

Polarography of Bismuth in Presence of Diethylenetriamine-pentaacetic Acid

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The polarographic behaviour of bismuth in the presence of excess DTPA has been studied. In strong acidic medium the chelate produces a diffusion controlled irreversible wave at the dropping mercury electrode. When pH of the supporting electrolyte is increased above 3.5 the wave is broken into two parts and a new wave appears at a more negative potential. A further increase in pH results in an increase in the height of the second wave at the expense of the original one and above pH 6 only the second wave is observed. The effect of temperature, drop time, pH, concentration of bismuth and various surface-active substances on the limiting current and the half-wave potentials of the two waves have been studied. The second wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by adsorption of the reduction product at the electrode surface.

Bismuth(III) forms very stable complexes with polyaminocarboxylic acids and the polarographic behaviour of bismuth in the presence of EDTA,¹⁻³ CDTA,⁴ DTPA,⁵ and TTHA⁶ has been reported in the literature. According to Dono *et al.*⁵ the current-voltage curve of the bismuth-diethylenetriamine-pentaacetic acid (DTPA) chelate exhibits a double wave at the dropping mercury electrode when recorded from solutions with pH values 3-5, whereas a single wave is observed at other pH values. The appearance of a double wave is very interesting as the first wave occurs at potentials much more negative than the reduction of simple bismuth aquo ions, and the bismuth complex should give only one reduction wave from trivalent bismuth to its metallic state as any intermediate reduction step for bismuth is not known.

The present study was carried out in order to investigate the polarographic behaviour of bismuth-DTPA in more detail and to verify whether the two waves are due to reduction of two different species or if the second wave is the result of an inhibited electrode reaction similar to the reduction of certain copper chelates^{7,8} where adsorption complicates the reduction process.

EXPERIMENTAL

Apparatus. D.C. polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werke, Bremen, Germany). The conventional types of dropping mercury electrode and of electrolysis cell were used. The capillary characteristics, measured in 0.1 M potassium nitrate (open circuit) at a corrected mercury height of 51.6 cm were $m = 2.899$ mg/sec and $t = 3.194$ sec. An external saturated calomel electrode (S.C.E.) served as reference electrode. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solutions during the electrolysis. All experiments were performed at $25 \pm 0.1^\circ\text{C}$. Halfwave potentials were determined by a manual set-up. Infrared spectra were obtained by a Beckman IR-5A spectrophotometer. The pH of all solutions was measured with a Beckman Zeromatic pH meter.

Reagents. Diethylenetriaminepentaacetic acid was obtained from Geigy Chemical Corp., New York, U.S.A. Stock solutions were prepared and standardized as described previously.⁷ A 0.01 M stock solution of bismuth(III) was prepared by dissolving the appropriate amount of reagent grade bismuth metal in nitric acid and diluting to one litre with distilled water. The solution was standardized by titration with EDTA⁸ and the titer checked by titration with standard DTPA solution following the same procedure.

Sodium dodecyl sulphate (L. Light and Co., Ltd., U.K.), dodecylamine perchlorate (Armour Chemical Industries, Ltd., U.K.), Triton X-100 (Rohm and Haas Co., Philadelphia, U.S.A.) and 10 % aqueous solutions of pyridine and α -aminopyridine were used as surface-active agents in some experiments.

Solutions of these substances were prepared as described previously.¹⁰ The remaining chemicals were of reagent grade and used without further purification. 0.1 M potassium nitrate together with 0.2 M citrate, acetate, phosphate, or ammonia buffer were used as supporting electrolyte.

RESULTS

Preliminary experiments indicated that the bismuth-DTPA chelate is not reduced at potentials less than -0.7 V *vs.* S.C.E. when acetate buffer is used as supporting electrolyte. Hence, the composition of the chelate was determined by amperometric titration of bismuth in acetate buffer pH 4.6 with standard DTPA at an applied potential -0.4 V *vs.* S.C.E. The limiting current of bismuth(III) ions decreases linearly with the amount of DTPA added and becomes zero after the addition of one mole DTPA per mole bismuth and implies that the metal/ligand ratio in the chelate is 1:1.

The solid bismuth-DTPA complex was prepared by addition of an equimolar amount of basic bismuth nitrate to 0.01 M DTPA solution. After two hours heating on a boiling waterbath the solution was cooled to room temperature, the precipitate thoroughly washed and recrystallized twice from distilled water. The product was dried and stored in vacuum desiccator.

