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Study of Polarographic Anodic Wave Controlled by the Rate of Precipitation Reaction in the Presence of Citrate Ion

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The anodic wave of mercury observed in the presence of citrate ions has been studied by a numerical method previously proposed by us. The anodic current increases with an increase of concentration of citrate ion. The anodic wave does not show any diffusion current plateau. The logarithm of the anodic current is plotted against the electrode potential, giving a straight line with a slope of 53—55 mV/unit. With the numerical method, it becomes clear that the anodic wave is controlled by the rate of precipitation, which is too low to attain equilibrium within a drop life and is independent of the surface area of the precipitates.

We reported the studies on the polarographic anodic wave, observed in the presence of chloride or sulfate ions, by a new numerical method.[1,2] Mercury(I) ion reacts with these ions to give sparingly soluble salts. The rate of the precipitation reaction with chloride ion is rapid enough to attain equilibrium within a drop life. However, it is a complexation reaction that controls the whole sequence of reactions with sulfate ion within a drop life, because the rate of precipitation reaction is quite slow. It was also proved that the numerical method used in our papers is a useful tool for analyzing anodic current-potential curves. This paper deals with an anodic wave observed in the presence of citrate ion, and it has been shown with the aid of the numerical method that the wave is controlled by the rate of precipitation reaction.

Theory

In the polarographic anodic wave in the presence of citrate ion, electrode mercury is dissolved into solution as mercury(I) ion, which reacts with citrate ion forming a sparingly soluble salt. The concentration of mercury(I) ion in the vicinity of the electrode surface decreases with the progress of the precipitation reaction. However, the decrease of the concentration of mercury(I) ion was partially compensated by further dissolution of electrode mercury. Thus, the anodic current increases with the extent of the precipitation reaction. The reaction sequence of precipitation is given as

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

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

$$\mathrm{H_3L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2L}^- + \mathrm{H}^+, \tag{3}$$

$$\mathrm{H_2L}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{HL}^{2-} + \mathrm{H}^+, \tag{4}$$

$$\mathrm{HL}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{L}^{3-} + \mathrm{H}^+, \tag{5}$$

$$\mathrm{Hg_2}^{2+} + \mathrm{HL}^{2-} \rightleftharpoons \mathrm{N}, \tag{6}$$

$$m\mathrm{N} \xrightarrow{k_4} \mathrm{P}, \tag{7}$$

and

$$\mathrm{Hg}^{2+} + \mathrm{L}^{3-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{HgL}^-, \tag{8}$$

where L^{3-} is citrate ion, N the dehydrated ion pair, P the precipitate particle assumed to be consisted of mercury(I) and hydrogen citrate ions, and k's are the rate constants. The precipitation begings when the concentration product of mercury(I) and HL^{2-} ions exceeds the solubility product. It is assumed that Reaction 6 is the rate-determining step, and controls the anodic current. Partial differential equations governing concentrations of the species in Reactions 1—8 are given as

$$\frac{\partial C_\mathrm{A}}{\partial t} = D_\mathrm{A}\left(\frac{\partial^2 C_\mathrm{A}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{A} - u\right)\frac{\partial C_\mathrm{A}}{\partial r} - f(C_\mathrm{A},C_\mathrm{E}), \tag{9}$$

$$\frac{\partial C_\mathrm{B}}{\partial t} = D_\mathrm{B}\left(\frac{\partial^2 C_\mathrm{B}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{B} - u\right)\frac{\partial C_\mathrm{B}}{\partial r} - k_5 C_\mathrm{B} C_\mathrm{F} + k_{-5} C_\mathrm{Q}, \tag{10}$$

$$\frac{\partial C_\mathrm{C}}{\partial t} = D_\mathrm{C}\left(\frac{\partial^2 C_\mathrm{C}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{C} - u\right)\frac{\partial C_\mathrm{C}}{\partial r} - k_1 C_\mathrm{C} + k_{-1} C_\mathrm{D} C_\mathrm{H}, \tag{11}$$

$$\frac{\partial C_\mathrm{D}}{\partial t} = D_\mathrm{D}\left(\frac{\partial^2 C_\mathrm{D}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{D} - u\right)\frac{\partial C_\mathrm{D}}{\partial r} + k_1 C_\mathrm{C} - k_{-1} C_\mathrm{D} C_\mathrm{H} - k_2 C_\mathrm{D} + k_{-2} C_\mathrm{E} C_\mathrm{H}, \tag{12}$$

