ELECTROCHEMICAL BEHAVIOR OF SULFIDE AT THE SILVER ROTATING DISC ELECTRODE

PART II. MECHANISM OF SILVER SULFIDE FILM FORMATION

KOICHI AOKI, KUNIO SHIMIZU and ROBERT A. OSTERYOUNG

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214 (U.S.A.)

(Received 27nd August 1980; in revised form 25th February 1981)

ABSTRACT

Steady-state anodic voltammograms were measured at a silver rotating disc electrode in a basic sulfide solution. Analysis of the voltammograms indicates that the rate-determining steps in the dissolution of silver are due to a combination of surface chemical reaction, forming silver sulfide, and the charge-transfer reaction between silver and silver ion. Kinetic parameters of each step are evaluated and an $I-E$ curve is reproduced from these parameters. The wave form is in good agreement with the voltammogram obtained experimentally.

INTRODUCTION

Although the anodic dissolution of metals, frequently producing insoluble substances, plays an important role in the process of metal corrosion, fundamental and kinetic knowledge of such processes has been accumulated only in recent years. The mechanism of anodic dissolution contains factors making quantitative measurements difficult, e.g. influence of crystal structure, adsorption, activity change of ad-atoms, volume reactions, passivation due to films, surface diffusion, formation of nuclei and crystallization [1,2], and hence quantitative descriptions of such processes have been limited [3–7]. However, to a certain extent it is possible to neglect some of these effects by controlling the time scale in measurements such as in ac impedance studies [5,6], in chronopotentiometric methods [4] and in steady-state measurements at the rotating disc electrode (RDE) [3].

Much recent work in this field has been concerned with dissolution studies of zinc [8] and cadmium [9] in alkaline solutions. They show contradictory results and conditions, depending on the investigators and their experimental methods. To describe anodic dissolution mechanisms comprehensively, it seems necessary to accumulate extensively many data with respect to many kinds of metals. The present work reports on the analysis of silver dissolution into sulfide solution as an extension of a previous study [10].

The previous experiments [10] describe the anodic dissolution of silver in basic

sulfide solution at a silver rotating disc electrode and can be summarized as follows:

(a) Silver sulfide films produced on the electrode do not block current through the electrode until the quantity of electricity passed at the electrode, Q_r, exceeds $8 \times 10^{-2}\, C\, cm^{-2}$. Thus, anodic currents can be regarded as steady-state currents, although silver sulfide is accumulated on the electrode surface as the reaction proceeds. The remarks that follow address only the case where $Q < Q_r$.

(b) The quantity of electricity passed on deposition of silver sulfide at the electrode surface, Q_a, is equal to the quantity of electricity of sulfide removed in the stripping process, Q_c.

(c) From the dependence of limiting currents on the rotation rate and concentration of sulfide, it was concluded that limiting currents are controlled by diffusion of sulfide to the electrode.

(d) The potential at which anodic currents begin to flow is $-0.78\, V$ (SCE), cathodically shifted from the equilibrium potential of Ag/Ag^+ by $1.34\, V$.

(e) Anodic currents less than those on the limiting current plateau are kinetically controlled, and plots of $I < I_1$ vs. $\omega^{1/2}$ are non-linear and are also independent of $\omega^{1/2}$ at the foot of the anodic wave.

Thus, the kinetic behavior represented by (d) and (e), supported by the rather simple results of (a)–(c), encouraged us to attempt to elucidate the kinetics of the mechanism in an effort to explain the shape of the current–potential curve.

EXPERIMENTAL

Chemicals, apparatus and experimental procedures have been described elsewhere [10]. Concentrations of sodium sulfide employed were 1.77×10^{-4}, 3.54×10^{-4}, 5.31×10^{-4}, 7.08×10^{-4} and $8.85 \times 10^{-4}\, mol\, dm^{-3}$. Rotation rates of the silver RDE were varied from 400 to 3600 rpm. The potential scan rate was $10\, mV\, s^{-1}$.