Infrared adsorption spectra of the solid bismuth-DTPA complex are very similar to the spectra of bismuth-EDTA¹¹ and a carboxylate peak at 1575 cm^{-1} implies that the bonding is primarily ionic.¹² A shoulder is observed at 1550 cm^{-1} and indicates that one or more of the carboxylate groups of DTPA probably is not bound to the metal.¹¹

Potentiometric pH titrations of a few samples of the solid complex dissolved in water were carried out, using carbonate-free potassium hydroxide as titrant. The titration curve (Curve A in Fig. 1) exhibits only one inflexion after the addition of two moles of alkali per mole bismuth chelate corresponding to a one-step neutralization of two hydrogen ions. The steep in-

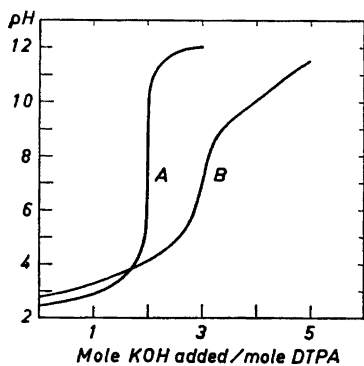


Fig. 1. Potentiometric titration curves of the bismuth-DTPA chelate (curve A) and of the free DTPA acid (curve B).

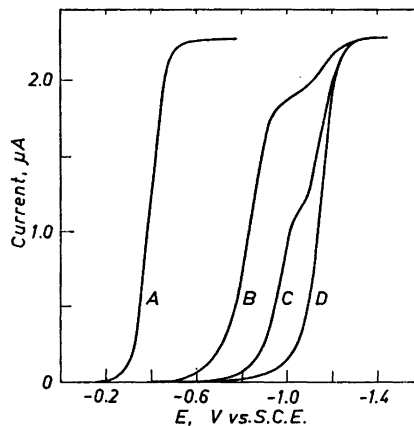


Fig. 2. Polarograms of 2×10^{-4} M bismuth and 2×10^{-3} M DTPA. Supporting electrolyte: Nitric acid, pH 1.5 (curve A), acetate buffer, pH 3.6 (curve B) and pH 4.4 (curve C), and ammonia buffer, pH 9.4 (curve D).

flexion and the low pH values of the chelate titration curve compared to the corresponding values for the free DTPA acid (Curve B, Fig. 1) indicates the presence of only one very stable bismuth chelate. The formula of the chelate is probably BiA^{2-} , where H_5A denotes DTPA and the chelate is probably completely deprotonized in aqueous solutions.

Polarography

Polarograms of bismuth in the presence of excess DTPA exhibit a large maximum when the concentration of bismuth is increased above 10^{-3} M. The maximum is easily suppressed by addition of surface-active agents but the half-wave potential is strongly affected by the presence of even small amounts of such substances. Hence, in the following experiments the bismuth concentration was kept below 10^{-3} M.

The effect of pH on the polarograms of 2×10^{-4} M bismuth in the presence of a ten-fold excess DTPA was tested using nitric acid, acetate, phosphate, and ammonia buffers as supporting electrolyte. The polarograms exhibit a single well-defined wave when recorded from electrolytes with pH values less than 3.5. Upon increasing pH of the supporting electrolyte above 3.5 the limiting current decreases and a new wave appears at a more negative potential. A further increase in pH results in an increase in the height of the second wave at the expense of the first one, the limiting current of the total wave remaining constant. At pH values above 6 only the second wave is observed on the polarograms. A few typical current-voltage curves are given in Fig. 2. At a given pH value the half-wave potentials and the height of the

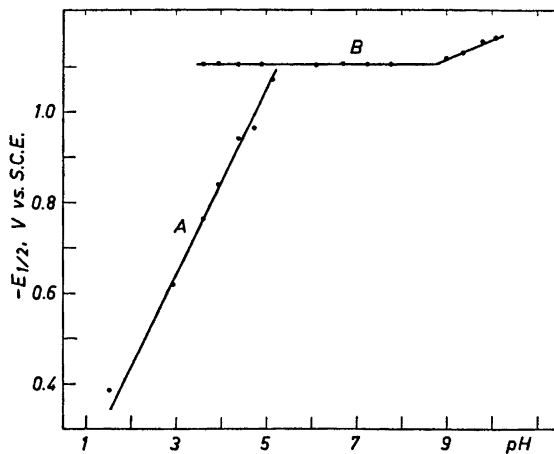


Fig. 3. Half-wave potentials of the first (curve A) and second (curve B) wave of 2×10^{-4} M bismuth and 2×10^{-3} M DTPA at various pH values.

two waves are independent of the kind of buffer used as supporting electrolyte, indicating that the double wave is not the result of a mixed ligand complex.