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

$$+ k_2C_{\mathrm{D}} - k_{-2}C_{\mathrm{E}}C_{\mathrm{H}} - k_3C_{\mathrm{E}} + k_{-3}C_{\mathrm{F}}C_{\mathrm{H}}, \qquad (13)$$

$$\frac{\partial C_{\mathrm{F}}}{\partial t} = D_{\mathrm{F}}\left(\frac{\partial^2 C_{\mathrm{F}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{F}} - u\right)\frac{\partial C_{\mathrm{F}}}{\partial r} + k_3C_{\mathrm{E}}$$

$$- k_{-3}C_{\mathrm{F}}C_{\mathrm{H}} - k_5C_{\mathrm{B}}C_{\mathrm{F}} + k_{-5}C_{\mathrm{Q}}, \qquad (14)$$

$$\frac{\partial C_{\mathrm{Q}}}{\partial t} = D_{\mathrm{Q}}\left(\frac{\partial^2 C_{\mathrm{Q}}}{\partial r^2}\right)$$

$$+ \left(\frac{2}{r}D_{\mathrm{Q}} - u\right)\frac{\partial C_{\mathrm{Q}}}{\partial r} + k_5C_{\mathrm{B}}C_{\mathrm{F}} - k_{-5}C_{\mathrm{Q}}, \qquad (15)$$

$$\frac{\partial C_{\mathrm{P}}}{\partial t} = -u\frac{\partial C_{\mathrm{P}}}{\partial r} - f(C_{\mathrm{A}},C_{\mathrm{E}}), \qquad (16)$$

$$f(C_{\mathrm{A}},C_{\mathrm{E}}) = k_4C_{\mathrm{P}}{}^{p}\{(C_{\mathrm{A}},C_{\mathrm{E}})^{a} - K_{\mathrm{sp}}{}^{a}\}^{b}, \qquad (17)$$

and

$$u = m/(4\pi\rho r^2), \quad \beta = k_5/k_{-5} = C_{\mathrm{Q}}/(C_{\mathrm{B}}C_{\mathrm{F}}). \qquad (18)$$

The notations in the above are as follows: A, B, C, D, E, F, and Q are $\mathrm{Hg_2^{2+}}$, $\mathrm{Hg^{2+}}$, $\mathrm{H_3L}$, $\mathrm{H_2L^-}$, $\mathrm{HL^{2-}}$, $\mathrm{L^{3-}}$, and $\mathrm{HgL^-}$, respectively; $f(C_{\mathrm{A}}, C_{\mathrm{E}})$ is the precipitation kinetics term; a, b, and p are numbers representing orders of corresponding quantities in the precipitation kinetics term; m is the flow rate of mercury; ρ is the density of mercury; β is the stability constant of a complex $\mathrm{HgL^-}$; D_{h} the diffusion coefficient of species h; and C_{h} the concentration of species h. In the above, it is assumed that the diffusion of the precipitate is negligible in comparison with that of ions. When the precipitation is controlled by a crystal growth process, the rate of precipitation reaction is proportional to the surface area of the precipitate particles, and the value of p is 2/3. In other cases the value of p is different from 2/3. For example, the value of p is zero in the nucleation process. When the concentration product is smaller than the solubility product of the salt, the value of $f(C_{\mathrm{A}}, C_{\mathrm{E}})$ is null.

