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Study of Polarographic Anodic Wave in the Presence of Sulfate Ions by a Numerical Method

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A polarographic anodic wave in the presence of sulfate ions increases with any increase in the concentration of sulfate ions, contrary to the expectation based on a free dissolution of electrode mercury. It does not show any diffusion current plateau. The precipitation of mercury(I) sulfate, the product of an electrode reaction, does not take place within a dropping time. An analysis using a new numerical method previously reported proved that the wave is caused by the formation of a mercury(I) complex, $[Hg_2(SO_4)]$, with a stability constant of 150 $mol^{-1}\,dm^3$.

Kolthoff and Miller reported that an anodic process involving the electrooxidation of mercury appeared as a free dissolution wave in a solution of 0.1 $mol\,dm^{-3}$ potassium nitrate, since nitrate ions do not depolarize a mercury electrode.[1)]

When sulfate ions are added into the solution, the anodic wave is expected to remain unchanged as long as the concentration of the mercury(I) sulfate produced is below its solubility. This means that the current-potential curve should be written as

$$E=E^0+(RT/2F)\ln \bar{i}. \tag{1}$$

In the above, E is the electrode potential of the dropping mercury electrode, E^0 the standard electrode potential, $\bar{i}$ the average current, and F is the Faraday constant. Equation 1 says that the anodic current is independent of the concentration of sulfate ions. This is not the case, however. The anodic current any increases with increase in the concentration of sulfate ions, as shown in Fig. 1. This fact contradicts Eq. 1.

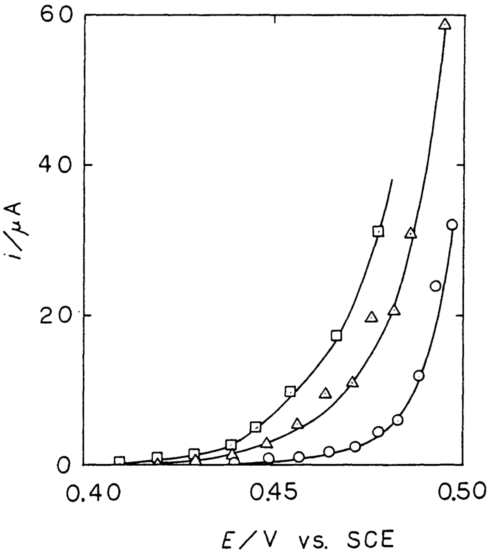

Fig. 1. Effect of the concentration of sulfate ions on the anodic current in a solution of pH 1.93. Concentration of a sodium sulfate, ○; 2 $mmol\,dm^{-3}$, △; 10 $mmol\,dm^{-3}$, □; 20 $mmol\,dm^{-3}$.

Figure 1 also shows that the anodic current does not attain the diffusion current plateau as expected for the anodic current with precipitate formation, of which a treatment was described in a previous paper.[2)]

The purpose of this paper is to clarify processes involving the anodic wave in the presence of sulfate ions by applying a numerical method which was developed in previous reports.[2,3)]

Theory

In the anodic process, mercury is dissolved into solution as a mercury(I) ion; a mercury(I) ion reacts with a sulfate ion to produce a mercury(I) sulfate complex. When the concentration of the complex exceeds its solubility, precipitate particles of mercury(I) sulfate appear in the solution. The sequence of the reactions can be written as follows:

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

$$HSO_4^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H^+ + SO_4^{2-} \tag{3}$$

$$Hg_2^{2+} + SO_4^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Hg_2SO_4 \tag{4}$$

$$Hg_2SO_4 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{precipitate} \tag{5}$$

In the above, k_2, k_{-2}, k_3, k_{-3}, k_4, and k_{-4} are the rate constants of Reactions 3—5. The rate of dissolution of precipitate particles in Reaction 5 is nil in the absence of a precipitate.

An analysis of the anodic current is carried out with using two alternative assumptions.

(1) The first assumption is that the mercury(I) sulfate precipitate particles are produced when the concentration of a mercury(I) sulfate complex exceeds its solubility.

When precipitate particles exist in a volume element or the concentration of the complex exceeds its solubility in it, the simultaneous equations governing the concentrations of species in the sequence of Reactions 2—5 are

$$\frac{\partial C_A}{\partial t} = D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right) + \left(\frac{2}{r}D_A - u\right)\frac{\partial C_A}{\partial r} - k_3 C_A C_B + k_{-3} C_C, \tag{6}$$

$$\frac{\partial C_B}{\partial t} = D_B\left(\frac{\partial^2 C_B}{\partial r^2}\right) + \left(\frac{2}{r}D_B - u\right)\frac{\partial C_B}{\partial r} + k_2 C_D - k_{-2}C_H C_B - k_3 C_A C_B + k_{-3}C_C \ , \tag{7}$$

$$\frac{\partial C_C}{\partial t} = D_C\left(\frac{\partial^2 C_C}{\partial r^2}\right) + \left(\frac{2}{r}D_C - u\right)\frac{\partial C_C}{\partial r} + k_3 C_A C_B - k_{-3}C_C - k_4 C_C + k_{-4} \ , \tag{8}$$

$$\frac{\partial C_D}{\partial t} = D_D\left(\frac{\partial^2 C_D}{\partial r^2}\right) + \left(\frac{2}{r}D_D - u\right)\frac{\partial C_D}{\partial r} - k_2 C_D + k_{-2}C_H C_B \ , \tag{9}$$

and

$$\frac{\partial C_P}{\partial t} = - u\frac{\partial C_P}{\partial r} + k_4 C_C - k_{-4} \ . \tag{10}$$

In the above

$$u = m/(4\pi\rho r^2), \tag{11}$$

where C_h is the concentration of species h, r the distance from the center of the electrode mercury drop, m the flow rate of mercury, and ρ the density of mercury. As for the subscript, A denotes the mercury(I) ion, B the sulfate ion, C the mercury(I) sulfate complex, D the hydrogen sulfate ion, and P the mercury(I) sulfate precipitate.