As indicated in Fig. 3 the half-wave potential of the first wave is shifted to more negative values with increasing pH of the supporting electrolyte whereas the half-wave potential of the second wave is independent of pH in the range 3.5–9. In the pH range 9–11 the half-wave potential is shifted slightly to more negative potentials with increasing pH of the supporting electrolyte.

When pH is increased above 11 by addition of sodium hydroxide a new wave appears at a more positive potential. At a given pH value the half-wave potential of this wave is constant and independent of the presence of DTPA and it coincides with the half-wave potential of bismuth in sodium hydroxide solutions.¹³ Apparently, the bismuth-DTPA chelate is broken down at high pH values and the more stable bismuth hydroxide complex (probably $\text{Bi}(\text{OH})_4^-$) is formed.

The reversibility of the electrode reaction was tested by plotting $\log i/(i_a - i)$ vs. the potential. The plots yield straight lines of slopes about -100 mV/log unit at all pH values in the range 1.5–10 and implies that the electrode reaction is completely irreversible.

The limiting current of the total wave is not affected by increasing the excess of DTPA from 2×10^{-4} to 2×10^{-2} M. However, the value i/C decreases with increasing concentration of bismuth. The data obtained for the double wave obtained at pH 4.65 and for the single wave at pH 9.4 are reported in Table 1. A maximum which appeared on the polarograms at bismuth concentrations greater than 10^{-3} M was suppressed by addition of 0.002 % dodecylamine perchlorate. The limiting current of the total wave is not affected by even large amounts of this surfactant. As indicated in Table 1 the diffusion current constant, $I = i/Cm^{2/3}t^{1/6}$, decreases with increasing concentration

Table 1. Limiting current of bismuth in the presence of a ten-fold excess DTPA. Supporting electrolytes: 0.2 M acetate buffer, pH 4.65, and 0.2 M ammonia buffer, pH 9.4.

Conc. of Bi mmole/l	pH 4.65		pH 9.4	
	$i, \mu\text{A}$	$i/Cm^{2/3}t^{1/6}$	$i, \mu\text{A}$	$i/Cm^{2/3}t^{1/6}$
0.02			0.26	5.16
0.04			0.47	4.99
0.05	0.60	4.85	0.61	4.94
0.10	1.16	4.70	1.20	4.86
0.20	2.24	4.53	2.38	4.82
0.40			4.68	4.74
0.50	5.35	4.33		
1.00	10.5	4.25	11.2	4.53
2.00			21.9	4.43
2.50	25.8	4.17		

of bismuth, but the order of magnitude indicates that the total wave is due to a 3-electron reduction of bismuth to its metallic state.

The half-wave potential of the second wave is also affected by increasing concentration of bismuth. Data obtained at low concentration of bismuth (in the absence of surfactants) indicate that the half-wave potential is shifted about 100 mV to more negative values upon a tenfold increase in the concentration of bismuth.

The effect of temperature on the current-voltage curve of bismuth in the presence of excess DTPA was tested in the region 25–50°C using acetate, phosphate, and ammonia buffers as supporting electrolytes. In the pH region 3.5–9.5 the temperature dependence of the limiting current is linear and the temperature coefficient, + 1.1 % per degree, indicates that the current is not controlled exclusively by diffusion. The temperature coefficient of the half-wave potential, + 1.5 and –0.46 mV/degree for the first and second wave, respectively, indicates irreversible electrode reaction.

