February, 1993] © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 437—443(1993) 437

Study of Polarographic Anodic Current in the Presence of Selenate Ion

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(Received July 7, 1992)

The polarographic anodic current observed in the presence of selenate ion has been studied using a numerical method previously proposed by us. Though there is no current plateau in the current-potential curve, the current increases with an increase in the concentration of selenate. The logarithmic plots of the current against the electrode potential give a straight line with a slope of 39—40 mV/unit. With the aid of the numerical method, it is concluded that the anodic current is controlled by the rate of precipitation, and that the rate can be expressed by a formula which is derived by assuming a reaction sequence for precipitation and represents the rate controlled by the nucleation step.

We studied polarographic currents in the presence of chloride, sulfate, and citrate ions.[1—3] Mercury(I) ions at and around the surface of a mercury electrode react with these ions, producing sparingly soluble salts. The precipitation reaction with chloride ion is rapid enough to attain an equilibrium within a drop life. The reaction with sulfate ion, however, is too slow to control the current. In this current, the dominant factor is a complexation reaction between mercury(I) and sulfate ions. The reaction controls a whole sequence of reactions taking place within a drop life. Another factor controls the current in the presence of citrate ion. It is the nucleation step of precipitation reaction. These conclusions were derived by analyzing the currents with the aid of a numerical method we devised.

In this report, we describe the similarity and dissimilarity between the anodic current observed in the presence of selenate ion and that observed in the presence of citrate ion.

Theory

At a potential corresponding to the anodic current, the electrode mercury dissolves into solution as mercury(I) ion, which reacts with selenate ion and produces a sparingly soluble salt. The concentration of mercury(I) ions in the vicinity of the electrode surface decreases with the progress of reaction of precipitation or complexation. The concentration decrease of mercury(I) ions is, however, partially compensated with further dissolution of electrode mercury. Thus, the anodic current (referred to an instantaneous one hereafter) increases with increasing extents of reactions of precipitation and complexation. The reaction sequence assumed is given as follows:

$$2\mathrm{Hg} \rightleftharpoons \mathrm{Hg_2}^{2+} + 2\mathrm{e}^-, \tag{1}$$

$$\mathrm{Hg} \rightleftharpoons \mathrm{Hg}^{2+} + 2\mathrm{e}^-, \tag{2}$$

$$\mathrm{HSeO_4}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{SeO_4}^{2-}, \tag{3}$$

$$\mathrm{Hg_2}^{2+} + \mathrm{SeO_4}^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Hg_2SeO_4}], \tag{4}$$

$$[\mathrm{Hg_2SeO_4}] \rightarrow \mathrm{P}, \tag{5}$$

$$[\mathrm{Hg_2SeO_4}] + \mathrm{SeO_4}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Hg_2(SeO_4)_2}]^{2-}, \tag{6}$$

$$\mathrm{Hg}^{2+} + \mathrm{SeO_4}^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [\mathrm{HgSeO_4}], \tag{7}$$

and

$$[\mathrm{HgSeO_4}] + \mathrm{SeO_4}^{2-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [\mathrm{Hg(SeO_4)_2}]^{2-}. \tag{8}$$

Here, P denotes a precipitate particle, and k's are rate constants. Precipitation Reaction 5 does not proceed unless the concentration product of mercury(I) and selenate ions exceeds the solubility product. The equilibrium constants for Reactions 3, 4, and 6 are given as follows:

$$K_1 = k_1/k_{-1}, \quad K_2 = k_2/k_{-2}, \quad \text{and} \quad K_3 = k_3/k_{-3}. \tag{9}$$

Reaction 3 is an acid dissociation reaction, and the rate, both in forward and backward directions, is considered to be very rapid compared with the other reactions. Hence, the concentrations of hydrogenselenate and selenate ions are described with the equilibrium constant K_1 and the total concentration of selenate,

$$C_\mathrm{L} = [\mathrm{HSeO_4}^-] + [\mathrm{SeO_4}^{2-}], \tag{10}$$

through

$$[\mathrm{HSeO_4}^-] = \frac{[\mathrm{H}^+]C_\mathrm{L}}{K_1 + [\mathrm{H}^+]} \tag{11}$$

and

$$[\mathrm{SeO_4}^{2-}] = \frac{K_1 C_\mathrm{L}}{K_1 + [\mathrm{H}^+]}. \tag{12}$$