When the precipitate particles do not exist in a volume element, or the concentration of the complex is below its solubility, partial derivatives in Eq. 10 become zero. This results in the relation $k_4C_C = k_{-4}$. Using this relation, Eqs. 6—9 become

$$\frac{\partial C_A}{\partial t} = D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right) + \left(\frac{2}{r}D_A - u\right)\frac{\partial C_A}{\partial r} - k_3 C_A C_B + k_{-3}C_C' \tag{12}$$

$$\frac{\partial C_B}{\partial t} = D_B\left(\frac{\partial^2 C_B}{\partial r^2}\right) + \left(\frac{2}{r}D_B - u\right)\frac{\partial C_B}{\partial r} + k_2 C_D - k_{-2}C_H C_B - k_3 C_A C_B + k_{-3}C_C' \ , \tag{13}$$

$$\frac{\partial C_C}{\partial t} = D_C\left(\frac{\partial^2 C_C}{\partial r^2}\right) + \left(\frac{2}{r}D_C - u\right)\frac{\partial C_C}{\partial r} + k_3 C_A C_B - k_{-3}C_C \ , \tag{14}$$

and

$$\frac{\partial C_D}{\partial t} = D_D\left(\frac{\partial^2 C_D}{\partial r^2}\right) + \left(\frac{2}{r}D_D - u\right)\frac{\partial C_D}{\partial r} - k_2 C_D + k_{-2}C_H C_B . \tag{15}$$

The initial conditions are

$$C_A = 0,\ C_B = C^*_B,\ C_C = 0,\ C_D = C^*_D,\ C_P = 0\ (t = 0,\ r = a), \tag{16}$$

and the boundary conditions are

$$C_A = C_{A0} = \exp\{2F(E - E^0)/RT\}/\gamma_A,\ (\partial C_B/\partial r)_{r=a} = 0,\ (\partial C_C/\partial r)_{r=a} = 0,\ (\partial C_D/\partial r)_{r=a} = 0\ (t>0,\ r=a) \tag{17}$$

$$C_A = 0,\ C_B = C^*_B,\ C_C = 0,\ C_D = C^*_D \text{ and } C_P = 0\ (t>0,\ r = \infty). \tag{18}$$

In the above, C_{A0} is the concentration of mercury(I) ions at the surface of the mercury electrode and γ_A is the activity coefficient of mercury(I) ions.

The relation between the concentration of hydrogen sulfate and sulfate ions is expressed by

$$C_F = C_D + C_B$$

and

$$(C_H + K_{a2})C_B/K_{a2} = (C_H + K_{a2})C_D/C_H. \tag{19}$$

In the above, C_H is the concentration of hydrogen ions, and K_{a2} the dissociation constant of the hydrogen sulfate ion. Equations 6—9 and 12—15 can be rewritten using Eq. 19. The following equations are derived from Eqs. 6—9 and 12—15:

$$\frac{\partial C_A}{\partial t} = D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right) + \left(\frac{2}{r}D_A - u\right)\frac{\partial C_A}{\partial r} - \frac{k_3 C_A C_F K_{a2}}{C_H + K_{a2}} + k_{-3}C_C, \tag{20}$$

$$\frac{\partial C_F}{\partial t} = D_F\left(\frac{\partial^2 C_F}{\partial r^2}\right) + \left(\frac{2}{r}D_F - u\right)\frac{\partial C_F}{\partial r} - \frac{k_3 C_A C_F K_{a2}}{C_H + K_{a2}} + k_{-3}C_C \ , \tag{21}$$

$$\frac{\partial C_C}{\partial t} = D_C\left(\frac{\partial^2 C_C}{\partial r^2}\right) + \left(\frac{2}{r}D_C - u\right)\frac{\partial C_C}{\partial r} + \frac{k_3 C_A C_F K_{a2}}{C_H + K_{a2}} - k_{-3}C_C - k_4 C_C + k_{-4} \ , \tag{22}$$

and

$$\frac{\partial C_C}{\partial t} = D_C\left(\frac{\partial^2 C_C}{\partial r^2}\right) + \left(\frac{2}{r}D_C - u\right)\frac{\partial C_C}{\partial r} + \frac{k_3 C_A C_F K_{a2}}{C_H + K_{a2}} - k_{-3}C_C \tag{23}$$

The initial conditions are transformed as

$$C_A = 0,\ C_F = C^*_F,\ C_C = 0,\ C_p = 0\ (t = 0,\ r = a). \tag{24}$$

The boundary conditions are

$$C_A = C_{A0},\ (\partial C_F/\partial r)_{r=a} = 0,\ (\partial C_C/\partial r)_{r=a} = 0\ (t>0,\ r=a) \tag{25}$$

$$C_A = 0,\ C_F = C^*_F,\ C_C = 0,\ C_p = 0\ (t>0,\ r = \infty). \tag{26}$$

The instantaneous current, i, is given by

$$i = 2FD_A S(\partial C_A/\partial r)_{r=a}, \tag{27}$$

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

The following parameters are used to simplify the description of the simultaneous equations:

$$y_A = C_A/C^*_F,\ y_F = C_F/C^*_F,\ y_C = C_C/C^*_F,\ y_P = C_P/C^*_F,\ y_H = C_H/C^*_F,\ d_A = D_A/D_F,\ d_F = D_F/D_F,\ d_C = D_C/D_F,\ x = (r - a)/L,\ s = 1 - 1/\{1 + (r - a)H/L\},\ T = D_F t/L^2,\ U = Lur^2/D_F a^2 \text{ and } K^*_{a2} = K_{a2}/C^*_F. \tag{28}$$

