

## Reduction of Bi(III) from highly concentrated perchloric acid

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In highly concentrated  $\text{HClO}_4$  solutions ( $\geq 8 \text{ mol dm}^{-3}$ ) the reduction of Bi(III) at dropping mercury electrode is reversible due to the low concentration of free water molecules. The mechanism of reduction which includes the formation of an adion:  $\text{Bi}(\text{OH}_2)_m^{3+} + \text{Hg}_k \rightleftharpoons \text{Bi}(\text{OH}_2)_{m-1}^{3+}(\text{Hg})_k + \text{H}_2\text{O}$  is proposed. Formation of the adion is prompted by the adsorption of the  $\text{Cl}^-$  ion at the mercury surface:  $\text{BiCl}(\text{OH}_2)_{m-1}^{2+} + \text{Hg}_k \rightleftharpoons \text{Bi}(\text{OH}_2)_{m-1}^{3+}(\text{Hg})_k + \text{Cl}_{\text{ads}}^-(\text{Hg})_k$ . The highest coordination number of  $\text{Bi}^{3+}$  for the  $\text{Cl}^-$  anion is 6.

The d.c. polarographic reduction of bismuth(III) ions on a mercury electrode in  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  is irreversible<sup>1-16</sup>. It is accepted widely that the electrode process:  $\text{Bi}(\text{OH}_2)_m^{3+} + 3e^- \rightleftharpoons \text{Bi}(\text{Hg}) + m\text{H}_2\text{O}$  is slow due to kinetically slow removal of coordinated water. The dehydration is the rate-determining step in redox reactions of many transition metal ions<sup>17-20</sup>. If the supporting electrolyte contains some anions which form complexes with bismuth ions, the reduction rate of Bi(III) may be significantly increased. Formation of covalently bonded ligands can increase the rate of removal of water, but the exact mechanism of such a reaction is still unknown. There is no satisfactory explanation for the fact that the activity of ligands depends not only on the stability of complexes formed, but also on the surface activity of ligand ions. For instance, bismuth forms stronger complexes with sulphate than with nitrate anions, but the latter are more active because of higher surface activity. In this paper it will be shown that the electroactivity of Bi(III) ions can be substantially improved if the activity of water in the supporting electrolyte is reduced.

### Materials and Methods

Square-wave voltammetric measurements were performed with a Harwell multi-mode polarograph<sup>21</sup>, an x-y recorder HP 7045 A (Hewlett-

Packard) and an electroanalytical cell EA 875-20 (Metrohm). The working electrode was the DME in a free-dropping mode ( $t_d = 18 \text{ s}$ ). The polarograph provides a square-wave voltammogram within the lifetime of a single mercury drop. The frequency was 225 Hz and the amplitude was 32 mV (peak to peak).

The supporting electrolyte was  $\text{HClO}_4$  (Merck, AR) in concentrations from 1 to  $11.6 \text{ mol dm}^{-3}$ . Water deionized in a Millipore Milli-Q column deionizer was used. The counter electrode was the Pt wire and the reference was the saturated Ag/AgCl(NaCl) electrode. Extra pure nitrogen was passed through the solutions for 30 min prior to measurements and a nitrogen blanket was maintained thereafter.

### Results and Discussion

To investigate the influence of water activity on the Bi(III)/Bi(Hg) redox reaction, the square-wave (S.W.) voltammetric measurements were performed in highly concentrated solutions of perchloric acid. The results are displayed in Fig. 1. The abscissa in Fig. 1A bears both the concentration of  $\text{HClO}_4$  and formal concentration of remaining water in solution. The concentration of free water molecules is probably smaller because of hydration of  $\text{H}^+$  and  $\text{ClO}_4^-$  ions. Under the influence of increased concentration of  $\text{HClO}_4$ , the s.w. peak potential shifts in positive direction. The shift is several in the concentration range between 3 and  $8 \text{ mol dm}^{-3}$ , but at  $\text{HClO}_4$  concentration  $\geq 8 \text{ mol}$