Partial differential equations governing C_L and concentrations of the species (except hydrogenselenate and selenate ions) in Reactions 1—8 are:

$$\frac{\partial C_\mathrm{A}}{\partial t} = D_\mathrm{A}\left(\frac{\partial^2 C_\mathrm{A}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{A} - u\right)\frac{\partial C_\mathrm{A}}{\partial r} - \frac{K_1 k_2 C_\mathrm{A} C_\mathrm{L}}{K_1 + C_\mathrm{E}} + k_{-2}C_\mathrm{F}, \tag{13}$$

$$\frac{\partial C_{\mathrm{B}}}{\partial t} = D_{\mathrm{B}}\left(\frac{\partial^2 C_{\mathrm{B}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{B}} - u\right)\frac{\partial C_{\mathrm{B}}}{\partial r} - \frac{K_1 k_4 C_{\mathrm{B}} C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} + k_{-4} C_{\mathrm{J}}, \tag{14}$$

$$\frac{\partial C_{\mathrm{F}}}{\partial t} = D_{\mathrm{F}}\left(\frac{\partial^2 C_{\mathrm{F}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{F}} - u\right)\frac{\partial C_{\mathrm{F}}}{\partial r} + \frac{(k_2 C_{\mathrm{A}} - k_3 C_{\mathrm{F}}) K_1 C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} - k_{-2} C_{\mathrm{F}} + k_{-3} C_{\mathrm{G}} - f, \tag{15}$$

$$\frac{\partial C_{\mathrm{G}}}{\partial t} = D_{\mathrm{G}}\left(\frac{\partial^2 C_{\mathrm{G}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{G}} - u\right)\frac{\partial C_{\mathrm{G}}}{\partial r} + \frac{K_1 k_3 C_{\mathrm{F}} C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} - k_{-3} C_{\mathrm{G}}, \tag{16}$$

$$\frac{\partial C_{\mathrm{J}}}{\partial t} = D_{\mathrm{J}}\left(\frac{\partial^2 C_{\mathrm{J}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{J}} - u\right)\frac{\partial C_{\mathrm{J}}}{\partial r} + \frac{(k_4 C_{\mathrm{B}} - k_5 C_{\mathrm{J}}) K_1 C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} - k_{-4} C_{\mathrm{J}} + k_{-5} C_{\mathrm{M}}, \tag{17}$$

$$\frac{\partial C_{\mathrm{L}}}{\partial t} = D_{\mathrm{D}}\left(\frac{\partial^2 C_{\mathrm{L}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{D}} - u\right)\frac{\partial C_{\mathrm{L}}}{\partial r} - \frac{(k_2 C_{\mathrm{A}} + k_4 C_{\mathrm{B}} + k_3 C_{\mathrm{F}} + k_5 C_{\mathrm{J}}) K_1 C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} + k_{-2} C_{\mathrm{F}} + k_{-3} C_{\mathrm{G}} + k_{-4} C_{\mathrm{J}} + k_{-5} C_{\mathrm{M}}, \tag{18}$$

$$\frac{\partial C_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}\left(\frac{\partial^2 C_{\mathrm{M}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{M}} - u\right)\frac{\partial C_{\mathrm{M}}}{\partial r} + \frac{K_1 k_5 C_{\mathrm{J}} C_{\mathrm{L}}}{K_1 + C_{\mathrm{E}}} - k_{-5} C_{\mathrm{M}}, \tag{19}$$

and

$$\frac{\partial C_{\mathrm{P}}}{\partial t} = -u\frac{\partial C_{\mathrm{P}}}{\partial r} + f, \tag{20}$$

where

$$u = m/\left(4\pi\rho r^2\right). \tag{21}$$

The following notations are used in the above equations: A, B, D, and E are mercury(I), mercury(II), selenate, and hydrogen ions, respectively; F, G, J, and M are selenatomercury(I), bis(selenato)mercurate(I), selenatomercury(II), and bis(selenato)mercurate(II) complexes, respectively; m is the flow rate of mercury; ρ is the density of mercury; D_{h} is the diffusion coefficient of species h; C_{h} is the concentration of species h. It is assumed that the diffusion of the precipitate particle is negligible before those of the ions and complexes. The diffusion coefficient of selenate ion is used in Eq. 18, instead of any average value of diffusion coefficients of selenate and hydrogenselenate ions. This is because selenate ion is the sole species to diffuse and hydrogenselenate ion is formed through protonation of selenate ion with protons supplied from solvent water. Function f is the precipitation kinetics term. The value of f remains zero as far as the concentration product of mercury(I) and selenate ions does not exceed the solubility product, but becomes finite and positive if the former exceeds the latter.

If the formation of selenatomercury(I) and bis(selenato)mercurate(I) plays no significant role in the anodic current to be discussed, Eqs. 15 and 16 and the terms containing C_{F} and C_{G} are eliminated from the above, and Eq. 13 is replaced by

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}}\left(\frac{\partial^2 C_{\mathrm{A}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{A}} - u\right)\frac{\partial C_{\mathrm{A}}}{\partial r} - f. \tag{22}$$