Initial conditions are

$$C_{\mathrm{A}} = 0,\ C_{\mathrm{B}} = 0,\ C_{\mathrm{C}} = C^*_{\mathrm{C}},\ C_{\mathrm{D}} = C^*_{\mathrm{D}},\ C_{\mathrm{E}} = C^*_{\mathrm{E}},$$

$$C_{\mathrm{F}} = C^*_{\mathrm{F}},\ C_{\mathrm{P}} = 0, \text{ and } C_{\mathrm{Q}} = 0 \quad (\mathrm{t} = 0,\ r > a), \qquad (19)$$

and boundary conditions are

$$C_{\mathrm{A}} = \frac{1}{\gamma_{\mathrm{A}}}\exp\{2(E - E^{\circ}{}_{\mathrm{A}})F/RT\},$$

$$C_{\mathrm{B}} = \frac{1}{\gamma_{\mathrm{B}}}\exp\{2(E - E^{\circ}{}_{\mathrm{B}})F/RT\},$$

$$\left(\frac{\partial C_{\mathrm{C}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{D}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{E}}}{\partial r}\right)_{r=a} = 0,\ \left(\frac{\partial C_{\mathrm{F}}}{\partial r}\right)_{r=a} = 0,$$

$$\left(\frac{\partial C_{\mathrm{Q}}}{\partial r}\right)_{r=a} = 0 \quad (t > 0,\ r = a), \qquad (20)$$

and

$$C_{\mathrm{A}} = 0,\ C_{\mathrm{B}} = 0,\ C_{\mathrm{C}} = C^*_{\mathrm{C}},\ C_{\mathrm{D}} = C^*_{\mathrm{D}},\ C_{\mathrm{E}} = C^*_{\mathrm{E}},$$

$$C_{\mathrm{F}} = C^*_{\mathrm{F}},\ C_{\mathrm{P}} = 0,\ C_{\mathrm{Q}} = 0, \quad (t > 0,\ r = \infty), \qquad (21)$$

where $\mathrm{C}^*_{\mathrm{h}}$ is the bulk concentration of the species h, γ_{h} the activity coefficient of the sppecies h, F the Faraday's constant, and $E^{\circ}{}_{\mathrm{A}}$ and $E^{\circ}{}_{\mathrm{B}}$ are the standard electrode potentials of $\mathrm{Hg_2^{2+}}$–Hg and $\mathrm{Hg^{2+}}$–Hg couples, respectively.

The current, i, is given by

$$i = 2FD_{\mathrm{A}}S\left(\frac{\partial C_{\mathrm{A}}}{\partial r}\right)_{r=a} + 2FD_{\mathrm{B}}S\left(\frac{\partial C_{\mathrm{B}}}{\partial r}\right)_{r=a}, \qquad (22)$$

where S is the mercury electrode surface area. The total concentration of the citrate, C_{L}, is defined as

$$C_{\mathrm{L}} = C_{\mathrm{C}} + C_{\mathrm{D}} + C_{\mathrm{E}} + C_{\mathrm{F}}. \qquad (23)$$

In Eqs. 9—16, the citrate ion and its protonated species are treated as the species which diffuse independently. However, citrate ion is only the species to diffuse, and other species are formed through protonation of citrate ion with protons supplied from solvent water. Hence, the number of independent equations may be reduced by use of the variable C_{L}. By using Eq. 23, Eqs. 9—16 become

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}}\left(\frac{\partial^2 C_{\mathrm{A}}}{\partial r^2}\right) + \left(\frac{2}{r}D_{\mathrm{A}} - u\right)\frac{\partial C_{\mathrm{A}}}{\partial r} - F(C_{\mathrm{A}},C_{\mathrm{L}}), \qquad (24)$$

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

$$- k_5\alpha_3C_{\mathrm{B}}C_{\mathrm{L}} + k_{-5}C_{\mathrm{Q}}, \qquad (25)$$

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

$$- F(C_{\mathrm{A}},C_{\mathrm{L}}) - k_5\alpha_3C_{\mathrm{B}}C_{\mathrm{L}} + k_{-5}C_{\mathrm{Q}}, \qquad (26)$$