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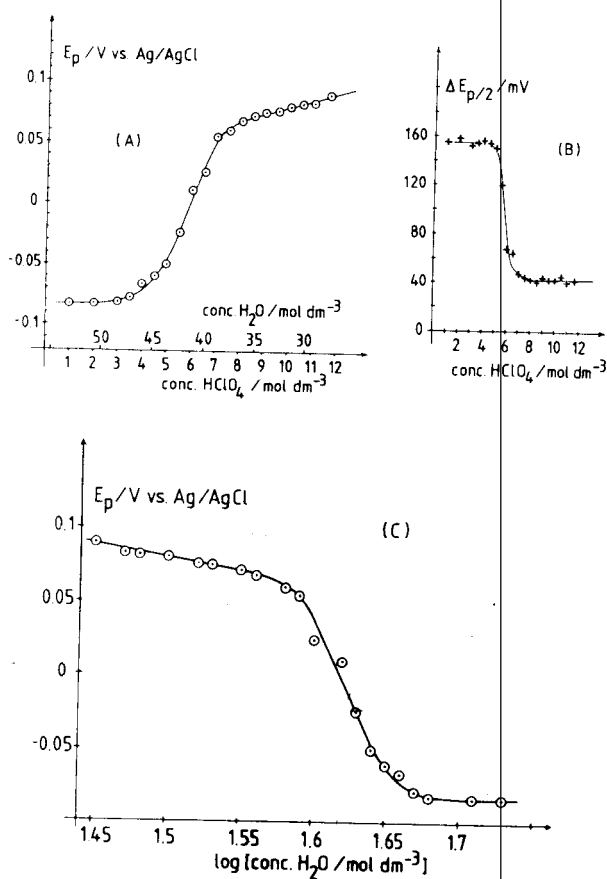
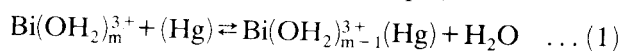


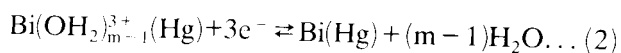
Fig. 1 - Square-wave voltammetry of  $1.10 \cdot 10^{-5} \text{ mol dm}^{-3}$  Bi(III) in highly concentrated  $\text{HClO}_4$  [The figure shows the dependence of s.w. peak potentials on concentrations of  $\text{HClO}_4$  and  $\text{H}_2\text{O}$  (A) and on the logarithm of the formal water concentration (C); and dependence of s.w. half-peak widths on  $\text{HClO}_4$  concentration (B) S.w. frequency 225 Hz; the amplitude 32 mv (peak to peak);  $dE/dt = -83 \text{ mV/s}$ ; delay time 4 s]

$\text{dm}^{-3}$ , the s.w. peak potential depends linearly upon  $\text{HClO}_4$  concentration. In the latter range the s.w. halfpeak widths are equal to 42 mV indicating that the redox reaction is reversible (see Fig. 1B). The linear relationship between  $E_p$  and  $\text{HClO}_4$  concentration starts approximately at  $E_p = +0.06 \text{ V}$  (vs Ag/AgCl). In the presence of  $1.10 \cdot 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Br}^-$  or  $\text{I}^-$  ions, the d.c. polarogram of Bi(III)/Bi(Hg) reaction indicates it to be reversible with the half-wave potential which is also equal to  $+0.060 \text{ V}$  (vs Ag/AgCl)<sup>15</sup>. It may be concluded that in  $8 \text{ mol dm}^{-3}$   $\text{HClO}_4$  the redox reaction Bi(III)/Bi(Hg) becomes reversible, with  $(E_{1/2})_r = +0.06 \text{ V}$  (vs Ag/AgCl). As  $\text{HClO}_4$  is an inert electrolyte, the observed phenomena can be ascribed entirely to change in the concentration of free water molecules (or of formal water concentration, as the former is not known). This is shown in Fig. 1C. The existence of  $\text{BiClO}_4^{2+}$  complex species<sup>22</sup>, which is possibly formed in con-