The system of partial differential equations should be solved under the following initial and boundary conditions:

$$\begin{aligned} &\text{at } t = 0 \text{ and } r > a \\ &\quad C_{\mathrm{A}} = 0,\ C_{\mathrm{B}} = 0,\ C_{\mathrm{F}} = 0,\ C_{\mathrm{G}} = 0,\ C_{\mathrm{J}} = 0, \\ &\quad C_{\mathrm{L}} = C_{\mathrm{L}}{}^{*},\ C_{\mathrm{M}} = 0, \text{ and } C_{\mathrm{P}} = 0. \end{aligned} \tag{23}$$

$$\begin{aligned} &\text{at } t > 0 \text{ and } r = a \\ &\quad C_{\mathrm{A}} = \frac{1}{\gamma_{\mathrm{A}}} \exp\left\{2\left(E - E_{\mathrm{A}}^{\circ}\right) F/RT\right\}, \\ &\quad C_{\mathrm{B}} = \frac{1}{\gamma_{\mathrm{B}}} \exp\left\{2\left(E - E_{\mathrm{B}}^{\circ}\right) F/RT\right\}, \\ &\quad \left(\frac{\partial C_{\mathrm{F}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{G}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{J}}}{\partial r}\right)_{r=a} = 0, \\ &\quad \left(\frac{\partial C_{\mathrm{L}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{M}}}{\partial r}\right)_{r=a} = 0, \text{and } \left(\frac{\partial C_{\mathrm{P}}}{\partial r}\right)_{r=a} = 0. \end{aligned} \tag{24}$$

$$\begin{aligned} &\text{at } t > 0 \text{ and } r = \infty \\ &\quad C_{\mathrm{A}} = 0,\ C_{\mathrm{B}} = 0,\ C_{\mathrm{F}} = 0,\ C_{\mathrm{G}} = 0,\ C_{\mathrm{J}} = 0, \\ &\quad C_{\mathrm{L}} = C_{\mathrm{L}}^{*},\ C_{\mathrm{M}} = 0, \text{ and } C_{\mathrm{P}} = 0. \end{aligned} \tag{25}$$

In the above, $C_{\mathrm{L}}{}^{*}$ is the bulk concentration of the total selenate, F is the Faraday's constant, γ_{h} is the activity coefficient of species h, E is the potential of the dropping mercury electrode, and E_{A}° and E_{B}° are, respectively, the standard electrode potentials of $\mathrm{Hg_2}^{2+}/\mathrm{Hg}$ and $\mathrm{Hg}^{2+}/\mathrm{Hg}$ couples.

The current, i, is given by

$$i = 2FSD_{\mathrm{A}}\left(\frac{\partial C_{\mathrm{A}}}{\partial r}\right)_{r=a} + 2FSD_{\mathrm{B}}\left(\frac{\partial C_{\mathrm{B}}}{\partial r}\right)_{r=a} \tag{26}$$

where S is the surface area of the dropping mercury electrode.

The residual current is defined as the anodic current observed in the absence of selenate ion. Partial differential equations governing concentrations of the participating species are given as follows:

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}}\left(\frac{\partial^2 C_{\mathrm{A}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{A}} - u\right)\frac{\partial C_{\mathrm{A}}}{\partial r} \tag{27}$$

and

$$\frac{\partial C_B}{\partial t} = D_B\left(\frac{\partial^2 C_B}{\partial r^2}\right) + \left(\frac{2}{r}D_B - u\right)\frac{\partial C_B}{\partial r}. \tag{28}$$

The initial and boundary conditions are:

at $t = 0$, and $r > a$

$$C_A = 0 \text{ and } C_B = 0. \tag{29}$$

at $t > 0$, and $r = a$

$$C_A = \frac{1}{\gamma_A}\exp\{2(E - E_A^\circ)F/RT\},$$

and

$$C_B = \frac{1}{\gamma_B}\exp\{2(E - E_B^\circ)F/RT\}. \tag{30}$$

at $t > 0$ and $r = \infty$

$$C_A = 0 \text{ and } C_B = 0. \tag{31}$$

The residual current, i_r, is given by

$$i_r = 2FSD_A\left(\frac{\partial C_A}{\partial r}\right)_{r=a} + 2FSD_B\left(\frac{\partial C_B}{\partial r}\right)_{r=a} \tag{32}$$

The corrected anodic current, i_C, is obtained by subtracting i_r from i, the anodic current in the presence of selenate ion.

$$i_C = i - i_r \tag{33}$$

Equations 13, 14, 15, 16, 17, 18, 19, 20, 27, and 28 are solved with procedures similar to those described in the previous papers.[1—3]

Experimental

All the chemicals used were of reagent grade. The concentration of selenate ions in stock solutions was calculated from the amount of sodium selenate dissolved. The salt was used after drying at 250°C for 2 h. The ionic strength of the test solution, containing 0.01% gelatin, was controlled to 0.1 mol dm^{-3} with sodium perchlorate. The current was measured at the end of the mercury drop life. Measurements were carried out using a Hokuto Denko Model HA-104 Potentio-Galvanostat, in conjunction with the three-electrode arrangement, at 25°C. The electric resistance of the electrolytic system was determined with the procedure described in a previous paper,[2] and was found to be 100—240 Ω. The dropping mercury electrode used had the following characteristics (in 0.1 mol dm^{-3} sodium perchlorate at zero applied potential vs. SCE, and at a mercury head of 80.0 cm): flow rate of mercury (m), 1.249 mg s^{-1}; the drop time (τ), 4.65 s; the capillary constant ($m^{2/3}\tau^{1/6}$), 1.499 $\text{mg}^{2/3}\,\text{s}^{-1/2}$.