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

$$- k_5\alpha_3C_{\mathrm{B}}C_{\mathrm{L}} + k_{-5}C_{\mathrm{Q}}, \qquad (27)$$

and

$$\frac{\partial C_{\mathrm{P}}}{\partial t} = -u\frac{\partial C_{\mathrm{P}}}{\partial r} - F(C_{\mathrm{A}},C_{\mathrm{L}}), \qquad (28)$$

where

$$\alpha_2 = \frac{Ka_1Ka_2}{\left\{1 + \frac{Ka_1}{[\mathrm{H}^+]} + \frac{Ka_1Ka_2}{[\mathrm{H}^+]^2} + \frac{Ka_1Ka_2Ka_3}{[\mathrm{H}^+]^3}\right\}[\mathrm{H}^+]^2}, \tag{29}$$

$$\alpha_3 = \frac{Ka_3\alpha_2}{[\mathrm{H}^+]}, \tag{30}$$

and

$$F(C_\mathrm{A},C_\mathrm{L}) = f(C_\mathrm{A},\alpha_2C_\mathrm{L}) = f(C_\mathrm{A},C_\mathrm{E})$$

$$= k_4C_\mathrm{P}{}^p\{(\alpha_2C_\mathrm{A}C_\mathrm{L})^a - K_\mathrm{sp}{}^a\}^b. \tag{31}$$

In the above, Ka_1, Ka_2, and Ka_3 are successive dissociation constants of citric acid, and D_L is the common diffusion coefficient of citric acid and its ionic species.

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

$$\frac{\partial C_\mathrm{A}}{\partial t} = D_\mathrm{A}\left(\frac{\partial^2 C_\mathrm{A}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{A} - u\right)\frac{\partial C_\mathrm{A}}{\partial r}, \tag{32}$$

and

$$\frac{\partial C_\mathrm{B}}{\partial t} = D_\mathrm{B}\left(\frac{\partial^2 C_\mathrm{B}}{\partial r^2}\right) + \left(\frac{2}{r}D_\mathrm{B} - u\right)\frac{\partial C_\mathrm{B}}{\partial r}. \tag{33}$$

The initial conditions are

$$C_\mathrm{A} = 0,\ C_\mathrm{B} = 0 \quad (t = 0,\ r > a), \tag{34}$$

and the boundary conditions are

$$C_\mathrm{A} = \frac{1}{\gamma_\mathrm{A}}\exp\{2(E - E^\circ{}_\mathrm{A})F/RT\},$$

$$C_\mathrm{B} = \frac{1}{\gamma_\mathrm{B}}\exp\{2(E - E^\circ{}_\mathrm{B})F/RT\}.$$

The residual current, i_r, is given as

$$i_r = 2FD_\mathrm{A}S\left(\frac{\partial C_\mathrm{A}}{\partial r}\right)_{r=a} + 2FD_\mathrm{B}S\left(\frac{\partial C_\mathrm{B}}{\partial r}\right)_{r=a}. \tag{36}$$

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

$$i_\mathrm{c} = i - i_r \tag{37}$$

Equations 24, 25, 26, 27, 28, 32, and 33 are solved by the procedure similar to one described in the previous papers.[1,2]

Experimental

All chemicals used were of the reagent grade. The concentration of citric acid was determined by titrating with a sodium hydroxide solution. The ionic strength of the test solution was controlled to 0.1 with sodium perchlorate. To the test solution, 0.03% gelatin was added as a maximum suppresser.[3] Measurements were carried out using a Hokuto Denko Model HA-104 Potentio-Galvanostat in conjunction with the three-electrode arrangement. The electric resistance of the electrolytic system was determined by the procedure described in the previous paper.[2] This procedure gave electric resistance values ranging from 180 to 240 Ω.

The dropping mercury electrode used had 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): the flow rate of mercury (m), 1.251 mg s^{-1}; the drop time (t), 4.65 s; the capillary constant ($m^{2/3}t^{1/6}$), 1.499 mg$^{2/3}$ s$^{-1/2}$.

The value of the common diffusion coefficient D_L was calclulated from the equivalent conductance of citrate ion at infinite dilution.[4] The equivalent conductance was measured with TOA conductivity meter CM-25E. The value of the diffusion coefficient was estimated to be 0.668×10^{-5} cm^2 s^{-1} from a value of the equivalent conductance at infinite dilution, 75.0 S cm^2 eq^{-1}. The value of diffusion coefficient of mercury(I) ion used is 0.847×10^{-5} cm^2 s^{-1},[1] and the value of the diffusion coefficient of mercury(II) ion was chosen to minimize difference between calculated and observed values of the currents.[5] This procedure gave a value of 0.724×10^{-5} cm^2 s^{-1}.

