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Retardation of Polarographic Oxidation of Ethylenediaminetetraacetatocobaltate(II) by Mercury(I) Iodide Film Formation

Nobuyuki TANAKA, Setsuko YAMAMOTO and Yuichi SATO

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The electrode process of ethylenediaminetetraacetatocobaltate(II) ($Co^{II}Y^{2-}$) at the dropping mercury electrode has been studied in the presence of iodide ions. It was found that polarographic anodic waves of $Co^{II}Y^{2-}$ were affected by the film of mercury(I) iodide which was formed electrolytically at the electrode surface. The measurement of current-time curves during the life of a mercury drop and the coulometric studies revealed that the electro-oxidation of $Co^{II}Y^{2-}$ was completely inhibited by the formation of monomolecular layer of mercury(I) iodide on the mercury surface.

The electrode processes of ethylenediaminetetraacetatocobaltates(II, III) at various kinds of electrodes have been studied by several investigators;[1-6] the polarographic behaviors of these complexes have been investigated in detail.[1-4] Anson[5] reported the effect of adsorbed halide ions on the electro-oxidation of ethylenediaminetetraacetatocobaltate(II) ($Co^{II}Y^{2-}$) at a platinum electrode. According to his paper, adsorbed halide ions act catalytically on the electro-oxidation of $Co^{II}Y^{2-}$ and inhibit the oxidation of the platinum electrode especially in acid solutions. Voltammetric and chronopotentiometric behaviors of the anodic oxidation of $Co^{II}Y^{2-}$ at a carbon paste electrode were reported by T. Kitagawa and S. Tsushima.[6] They found, however, that the adsorbable halide ions did not show any pronounced effect on the kinetics of the electrode reaction at the carbon paste electrode.

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[1] C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, **28**, 450 (1956).

[2] N. Maki, This Bulletin, **37**, 765 (1964).

[3] N. Tanaka and H. Ogino, *ibid.*, **38**, 1054 (1965).

[4] H. Ogino, *ibid.*, **38**, 771 (1965).

[5] F. C. Anson, *J. Electrochem. Soc.*, **110**, 436 (1963).

[6] T. Kitagawa and S. Tsushima, *Review of Polarography (Kyoto)*, **14**, 17 (1966).

The present paper is concerned with the effect of iodide ions on the electro-oxidation of $Co^{II}Y^{2-}$ to $Co^{III}Y^{-}$ at the dropping mercury electrode (DME). Iodide ions depolarize the dropping mercury anode with the formation of slightly soluble merucry(I) iodide. In the presence of iodide ions, a direct current (d. c.) polarogram showed the decrease in anodic limiting current of $Co^{II}Y^{2-}$ and a current-time curve during the life of a mercury drop showed a peculiar shape. The influence of iodide ions on the polarogram and current-time curve of $Co^{II}Y^{2-}$ was explained as a result of the film formation of mercury(I) iodide on the electrode surface.

Experimental

A standard solution of cobalt(II) nitrate was obtained by the same procedure as reported previously.7) Its concentration was determined with a standardized disodium dihydrogen ethylenediaminetetraacetate solution by amperometric titration. The concentration of iodide ions was determined by the Volhard method. All other chemicals used were of analytical reagent grade.

D.c. polarograms were recorded with a Yanagimoto Galvarecorder Model AP-1 with an automatic potential scanner. A Rikendenshi SP-J1 recorder with a Rikadenki DC-201 preamplifier was used to measure current-time curves. The dropping mercury electrode used had an m value of 1.397 mg/sec and a drop time t_d of 5.38 sec, being measured in an air-free 1 M potassium chloride solution containing 0.01% gelatin at 25°C and −0.5 V *vs.* SCE at a 70 cm height of the mercury reservoir. A saturated calomel electrode (SCE) was used as a reference electrode. All measurements were carried out in a thermostat of 25°C, and the dissolved oxygen in the solution was removed by passing pure nitrogen gas through the solution.

Current-potential and current-time curves presented in this paper are all corrected for residual currents. In the case of current-potential curves, the average current was measured and denoted by $\bar{i}$. The plus sign is given for the anodic current and the minus sign for the cathodic one according to the electrochemical nomenclature and definitions by CITCE. The quantity of electricity was calculated by weighing the area of current-time recording chart with a maximum relative error due to weighing of ±1%.