The diffusion coefficient of selenate ion, D_D, was calculated from the equivalent conductance of selenate ion at infinite dilution.[4] The equivalent conductance was measured with a TOA conductivity meter CM-25E. The diffusion coefficient was thus estimated to be 1.172×10^{-5} $\text{cm}^2\,\text{s}^{-1}$ from the equivalent conductance at infinite dilution, 87.8 S cm^2 equiv^{-1}. Values of diffusion coefficients of mercury(I) and mercury(II) ions, 0.845×10^{-5} and 0.721×10^{-5} $\text{cm}^2\,\text{s}^{-1}$, respectively, were taken from previous papers.[3,5] A value of 2.0×10^{-2} mol dm^{-3} was used for the dissociation constant, K_1, of hydrogenselenate ion.[6]

Results and Discussion

The anodic current was measured in a solution with pH ranging from 1.2 to 2.2. Figure 1 shows the anodic polarograms in the presence of selenate ion at pH 1.93. The anodic current i_C increases with an increase in the concentration of sodium selenate, though the current-potential curve exhibits no current plateau.

Plots of log i_C against the electrode potential produce a straight line with a reciprocal slope of 39—41 mV/unit, as shown in Fig. 2, provided i_C does not exceed 1.0 μA.

Figure 3 presents the linear variation of i_C observed at fixed electrode potentials with increasing concentration of selenate.

Figure 4 shows the variation of the electrode potential, corresponding to fixed values of i_C, with an increase in the concentration of sodium selenate. The plots give straight lines with a slope of −29 mV/unit.

The results described above are very similar to those for currents observed in the presence of sulfate or citrate ion. Those currents are caused by complexation and precipitation reactions, respectively. By analogy with those, it is most probable that the current in the presence of selenate ion is caused by either complexation reaction or precipitation reaction, or both.

First, the possibility of complexation reaction is examined by assuming a value of zero for the precipitation

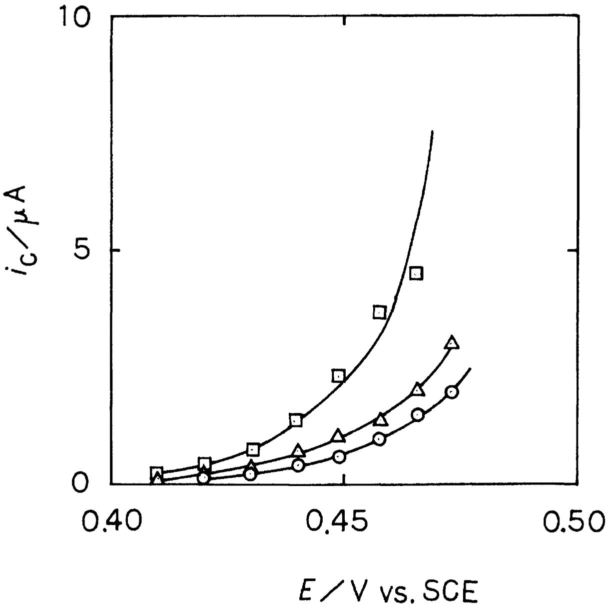

Fig. 1. Polarograms of the anodic current in the presence of sodium selenate in a solution of pH 1.93. Concentration of sodium selenate (in mmol dm^{-3}): ○, 1.0; △, 2.0; □, 4.0.

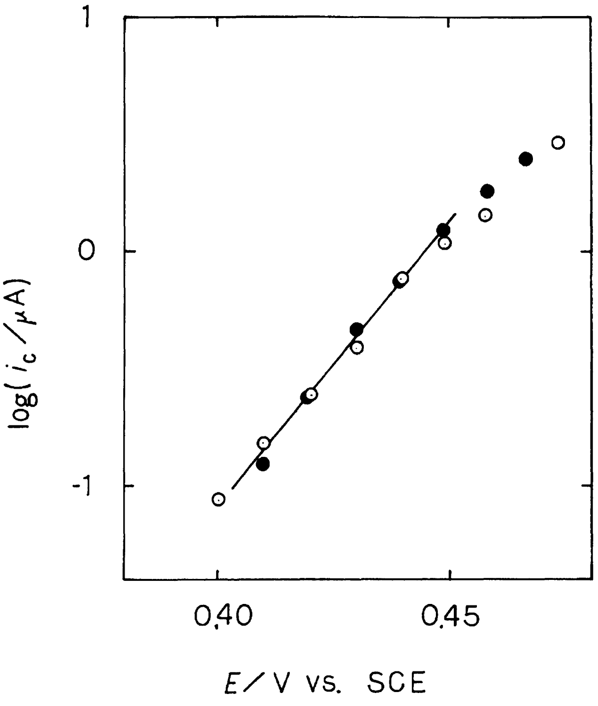

Fig. 2. Logarithmic plots of the anodic current in the presence of 2.0 mmol dm^{-3} sodium selenate in a solution of pH 1.93. ○, observed; ●, calculated.