RESULTS AND DISCUSSION

An experimental voltammogram is shown in Fig. 1 as curve a. As described in prior work [10], the overall reaction which forms a silver sulfide film on the electrode is given by

$$2\, Ag + S^{2-} \rightleftharpoons Ag_2S + 2\, e^- \qquad (I)$$

This reaction can be divided intuitively into a charge-transfer reaction and a chemical one as follows:

$$2\, (Ag \rightleftharpoons Ag^+ + e^-) \qquad (II)$$

$$2\, Ag^+ + S^{2-} \rightleftharpoons Ag_2S \qquad (III)$$

First we tentatively apply the theory for the anodic dissolution of mercury into a solution of halide ions, developed by Heyrovský and Kůta [11], to the present system. The theory assumes that anions which produce sparingly soluble salts diffuse
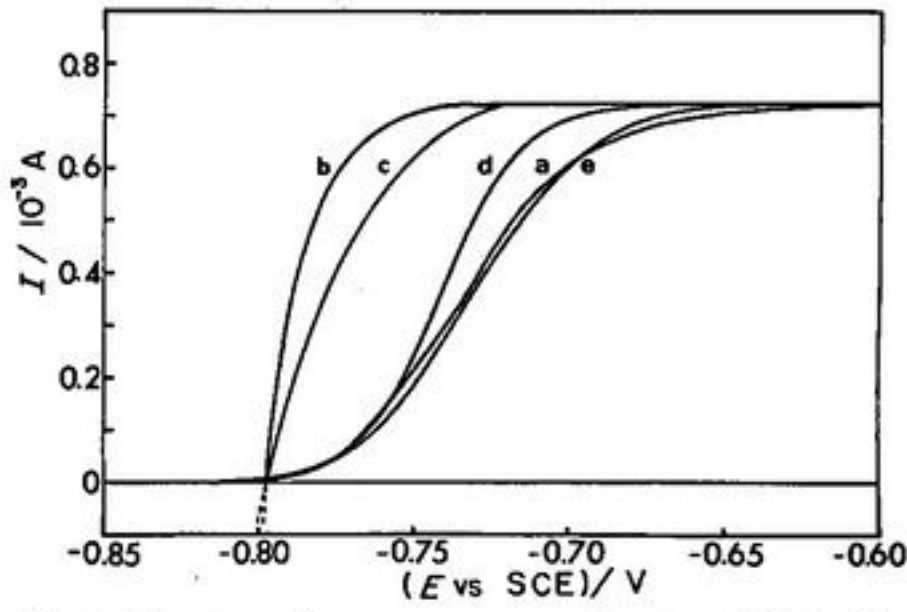
Fig. 1. Anodic voltammograms at the silver RDE: (a) experimentally obtained curve; (b) calculated from eqn. (4); (c) calculated from eqn. (6); (d) calculated from eqn. (10); (e) calculated from eqns. (11) and (12) under the conditions of $c_0 = 5.31 \times 10^{-4}$ mol dm^{-3}, rotation speed 1600 rpm and $I_d = 0.725$ mA.

to the electrode and equilibrate on the electrode surface, with metal ions dissolving reversibly from a metal lattice. This predicts that the rate-determining step is not due to reaction rates but to the diffusion of anions from the bulk solution to the electrode. Then the conditions of the equilibrium in reactions (II) and (III) are given by

$$(c_{Ag^+})_s/c^{\ominus} = \exp\left((F/RT)(E - E^{0\prime})\right) \tag{1}$$

$$(c_{Ag^+})_s^2(c_{S^{2-}})_s = K_{sp} \tag{2}$$

$$(c_{HS^-})_s/(c_{S^{2-}})_s/(c_{H^+})_s = K_1 \ldots \tag{3}$$

where $(c_{Ag^+})_s$, $(c_{S^{2-}})_s$, $(c_{HS^-})_s$ and $(c_{H^+})_s$ are concentration of Ag$^+$, S^{2-}, HS$^-$ and H$^+$ respectively, on the electrode surface, $c^{\ominus}$ the standard concentration (1 mol dm^{-3}) of silver ion, $E^{0\prime}$ the formal potential of eqn. (II), K_{sp} the solubility product of Ag$_2$S and K_1 the formation constant of the reaction, S^{2-} + H$^+$ $\rightleftharpoons$ HS$^-$. The solution of the convective diffusion equation at the RDE is, in general,