An introduction of the above parameters into Eq. 20 results in

$$\frac{\partial y_A}{\partial T} = d_A H^2(1-s)^4\frac{\partial^2 y_A}{\partial s^2} + \left\{\frac{2d_A}{x + a/L} + \frac{x(x + 2a/L)}{(x + a/L)^2}U - 2d_A H(1-s)\right\}H(1-s)^2\frac{\partial y_A}{\partial s} - \frac{L^2 C^*_F k_3 y_A y_F K^*_{a2}}{D_F(y_H + K^*_{a2})} + k_{-3}y_C L^2/D_F \ . \tag{29}$$

The space and time coordinates are expressed as

$$s_i=i\Delta s,\ T_j=j\Delta T,\ x_i=i\Delta s/H(1+i\Delta s)$$

and

$$y_{\mathrm{A}}(s,t)=y_{\mathrm{A}}(s_i,T_j)=y_{\mathrm{A},i,j}. \tag{30}$$

The reaction rate constants are replaced by following parameters:

$$k^*_3=\Delta TL^2C^*_{\mathrm{F}}K^*_{\mathrm{a2}}k_3/D_{\mathrm{F}}(y_{\mathrm{H}}+K^*_{\mathrm{a2}}),$$

$$k^*_{-3}=\Delta TL^2k_{-3}/D_{\mathrm{F}},\ k^*_4=\Delta TL^2k_4/D_{\mathrm{F}},$$

and

$$k^*_{-4}=\Delta TL^2k_{-4}/D_{\mathrm{F}}C^*_{\mathrm{F}}. \tag{31}$$

The centered space difference method and the forward time method are used for converting the diffusion equations, except for one involving the concentration of precipitate particles.3)

By using a method reported by Morihara and Cheng,4) the chemical kinetics term involving the concentration of mercury(I) sulfate complex can be reformulated as

$$k^*_3(y_{\mathrm{A},i,j+1}y_{\mathrm{F},i,j+1}+y_{\mathrm{A},i,j}y_{\mathrm{F},i,j})/2$$
$$=k^*_3(y_{\mathrm{A},i,j+1}y_{\mathrm{F},i,j}+y_{\mathrm{A},i,j}y_{\mathrm{F},i,j+1})/2. \tag{32}$$

The introduction of Eqs. 30, 31, and 32 to Eq. 29 gives the following equations:

$$\begin{aligned}(E_{\mathrm{A},i}+k^*_3y_{\mathrm{F},i,j}/2)y_{\mathrm{A},i,j+1}&=F_{\mathrm{A},i,j+1}y_{\mathrm{A},i+1,j+1}\\&+G_{\mathrm{A},i,j+1}y_{\mathrm{A},i-1,j+1}+D_{\mathrm{A},i,j}-k^*_3y_{\mathrm{F},i,j+1}y_{\mathrm{A},i,j}/2\\&+k^*_{-3}(y_{\mathrm{C},i,j+1}+y_{\mathrm{C},i,j})/2,\end{aligned} \tag{33}$$

$$E_{\mathrm{A},i}=1+\Delta TH(1-s_i)^4/(\Delta s)^2, \tag{34}$$

$$\begin{aligned}F_{\mathrm{A},i,j+1}&=\Delta TH(1-s_i)^2\{d_{\mathrm{A}}H(1-s_i)^2/\Delta s+d_{\mathrm{A}}/(x_i+a_{j+1}/L)\\&+x_i(x_i+2a_{j+1}/L)U_{j+1}/2(x_i+a_{j+1}/L)^2-d_{\mathrm{A}}H(1-s_i)\}/2\Delta s,\end{aligned} \tag{35}$$

$$\begin{aligned}G_{\mathrm{A},i,j+1}&=\Delta TH(1-s_i)^2\{d_{\mathrm{A}}H(1-s_i)^2/\Delta s-d_{\mathrm{A}}/(x_i+a_{j+1}/L)\\&-x_i(x_i+2a_{j+1}/L)U_{j+1}/2(x_i+a_{j+1}/L)^2+d_{\mathrm{A}}H(1-s_i)\}/2\Delta s,\end{aligned} \tag{36}$$

and

$$\begin{aligned}D_{\mathrm{A},i,j}&=F_{\mathrm{A},i,j+1}y_{\mathrm{A},i+1,j}+G_{\mathrm{A},i,j+1}y_{\mathrm{A},i-1,j}\\&+\{1-\Delta Td_{\mathrm{A}}H^2(1-s_i)^4/\Delta s^2\}y_{\mathrm{A},i,j}.\end{aligned} \tag{37}$$

In much the same way, Eq. 22 is transformed as

$$\begin{aligned}(E_{F,i}+k^*_3y_{\mathrm{A},i,j}/2)y_{\mathrm{F},i,j+1}&=F_{\mathrm{F},i,j+1}y_{\mathrm{F},i+1,j+1}\\&+G_{\mathrm{F},i,j+1}y_{\mathrm{F},i-1,j+1}+D_{\mathrm{F},i,j}-k^*_3y_{\mathrm{A},i,j+1}y_{\mathrm{F},i,j}/2\\&+k^*_{-3}(y_{\mathrm{C},i,j+1}+y_{\mathrm{C},i,j})/2.\end{aligned} \tag{38}$$