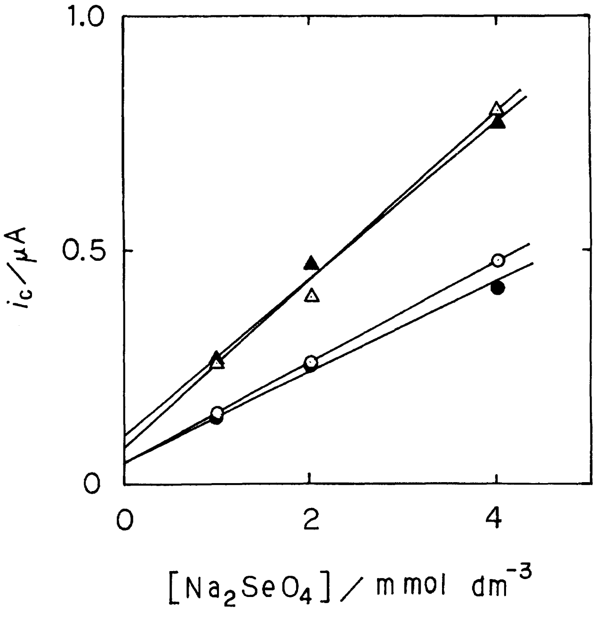

Fig. 3. Variation of i_C at fixed electrode potentials with increasing concentration of sodium selenate in a solution of pH 1.93. Electrode potential (in V vs. SCE): ○ (obsd) and ● (calcd), 0.42; △ (obsd) and ▲ (calcd), 0.43.

kinetics term in the differential equations.

Figure 5 shows logarithmic plots of i_C observed as open symbols. Thses plots are examined by use of the assumption that the formation of selenatomercury(I) and bis(selenato)mercurate(I) complexes is predominant. The plots are numerically simulated by assuming various values for k_2, k_{-2}, k_3, and k_{-3}. However, large values of K_2 and K_3, ratios of forward and reverse rate constants, should be excluded from consideration, because no current plateaus are observed on the polarogram. The solid symbols in Fig. 5 represent the data calculated with values of 300 mol^{-1} dm^3 and 100 mol^{-1} dm^3 for K_2 and K_3, respectively. (The values were selected to reproduce the observed data as closely as possible.) The curve constructed with the calculated data shifts to a less positive potential with increasing k_2 and k_3. The plots of i_C calculated, not exceeding 5.0 μA, give straight lines with a slope of 29—30 mV/unit, irrespective of the values of k_2 and k_3. The calculated results are not consistent with the observed one. Similar results are obtained under an alternative assumption that the formation of mercury(II) complexes is the dominant factor. These show that the complexation does not take place at all, or that at least the values of stability constants are too small to take into consideration the formation of the complexes.

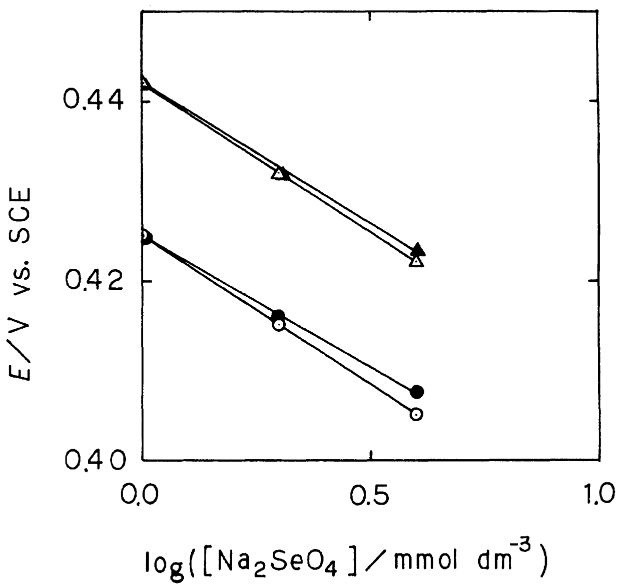

Fig. 4. Variation of the electrode potential, corresponding to fixed values of i_C, with increasing concentration of sodium selenate in a solution of pH 1.93. i_C (in μA): ○ (obsd) and ● (calcd), 0.2; △ (obsd) and ▲ (calcd), 0.4.

