

POLAROGRAPHIC ELECTRODE PROCESS OF ANTIMONY(III) COMPLEXES WITH COMPLEXONES

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Antimonous ions yield in a solution of 4M sodium chloride a well-defined reduction wave. With increasing concentration of EDTA or CDTA a new cathodic wave appears at more negative potentials. The first (more positive) wave is kinetically controlled. We calculate the stability constant and the thermodynamic functions of antimony(III) complexone complexes from the shift of half-wave of the kinetic wave and their dissociation constant from the kinetic current under given conditions, $\beta = 3 \cdot 10^{19}$, $k_d = 2.8 \cdot 10^{13} \text{ s}^{-1}$ for SbY, $\beta = 6 \cdot 10^{24}$, $k_d = 8.8 \cdot 10^{18} \text{ s}^{-1}$ for SbZ. The rate constant of electrode reaction proper of the antimony(III) complexes with complexone is also calculated and the mechanism of the whole process is discussed.

The properties of complexes of antimony(III) with complexones such as their polarographic behaviour, their stability constants and thermodynamic functions and the mechanism of their formation and electrode reaction proper, has not been reported in detail¹⁻⁴.

Antimonous ions yield in a solution of 4M sodium chloride in the presence of ethylenediaminetetraacetic acid(EDTA) or 1,2-diaminocyclohexanetraacetic acid (CDTA) two well-defined waves; Koryta's method⁵ allows to calculate the stability constant and the thermodynamic functions of antimony(III) complexes with EDTA or CDTA from the shift of half-wave potential of the kinetic wave under given conditions (concentration of sodium chloride and complexones, pH, etc.), Hanu's method⁶ to calculate their dissociation constant from the kinetic current. The rate constant of electrode reaction proper of the antimony(III) complexes with complexones is also calculated and the mechanism of the whole process is discussed.

EXPERIMENTAL

All polarographic and oscillopolarographic measurements were done using conventional polarograph and multipurpose oscillopolarograph made in this laboratory⁷. The Kalousek vessel was used with a saturated calomel reference electrode. Two dropping mercury electrodes were used ($m = 2.16 \text{ mg/s}$ and $t_f = 2.65 \text{ s}$ at a height of mercury column 49 cm, and $m = 1.69 \text{ mg/s}$ and 2.77 s at 64 cm; 0.1M-KCl, open circuit). A drop time controller and the hanging mercury drop electrode used was of Vogel's type, all made in this laboratory⁷. The measured solutions

were deaerated by bubbling nitrogen for 10 min. The temperature of the vessel was maintained at $25 \pm 0.5^\circ\text{C}$.

Antimonous chloride was dissolved in a saturated solution of sodium chloride, heated nearly to boiling, filtered and then diluted to a certain concentration (e.g. 0.013 mol/dm^3) with a saturated solution of sodium chloride. The concentration of antimony in the solution was determined volumetrically with potassium bromate. The solution of complexones in concentration of 0.05 mol/dm^3 was prepared, the accurate concentration of which was determined with a standard solution of zinc, with Eriochrome Black T (EBT) used as indicator. The solution of sodium chloride (A.R. and recrystallized) in concentration of 4 mol/dm^3 was used as supporting electrolyte. The ionic strength was kept at 4 with sodium nitrate. All reagents were chemically or analytically pure.

RESULTS AND DISCUSSION

Antimonous ions yield in a solution of 4M sodium chloride a well-defined diffusion-controlled reduction wave. The logarithmic analysis of the relation between average limiting current and drop time is $\partial \log \bar{i}_l / \alpha \log t_1 = 0.2$. The half-wave potential $E_{1/2}$ is equal to -0.132 V (vs S.C.E.) at pH 1.63. The logarithmic analysis of the wave produces a straight line with a slope of 20 mV for 25°C . The half-wave potential is linearly dependent on pH (between 0.5 and 2.0) of the solution with a slope of 30 mV showing that two hydrogen ions take part in the reaction. The concentration of chloride ions, when larger than 2.2 mol/dm^3 , does not influence the half-wave potential, but with decrease of the concentration the half-wave potential is shifted towards negative potentials and the wave shape becomes drawn out.

The dependence of $E_{1/2}$ on the logarithm of concentration of chloride ions is linear with a slope of 22 mV. With increasing concentration of EDTA or CDTA a new cathodic wave appears at more negative potentials, the height of which increases at the expense of the original wave, the half-wave potential of the original wave being shifted slightly towards the negative values. The height of the first (more positive) wave is kinetically controlled. The sum of the heights of both the first and the second waves has a diffusion character. The slope of the logarithmic analysis of the relation between the average limiting current and the drop time is $\partial \log \bar{i}_l / \partial \log t_1 = 0.60$. The temperature coefficient of the sum of these two waves is $1.2\%/^\circ\text{C}$ in the range from 14.3°C to 50°C in the presence of EDTA and $1.4\%/^\circ\text{C}$ in the range from 11°C to 45°C in the presence of CDTA. On the contrary, the temperature coefficient of the first wave is $3.6\%/^\circ\text{C}$ in the presence of EDTA and $3.5\%/^\circ\text{C}$ in the presence of CDTA. The logarithmic analysis of the first wave produces a straight line with a slope of 20 mV and thus shows a reversible process of the three electron reaction.

