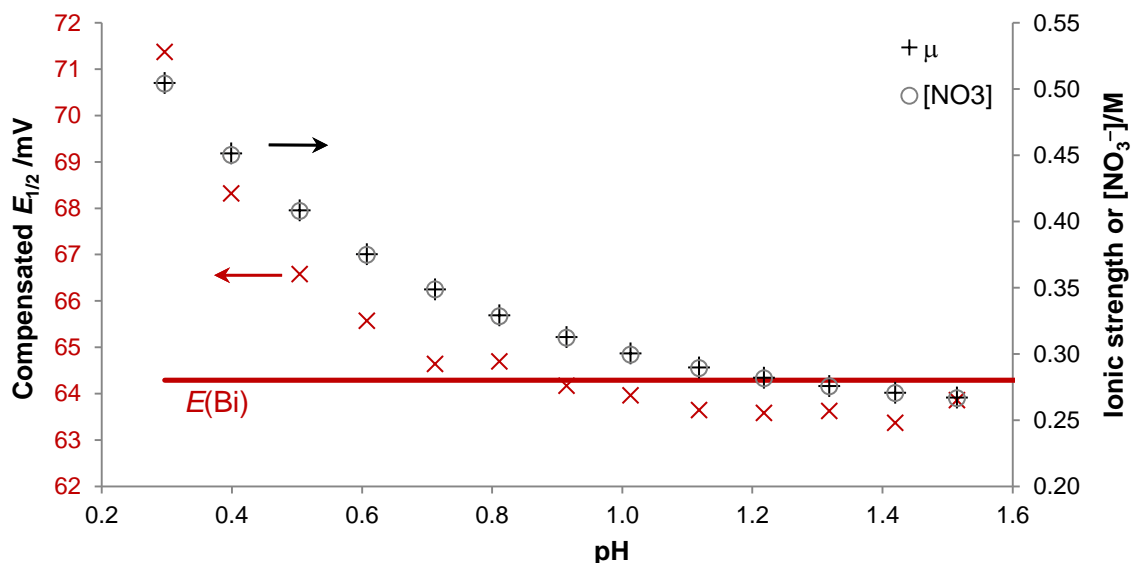


#### 4. Species distribution diagrams



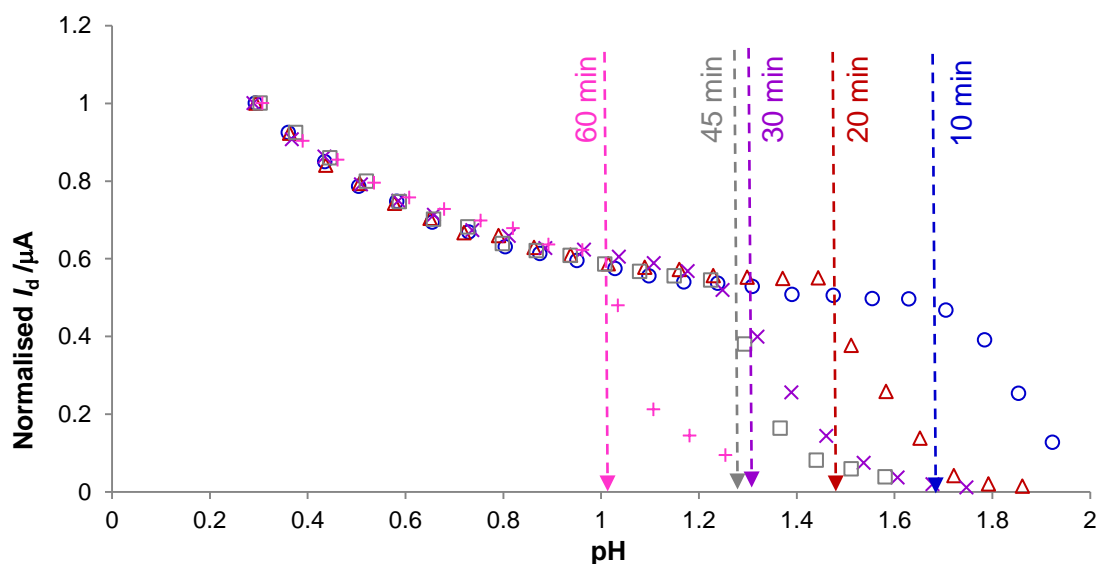
**Figure S4:** Species distribution diagrams plotted using log  $\beta$  values in Table 1 (indicated by \*) and Table 3. (a)  $[\text{Bi(III)}] = 5 \times 10^{-5} \text{ M}$  (Bi(III) nitrates omitted); (b)  $[\text{Bi(III)}] = 5 \times 10^{-5} \text{ M}$  and  $[\text{NO}_3^-] = 0.5 \text{ M}$ ; (c)  $[\text{Bi(III)}] = 1 \times 10^{-5} \text{ M}$  and  $[\text{NO}_3^-] = 0.5 \text{ M}$ .