$$c_s = c_0(1 - I/I_d) \tag{4}$$

where c_s and c_0 are analytical concentrations of sulfide ($c_{S^{2-}} + c_{HS^-}$) at the electrode and in the bulk solution respectively, and I_d and I the diffusion-controlled current and a current depending on potential respectively. This simple expression results from uniform accessibility of the RDE [12] and also holds for other conditions described below. From eqns. (3) and (4) one can obtain eqn. (5):

$$(c_{S^{2-}})_s\{1 + (c_{H^+})_s K_1\} = c_0(1 - I/I_d) \tag{5}$$

Substituting eqn. (1) into eqn. (2) and eliminating $(c_{S^{2-}})_s$ from eqns. (2) and (5) yields:

$$I = I_d\left\{1 - \left(K'_{sp}/c_0(c^{\ominus})^2\right)\exp\left(-2F(E - E^{0\prime})/RT\right)\right\} \tag{6}$$

where K'_{sp} is an apparent solubility product given by $K_{sp}\{1 + (c_{H^+})_s K_1\}$. The I–E curve calculated from eqn. (6) is shown as curve b in Fig. 1 for $K_{sp} = 1.6 \times 10^{-50}$ mol^3 dm^{-9} [13], $(c_{H^+})_s = 5 \times 10^{-4}$ mol dm^{-3}, $K_1 = 10^{14.0}$ mol dm^3 [14] and $E^{0'} = 0.555$ V (SCE) [15], together with curve a, which is experimental. Curve b is shifted cathodically from curve a by approximately 50 mV and rises steeply at $E = -0.798$ V (SCE), ascending more steeply than curve a to reach the diffusion-controlled current plateau. Therefore, assuming the establishment of the equilibrium of reactions (II) and (III) at the electrode surface fails to reproduce the experimentally observed curve.

An alternative possibility is to introduce the kinetics of the charge-transfer process represented by the Butler equation instead of the Nernst equation. Then reaction (II) is formulated as

$$I = 2FAk_c^{\ominus}\{c^{\ominus}\exp[(1-\alpha)F(E-E^{0'})/RT] - (c_{Ag^+})_s\exp[-\alpha F(E-E^{0'})/RT]\}$$
(7)

where $k_c^{\ominus}$ is the conditional electrode reaction-rate constant for reaction (II), α the cathodic charge-transfer coefficient and A the surface area of the electrode. Combining eqn. (7) with eqns. (2) and (3) yields:

$$I = 2FAk_c^{\ominus}\{c^{\ominus}\qquad\exp[(1-\alpha)F(E-E^{0'})/RT]$$
$$- (K'_{sp}I_d/c_0(I_d - I))^{1/2}\exp[-\alpha F(E-E^{0'})/RT]\}$$
(8)

which is a cubic equation with respect to I. Values of I computed numerically for $k_c^{\ominus} = 2.3 \times 10^{-5}$ cm s^{-1} and $\alpha = 1$ were plotted against potentials in Fig. 1 (curve c). The values of $k_c^{\ominus}$ and α referred here are those which will be determined in a later discussion. Curve c still has a sharp rise at $E_e = -0.798$ V equal to $E^{0'} + (RT/2F)$ $\ln(K'_{sp}/c_0(c^{\ominus})^2)$ and is very similar to curve b at the foot of the wave. Slopes of curves b and c at $E = E_e$ are given by $2FI_d/RT$ and

$$2F^2Ak_c^{\ominus}/\left[RT\left\{\left(c_0(c^{\ominus})^2/K'_{sp}\right)^{(1-\alpha)/2} + FAk_c^{\ominus}/I_d\right\}\right]$$

respectively, as a result of differentiating eqns. (6) and (8). Obviously, they do not become zero for any choice of $k_c^{\ominus}$ and α within reasonable physical meaning. Further efforts to force curve c to fit curve a for several values of $k_c^{\ominus}$ and α, in terms of numerical calculation, failed. Therefore, it is concluded that a smooth increase in the current does not result solely from kinetics of the charge transfer but some other chemical reaction observed experimentally in curve a.