The cyclic voltammetry on a hanging mercury drop electrode of the antimonous ion in the absence of complexone gives a sharp peak with diffusion character, while in the presence of complexone a flat wave of kinetic character occurs. The half-wave potential of the cathodic branch of the first wave is the same as that of the anodic

one, thus showing the reversible process. The cathodic branch of the second wave becomes more rounded and does not manifest the corresponding anodic branch, showing the irreversible character. Oscillopolarographic measurements ($dV/dt - V$) give analogous results.

The kinetic wave decreases with increasing concentration of complexone and its half-wave potential shifts to more negative values; the sum of the two waves remains constant. The slope obtained by plotting the corrected difference of the half-wave potential against $\log C_Y^0$ or $\log C_Z^0$ is

$$(E_{1/2}^{\text{corr}}/\log C_Y^0)_{[H^+],[Cl^-]} = 20 \text{ mV}, \quad (E_{1/2}^{\text{corr}}/\log C_Z)_{[H^+],[Cl^-]} = 24 \text{ mV} \quad (1), (2)$$

$$(\Delta E_{1/2})^{\text{corr}} = (E_{1/2})_S - (E_{1/2})_K + \frac{RT}{nF} \ln \frac{\bar{i}_d}{\bar{i}_1} = \Delta E_{1/2} + \frac{RT}{nF} \ln \frac{\bar{i}_d}{\bar{i}_1}. \quad (3)$$

In these relations C_Y^0 and C_Z^0 denote the actual total concentration of EDTA and CDTA in solution, c_Y and c_Z the analytical concentration of EDTA, c_M the analytical concentration of trivalent antimony, \bar{i}_d the total average limiting diffusion current, \bar{i}_1 the average limiting current of the kinetic wave, $(E_{1/2})_S$ the half-wave potential of antimonous ion in the absence of complexone and $(E_{1/2})_K$ the half-wave potential of the kinetic wave. For simplicity the charge of the ions is neglected.

The kinetic wave decreases with increasing pH. The following expressions are obtained experimentally:

$$(\partial(\Delta E_{1/2})^{\text{corr}}/\partial \text{pH})_{C_Y,[Cl^-]} = 47 \text{ mV} \quad (4)$$

$$(\partial(E_{1/2})_K/\partial \text{pH})_{C_Y,[Cl^-]} = 78 \text{ mV} \quad (5)$$

$$(\partial(\Delta E_{1/2})^{\text{corr}}/\partial \text{pH})_{C_Z,[Cl^-]} = 47 \text{ mV}. \quad (6)$$

The kinetics wave increases with increasing concentration of antimonous ions, but the relation is not a linear one. The sum of the height of the two waves shows a linear dependence on concentration of antimonous ions and the line passes through the origin.

The concentration of chloride ions also influences the kinetic wave, the height of which increases with increasing concentration of chloride, but at $[Cl^-] \geq 2 \cdot 2 \text{ mol/dm}^3$ the half-wave potential has a constant value; with decreasing concentration of chloride, the half-wave potential is shifted towards the more negative potentials and the wave shape is drawn out.

From the above experiments it is realized that trivalent antimony in a solution of 4M sodium chloride in the absence of complexone exists in the form of $Sb(OH)_2Cl$. The appearance of a new cathodic wave at more negative potentials with increasing

concentration of EDTA shows that in the solution there is at least one other complex of antimony(III) with complexone. It is considered that antimony(III) in solution exists essentially in the form of complex with complexone under experimental conditions of appearance of the kinetic wave. The kinetic wave is controlled by the dissociation rate of the complex of antimony(III) with complexone.

Composition, Stability Constant and Thermodynamic Functions of Antimony(III) Complex with Complexone from the Half-Wave Potential of the Kinetic Wave

Since the first wave has kinetic character and reflects a reversible electrode process Koryta's method⁵ is applicable here:

$$\Delta E_{1/2} = (E_{1/2})_s - (E_{1/2})_k = \frac{RT}{3F} \ln \left\{ \sum_{j=k}^x k_0 k_1 \dots k_j [Y]^j + \sum_{j=0}^p k'_0 k'_1 \dots k'_j [A]^j \right\} + \frac{RT}{3F} \ln \frac{i_1}{i_d}, \quad (7)$$

where k_0, k_1, \dots, k_j are the successive stability constants of antimony(III) complex with EDTA, k'_1, k'_1, \dots, k'_j that of antimony(III) complex with supporting electrolyte, $[A]$ the concentration of the corresponding ligand, and j the ligand number.