The following equations are derived from Eqs. 22 and 23:

$$\begin{aligned}\{E_{\mathrm{C},i}-(k^*_{-3}-k^*_4)/2\}y_{\mathrm{C},i,j+1}&=\\F_{\mathrm{C},i,j+1}y_{\mathrm{C},i+1,j+1}&+G_{\mathrm{C},i,j+1}y_{\mathrm{C},i-1,j+1}+D_{\mathrm{C},i,j}\\&-k^*_3(y_{\mathrm{A},i,j+1}y_{\mathrm{F},i,j}/2+y_{\mathrm{A},i,j}y_{\mathrm{F},i,j+1})/2\\&+(k^*_{-3}-k^*_4)y_{\mathrm{C},i,j}/2,\end{aligned} \tag{39}$$

and

$$\begin{aligned}(E_{\mathrm{C},i}-k^*_{-3}/2)y_{\mathrm{C},i,j+1}&=\\F_{\mathrm{C},i,j+1}y_{\mathrm{C},i+1,j+1}&+G_{\mathrm{C},i,j+1}y_{\mathrm{C},i-1,j+1}+D_{\mathrm{C},i,j}\\&-k^*_3(y_{\mathrm{A},i,j+1}y_{\mathrm{F},i,j}/2+y_{\mathrm{A},i,j}y_{\mathrm{F},i,j+1})/2\\&+k^*_{-3}y_{\mathrm{C},i,j}/2.\end{aligned} \tag{40}$$

The backward space difference method must be used in order to obtain the difference equations of Eq. 10 for a precipitate, as was done in a previous study.2) Equation 10 is transformed as follows. For $i=1$, the difference equation is expressed with concentrations at nodes $(1, j)$, $(2, j)$, $(3, j)$, $(4, j)$, $(1, j+1)$, $(2, j+1)$, $(3, j+1)$, and $(4, j+1)$.

$$\begin{aligned}(1+11M_{\mathrm{P},1,j+1})y_{\mathrm{P},1,j+1}&=M_{\mathrm{P},1,j+1}(18y_{\mathrm{P},2,j+1}\\&-9y_{\mathrm{P},3,j+1}+2y_{\mathrm{P},4,j+1})+M_{\mathrm{P},1,j+1}(-11y_{\mathrm{P},1,j}\\&+18y_{\mathrm{P},2,j}-9y_{\mathrm{P},3,j}+2y_{\mathrm{P},4,j})+y_{\mathrm{P},1,j}\\&+k^*_4(y_{\mathrm{C},1,j+1}+y_{\mathrm{C},1,j})/2-k^*_{-4}\end{aligned} \tag{41}$$

For $1<i<99$, the difference equation is expressed with concentrations at nodes $(i-1, j)$, (i, j), $(i+1, j)$, $(i+2, j)$, $(i-1, j+1)$, $(i, j+1)$, $(i+1, j+1)$, and $(i+2, j+1)$.

$$\begin{aligned}(1+3M_{\mathrm{P},i,j+1})y_{\mathrm{P},i,j+1}&=M_{\mathrm{P},i,j+1}(-2y_{\mathrm{P},i-1,j+1}\\&+6y_{\mathrm{P},i+1,j+1}-y_{\mathrm{P},i+2,j+1})+M_{\mathrm{P},i,j+1}(-2y_{\mathrm{P},i-1,j}\\&-3y_{\mathrm{P},i,j}+6y_{\mathrm{P},i+1,j}-y_{\mathrm{P},i+2,j})+y_{\mathrm{P},i,j}\\&+k^*_4(y_{\mathrm{C},i,j+1}+y_{\mathrm{C},i,j})/2-k^*_{-4}\end{aligned} \tag{42}$$

For a node with $i=99$, only an outer node is a node with $i=100$. Therefore, the backward space difference method is not applicable for a transformation; thus, the forward space difference method is used for this purpose. The difference equation is expressed with the concentrations at nodes $(97, j)$, $(98, j)$, $(99, j)$, $(100, j)$, $(97, j+1)$, $(98, j+1)$, $(99, j+1)$, and $(100, j+1)$.

$$\begin{aligned}(1-3M_{\mathrm{P},99,j+1})y_{\mathrm{P},99,j+1}&=M_{\mathrm{P},99,j+1}(y_{\mathrm{P},97,j+1}\\&-6y_{\mathrm{P},98,j+1}+2y_{\mathrm{P},100,j+1})+M_{\mathrm{P},99,j+1}(y_{\mathrm{P},97,j}\\&-6y_{\mathrm{P},98,j}+3y_{\mathrm{P},99,j}+2y_{\mathrm{P},100,j})+y_{\mathrm{P},99,j}\\&+k^*_4(y_{\mathrm{C},99,j+1}+y_{\mathrm{C},99,j})/2-k^*_{-4}\end{aligned} \tag{43}$$

$$\begin{aligned}&M_{\mathrm{P},i,j+1}\\&=\Delta TH(1-s_i)^2U_{j+1}x_i(x_i+2a_{j+1}/L)/6\Delta s(x_i+a_{j+1}/L)^2\end{aligned} \tag{44}$$

The derived expression of the boundary condition in Eq. 25 can be rewritten with concentrations at nodes $(0, j)$, $(1, j)$, $(2, j)$, $(3, j)$, $(0, j+1)$, $(1, j+1)$, $(2, j+1)$, and $(3, j+1)$ by a previously reported procedure:2)

$$y_{\mathrm{F},0,j+1}=(18y_{\mathrm{F},1,j+1}-9y_{\mathrm{F},2,j+1}+2y_{\mathrm{F},3,j+1})/11 \tag{45}$$

$$y_{\mathrm{C},0,j+1}=(18y_{\mathrm{C},1,j+1}-9y_{\mathrm{C},2,j+1}+2y_{\mathrm{C},3,j+1})/11 \tag{46}$$

Values of $y_{\mathrm{A},i,j+1}$, $y_{\mathrm{C},i,j+1}$, and $y_{\mathrm{F},i,j+1}$ are calculated by using Eqs. 33, 38, 40, 45, and 46 when precipitate particles do not exist in a volume element; these and the value of $y_{\mathrm{P},i,j+1}$ are calculated by using Eqs. 33, 39, 41, 42, 43, 45, and 46 when precipitate particles exist in a volume element.

(2) The second alternative assumption consists of two parts. The first part is that the concentration of the mercury(I) sulfate complex is negligible compared with the concentrations of the mercury(I) and sulfate

ions. A corollary to this is that derivatives in Eqs. 8 and 14 are zero. The second part is that the reaction rates of Reactions 4 and 5 are so large that reactions attains equilibrium within the dropping time. This latter condition is usually assumed for an analysis of a wave involving a precipitation reaction.