## 5. Effect of varying ionic strength



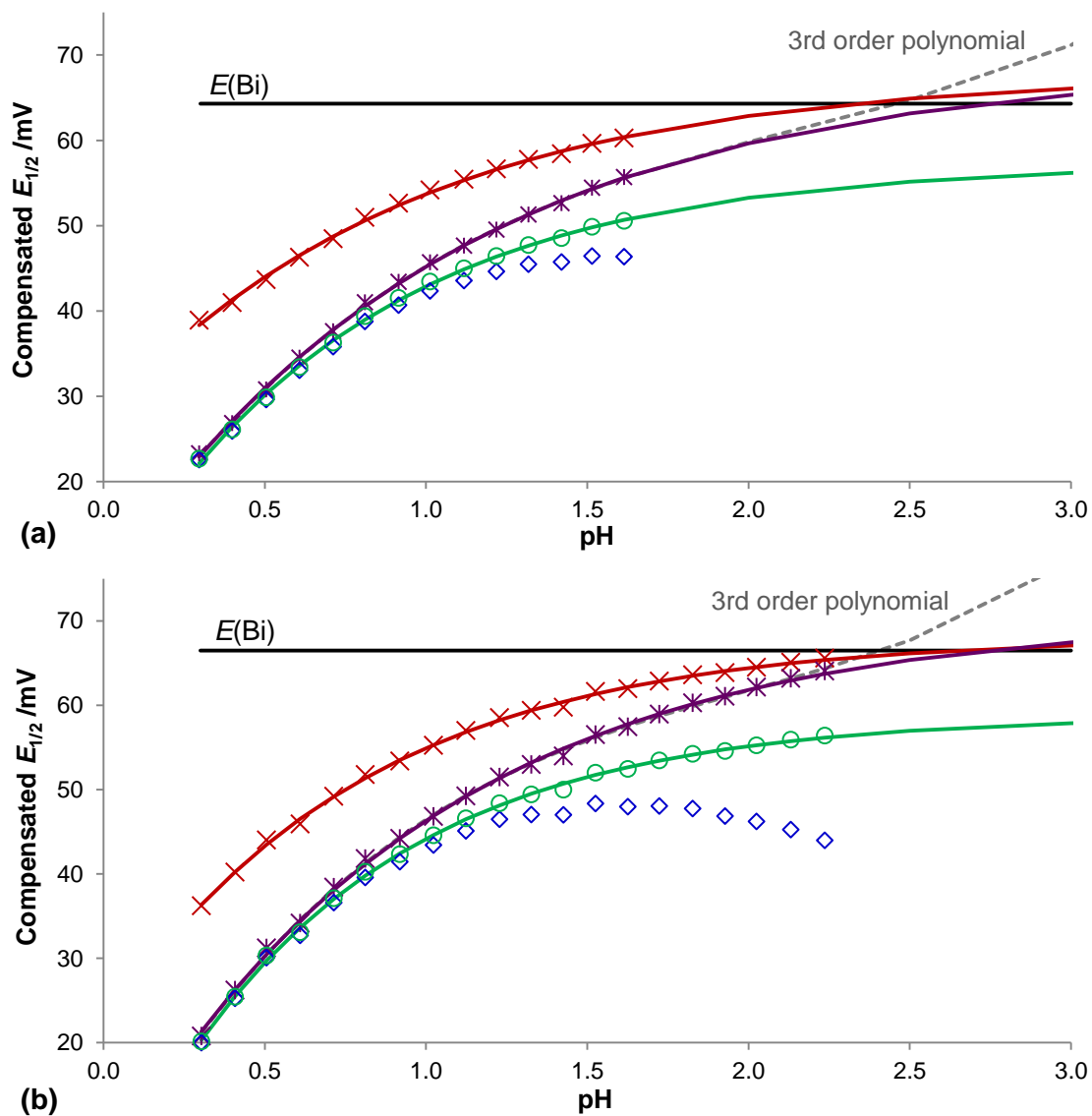
**Figure S5:** As for Fig. 2a, the  $E_{1/2}(\text{Bi})$  values compensated for  $E_j$  and for potential shifts due to  $\text{Bi}(\text{OH})_2^{2+}$ ,  $\text{Bi}(\text{OH})_2^+$  and  $\text{Bi}(\text{III})$  nitrate species ( $\times$ ) is given. Also shown is the concentration of nitrate ( $\circ$ ) and the ionic strength ( $+$ ) of the solution as the titration proceeds.

## 6. Kinetics of precipitate formation



**Figure S6:** Normalised  $I_d$  for the reduction of  $\text{Bi}(\text{III})$  (initial  $[\text{Bi}(\text{III})] = 4.99 \times 10^{-5} \text{ M}$ ) for titration experiments with varying time intervals between  $\text{OH}^-$  addition and polarographic data collection. The approximate pH at which precipitation starts is also indicated by the arrows.

## 7. Determining $E(\text{Bi})$ by extrapolation



**Figure S7:** Experimental  $E_{1/2}(\text{Bi})$  values ( $\diamond$ ) are given for experiments with initial  $[\text{Bi(III)}]$  of (a)  $5 \times 10^{-5}$  M (as for Fig. 2) and (b)  $1 \times 10^{-5}$  M (as for Fig. 4). The  $E_{1/2}(\text{Bi})$  values were corrected for potential shifts due to  $\text{Bi(OH)}^{2+}$  and  $\text{Bi(OH)}_2^+$  formation only ( $*$ ),  $\text{Bi(OH)}^{2+}$ ,  $\text{Bi(OH)}_2^+$  and  $\text{Bi(III)}$  nitrate species ( $\times$ ) or just  $\text{Bi(OH)}^{2+}$  and  $\text{Bi(OH)}_2^+$  in the presence of nitrate ( $\circ$ ). The function  $y = a + b \exp(cx)$  was fitted to the corrected  $E_{1/2}(\text{Bi})$  values. The  $E(\text{Bi})$  values obtained using the methodology proposed in this work is also shown. The third order polynomials fitted to data ( $*$ ) illustrate why this function could not be extrapolated to determine  $E(\text{Bi})$ .