Since the current is proportional to a rate of a chemical reaction, the following equation can be written, assuming constant concentration of sulfide at the surface, as

$$I = k'(c_{Ag^+})_s^r$$
(9)

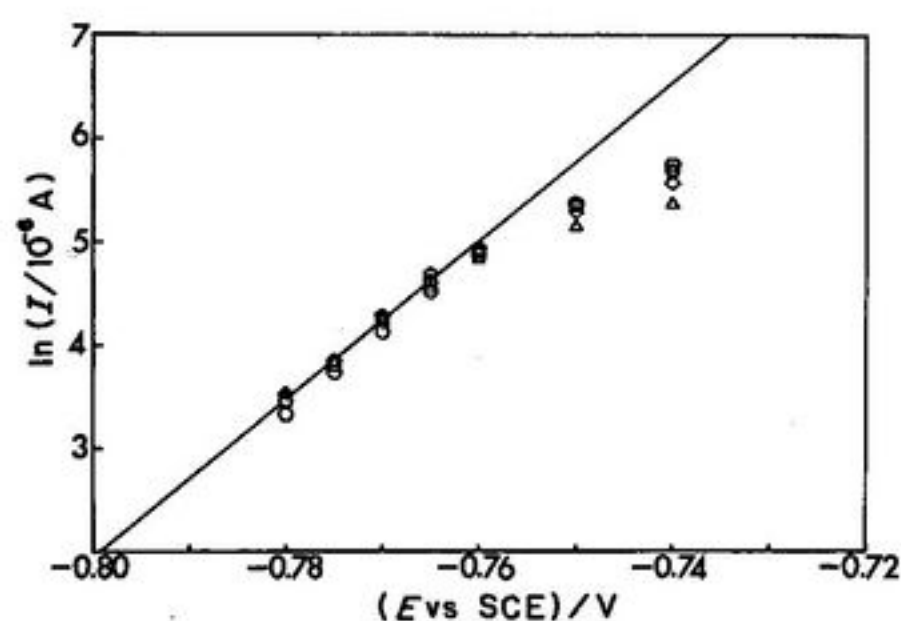In order to find the order, r, of the reaction, the logarithm of current values at the

Fig. 2. Variations of $\ln(I/10^{-6} \text{A})$ with E in the 5.31×10^{-4} mol dm^{-3} sodium sulfide solution at rotation speeds of: ($\triangle$) 400 rpm; ($\lozenge$) 900 rpm; ($\circ$) 1600 rpm; ($\circ$) 2500 rpm; ($\bigcirc$) 3600 rpm.

foot of the kinetically controlled waves were plotted against E (Fig. 2). This is equivalent to assuming that the charge-transfer process is reversible at the foot of the wave, but that the current is limited by an irreversible chemical reaction which (see below) is a surface reaction. Values of E at the foot of the wave determine the concentration of silver ions at the electrode surface (eqn. 1), because the charge-transfer kinetics have little influence on currents at the foot of the waves, as discussed in the previous section.

Then eqn. (9) becomes

$$\ln(I/k'') = rFE/RT \tag{10}$$

Values of $r = 2$ were obtained from the plots and are given in Table 1 for five concentrations of sulfide solutions. Hence eqn. (9) can be rewritten, combined with reaction (III), as

$$I = FAk \left(c_{\text{Ag}^+} \right)_s^2 \left(c_{\text{S}^{2-}} \right)_s \tag{11}$$

Since the dimensions of k are ms$^{-1}M^{-2}$, when M is molarity, k is the rate constant of a surface reaction. The conclusion that reaction (III) is a surface reaction is further supported by the fact that silver sulfide does not escape from the electrode

TABLE 1

Reaction order, r, for silver ion obtained from plots of $\ln(I/10^{-6} \text{A})$ vs. E

$c_0 \times 10^4/\text{mol dm}^{-3}$	Reaction order, r
1.77	1.91
3.54	1.89
5.31	2.06
7.08	2.06
8.85	1.91
Average	1.97

surface to the bulk solution during anodic polarization [10], see above.