Comparing Eq. (7) with Eqs (1), (4) and (5), it seems that the antimony(III) complex with EDTA is in the form of SbY , with CDTA in the form of SbZ and that the

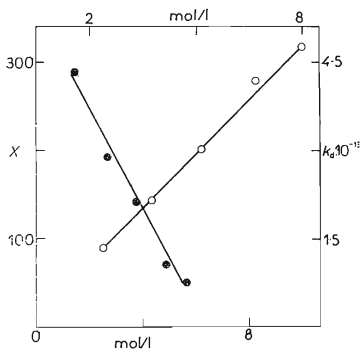


FIG. 1

Dependence of $\exp[(nF/RT)(\Delta E_{1/2})^{corr}]$ on the concentration of EDTA anion \circ . Dependence of dissociation velocity constant k_d of complex SbY on the concentration of EDTA \bullet . 4M-NaCl + 0.01% gelatin + 2.5 mM-SbCl₃, pH 1.63

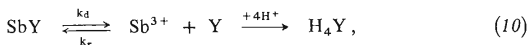
kinetic wave is controlled by the dissociation rate of SbY or SbZ. Hence Eq. (7) can be simplified to

$$\begin{aligned} (\Delta E_{1/2})^{\text{corr}} &= RT/3F \ln \beta [Y]; \\ \beta &= [\text{SbY}]/[\text{Sb}][Y]. \end{aligned} \quad (8), (9)$$

It is evident from Eq. (8) that a plot of $\exp [(3F/RT)(\Delta E_{1/2})^{\text{corr}}]$ against $[Y]$ should give a straight line with a slope equal to the β value (Fig. 1); one finds $\beta = 3 \cdot 10^{19}$ for SbY, $\beta = 6 \cdot 10^{24}$ for SbZ. The obtained straight line (1 in Fig. 1) passes nearly through the origin. Hence it follows that the stability of the complex $\text{Sb}(\text{OH})_2\text{Cl}_2$ is quite small and that in the formation or dissociation of antimony (III) complex with EDTA no chloride ions take part. The thermodynamic functions may be found from the β values and the dependence of $\log \beta$ on $1/T$. We find the change of free energy $\Delta G = -51\,537$ J, the enthalpy change $\Delta H = -25\,140$ J and the entropy change $\Delta S = 88$ JK $^{-1}$ for SbY; $\Delta G = 142\,460$ J, $\Delta H = 71\,230$ J, $\Delta S = 234.6$ JK $^{-1}$ for SbZ.

Composition, Dissociation Velocity Constants and Activation Energy of the Antimony(III) Complex with Complexone

From the above results the mechanism of the appearance of the kinetic wave can be written schematically as



where k_d and k_r are respectively the dissociation and formation velocity constants of the complex and

$$\beta = k_r/k_d. \quad (11)$$

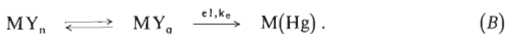
By the assumption of equality of diffusion coefficients of all forms of antimony(III) and of complexone, i.e. $D_{\text{Sb}^{3+}} = D_{\text{SbY}} = D$, we get⁶

$$k_d = \frac{\beta c_M}{0.664t_1} \left[\left(\frac{i_1}{i_d} \right)^3 / \left(1 - \frac{i_1}{i_d} \right)^2 \right]^2, \quad (12)$$

(t_1 drop time, c_M concentration of all forms of the metal) and further

$$N = \frac{k_d t_1}{c_M}, \quad (13)$$

mercury electrode. Now we discuss the case of antimony(III)–EDTA complex. The logarithmic analysis of the wave produces a straight line with a slope of 57 mV. The half-wave potential is linearly dependent on $\log t$ with a slope $\partial E_{1/2}/\partial \log t = 32$ mV. At the head of the wave, the wave height is nearly independent of the height of the mercury reservoir, i.e. $i \partial h^0$ and dependent on the drop time with the exponent $2/3$, i.e. $i \partial t^{2/3}$; at the end of the wave, $i \partial h_{1/2}$ and $i \partial t^{1/6}$. In the cyclic voltammetric curves on a hanging mercury drop electrode or on oscillographic polarograph with triangle voltage sweep the anodic process disappears. This indicates that antimony(III) complex with complexone gives a completely irreversible wave. Also from the experimental data $\partial E_{1/2}/\partial \log c_Y = 57$ mV, $\partial \log [i/i_d - i] : \partial \log c_Y = -1$, $\partial E_{1/2}/\partial \text{pH} = 102$ mV and $\partial \log [i]/(i_d - i) : \partial \text{pH} = -1.8$, it is realized that the electrode process may be of the type (B) (ref.^{5,6}):