Next, the possibility of the precipitation reaction is examined. In view of the similarity to the anodic current observed in the presense of citrate ion,[3] this is a promising alternative. After publication of the report about anodic current in the presence of citrate ion, we succeeded in deriving a formula for f from a sequece of reactions for precipitation. It is written as

$$f = k_6 k_a \left\{-1 + (1 + k_b C_A C_D)^{1/2}\right\} \qquad (34)$$

where k_6, k_a, and k_b are constants. Derivation of Eq. 34

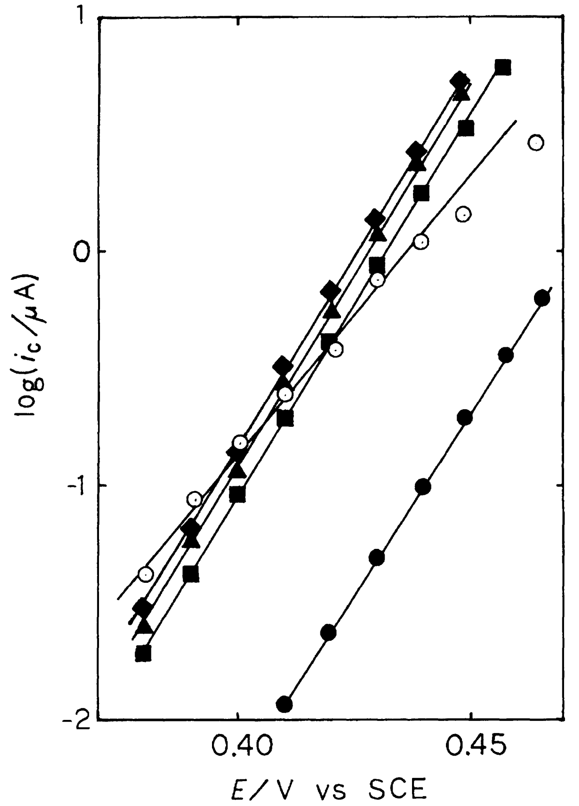

Fig. 5. Logarithmic plots of the anodic current in the presence of 4.0 mmol dm^{-3} sodium selenate in a solution of pH 1.93. ○, observed. Solid symbols represent the data calculated on the basis of an assumption that formation of selenatomercury(I) and bis(selenato)mercurate(I) controls the current. Values of K_2 and K_3 used in the calculation are 300 mol^{-1} dm^3 and 100 mol^{-1} dm^3, respectively. The rate constants k_2/mol^{-1} dm^3 s^{-1} and k_3/mol^{-1} dm^3 s^{-1}, respectively, are: ●, 10 and 0; ■, 1000 and 0; ▲, 100000 and 0; ◆,100000 and 10000.

is described in Appendix.

If a condition $(k_b C_A C_D)^{1/2} \gg 1$ is fulfilled, Eq. 34 becomes Eq. 35.

$$f = k_6 k_a k_b{}^{1/2} (C_A C_D)^{1/2} \tag{35}$$

Equation 35 corresponds to Eq. 43 in the previous report.[3] Although the latter equation reproduced the anodic current in the presence of citrate ion, Eq. 35 is not successful for reproducing the anodic current being discussed now.

Then the current is examined with Eq. 34. Figure 6 shows how the calcurated anodic current varies with the value of the solubility product. Best agreement with the observed results is obtained by using (13.0±2.0) mol dm^{-3} s^{-1}, (4.5±0.4)×10^6 mol^{-2} dm^6, and 2.0×10^{-10} mol^2 dm^{-6}, respectively, for $k_6 k_a$, k_b, and the solubility product. Further discussion described below is based on Eq. 34 and the numerical values cited above.