If reaction (III) were controlled by a volume reaction in place of a surface reaction, the order r should be 1.5. This can be demonstrated as follows. The mass transport equation for the case of fast chemical reactions within the reaction layer $(0 \leqslant x \leqslant \mu)$ is given by [12]

$$d^2 c_{Ag^+}/dx^2 = k'''(c_{Ag^+})^2(c_{X^{2-}}) \tag{12}$$

At the foot of the anodic wave, the region being considered here, the concentration of sulfide ion is constant in the vicinity of the electrode, which is expressed as $(c_{S^2})_\mu$. Multiplying dc_{Ag^+}/dx on both sides and integrating the resulting equation from 0 to μ yields:

$$(I/F)^2 = (2/3)k'''D^2(c_{S^{2-}})_\mu(c_{Ag^+})_s^3$$

which would yield a reaction order of 1.5. This is obviously inconsistent with the experimentally determined value of r. It has been reported by Bockris et al. [16] that a dissolution–precipitation mechanism of calomel formation on the mercury electrode contains the rate-determining step of a homogeneous chemical reaction of disproportionation of the Hg_2Cl^+ ion.

The expression for the current complicated by the surface-chemical reaction can be derived by substituting eqns. (1) and (4) into eqn. (11) if the charge-transfer step takes place reversibly. Then, it becomes

$$\ln(I/I_d - I) = \ln\left(FAkc_0(c^\ominus)^2/I_d\right) + 2F(E - E^{0\prime})/RT \tag{3}$$

Plots of $\ln(I/I_d - I)$ against E for the foot of the wave are shown in Fig. 3. Linearity is observed at the foot of the wave and slopes of the lines are equal to $2F/RT$ and values of $FAkc_0/I_d$ can be evaluated from the intercept through use of $E^{0\prime} = 0.555$ V. Taking into account that I_d is given by $2 \times 6.2 \times 10^{-4}$ $FAc_0D^{2/3}\nu^{-1/6}\omega^{1/2}$ [12], we notice that $FAkc_0/I_d$ should be proportional to $\omega^{1/2}$, where ω is the rotation rate (rad s^{-1}) of the RDE. Variation of $FAkc_0/I_d$ with $\omega^{-1/2}$
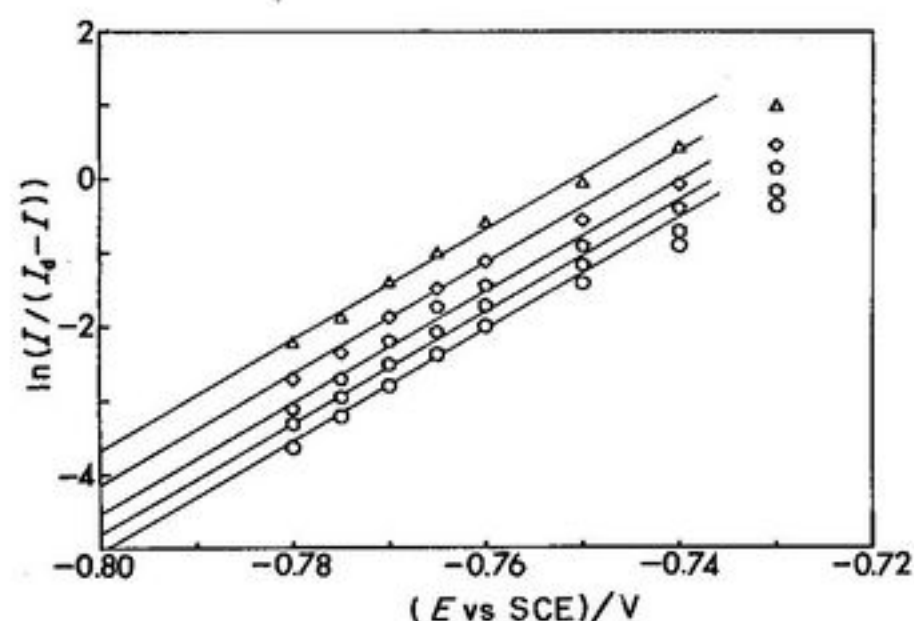