The value of β, Ka_1, Ka_2, and Ka_3 is 7.94×10^{10} mol^{-1} dm^3, 1.35×10^{-3} mol dm^{-3}, 4.47×10^{-5} mol dm^{-3}, and 2.04×10^{-6} mol dm^{-3}.[6]

The numerical method described in the present paper was performed by an IBM 4361-L03 computer at Shiga Prefectural Junior College.

Results and Discussion

The anodic wave was measured in solutions with pH values ranging from 1.2 to 2.2. Figure 1 shows the

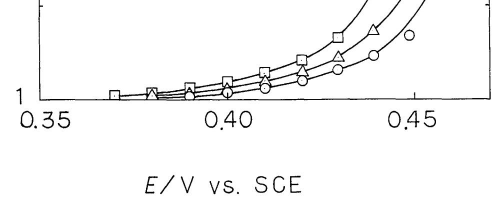

Fig. 1. The anodic waves in the presence of citrate ions. pH of solutions, 1.99. Total concentration of the citrate (mmol dm^{-3}): ○, 1.0; △, 2.0; □, 4.0.

anodic waves in the presence of citric acid in a solution of pH 1.99. The anodic current increases with an increase of the total concentration of the citrate, but the waves lack any current plateau.

Figure 2 shows the plots of log i_c against the electrode potential. The reciprocal slope of asymptotes to these plots is 53—55 mV/unit.

Figure 3 shows the variation of i_c observed at fixed electrode potentials with the total concentration of the citrate. The plots are straight lines with a slope of 0.53.

Figure 4 shows the variation of the electrode potential corresponding to a constant value of i_c with the total concentration of the citrate. The plot gives a straight line with a slope of −29 mV/unit. Kolthoff and Miller derived an equation describing the anodic wave in the presence of halide ion.[7] The equation is modified in our case as follows:

$$E = E^\circ + \frac{RT}{2F}\ln a_A = E^\circ + \frac{RT}{2F}\ln K_{sp}\gamma_A/(\alpha_2 C_{Lo}). \qquad (38)$$

In the above, a_A is the activity of Hg_2^{2+}, K_{sp} the solubility product of Hg_2HL, and C_{Lo} the total concentration of the citrate at the electrode surface. However, the wave in question is assumed to be controlled by the rate of precipitation, and that the citrate at the electrode surface is not consumed as much as expected from the solubility product relationship, al least, within a drop life. Hence, the value of C_{Lo} may be assumed to remain constant during a drop life. One may write as

$$C_{Lo} \propto C_L. \qquad (39)$$

Introducing this into Eq. 38, one obtains

$$E = E^\circ - \frac{RT}{2F}\ln \alpha_2 C_L + \text{const.} \qquad (40)$$

From Eq. 40, it is expected that the plots of E against log C_L form a straight line, of which reciprocal slope is −29 mV/unit. This value agrees well with the observed value.

The value of α_2 in Eq. 40 depends on pH of the solution. Figure 5 shows the variation of the electrode potential corresponding to a constant value of i_C with increasing pH in the solution of 2.0 mmol dm^{-3} of C_L.

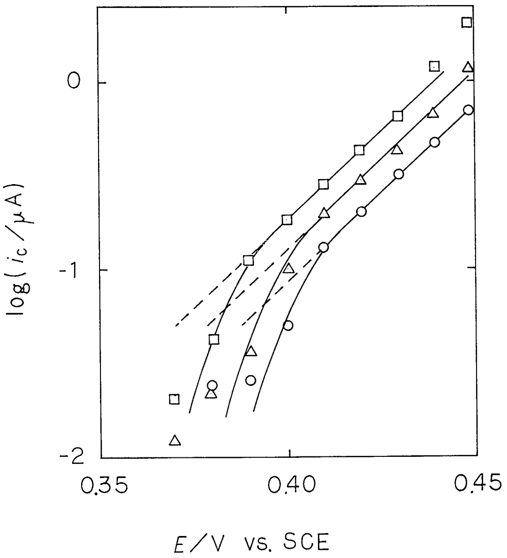

Fig. 2. Plots of log i_c against the electrode potential. Conditions are same as in Fig. 1.