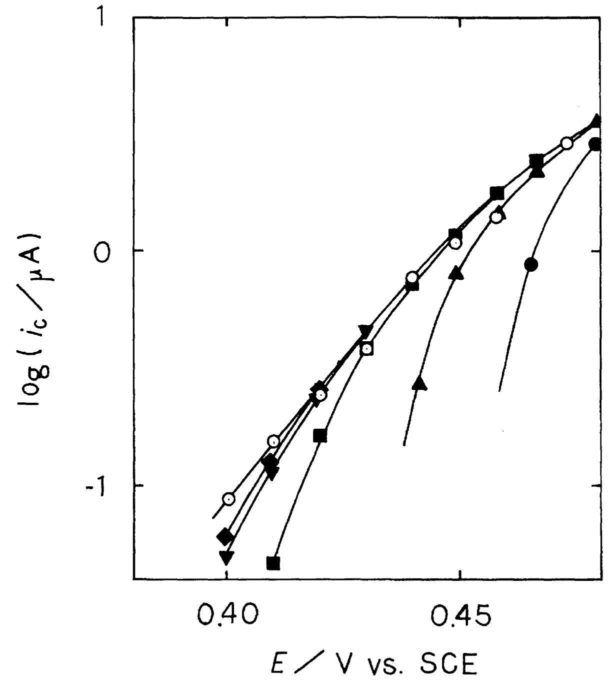

Fig. 6. Logarithmic plots of the anodic current in the presence of 2.0 mmol dm^{-3} sodium selenate in a solution of pH 1.93. ○, observed. Solid symbols represent the calculated data based on Eq. 34. Values of $k_6 k_a$ and k_b used in the calculation are 13.0 mol dm^{-3} s^{-1} and 4.5×10^6 mol^{-2} dm^6, respectively. Solubility product (in mol^2 dm^{-6}): ●, 2.0×10^{-6}; ▲, 2.0×10^{-7}; ■, 2.0×10^{-8}; ◆, 2.0×10^{-9}; ◆, 2.0×10^{-10}.

Figure 2 shows the logarithmic plots of the anodic current calculated. The plots with solid symbols falls on a straight line of the observed current not exceeding 1.0 μA.

The relation between i_C at fixed electrode potentials and the total concentration of selenate is shown in Fig. 3, where solid symbols represent the calculated i_C. The calculated data are in harmony with the observed ones.

Figure 4 shows the effect of the increase in the total selenate concentration to the electrode potential corresponding to fixed values of i_C. Solid symbols, denoting calculated values, give straight lines with a slope of −27 mV/unit, which is compared favorably with the experimental value of −29 mV/unit.

Conclusion

The numerical method proposed by us has been applied to the polarographic anodic current observed in the presence of selenate ion. Analysis with the numerical method shows that the precipitation reaction between selenate and mercury(I) ions, occurring at and around the surface of the mercury electrode, does not attain an equilibrium within a drop life of the dropping mercury electrode, and that the corrected anodic current is controlled by the rate of the reaction. The precipitation kinetics term is written as

$$f = k_6 k_a \left\{-1 + (1 + k_b C_A C_D)^{1/2}\right\},$$

where the values of $k_6 k_a$ and k_b are (13.0±2.0) $\mathrm{mol\,dm^{-3}\,s^{-1}}$ and $(4.5\pm0.4)\times10^6$ $\mathrm{mol^{-2}\,dm^6}$, respectively.

Appendix

When the concentration product of mercury(I) and selenate ions exceeds the solubility product, a precipitation nucleus N is formed from a complex [Hg_2SeO_4], and the following sequence of reactions begins to proceed:

$$\mathrm{Hg_2}^{2+} + \mathrm{SeO_4}^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Hg_2SeO_4}], \tag{36}$$

$$[\mathrm{Hg_2SeO_4}] \xrightarrow{k_6} \mathrm{N}, \tag{37}$$

$$2[\mathrm{Hg_2SeO_4}] \xrightarrow{k_7} \mathrm{Hg_2}^{2+} + \mathrm{SeO_4}^{2-} + [\mathrm{Hg_2SeO_4}], \tag{38}$$

$$\mathrm{N} + \mathrm{Hg_2}^{2+} \rightarrow \mathrm{N\text{-}Hg_2}^{2+}, \tag{39}$$

$$\mathrm{N} + \mathrm{SeO_4}^{2-} \rightarrow \mathrm{N\text{-}SeO_4}^{2-}, \tag{40}$$

$$\mathrm{N\text{-}Hg_2}^{2+} + \mathrm{SeO_4}^{2-} \rightarrow \mathrm{P(2)}, \tag{41}$$

$$\mathrm{N\text{-}SeO_4}^{2-} + \mathrm{Hg_2}^{2+} \rightarrow \mathrm{P(2)}, \tag{42}$$

$$\mathrm{P(2)} + \mathrm{Hg_2}^{2+} \rightarrow \mathrm{P(2)\text{-}Hg_2}^{2+}, \tag{43}$$

$$\mathrm{P(2)} + \mathrm{SeO_4}^{2-} \rightarrow \mathrm{P(2)\text{-}SeO_4}^{2-}, \tag{44}$$

$$\mathrm{P(2)\text{-}Hg_2}^{2+} + \mathrm{SeO_4}^{2-} \rightarrow \mathrm{P(3)}, \tag{45}$$

$$\mathrm{P(2)\text{-}SeO_4}^{2-} + \mathrm{Hg_2}^{2+} \rightarrow \mathrm{P(3)}, \tag{46}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

and

$$\mathrm{P(i)} + \mathrm{Hg_2}^{2+} + \mathrm{SeO_4}^{2-} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \mathrm{P(i+1)}, \tag{47}$$

where P(i) is a precipitate particle comprising i pairs of Hg_2^{2+} and SeO_4^{2-}. Growth of precipitate particles is composed of addition reactions of Hg_2^{2+} and SeO_4^{2-} ions. The rate constants of the reactions decrease with an increase in the size, i, of the precipitate particle, owing to decreasing chance of the collision with good orientation of the ions to the precipitate particle. On the other hand, dissociation reactions of ions from the precipitate particle, the reverse reactions, are not so susceptible to i as the forward reactions are. Hence, the reverse reactions become increasingly important, and process of the growth of the precipitate particle should be correctly expressed by Reaction 47 when i increases beyond a certain value.