When precipitate particles exist in a volume element, Eq. 47 can be derived from Eq. 8:

$$C_C=(k_3C_AC_B+k_{-4})/(k_{-3}+k_4) \tag{47}$$

By the introduction of Eq. 47 to Eqs. 6, 7, 9, and 10, the following equations are obtained:

$$\frac{\partial C_A}{\partial t}=D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right)+\left(\frac{2}{r}D_A-u\right)\frac{\partial C_A}{\partial r}-\frac{k_3k_4C_AC_B-k_{-3}k_{-4}}{k_{-3}+k_4}\,, \tag{48}$$

$$\begin{aligned}\frac{\partial C_B}{\partial t}&=D_B\left(\frac{\partial^2 C_B}{\partial r^2}\right)+\left(\frac{2}{r}D_B-u\right)\frac{\partial C_B}{\partial r}+k_2C_D-k_{-2}C_HC_B\\&\quad-\frac{k_3k_4C_AC_B-k_{-3}k_{-4}}{k_{-3}+k_4}\,,\end{aligned} \tag{49}$$

$$\frac{\partial C_D}{\partial t}=D_D\left(\frac{\partial^2 C_D}{\partial r^2}\right)+\left(\frac{2}{r}D_D-u\right)\frac{\partial C_D}{\partial r}-k_2C_D+k_{-2}C_HC_B\,, \tag{50}$$

and

$$\frac{\partial C_P}{\partial t}=-u\frac{\partial C_P}{\partial r}+\frac{k_3k_4C_AC_B-k_{-3}k_{-4}}{k_{-3}+k_4}\,. \tag{51}$$

The solubility product is related to the reaction rate constants by

$$K_{sp}=C_AC_B=k_{-3}k_{-4}/k_3k_4. \tag{52}$$

When precipitate particles do not exist in a volume element, the simultaneous equations governing the concentration of species involving Reactions 2 and 3 are given as

$$\frac{\partial C_A}{\partial t}=D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right)+\left(\frac{2}{r}D_A-u\right)\frac{\partial C_A}{\partial r}\,, \tag{53}$$

$$\frac{\partial C_B}{\partial t}=D_B\left(\frac{\partial^2 C_B}{\partial r^2}\right)+\left(\frac{2}{r}D_B-u\right)\frac{\partial C_B}{\partial r}+k_2C_D-k_{-2}C_HC_B\,, \tag{54}$$

and

$$\frac{\partial C_D}{\partial t}=D_D\left(\frac{\partial^2 C_D}{\partial r^2}\right)+\left(\frac{2}{r}D_D-u\right)\frac{\partial C_D}{\partial r}-k_2C_D+k_{-2}C_HC_B\,. \tag{55}$$

Equations 48—51 and 53—55 are rewritten by use of Eq. 19:

$$\begin{aligned}\frac{\partial C_A}{\partial t}&=D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right)+\left(\frac{2}{r}D_A-u\right)\frac{\partial C_A}{\partial r}-\frac{k_3k_4C_AC_FK_{a2}}{(k_{-3}+k_4)(C_H+K_{a2})}\\&\quad+\frac{k_{-3}k_{-4}}{k_{-3}+k_4}\,,\end{aligned} \tag{56}$$

$$\begin{aligned}\frac{\partial C_F}{\partial t}&=D_F\left(\frac{\partial^2 C_F}{\partial r^2}\right)+\left(\frac{2}{r}D_F-u\right)\frac{\partial C_F}{\partial r}\\&\quad-\frac{k_3k_4C_AC_FK_{a2}}{(k_{-3}+k_4)(C_H+K_{a2})}+\frac{k_{-3}k_{-4}}{k_{-3}+k_4}\,,\end{aligned} \tag{57}$$

$$\frac{\partial C_P}{\partial t}=-u\frac{\partial C_P}{\partial r}+\frac{k_3k_4C_AC_FK_{a2}}{(k_{-3}+k_4)(C_H+K_{a2})}-\frac{k_{-3}k_{-4}}{k_{-3}+k_4}\,, \tag{58}$$

$$\frac{\partial C_A}{\partial t}=D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right)+\left(\frac{2}{r}D_A-u\right)\frac{\partial C_A}{\partial r}\,, \tag{59}$$

and

$$\frac{\partial C_F}{\partial t}=D_F\left(\frac{\partial^2 C_F}{\partial r^2}\right)+\left(\frac{2}{r}D_F-u\right)\frac{\partial C_F}{\partial r}\,. \tag{60}$$

In much the same way as Eq. 20 was transformed to a difference equation, Eqs. 56, 57, 58, and 60 can be transformed as follows:

$$\begin{aligned}&\{E_{A,i}+k^*_3k^*_4y_{F,i,j}/2(k^*_{-3}+k^*_4)\}y_{A,i,j+1}=\\&\quad F_{A,i,j+1}y_{A,i+1,j+1}+G_{A,i,j+1}y_{A,i-1,j+1}+D_{A,i,j}\\&\quad-k^*_3k^*_4y_{A,i,j}y_{F,i,j+1}/2(k^*_{-3}+k^*_4)\\&\quad+k^*_{-3}k^*_{-4}/(k^*_{-3}+k^*_4),\end{aligned} \tag{61}$$

$$\begin{aligned}&\{E_{F,i}+k^*_3k^*_4y_{A,i,j}/2(k^*_{-3}+k^*_4)\}y_{F,i,j+1}=\\&\quad F_{F,i,j+1}y_{F,i+1,j+1}+G_{F,i,j+1}y_{F,i-1,j+1}+D_{F,i,j}\\&\quad-k^*_3k^*_4y_{A,i,j+1}y_{F,i,j}/2(k^*_{-3}+k^*_4)\\&\quad+k^*_{-3}k^*_{-4}/(k^*_{-3}+k^*_4),\end{aligned} \tag{62}$$

$$\begin{aligned}&E_{A,i}y_{A,i,j+1}=\\&\quad F_{A,i,j+1}y_{A,i+1,j+1}+G_{A,i,j+1}y_{A,i-1,j+1}+D_{A,i,j},\end{aligned} \tag{63}$$

and

$$\begin{aligned}&E_{F,i}y_{F,i,j+1}=\\&\quad F_{F,i,j+1}y_{F,i+1,j+1}+G_{F,i,j+1}y_{F,i-1,j+1}+D_{F,i,j}.\end{aligned} \tag{64}$$