Fig. 3. Plots of $\ln(I/(I_d - I))$ vs. E in the 5.31×10^{-4} mol dm^{-3} sodium sulfide solution at rotation speeds of: ($\triangle$) 400 rpm; ($\diamond$) 900 rpm; ($\circ$) 1600 rpm; ($\circ$) 2500 rpm; ($\bigcirc$) 3600 rpm.
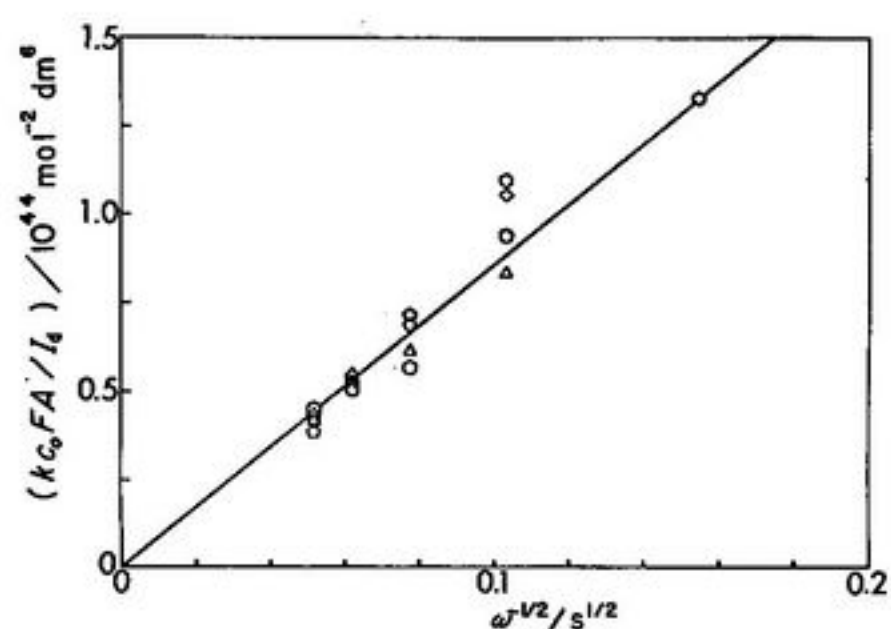
Fig. 4. Dependence of $kc_0 FA/I_d$ on inverse square roots of rotation speeds in: ($\triangle$) 1.77; ($\lozenge$) 3.54; ($\circ$) 5.31; ($\mathbf{o}$) 7.08; ($\bigcirc$) 8.85×10^{-4} mol dm^{-3} sodium sulfide solutions.

is shown in Fig. 4. The slope of the line is $0.807D^{-1/2}\nu^{1/6}k$, and hence $k = 2.0 \times 10^{43}$ cm s^{-1} M^{-2}. If the units of k are converted into cm s^{-1} per atom, k is given by 5.6×10^{-5} cm s^{-1} per atom, which corresponds to a conditional electrode reaction rate constant for the totally irreversible system. This linearity also demonstrates that the reaction order of S^{2-} is unity, since if c_0 were other than first order, non-linearity would result in these plots as a result of the various concentrations of sulfide employed.

Curve d in Fig. 1 is the wave calculated from eqn. (13) with the value of k thus obtained. It overlaps the experimental curve a at the lower part of the wave, while deviating from it at the upper part.

As described previously, consideration of the kinetics of charge transfer contributes to the shape of the upper part of the wave, hence the deviation of curve d from curve a can be attributed to the kinetics of the charge transfer. In fact, the charge transfer of Ag/Ag^+ takes place quasi-reversibly [17], and hence this effect can be taken into account.

To derive the expression for a current controlled by both the surface-chemical reaction (at the foot of the wave) and the charge-transfer reaction (at the upper portion of the wave), we combine eqns. (4), (7) and (11) by eliminating $(c_{Ag^+})_s$ as well as $(c_{S^{2-}})_s$. By simple calculation, we have

$$\ln Hk_c^\ominus = -(1-\alpha)F(E - E^{0\prime})/RT \tag{14}$$

where

$$H = (2FA/I)\left[c^\ominus - \{(I_d/FAkc_0)(I/(I_d - I))\}^{1/2} \exp\{-F(E - E^{0\prime})/RT\}\right] \tag{15}$$