centrated  $\text{HClO}_4$  solutions, has been ignored. It is assumed that the reactivity of  $\text{BiClO}_4^{2+}$  is not higher than that of a simple hydrate  $\text{Bi}(\text{OH}_2)_m^{3+}$ . In the range of reduced water concentrations, the redox reaction is reversible and the s.w. peak potentials depend linearly on the logarithm of formal water concentration. For the reversible reaction:  $\text{Bi}(\text{OH}_2)_m^{3+} + 3e^- \rightleftharpoons \text{Bi}(\text{Hg}) + m\text{H}_2\text{O}$ , the slope  $\Delta E_p / \Delta \log(\text{H}_2\text{O concentration})$  is equal to  $-(2.303 \text{ mRT}/3F)$ . The slope in Fig. 1C indicates that  $m=9$ . This number seems reasonable, but it is perhaps too high because the concentration of free water molecules decreases faster than the formal water concentration. As the water concentration increases, the reaction becomes quasireversible and eventually totally irreversible, so that the s.w. peak potential shifts significantly towards negative direction. To understand such a relationship between  $E_p$  and concentration of  $\text{H}_2\text{O}$ , the concept of an adion formation is adopted<sup>19,23</sup>. (The adion is the ion immobilized at the interface, partially hydrated and partially coordinated by the atoms of the mercury electrode surface. It is imagined to be a short-lived intermediate in the reduction process. Its surface concentration and its energy of stabilization are extremely low). Keeping this in view, the first step of the proposed mechanism of Bi(III) reduction is the substitution of one water molecule from the coordinative sphere of  $\text{Bi}^{3+}$  ion by one mercury atom from the electrode surface (see Eq. 1).



The rate of formation of new coordinative bond depends on the density of electrons on the surface of the electrode because the process can be regarded as the substitution of electrons donated by a water molecule with electrons donated by the mercury surface. So, the activity of the mercury surface can be written as  $a_{\text{Hg}} = f(E)$  where  $f(E)$  is an unknown function of the electrode potential. The rate of dehydration depends also on the strength of Bi-OH<sub>2</sub> bond<sup>24-26</sup>. The adion formation does not depend on the rate of a spontaneous dehydration,  $\text{Bi}(\text{OH}_2)_m^{3+} \rightleftharpoons \text{Bi}(\text{OH}_2)_{m-1}^{3+} + \text{H}_2\text{O}$ , in the bulk of the solution, but on the completion between water molecules and the electrons of the mercury surface for the place in the coordinative sphere of  $\text{Bi}^{3+}$  ion. The second step of the reduction is the charge transfer followed by the dissolution of Bi in Hg (see Eq. 2).



This step is regarded as fast and reversible. In dilute solutions of  $\text{HClO}_4$ , the adion formation is

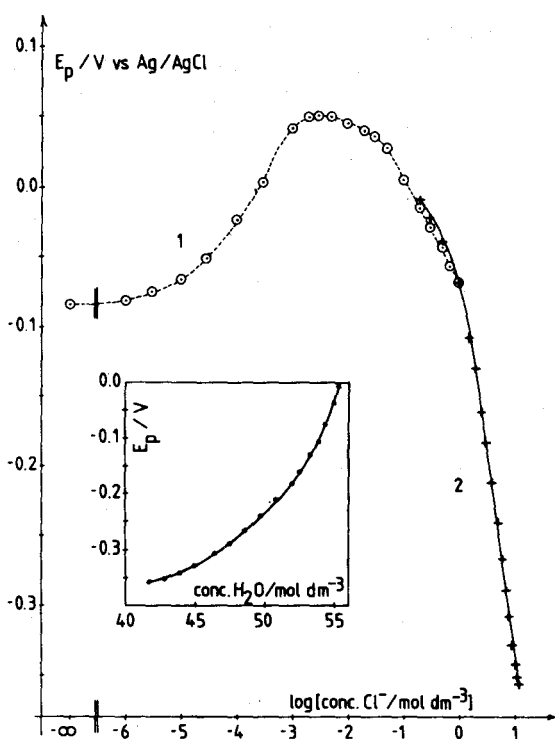
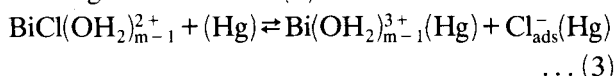