The following equation is derived from Eq. 58 by the same procedure as applied Eq. 10:

$i=1$

$$\begin{aligned}&(1+11M_{P,1,j+1})y_{P,1,j+1}=M_{P,1,j+1}(18y_{P,2,j+1}\\&\quad-9y_{P,3,j+1}+2y_{P,4,j+1})+M_{P,1,j+1}(-11y_{P,1,j}\\&\quad+18y_{P,2,j}-9y_{P,3,j}+2y_{P,4,j})+y_{P,1,j}\\&\quad+k^*_3k^*_4(y_{A,1,j+1}y_{F,1,j}+y_{A,1,j}y_{F,1,j+1})/2(k^*_{-3}+k^*_4)\\&\quad-k^*_{-3}k^*_{-4}/(k^*_{-3}+k^*_4),\end{aligned} \tag{65}$$

$1<i<99$

$$\begin{aligned}&(1+3M_{P,i,j+1})y_{P,i,j+1}=M_{P,i,j+1}(-2y_{P,i-1,j+1}\\&\quad+6y_{P,i+1,j+1}-y_{P,i+2,j+1})+M_{P,i,j+1}(-2y_{P,i-1,j}\\&\quad-3y_{P,i,j}+6y_{P,i+1,j}-y_{P,i+1,j})+y_{P,i,j}\\&\quad+k^*_3k^*_4(y_{A,i,j+1}y_{F,i,j}+y_{A,i,j}y_{F,i,j+1})/2(k^*_{-3}+k^*_4)\\&\quad-k^*_{-3}k^*_{-4}/(k^*_{-3}+k^*_4),\end{aligned} \tag{66}$$

and

$i=99$

$$\begin{aligned}&(1-3M_{P,99,j+1})y_{P,99,j+1}=M_{P,99,j+1}(y_{P,97,j+1}\\&\quad-6y_{P,98,j+1}+2y_{P,100,j+1})+M_{P,99,j+1}(y_{P,97,j}\\&\quad-6y_{P,98,j}+3y_{P,99,j}+2y_{P,100,j})+y_{P,99,j}\\&\quad+k^*_3k^*_4(y_{A,99,j+1}y_{F,99,j}+y_{A,99,j}y_{F,99,j+1})/2(k^*_{-3}+k^*_4)\\&\quad-k^*_{-3}k^*_{-4}/(k^*_{-3}+k^*_4),\end{aligned} \tag{67}$$

When precipitate particles exist in a volume element, the values of $y_{A,i,j+1}$, $y_{F,i,j+1}$ and $y_{P,i,j+1}$ are calculated from Eqs. 45, 46, 61, 62, 65, and 66. When the precipitate particles do not exist in a volume element, the values of $y_{A,\,i,\,j+1}$ and $y_{F,\,i,\,j+1}$ are calculated from Eqs. 45, 46, 63, and 64.

The observed corrected anodic current is obtained by subtracting the anodic current in the absence of sulfate ions from one in the presence of a sulfate ion. A numerical method to calculate an anodic current of mercury in the absence of sulfate ion will now be described.

The differential equation governing the concentration of the mercury(I) ion is given as

$$\frac{\partial C_A}{\partial t}=D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right)+\left(\frac{2}{r}D_A-u\right)\frac{\partial C_A}{\partial r}. \tag{68}$$

The initial condition is

$$C_A=0 \qquad (t=0,\ r=a). \tag{69}$$

The boundary conditions are

$$C_{A0}=C_{A0} \qquad (t=0,\ r=a),\ \text{and} \tag{70}$$

$$C_A=0 \qquad (t>0,\ r=\infty). \tag{71}$$

The difference equation form of Eq. 68 is

$$E_{A,\,i}y_{A,\,i,\,j+1}= F_{A,\,i,\,j+1}y_{A,\,i+1,\,j+1}+G_{A,\,i,\,j+1}y_{A,\,i,\,j+1}+D_{A,\,i,\,j}. \tag{72}$$

The instantaneous anodic current in the absence of a sulfate ion, i_r, is given by

$$i_r=2FD_AS(\partial C_A/\partial_r)_{r=a}. \tag{73}$$

The corrected anodic current, i_C, is obtained by

$$i_C=i-i_r. \tag{74}$$

The corrected current is the current mainly caused by either a complex formation reaction or a precipitation reaction.

Experimental

The chemicals used were of reagent grade. The concentration of sodium sulfate in the stock solution was calculated from a weighed amount of anhydrous sodium sulfate after drying 150 °C for 2 h. The concentration of hydrogen ions in the test solution was controlled with sodium carbonate and perchloric acid. The ionic strength of the solution was also adjusted to 0.1 mol dm^{-3}.

Measurements were carried out using a Hokuto Denko Model HA-104 Potentio-Galvanostat in conjunction with the three-electrode method. Precautions were taken in order to prevent any permeation of both chloride and potassium ions from the salt bridges.