We get

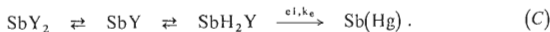
$$\frac{i}{i_d - i} = 0.886 t^{1/2} D^{-1/2} k_e \frac{\beta_q [\text{Y}]^q}{\beta_n [\text{Y}]^n}. \quad (15)$$

Comparing Eq. (15) with the experimental data, one obtains

$$q - n = -1. \quad (16)$$

At higher pH or concentration of EDTA it is possible that there exists a complex of Sb(III) with EDTA in the ratio of 1 : 2, i.e. $n = 2$, $q = 1$; the complex discharged directly at dropping mercury electrode is SbY . The experimental data give evidence that in the electrode reaction proper two hydrogen ions take part; this is evidently due to the fact that the hydrocomplexes SbHY and SbH_2Y are easier reducible¹⁰.

Fig. 2 shows the dependence of $\log [i/(i_d - i)]$ on ΔE at various pH, where $\Delta E = E - E^0$. In our experiments the half-wave potential of antimony(III) in the absence of EDTA $(E_{1/2})_S$ can be taken as reference potential E^0 , i.e. $\Delta E = E - (E_{1/2})_S$. It shows from Fig. 2 that the rate constant of the electrode reaction proper k_s^0 increases linearly with increasing potential. Taking $(E_{1/2})_S$ as reference potential, the rate constant k_s is found to be $4 \cdot 10^{-10}$ cm/s. The mechanism of the system studied can thus be expressed by the following scheme:



The irreversible wave of Sb(III)–EDTA complex is controlled by the rate of its electrode reaction proper.

In case of the presence of CDTA, the electrode process is very complicated. The experimental results are similar to the system with EDTA. However, the value

of $\partial E_{1/2}/\partial \log c_Z$ is about twice as that of $\partial E/\partial \log [i/(i_d - i)]$ while $\partial \log [i/(i_d - i)] : \partial \log c_Z = 2$.

Let us suppose the case, where the primary unstable product (amalgam) is completely inactivated. The following expression holds^{5,9}

$$E = E^0 - \frac{RT}{3F} \ln \beta_n[Z] + \frac{RT}{3F} \ln kt_1 - \frac{RT}{3F} \ln \frac{i}{i_d - i} \quad (17)$$

k is the inactivation rate constant of the product of electrode reaction. From Eq. (17) it follows $\partial \log [i/(i_d - i)] : \partial \log c_Z = -n$; hence $n = 2$. Thus at higher pH and concentration of CDTA the complex in the ratio of Sb : Z = 1 : 2 exists in the solution.

From the experimental results at fixed potential it follows that in contradiction to the Sb(III)-EDTA complex the expression $\log [i/(i_d - i)]$ is independent of pH; here the species taking part in the electrode reaction is not the hydrocomplex of antimony(III)-CDTA.

Thus the mechanism of the system studied above can be expressed by the following scheme

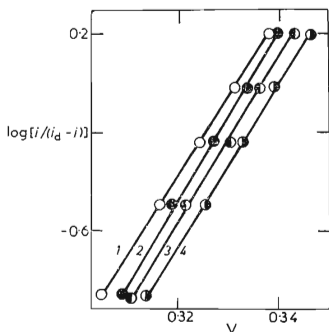
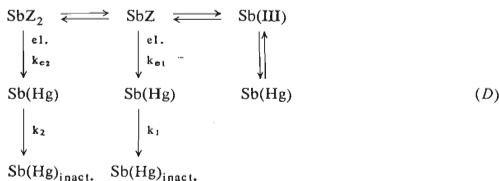


FIG. 2

Dependence of $\log [i/(i_d - i)]$ on ΔE at various pH. 4.75M-NaCl + 10 mM-EDTA + 0.2 mM-SbCl₃. pH 1 2.06, 2 2.26, 3 2.40, 4 2.61

The rate constant at standard equilibrium potential k_s^0 has been calculated to be $6 \cdot 10^{-11}$ cm/s.

The apparent activation energy of the electrode reaction proper can be determined either from the dependence of the rate constant of the electrode reaction on temperature or from that of $\log [i/(i_d - i)]$ on $1/T$ (ref.⁹).

$$Q_e = Q_e^0 + \partial nF(E - E^0), \quad (18)$$

$$\log \frac{i}{i_d - i} = \log A^* - \frac{Q_e - \frac{1}{2}Q_D}{2 \cdot 303RT}. \quad (19)$$

A^* collects all the temperature independent terms, Q_D is the activation energy of diffusion which can be obtained from the plot $\log i_d - (1/T)$; it is a linear relation with the slope of $1/2(Q_D/2 \cdot 3RT)$. In this way 22 207 J and 62 850 K has been obtained for Q_D and Q_e , respectively.

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