Results and Discussion

Inhibition of the Electrode Reaction by Mercury(I) Iodide Film Formation. Cobalt(II)-EDTA anions gave a polarographic anodic wave as a result of the electrode reaction,

$$Co^{III}Y^{-} + e \rightleftharpoons Co^{II}Y^{2-} \qquad (1)$$

Its half-wave potential $E_{1/2}$ was obtained at $+0.13_8$ V *vs.* SCE, independent of the ionic strength from 0.1 to 1.0 and of the concentration of gelatin from zero to 0.05%. This value of $E_{1/2}$ is in good agreement with that reported by Reilley *et al.*1) independent of pH from 4.5 to 10.5. The limiting current of the oxidation wave was diffusion-controlled.

It is also well known that iodide ions give a polarographic anodic wave based on the electrode reaction,8)

$$Hg_2I_2 + 2e \rightleftharpoons 2Hg + 2I^{-} \qquad (2)$$

The wave showed a well-defined shape at a small concentration of iodide, but when the concentration of iodide was greater than about 5×10^{-4} M the limiting current showed irregular fluctuations. Accordingly, 0.05% gelatin was used in this experiment to improve the iodide limiting current.

The current-time curve of iodide ions showed a normal shape, provided that an appropriate concentration of gelatin was present in the solution. However, in the presence of iodide ions, polarograms of $Co^{II}Y^{2-}$ were found not to be diffusion-controlled and current-time curves of $Co^{II}Y^{2-}$ showed peculiar shapes. In Fig. 1 are shown polarograms of 1.0 mM $Co^{II}Y^{2-}$ which were obtained in the solution containing 3×10^{-4} M potassium iodide, 0.1 M acetate buffer (pH 4.59) and 0.05% gelatin. Comparing curve 2 with curve 1, it is clear that the limiting current of $Co^{II}Y^{2-}$ is much smaller in the presence of iodide ions, whereas iodide ions yield a wave proportional to their concentration even in the presence of the complex. This phenomenon was also observed in the measurement of current-time curves.

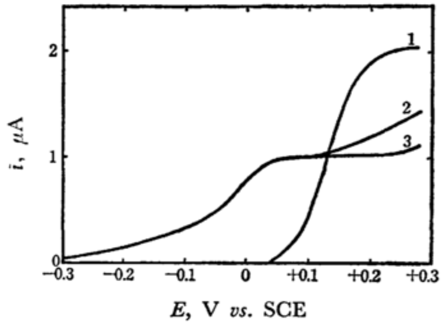

Fig. 1. Polarograms of 1.0 mM $Co^{II}Y^{2-}$ obtained in the solutions containing 0.1 M acetate buffer and 0.05% gelatin (1) in the absence and (2) in the presence of 3×10^{-4} M KI. Curve 3 is a polarogram of 3×10^{-4} M KI in 0.1 M acetate buffer containing 0.05% gelatin.

Figure 2 presents the current-time curves during the life of a mercury drop measured at +0.25 V *vs.* SCE where the electrode reactions according to Eqs. (1) and (2) can take place. The abnormal

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7) N. Tanaka and H. Ogino, This Bulletin, **38**, 439 (1965).

8) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York (1952), p. 577.

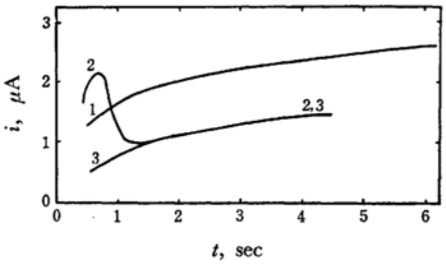

Fig. 2. Current-time curves obtained at +0.25 V *vs.* SCE with the same solutions as given in Fig. 1.