The effect of drop time was investigated by recording polarograms at various heights of the mercury column. The height of the single wave obtained at pH values less than 3.5 and of the first wave obtained in the pH range 3.5–5.5, increases with the height of the mercury and the value i/\sqrt{h} , where h is the height of the column after correction for the "back pressure", is constant indicating that this electrode reaction is diffusion controlled. The height of the second wave obtained at pH values 3.5–5.5 increases proportionally to the height of the mercury column and implies that this wave is from an

Table 2. Effect of pressure of mercury. 2×10^{-4} M bismuth and 10^{-3} M DTPA in 0.1 M acetate buffer with pH 4.67.

h_{corr} cm	First wave		Second wave	
	$i_d, \mu\text{A}$	$i_d/\sqrt{h_{\text{corr}}}$	$i, \mu\text{A}$	i/h_{corr}
41.2	1.08	0.168	1.01	0.0246
46.2	1.14	0.168	1.15	0.0249
51.2	1.20	0.168	1.26	0.0246
56.2	1.26	0.168	1.40	0.0249

adsorption on the electrode and that the current is controlled by the rate of penetration of the chelate through an adsorbed film.^{7,14} The data obtained from acetate buffer pH 4.67 are reported in Table 2. At this pH the two waves are fairly well separated and the effect of the drop time on both waves could be measured. The height of the single wave obtained at pH values above pH 7 also increases with the height of the mercury column. However, the current does not increase proportionally to neither h nor \sqrt{h} but is always intermediate between these values, indicating that the limiting current of this wave is controlled by both diffusion and the rate of penetration through an adsorbed film.¹⁴ Further measurements of the h -dependence performed at potentials on the rising part of the curve indicate that the lower part of the curve is diffusion controlled. Apparently, the single irreversible wave observed at pH values above 7 is due to two electrode reactions occurring at almost the same potential. The first reaction is a diffusion controlled reduction of bismuth-DTPA which is followed by an electrode reaction involving a rate determining step, probably penetration through the adsorbed layer of the reduction products in the first reaction.

The effect of surface-active substances on the polarographic waves of bismuth-DTPA was investigated using strongly adsorbed ionic and non-ionic surfactants. The polarograms are strongly distorted in the presence of even very small amounts of the nonionic substance Triton X-100 and the anionic substance sodium dodecyl sulphate. In the presence of 0.006 % Triton X-100 or 0.003 % sodium dodecyl sulphate the electrode reaction is completely inhibited and the whole wave is shifted to the desorption potential of the surfactant (-1.2 V and -1.5 V *vs.* S.C.E. for dodecylsulphate and Triton X-100, respectively). The polarogram of bismuth-DTPA is not distorted and the limiting current is not affected by the presence of dodecylamine perchlorate. However, the first wave is shifted to more negative potentials and the second wave is shifted to more positive potentials in the presence of this cationic substance (Fig. 4). A similar effect is observed by addition of pyridine or α -aminopyridine to the supporting electrolyte.

Further experiments showed that the half-wave potential of the second wave is strongly affected also by the presence of alkali salts. The half-wave potential is shifted 50 mV to more positive values upon addition of 0.2 M potassium nitrate to bismuth-DTPA in 0.2 M ammonia buffer with pH 9.1, and if phosphate buffer with pH 7.9 is used as supporting electrolyte the half-wave potential of bismuth-DTPA is shifted 40 mV to more positive values when 0.05 M potassium chloride is added to the electrolyte. In the presence of higher concentrations of potassium chloride a maximum appears on the polarogram and the half-wave potential cannot be measured. The effect of potassium chloride on the polarogram of bismuth-DTPA in acetate buffer with pH 4.5 is shown in Fig. 5. At this pH value the maximum is not observed at potassium chloride concentrations less than 0.5 M. As indicated in Fig. 5 the half-wave potential of the first wave is not affected by the presence of potassium chloride. However, the half-wave potential of the second wave is shifted to more positive values and the height of the first wave increases at the expense of the second one with increasing amount of potassium chloride in the supporting electrolyte.

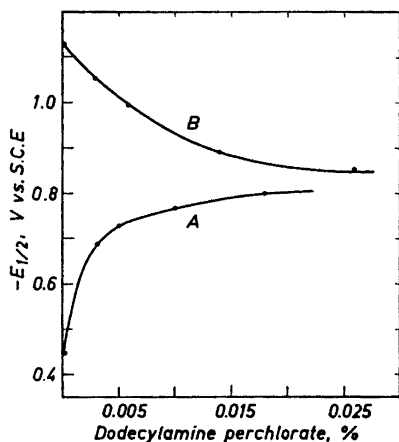


Fig. 4. Effect of dodecylamine perchlorate on the half-wave potential of the first wave obtained at pH 1.9 (curve A) and of the second wave obtained at pH 4.4 (curve B) of 5×10^{-4} M bismuth and 5×10^{-3} M DTPA.