The electric resistance of the test solution in the electrolytic system was determined from the free dissolution wave of electrode mercury. The method used was as follows. The value of the resistance was assumed and the electrode potential (E) was corrected by subtracting the iR drop. The corrected electrode potential was plotted against log i. Such a plot does not necessarily produce a straight line. When the assumed value of the resistance is incorrect, the plot is curved. In this case, plotting is repeated with a slightly different value of resistance. This procedure was repeated until the plotting produced a straight line. When plotting produces a straight line, the value of resistance used is the correct value of the resistance of the circuit. This procedure gave 200 Ω for the corrected value of the resistance. The value of the slope of the straight line, ranging from 32.5 mV/unit to 33.0 mV/unit,[1] agrees with the value reported by Kolthoff and Miller. All potentials reported in this paper were corrected for the iR drop and all polarographic currents were corrected for the residual current.

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): a flow rate of mercury (m) of 1.86 mg s^{-1}, a drop time (t) of 3.20 s, and a capillary constant ($m^{2/3}t^{1/6}$) of 1.846 mg$^{2/3}$ s$^{-1/2}$.

Results and Discussion

The anodic current in a solution of sulfate ion was examined by our numerical method.

The value of the diffusion coefficient of the mercury(I) ion was chosen so as to give the smallest difference between the calculated diffusion currents and the observed ones.[3] This procedure gave a value of 0.847×10^{-5} cm^2 s^{-1}. A value of 1.08×10^{-5} cm^2 s^{-1} for a sulfate ion was taken from Ref. 5. The value of the diffusion coefficient of a mercury(I) complex is assumed to be equal to that for mercury(I) ion. Values of pK_{a2} and K_{sp} used are 1.99 and 7.4×10^{-7} mol^2 dm^{-6}.[6,7]

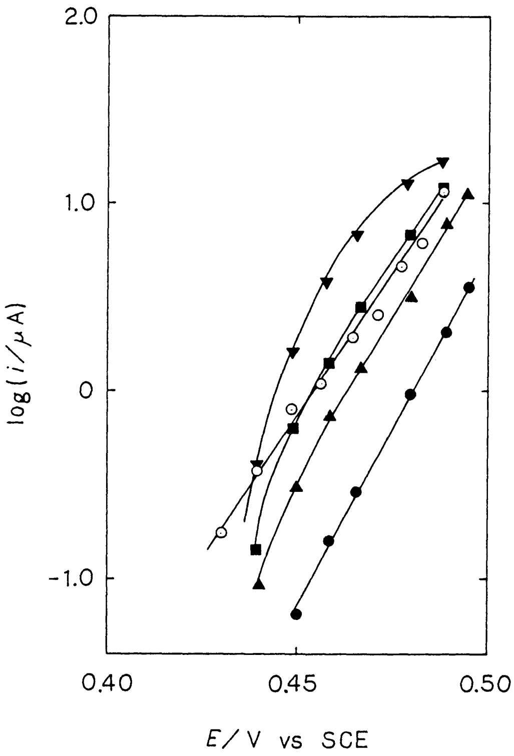

Fig. 2. Effect of the dissolution rate constant on the logarithmic plot in a solution of 2×10^{-3} mol dm^{-3} sodium sulfate and pH 1.93. Computation was carried out using the second alternative assumption. The value of K_{sp} is 0.25×10^{-7} mol^{2}dm^{-6}. ○; observed. Precipitation reaction rate constant (mol^{-1} dm^3 s^{-1}), ●; 10, ▲; 50, ■; 100, ▼; 300.

At first, the anodic current was analyzed using the second assumption, that the concentration of mercury(I) sulfate complex is negligible compared with the concentrations of mercury(I) and sulfate ions. The observed anodic current does not show any diffusion current plateau. It was shown in a previous report[2] that a diffusion current plateau is observed in the case of a large precipitation rate, even with a large value of K_{sp}. Hence, the absence of a plateau indicates that the rate of Reaction 5 is not so large.

Figure 2 shows the effect of the precipitation reaction rate k_4 on the plots of log i against E, constructed from observed and computed polarograms. The anodic current increased with an increase in the value of k_4. For a value of 100 mol^{-1} dm^3 s^{-1} for k_4, the difference between the calculated and observed current at 0.47 V vs. SCE is smallest compared with other values. However, this value is not sufficiently large to give a plateau.

Figure 3 shows plots of log i against E, constructed from observed and computed polarograms. The observed polarograms give straight lines, of which slope is 30—32 mV/unit. The calculated points approach to the observed points with a decrease in K_{sp}. A fair agreement between the calculated and observed points was obtained with a value of K_{sp} which was smaller than 1/50 of the accepted value.[7] This shows that the second assumption is in contradiction with the observed polarograms.

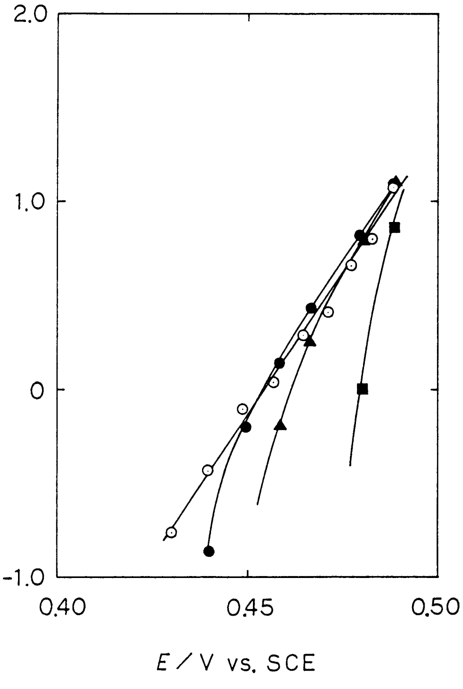

Fig. 3. Logarithmic plots of the anodic current in the solution of 2×10^{-3} mol dm^{-3} sodium sulfate and pH 1.93. Computation was carried out using the second assumption. The value of precipitation reaction rate is 100 mol^{-1} dm^3 s^{-1}. ○; observed data. The value of K_{sp} ($mol^2 dm^{-6}$), ●; 0.25×10^{-7}, ▲; 0.93×10^{-7}, ■; 7.40×10^{-7}.