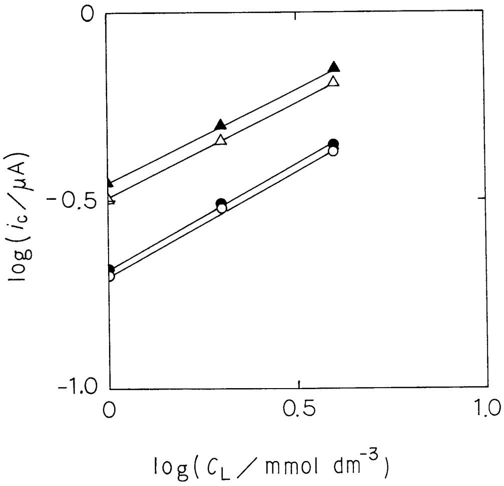

Fig. 3. Variation of i_c at fixed electrode potentials with increasing the total concentration of the citrate. pH of solution, 1.99. Electrode potential: ○, 0.42 V; △, 0.43 V. Filled symbols represent the computed data.

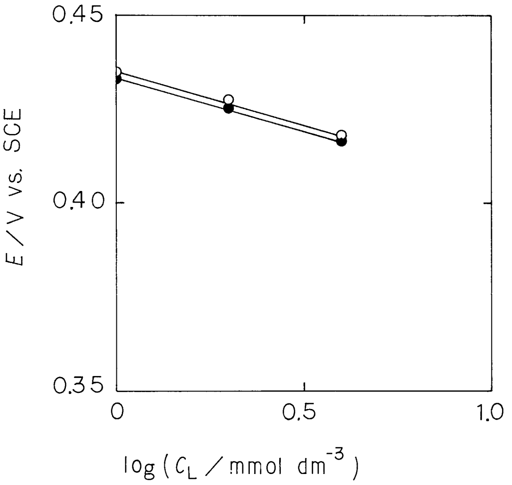

Fig. 4. Variation of the electrode potentials corresponding to a constant value of i_c with increasing the total concentration of the citrate. pH of solution 1.99. i_c, 0.4 μA. ○, observed; ●, computed by assuming that k_4, a, b, and p are 3.0 s^{-1}, 1, 0.5, and 0, respectively.

This plot gives a straight line with a slope of −55 mV/pH which is in good agreement with the calculated value of −54.4 mV/pH.

Although, as described above, some behaviors of the wave may be understood by Eq. 40, the explanation seems to be incomplete. Hence it is desirable to analyze the wave with the numerical method proposed in the previous papers.[1,2)]

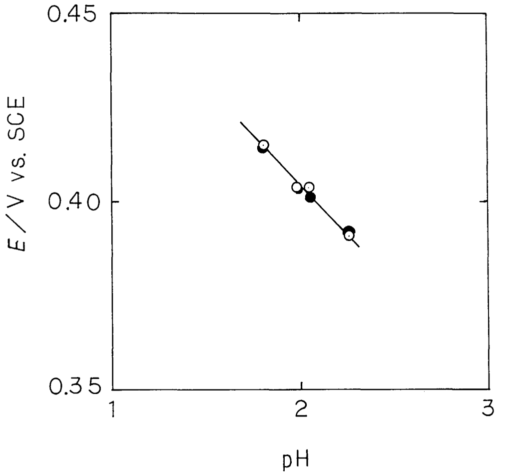

Fig. 5. Variation of the electrode potential corresponding to a constant value of i_c with increasing pH. Total concentration of the citrate, 2.0 mmol dm^{-3}. i_c, 0.15 μA. ○, observed; ●, computed by assuming that k_4, a, b, and p are 3.0 s^{-1}, 1, 0.5, and 0, respectively.