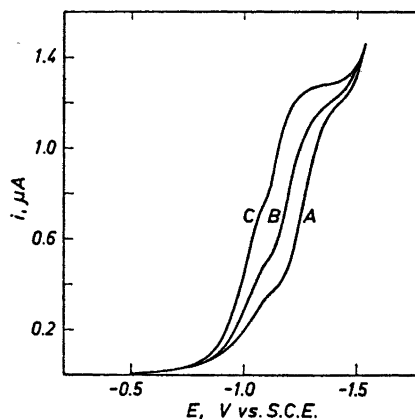
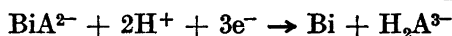


Fig. 5. Polarograms of 10^{-4} M bismuth and 10^{-3} M DTPA in 0.2 M acetate buffer with pH 4.55 in the absence (curve A) and in the presence of 0.05 M KCl (curve B) and 0.25 M KCl (curve C).

CONCLUSION

It is evident from the experimental results that only one bismuth complex is formed in the presence of excess DTPA. In strong acidic medium the chelate gives rise to a diffusion controlled irreversible polarographic wave. The half-wave potential is shifted to more negative values with increasing pH of the supporting electrolyte and the diffusion current constant indicates a 3-electron reduction to bismuth metal. The electrode reaction is probably:



where H_5A denotes DTPA.

The second wave which appears on the polarogram when pH of the supporting electrolyte is increased above 3.5 must be the result of an inhibited electrode reaction. The H_2A^{3-} liberated at the electrode during the reduction is probably surface-active and accumulates on the electrode surface during the life of the drop. The adsorbed layer has a negative charge and the negatively charged depolarizer is electrostatically repelled from the surface. The depolarizer has to cross a potential energy barrier before it can be reduced and the polarographic wave is shifted to more negative potentials. The effect of drop time on the height of the two waves clearly indicates that the first wave is diffusion controlled and that the current of the second wave is controlled by the rate of penetration through an adsorbed film. Hence, at pH values above 3.5 two electrode reactions will occur, one at the clean electrode surface and the other at the surface covered with adsorbed DTPA species.

The limiting current is not affected by a large excess of DTPA. However, the diffusion current constant decreases with increasing concentration of the bismuth chelate (Table 1) and indicates that only the DTPA species liberated at the electrode during the electrolysis (and not the free DTPA acid) is surface active.

The half-wave potential of the second wave is independent of pH but it is very dependent of the charge and structure of surfactants which are more strongly adsorbed than the DTPA species. For instance the adsorbed Triton X-100 film has a very compact structure and the electrode reaction of bismuth-DTPA is mechanically inhibited. Sodium dodecyl sulphate forms an adsorbed film with a more loose structure¹⁰ but as it carries a negative charge the depolarizer is electrostatically repelled from the electrode. In both cases the whole reduction wave of bismuth-DTPA is shifted to the desorption potential of the particular surfactant. On the other hand, if the adsorbed layer has a loose structure and it carries a positive charge as in the case of dodecylamine, pyridine, and α -aminopyridine there is no electrostatic repulsion and the first wave is shifted only slightly to more negative values. Moreover, the adsorption of surface-active DTPA species is partly prevented and the second wave of bismuth-DTPA is shifted to more positive values in the presence of these cationic substances. (Fig. 4).

The polarograms of bismuth-DTPA are strongly affected also by the presence of potassium chloride and potassium nitrate. The shift in the half-wave potential of the second wave to more positive potentials in the presence of these electrolytes is probably not due to an increase in the ionic strength. As indicated in Fig. 5 the height of the first diffusion controlled wave increases in the presence of potassium chloride and implies that the area of the electrode surface covered with adsorbed DTPA decreases in the presence of potassium chloride. Potassium ions are probably adsorbed on the electrode and prevent adsorption of the surface-active DTPA species and the effect of large concentrations of the weakly adsorbed potassium ions becomes similar to that of small amounts of the strongly adsorbed positively charged surfactants.

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