shape of current-time curve of $Co^{II}Y^{2-}$ was obtained in the presence of iodide ions (curve 2 in Fig. 2). During the earlier period of the growth of the mercury drop, the current-time curve (curve 2) follows the pattern of the normal diffusion-controlled current-time relationship, that is, the current observed is equal to the sum of the anodic current of $Co^{II}Y^{2-}$ (curve 1) and that of iodide (curve 3). Then, the current begins to decrease and at the end of the drop life it coincides exactly with the curve obtained in the solution containing only iodide ions. This suggests that mercury(I) iodide, which is the product of the electrode reaction according to Eq. (2), is adsorbed on the mercury surface and inhibits the electro-oxidation of $Co^{II}Y^{2-}$. In the earlier period of the drop life, the amount of adsorbed mercury(I) iodide is not enough to retard the electrode reaction of $Co^{II}Y^{2-}$, so that no deviation from the diffusion-controlled current occurs.

As the rate of mercury(I) iodide film formation is greater than the rate of the growth of the mercury drop, the ratio of the area occupied by the adsorbed mercury(I) iodide to the area of the mercury surface, *i. e.* the surface coverage θ, becomes larger with the time. This results in the retardation of the electro-oxidation of $Co^{II}Y^{2-}$ and the decrease in the current.

In Fig. 3 are shown the current-time curves obtained at various concentrations of iodide in the presence and the absence of $Co^{II}Y^{2-}$. These current-time curves demonstrate systematically the effect of adsorbed mercury(I) iodide on the oxidation of $Co^{II}Y^{2-}$ with increasing concentrations of iodide; the increase in the iodide concentration gradually changes the shape of the current-time curve. At a very low concentration of iodide such as 4×10^{-5} M, the current-time curve showed a normal shape during the whole life of the mercury drop (curve 1); this concentration of iodide is not sufficiently large enough to cause the retardation of the electro-oxidation of $Co^{II}Y^{2-}$. As the concentration of iodide increases, a remarkable change appears in the current-time curves (curves 2 and 3). When the concentration of iodide ions is equal to 1×10^{-3} M, the oxidation reaction of $Co^{II}Y^{2-}$ does not occur even at the very beginning of the drop life; curves 4 and 4′ are almost the same. In Fig. 4 are shown the d. c. polarograms which were obtained with the same solutions as shown in Fig. 3. Polarographic behaviors were found to be analogous to those of the current-time curves. With increasing concentrations of iodide, the anodic current of $Co^{II}Y^{2-}$ gradually decreases, until no difference could be seen between two polarograms of iodide ions with (curve 4) and without $Co^{II}Y^{2-}$ ions (curve 4′).

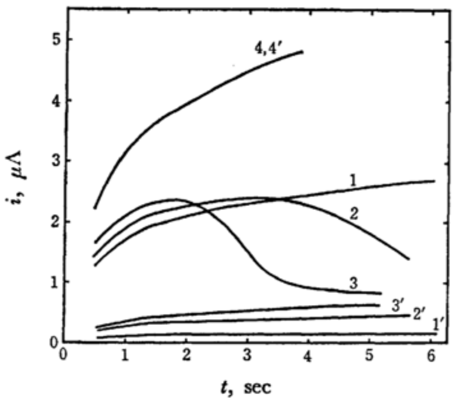

Fig. 3. Current-time curves of 1.0 mM $Co^{II}Y^{2-}$ obtained at +0.25 V *vs.* SCE in the solutions containing 0.1 M acetate buffer and 0.05% gelatin in the presence of (1) 4×10^{-5} M, (2) 1×10^{-4} M (3) 1.4×10^{-4} M and (4) 1×10^{-3} M KI. Curves 1′ to 4′ are current-time curves obtained in the same solutions as curves 1 to 4 but in the absence of $Co^{II}Y^{2-}$.

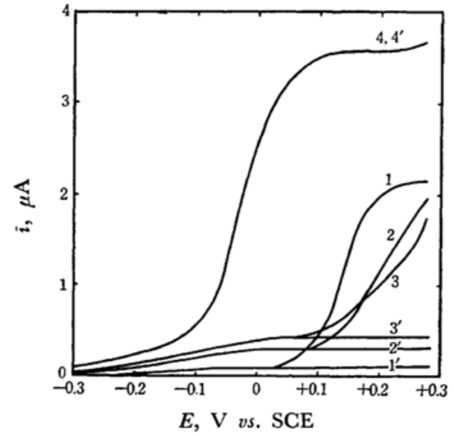

Fig. 4. Polarograms obtained with the same solutions as given in Fig. 3.