Fig. 2 - Square-wave voltammetry of  $2 \cdot 10^{-5} \text{ mol dm}^{-3}$  Bi(III) in  $(1-x) \text{ mol dm}^{-3} \text{ HClO}_4 + x \text{ mol dm}^{-3} \text{ HCl}$  (curve 1) and in highly concentrated HCl solutions of various ionic strengths (curve 2). [The figure shows the dependence of s.w. peak potentials on the logarithm of the concentration of chloride ions. The inset shows the dependence of peak potentials of s.w. voltammograms recorded in highly concentrated HCl solutions on the formal concentration of water. Experimental conditions as in the Fig. (1)]

the rate-determining step of the whole redox mechanism. In highly concentrated  $\text{HClO}_4$  solutions, the concentration of water is reduced and the equilibrium of the reaction (1) shifts in favour of the adion formation. Also, the rate of adion formation may increase if there are not enough free water molecules to fill the coordinative spheres of all  $\text{Bi}^{3+}$  ions. Under these conditions reaction (1) may become fast and reversible.

The proposed mechanism satisfactorily explains the influence of surface active ligands on the degree of reversibility of Bi(III)/Bi(Hg) redox reaction. Such ligands exhibit the affinity for  $\text{Bi}^{3+}$  as a central ion of a complex as well as for the mercury surface (adsorption). At the electrode surface, the mercury and  $\text{Bi}^{3+}$  compete for the ligand according to the reaction (3).



Mercury at the electrode surface attracts chloride ion of the complex forming the adsorbed chloride ion and the adion of the bismuth. Adsorption of  $\text{Cl}^-$  promotes dissociation of the complex and

formation of the adion. If the ligand exhibits a much stronger affinity for  $\text{Bi}^{3+}$  than for mercury, the equilibrium of reaction (3) shifts in favour of complex formation and the rate of adion formation decreases (e.g.  $\text{SO}_4^{2-}$  anion). Similarly, if the ligand has no affinity for mercury and only a weak affinity for  $\text{Bi}^{3+}$  (e.g.  $\text{ClO}_4^-$ ), the adion formation follows reaction (1). This is the reason why the complex species  $\text{BiClO}_4^{2+}$  is not more reactive than the simple hydrate  $\text{Bi}(\text{OH}_2)_m^{3+}$ .

The dependence of reversible half-wave potentials of d.c. polarograms on the concentration of ligand ions can be used for the determination of stability constants of complexes<sup>27</sup>. In the case of bismuth, these calculations are prevented by simultaneous change of reversibility of redox reaction under the influence of ligands<sup>13,15</sup>. In the system  $(1-x) \text{ mol dm}^{-3} \text{ HClO}_4 + x \text{ mol dm}^{-3} \text{ HCl}$ , the s.w. peak potentials of Bi(III)/Bi(Hg) redox reaction depend on the logarithm of HCl concentration as shown in Fig. 2 (curve 1). The shift of  $E_p$  in the positive direction for  $\log(\text{conc. Cl}^-/\text{mol dm}^{-3}) \leq -2.5$  is caused by the increased reversibility of Bi(III) reduction. The peak potential becomes equal to the reversible half-wave potential (+0.06 V vs Ag/AgCl) if  $\text{Cl}^-$  concentration =  $3 \cdot 10^{-3} \text{ mol dm}^{-3}$ . A further increase in  $\text{Cl}^-$  concentration shifts  $E_p$  in the negative direction, because of the dissociation of complexes between  $\text{Bi}^{3+}$  and  $\text{Cl}^-$  ions. The results of additional square-wave measurements, performed in pure HCl solutions (without  $\text{HClO}_4$ ), are shown in Fig. 2 (curve 2). The concentration of HCl changed from 0.2 to 12  $\text{mol dm}^{-3}$ . In highly concentrated acidic solutions the shift of peak potentials becomes severe, with an extremely high slope:  $\partial E_p / \partial \log(\text{conc. Cl}^-/\text{mol dm}^{-3}) = -300 \text{ mV/du}$ . This can be ascribed to the change in the formal concentration of water from 55.3  $\text{mol dm}^{-3}$  (in 0.2  $\text{mol dm}^{-3}$  HCl) to 42  $\text{mol dm}^{-3}$  in 12  $\text{mol dm}^{-3}$  HCl. The concentration of free water molecules decreases even faster because a significant amount of water must be engaged in the hydration of  $\text{H}^+$  and  $\text{Cl}^-$  ions (from HCl). If a reversible redox reaction  $\text{M}^+ + e^- \rightleftharpoons \text{M}(\text{Hg})$  is complicated by simultaneous formation of the hydrate and several complex species:  $\text{M}^+ + m \text{ H}_2\text{O} \rightleftharpoons \text{M}(\text{OH}_2)_m^+$  and  $\text{M}(\text{OH}_2)_m^+ + n\text{x}^- \rightleftharpoons \text{MX}_n(\text{OH}_2)_{m-n}^{1-n} + n \text{ H}_2\text{O}$  (where  $n=1,2,3,\dots,m$ ), the reversible half-wave potential will depend on the concentrations of both water and the ligand:

$$(E_{1/2})_{r,c} = (E_{1/2})_{r,c} \cdot \text{M} - (RT/F) \ln(K_{\text{H}_2\text{O}} \cdot \sum_{j=0}^m K_j (c_x^*)^j (c_{\text{H}_2\text{O}}^*)^{m-j}) \quad \dots (4)$$

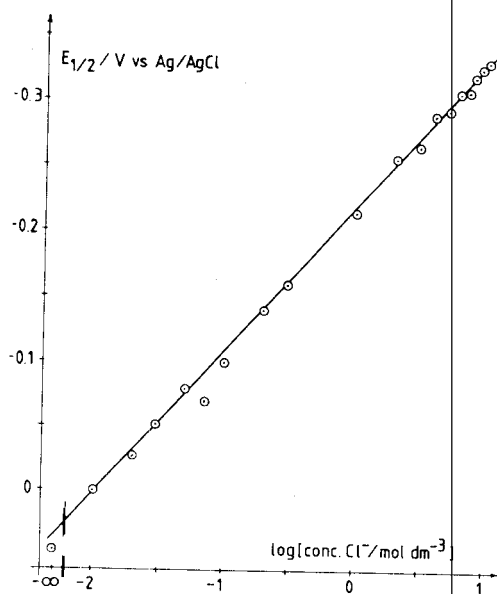


Fig. 3—The d.c. polarography of  $1.10^{-4} \text{ mol dm}^{-3}$  Bi(III) in the system  $(10-x) \text{ mol dm}^{-3} \text{ HClO}_4 + x \text{ mol dm}^{-3} \text{ HCl}$  [The figure shows the dependence of half-wave potentials on the logarithm of chloride anions concentration. For recording the polarogram a static mercury drop electrode combined with the PAR 384B polarographic analyzer was used. The drop life time was 0.5 s and the scan rate, 5 mV/s]

$$\text{In Eq. (4)} \quad K_{\text{H}_2\text{O}} = c_{\text{M}(\text{OH})_2}^* (c_{\text{M}}^* + c_{\text{H}_2\text{O}}^m)^{-1},$$

$$K_n = c_{\text{MX}_n(\text{OH})_{2-n}}^* c_{\text{H}_2\text{O}}^n (c_x^* c_{\text{M}(\text{OH})_2}^m)^{-1}$$

and  $K_0 = 1$ . (The asterisks indicates bulk concentrations of water, ligand and complexes). As the concentration of water is not known, the calculation of stability constants is prevented.