Table 1. The Time Necessary for Appearance of Precipitate Particles after Mixing of Solution of Mercury(I) and Sulfate Ions. The Appearance was Observed Visually

$[Hg_2^{2+}][SO_4^{2-}]$ / 1×10^{-5} $mol^2 dm^{-6}$	$[Hg_2^{2+}][SO_4^{2-}]/K_{sp}$	Time / min
1.5	2.54	150
3.0	5.08	20
4.5	7.62	1
7.5	12.7	0.5
15.0	25.4	0.5

The solutions of sulfate ion in pH 1.93 are mixed with a solution of 8.03 mM mercury(I) ion in pH 1.93.

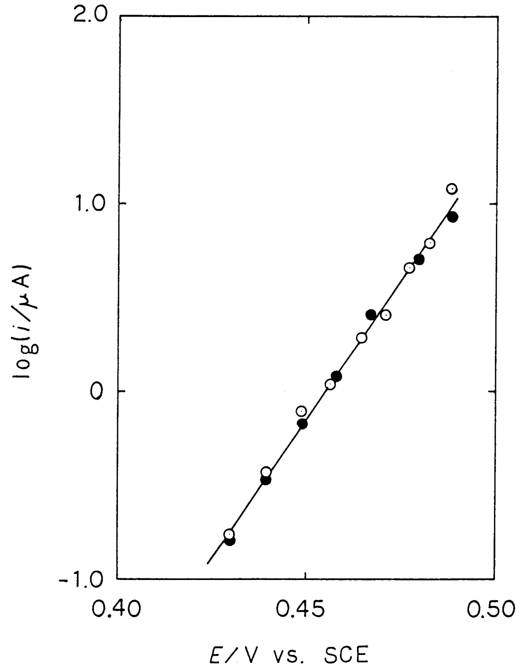

Fig. 4. Logarithmic plots of the anodic current in the solution of 2×10^{-3} mol dm^{-3} soddium sulfate and pH 1.93. Computation was carried out using the first assumptions.
○; observed data, ●; calculated data.

Table 1 shows the time necessary for the appearance of precipitate particles after mixing of solutions of mercury(I) and sulfate ions. The appearance was observed visually. It has been found that the time necessary for the appearance of precipitate particles is too large compared with the dropping time. This means that the values of k_4 and k_{-4} are nearly equal to zero.

Figure 4 shows the anodic current computed by using the first assumption that the mercury(I) sulfate precipitate is produced when the concentration of the mercury(I) sulfate complex exceeds its solubility. The calculated anodic currents are in fair agreement with the observed values. Calculated points were computed with a value of 150 $mol^{-1} dm^3$ for the equilibrium constant of Reaction 4.

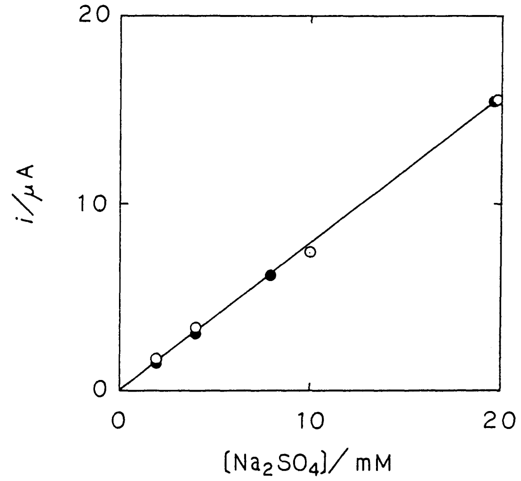

Fig. 5. Effect of the concentration of sodium sulfate on the anodic current at 0.46 V vs. SCE in the solution of pH 1.93. ○; observed data, ●; calculated data.

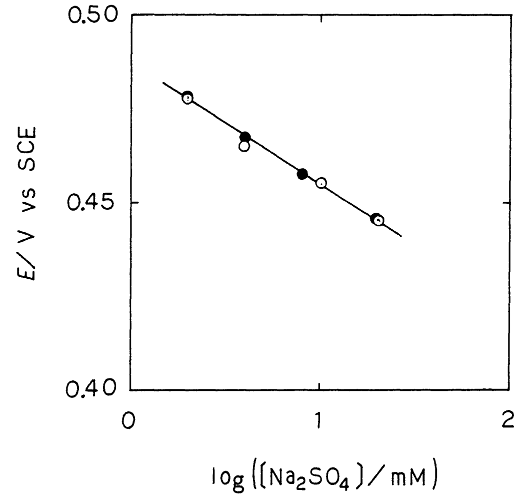

Fig. 6. Effect of the concentration of sodium sulfate on the electrode potential with the value of 5 μA for anodic current in the solution of pH 1.93.
○ ; observed data, ●; calculated data.

Figure 5 shows the relation between the concentration of the sulfate ions and the anodic current at 0.46 V vs. SCE. It shows that the observed currents agree well with calculated values, and that both are proportional to the concentration of sulfate ions.

Figure 6 shows the relation between the concentration of sulfate ions and the electrode potential where the anodic current is 5 μA. The calculated values agree well with the observed ones.

From the above discussion, it is certain that the anodic current is caused by the formation of a mercury(I) sulfate complex and that the precipitation reaction is slow and negligible within the dropping time.

Conclusion

An anodic wave in the presence of sulfate ions has been studied by a new numerical method. It was found that the value of the anodic current increases with an increase in the concentration of sulfate ions, and that the current is caused by the formation reaction of a mercury(I) sulfate complex. It has been confirmed by a numerical method that the precipitation reaction of mercury(I) sulfate does not take place within a dropping time. The value of the stability constant of a mercury(I) sulfate complex has been determined to be 150 mol^{-1} dm^3.

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