From the results mentioned above, it may be said that adsorbed mercury(I) iodide inhibits the electro-oxidation of $Co^{II}Y^{2-}$, but not that of mercury taking place in the presence of iodide ions. The electro-oxidation of mercury which took place in the presence of ethylenediaminetetraacetate anion to form ethylenediaminetetraacetatomercurate(II) (HgY^{2-}) was also observed. It occurred at almost the same potentials as the electro-oxidation of $Co^{II}Y^{2-}$, but it was not so inhibited as $Co^{II}Y^{2-}$ in the presence of iodide ions.

Quantitative Evaluation of Adsorbed Mercury(I) Iodide. The inhibition of the electrode reaction of $Co^{II}Y^{2-}$ by mercury(I) iodide film formation at the surface of the dropping mercury electrode was investigated quantitatively in the following way. The quantity of electricity q which was consumed to form mercury(I) iodide (Hg_2I_2) at the electrode surface was measured from the area of the current-time curve of iodide ions. Let us denote the time when the current-time curve of $Co^{II}Y^{2-}$ began to decrease in the presence of iodide to be t_1, and the quantity of electricity consumed until t_1 to be q_1. The former was determined from the current-time curve which was prepared by subtracting the current-time curve obtained with the solution containing iodide only from that obtained with the solution containing $Co^{II}Y^{2-}$ and iodide. (See Fig. 5). The values of q were determined at various concentrations of iodide ions. Plots of q_1 *vs.* A_1 gave a straight line passing through the origin, where A_1 is the area of the electrode surface at time t_1 expressed in cm² ((1) in Fig. 6). Therefore it can be concluded that when the inhibition of the electro-oxidation of $Co^{II}Y^{2-}$ begins during the life of a mercury drop the extent of coverage of the electrode surface by mercury(I) iodide is constant irrespective of the iodide ion concentrations. A linear relationship between q_2 and A_2 was also obtained, as is shown by (2) in Fig. 6, where q_2 and A_2 mean the electricity consumed and the surface area, respectively, at time t_2 when the electro-oxidation of $Co^{II}Y^{2-}$ at the DME is completely inhibited.

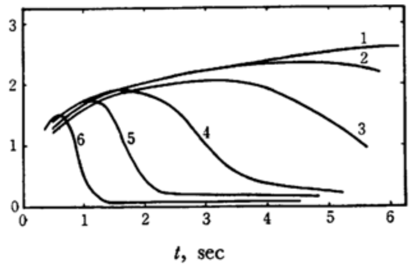

Fig. 5. Current-time curves of 1.0 mM $Co^{II}Y^{2-}$ at +0.25 V *vs.* SCE after correction for those of the corresponding concentration of iodide. The supporting electrolyte solutions contain 0.1 M acetate buffer and 0.05% gelatin. Concentrations of iodide ions are (1) none, (2) 8×10^{-5} M, (3) 1×10^{-4} M, (4) 1.4×10^{-4} M, (5) 2×10^{-4} M and (6) 3×10^{-4} M.

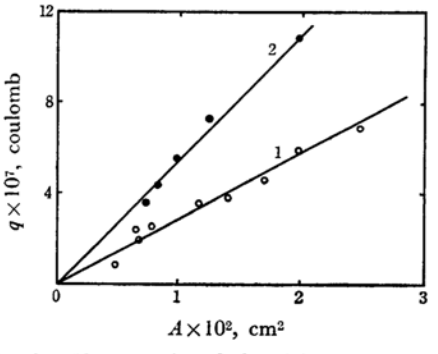

Fig. 6. The quantity of electricity versus the area of the DME (1) when inhibition of the electrode reaction begins and (2) when the electrode reaction is completely inhibited.

The surface coverage θ can be calculated with the equation,

$$\theta = \frac{n \times S}{A} \tag{3}$$

where n is the number of mercury(I) iodide molecules formed on the mercury surface, S is the area covered by one adsorbed molecule of mercury(I) iodide in cm², and A is the area of the electrode surface in cm². The value of n was calculated from the quantity of electricity consumed.