The variation of water concentration becomes less significant when the total concentration of acids is constant. In a system  $(10-x) \text{ mol dm}^{-3} \text{ HClO}_4 + x \text{ mol dm}^{-3} \text{ HCl}$  the formal concentration of water changes from  $32 \text{ mol dm}^{-3}$  (in  $10 \text{ mol dm}^{-3} \text{ HClO}_4$ ) to  $44 \text{ mol dm}^{-3}$  in  $10 \text{ mol dm}^{-3} \text{ HCl}$ . In this system the d.c. polarograms of Bi(III) are all reversible. Their half-wave potentials are plotted against the logarithm of chloride concentration in Fig. 3. The slope,  $\Delta E_{1/2} / \Delta \log(\text{conc. Cl}^-)$ , indicates that the number of ligands in the complex is 6. It may hence be concluded that 6 is the highest coordination number of  $\text{Bi}^{3+}$  for  $\text{Cl}^-$  anion. It is in good agreement with the literature data<sup>13,28,29</sup> because no species with the coordination number higher than 6 has yet been observed. Besides, this result suggests that the complex species with the highest coordination may appear even for the chloride concentration as low as  $0.01 \text{ mol dm}^{-3}$  if the concentration of free water molecules is sufficiently reduced.

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### References

- Heyrovsky J, *Disc Faraday Soc*, 1 (1947) 212.
- Randles J E B, Somerton K W, *Trans Faraday Soc*, 48 (1952) 951.
- Breyer B, Gutman F, Hacobian S, *Austr J Sci*, A4 (1951) 595.
- Moussa A A, Sammour H M, *J chem Soc*, (1960) 2151.
- Bauer H H, Elving P J, *Electrochim Acta*, 2 (1960) 240.
- Kambara T, Ishii T, *Rev Polarog*, 9 (1961) 30.
- Bond A M, *J electroanal Chem*, 23 (1969) 269.
- Johansson R, *Acta Chem Scand*, 18 (1964) 1809.
- Hamelin A, Valette E, *J chim Phys*, (1966) 1285.
- Gorodetskii V V, Losev V V, *Elektrokhimiya*, 2 (1966) 656, 664; 3 (1967) 1192; 7 (1971) 631.
- Gorodetskii V V, Mishenina K A, Losev V V, Grimberg A N, Ostrovsky G M, *Elektrokhimiya*, 4 (1968) 46.
- Lovreček B, Mekjavić J, *Electrochim Acta*, 14 (1969) 301.
- Bond A M, *Electrochim Acta*, 17 (1972) 769.
- Kopitsko O A, Grushina N V, *J electroanal Chem*, 178 (1984) 21.
- Lovrić M, Branica M, *J electroanal Chem*, 214 (1986) 103.
- Komorsky-Lovrić Š, Lovrić M, Branica M, *J electroanal Chem*, 241 (1988) 329.
- Tamamushi R, *J electroanal Chem*, 109 (1980) 353.
- Zielinska-Ignaciuk M, Galus Z, *J electroanal Chem*, 50 (1974) 41.
- Gorski W, Lipkowski J, *J electroanal Chem*, 123 (1981) 157.
- Maksymiuk K, Galus Z, *J electroanal Chem*, 234 (1987) 361.
- Barker G C, Gardner A W, Williams M J, *J electroanal Chem*, 42 (1973) app. 21.
- Prokić B, Pučar Z, *J inorg nucl Chem*, 35 (1973) 3287.
- Conway B E, Beckris J O'M, *Electrochim Acta*, 3 (1961) 340.
- Vijh A, Randin J P, *J phys Chem*, 79 (1975) 1252.
- Vlček A, *Chem Listy*, 50 (1956) 828.
- Hush N S, Scarrot I W, *J electroanal Chem*, 7 (1964) 26.
- DeFord D, Hume N, *J Am chem Soc*, 73 (1951) 5321.
- Smith R M, Martell A E, *Critical stability constants*, Vol. 4, (Plenum Press, New York) 1976; Vol. 5, 1982.
- Sillen G L, Martell A E, *Stability constants of metal-ions complexes* (The Chemical Society, London) 1964; 1971.