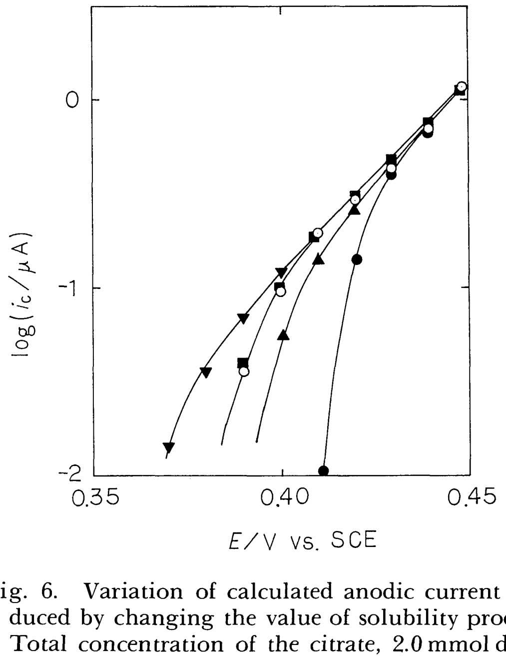

Fig. 6. Variation of calculated anodic current produced by changing the value of solubility product. Total concentration of the citrate, 2.0 mmol dm^{-3}. pH of solution, 1.99. Computations were performed by assuming that k_4, a, b, and p are 3.0 s^{-1}, 1, 0.5, and 0, respectively. ○, observed data. Solubility product (K_{sp}/mol^2 dm^{-6}): ▼, 5×10^{-13}; ■, 2×10^{-12}; ▲, 5×10^{-12}; ●, 2×10^{-11}.

At first, we will examine the case of being a=1, b=0.5, and p=0.

Figure 6 shows the variation of calculated anodic current obtained by changing the solubility product value. The value of k_4 used is 3 s^{-1}, which makes the difference between the calculated and observed currents at 0.44 V vs. SCE to be smallest. The current calculated using the solubility product of 0.2×10^{-11} mol^2 dm^{-6} agrees well with the observed data.

The calculated variation of i_c at fixed electrode potentials with increassing the total concentration of the citrate is shown as filled symbols in Fig. 3. The plots produce straight lines with a slope of 0.53. The calculated results are well consistent with the observed ones.

Figure 4 shows the calculated variation of the electrode potential, corresponding to a constant value of i_c with the total concentration of the citrate, with filled symbols. This plot gives a straight line with a slope of −27 mV/unit in agreement with the observed results.

The similar results with the change of pH are shown as filled symbols in Fig. 5, illustrating good agreement with the observed results.

In the above we have examined the case that a=1, b=0.5, and p=0. Next, we will examine the case that a=0.5, b=1, and p=0. Figure 7 shows the calculated variations of i_c at fixed electrode potentials and of the electrode potential corresponding to a constant value of i_c with the total concentration of the citrate using filled symbols. These results are in fair agreement with observed ones. Fair agreement was also obtained for the relation between the electrode potential and

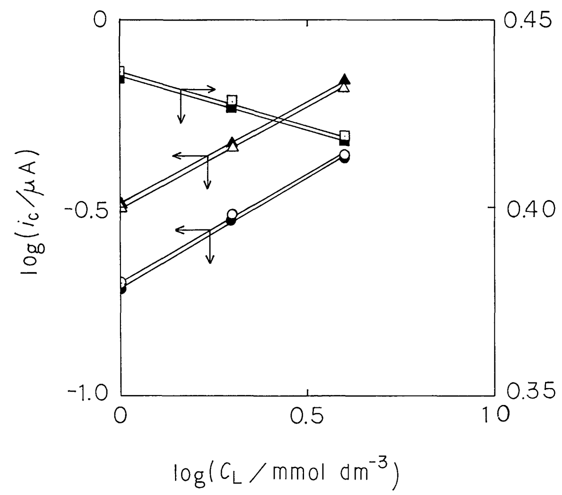

Fig. 7. Variation of i_c at fixed electrode potentials and of the electrode potential corresponding to a constant value of i_c with increasing the total concentration of the citrate. pH of solution, 1.99. Fixed electrode potential: ○, 0.42 V; △, 0.43 V. i_c: 0.4 μA. Filled symboles represent corresponding computed data obtained by assuming that k_4, a, b, and p are 3.0 s^{-1}, 0.5, 1, and 0, respectively.