At the initial stage of the growth, addition of ions mainly produces linear extension of the precipitate particle. After some elongation, however, the precipitate particle begins to accept ions not only at its ends but also at its sides. This results in three-dimensional extension of the precipitate particle. That also causes slow standstill of the decrease of rate constants, and guarantees a constant value of the solubility product for aged precipitates.

At the beginning of the precipitation, it is possible to take account of only Reactions 36, 37, and 38, and to ignore others.

Further it is assumed that although the equilibrium 36 lies fairly in the left side, the reaction, both in forward and reverse directions, is more rapid than Reactions 37 and 38. Equation 48 is obtained by applying the steady-state approximation.

$$\frac{\partial C_F}{\partial t} = k_2 C_A C_D - (k_{-2} + k_6) C_F - k_7 C_F^{\,2} = 0 \tag{48}$$

Hence

$$C_F = k_a \left\{-1 + (1 + k_b C_A C_D)^{1/2}\right\} \tag{49}$$

where

$$k_a = (k_{-2} + k_6) / (2k_7) \tag{50}$$

and

$$k_b = 4k_2 k_7 / (k_{-2} + k_6)^2 . \tag{51}$$

Because $\partial C_F/\partial t=0$, the time variation of C_A is equal to the consumed quantity of the complex [Hg_2SeO_4] in unit volume in unit time.

$$-\frac{\partial C_A}{\partial t} = k_6 C_F - k_7 C_F^{\,2} \tag{52}$$

The left-hand side of above equation represents the precipitation kinetics term *f*, because Hg_2^{2+} is consumed only by the precipitation process under these conditions. If the second term in the right-hand side of Eq. 52 is negligibly small compared to the first, the above equation may be rewritten as

$$f = k_6 k_a \left\{-1 + (1 + k_b C_A C_D)^{1/2}\right\}. \tag{53}$$

This is the precipitation kinetics term for the anodic current controlled by nucleation step.

If a condition

$$(k_b C_A C_D)^{1/2} \gg 1 \tag{54}$$

is fulfilled, one may obtain Eq. 55 from Eq. 53.

$$f = k_6 k_a k_b^{\,1/2} (C_A C_D)^{1/2} \tag{55}$$

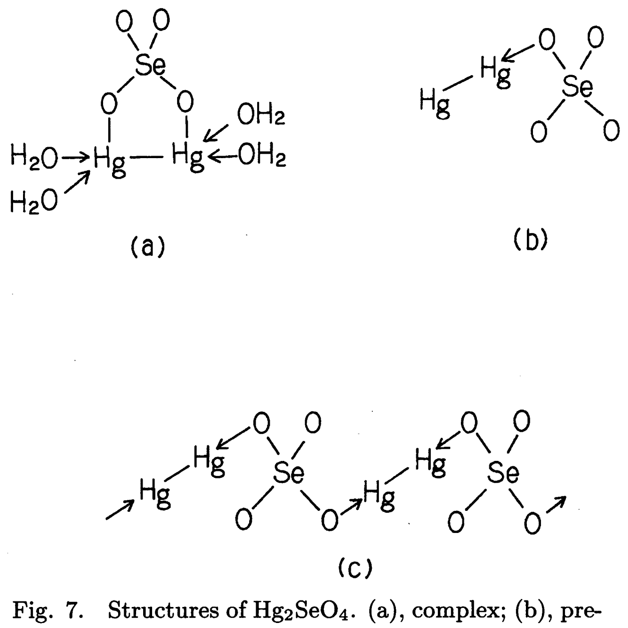

Fig. 7. Structures of Hg_2SeO_4. (a), complex; (b), precipitation mucleus; (c), linear molecule in solid.

Equations 53 and 55 correspond to the precipitation kinetics terms in the currents observed in the presence of selenate and citrate ions, respectively.

In the above discussion, we assume, without giving any reason, that N is different from the complex [Hg_2SeO_4]. The reason is described in what follows.

The structure of solid mercury(I) selenate is known as consisting of infinite linear molecules.7,8) The precipitation nucleus N is considered as a fragment of the linear molecule. Hence its structure is easily deduced from the structure of the linear molecule. However, the complex is not a fragment of the linear molecule. It is unnatural to consider that in the solution a linear cation $Hg_2{}^{2+}$ approaches a tetrahedral anion $SeO_4{}^{2-}$ with one of two its linear ends to form a complex. The coulomb's law dictates that the cation should approach the anion orienting its side toward $SeO_4{}^{2-}$. It is natural to consider that the ions combine themselves into the complex in a side-on fashion. The structure of the resulting complex is shown in Fig. 7, where the structures of N and the linear molecule in solid are also given.

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