The crystal structure of mercury(I) iodide has been investigated by Havighurst.[9] If it is assumed that mercury(I) iodide forms a molecular film of the same structural arrangement as in the crystal, the effective area which one molecule of mercury(I) iodide occupies on the surface of mercury can be calculated with the aid of the structural parameters. When the amount of mercury(I) iodide produced by the electro-oxidation is less, the molecule is considered to be adsorbed in such a way that the c axis (the direction of I-Hg-Hg-I) is parallel with the surface of mercury. In this case, if the (110) plane is parallel with the surface, the effective area S is equal to 4.04×10^{-15} cm², while if the (100) plane is parallel with the surface, the value of S is equal to 5.71×10^{-15} cm².

On the other hand, if mercury(I) iodide is assumed to form a monomolecular film at time t_2 when the electro-oxidation of $Co^{II}Y^{2-}$ is completely inhibited, the effective area of one adsorbed molecule of mercury(I) iodide (Hg_2I_2) is calculated,

TABLE 1. EFFECTIVE SURFACE AREA S_2 OF MERCURY(I) IODIDE AT TIME t_2

$[I^-]\times10^4$ mol/l	t_2 sec	$q_2\times10^7$ coulomb	$A_2\times10^2$ cm²	$S_2\times10^{15}$ cm²
2.0	2.52	10.8	2.0	5.9
3.0	1.26	7.3	1.2	5.4
4.0	0.88	5.5	1.0	5.7
5.0	0.69	4.4	0.8	6.1
6.0	0.57	3.6	0.7	6.5
			Average	5.9×10^{-15} cm²

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[9] R. T. Havighurst, *J. Am. Chem. Soc.*, **48**, 2113 (1926).

with the values of q_2 and A_2 obtained experimentally, to be approximately 5.9×10^{-15} cm^2 irrespective of the iodide concentration (see Table 1). This value is very close to the value of 5.71×10^{-15} cm^2 which was obtained with the assumption that the (100) plane of mercury(I) iodide covers the mercury surface.

As was mentioned above, the retardation of the electro-oxidation of $Co^{II}Y^{2-}$ begins at time t_1, when the mercury surface is covered by a smaller amount of mercury(I) iodide. The surface coverage θ_1 at time t_1 was calculated with the effective area of 5.71×10^{-15} cm^2 for mercury(I) iodide as given in Table 2, which seems to indicate that the retardation of the electro-oxidation of $Co^{II}Y^{2-}$ begins to occur when the fraction of the covered surface reaches nearly a half of the whole area of the electrode, again irrespective of the iodide concentration.

TABLE 2. SURFACE COVERAGE θ_1 AT TIME t_1

$[I^-] \times 10^4$ mol/l	t_1 sec	$q_1 \times 10^7$ coulomb	$A_1 \times 10^2$ cm^2	θ_1
0.8	3.53	6.9	2.5	0.5
1.0	2.52	5.9	2.0	0.5
1.2	2.02	4.6	1.7	0.5
1.4	1.51	3.8	1.4	0.5
2.0	1.13	3.6	1.2	0.6
3.0	0.63	2.6	0.8	0.6
4.0	0.50	1.9	0.7	0.5
5.0	0.47	2.4	0.7	0.7
6.0	0.32	0.8	0.5	0.3

Conclusion. The electro-oxidation of ethylenediaminetetraacetatocobaltate(II) at the DME was found to be retarded and inhibited by the film formation of mercury(I) iodide. The effective area of one adsorbed molecule of mercury(I) iodide (Hg_2I_2) agreed with the area which one molecule of mercury(I) iodide covers if the (100) plane is considered to be parallel with the surface of mercury, being calculated with the aid of the structural parameters of the compound. It seems difficult, however, to decide at the present moment whether this agreement is fortuitous or not.

The film formation of mercury(I) iodide did not interfere with the electro-oxidation of mercury to form mercury(I) iodide, and less interfere with that of mercury to form ethylenediaminetetraacetatomercurate(II) under the conditions that the electro-oxidation of ethylenediaminetetraacetatocobaltate(II) is completely inhibited.

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