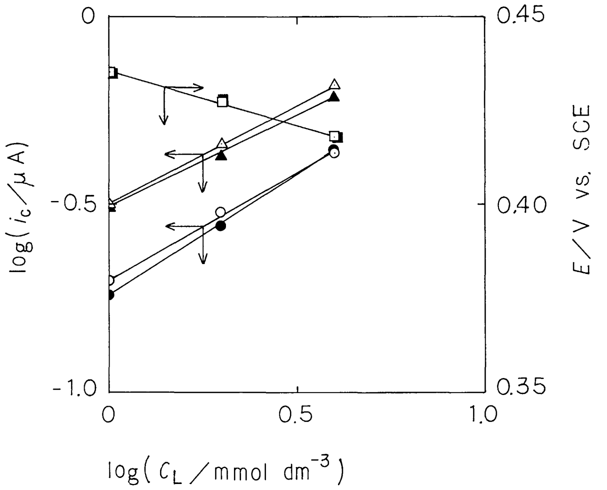

Fig. 8. Variation of i_c at fixed electrode potentials and of the electrode potential corresponding to a constant value of i_c with increasing the total concentration of the citrate. pH of solution, 1.99. Fixed electrode potential: ○, 0.42 V; △, 0.43 V. i_c: 0.4 μA. Filled symboles represent corresponding computed data obtained by assuming that k_4, a, b, and p are 1.4 s^{-1}, 1, 1/6, and 2/3, respectively.

pH.

Now we will extent the examination to other possibilities. An interesting question is whether or not the rate of the precipitation reaction depends on the surface area of the precipitates (in that case p=2/3). Results of computation, based on an assumption that a=1, b=1/6, and p=2/3, are given in Fig. 8, where filled symbols represent computed results for the variations of i_c at fixed electrode potentials and of the electrode potential corresponding to a constant value of i_c with the total concentration of the citrate. Although the results for the variation of the electrode potential are in good agreement with those observed, the ones for the variation of i_c give straight lines with slopes different from that of the straight line from observed results. Other assumptions, for example, that a=1/6, b=1, and p=2/3, lead a wider discrepancy between the observed results and the computed ones.

From the computational results described above, it is concluded that the precipitation kinetics term is expressed by Eqs. 41 or 42.

$$f(C_A,C_E) = k_4(C_AC_E - K_{sp})^{0.5} \tag{41}$$

or

$$f(C_A,C_E) = k_4\{(C_AC_E)^{0.5} - K_{sp}^{0.5}\}. \tag{42}$$

Under the experimental conditions of this study, the degree of supersaturation (C_AC_E/K_{sp}) is larger than 5. In that case the difference between above two expressions is meaningless, and they reduce to

$$f(C_A,C_E) = k_4(C_AC_E)^{0.5}. \tag{43}$$

The precipitation reaction may be divided into three processes: nucleation, crystal growth, and aggregation of crystals. The change of the concentration of ion in the process of nucleation does not depend on the surface area of the precipitates but on the degree of supersaturation.

The precipitation reaction rate equation expressed by Eq. 43 indicates that the precipitation rate does not depend on the surface area of the precipitate particles but on $(C_AC_E)^{0.5}$. It means that the rate-determining step of the precipitation reaction is the process of nucleation.

Conclusion

The numerical method proposed by us has been successfully applied to the anodic wave caused by the precipitation reaction of mercury(I) and hydrogen citrate ions. The precipitation reaction does not attain the equilibrium within a drop life of the electrode mercury. The anodic current is controlled by the rate of the precipitation reaction. It is a good assumption that the precipitates consist of Hg_2HL. The assumption leads to the reaction rate equation and the value of the reaction rate constant. The reaction rate equation is expressed by $k_4([Hg_2^{2+}][HL^{2-}])^{1/2}$ and the value of the rate constant of the precipitation reaction is 3.0 s^{-1}. The rate equation shows that the rate of the precipitation reaction is independent of the surface area of the precipitates, and that the rate-determining step is the process of nucleation.

References

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