All of the variables involved in H are known since k has already been evaluated. Plots of $\ln(H/\text{cm}^{-1}\text{s})$ vs. E in Fig. 5 shows that $\ln(H/\text{cm}^{-1}\text{s})$ is independent of the variation of E. This requires (eqn. 13) that $\alpha = 1$, and results in a value of
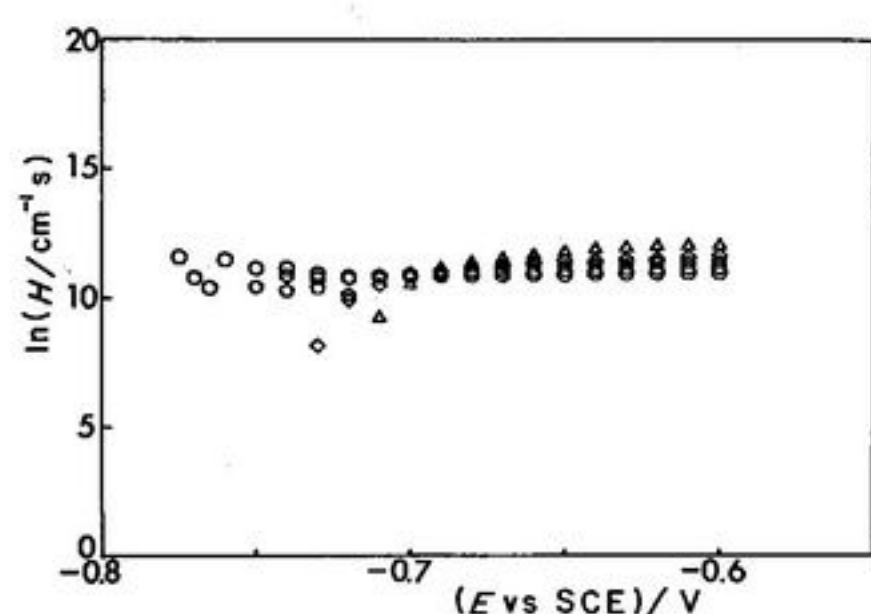
Fig. 5. Variations of $\ln(H/\text{cm}^{-1}\,\text{s})$ with E in 5.31×10^{-4} mol dm^{-3} sodium sulfide solution at rotation speeds of: ($\triangle$) 400 rpm; ($\Diamond$) 900 rpm; ($\circ$) 1600 rpm; ($\circ$) 2500 rpm; ($\bigcirc$) 3600 rpm.

$k_c^{\ominus} = 2.3 \times 10^{-5}$ cm s^{-1}. Literature values of the kinetic parameters are $k_c^{\ominus} = 2.3 \times 10^{-3}$ cm s^{-1}, $\alpha = 0.55$ [18] and $k_c^{\ominus} = 1.5 \times 10^{-4}$ cm s^{-1} [19], where $k_c^{\ominus}$ values have been evaluated from the exchange densities and α has been assumed to be 0.5.

The result, $\alpha = 1$, implies that all the electrical part of the activation energy for the charge transfer contributes to the reduction of silver ions to silver atoms, while the oxidation of silver atoms proceeds by surmounting the energy barrier which is associated only with structural chemical changes [20]. Therefore, the reduction takes place as if it were a chemical reaction independent of applied potential. This is equivalent to the intuitive reaction model that sulfide ions at the electrode surface stimulate silver atoms to make the charge transfer occur and then form silver sulfide as if they plucked silver atoms from the silver lattice. In other words, the chemical affinity of sulfide and silver predominantly overcomes the strength of the electric field due to the applied potential difference in the double layer. A voltammogram calculated from eqns. (14) and (15) by means of the iterated numerical computation is drawn in Fig. 1 as curve e, and is in excellent agreement with the experimentally obtained curve a.

Since the major S-containing anion in 0.2 M NaOH solution is HS$^-$ $((c_{\text{HS}^-}/c_{\text{S}^{2-}}) \approx 7)$, it may be necessary to take into account the dissociation rate of HS$^-$ into H$^+$ and S^{2-}. S^{2-} would then correspond to the electroactive species in the sense of a preceding chemical reaction. Then the thickness of the reaction layer is defined as $\mu = \sqrt{D/k_f[H^+]}$ [21], where k_f is the formation rate constant of HS$^-$ from H$^+$ and S^{2-}. Thus, the dissociation rate, v_1, the change in the number of moles of HS$^-$ within the reaction layer, is given by $v_1 = k_d c_{\text{HS}^-} A\mu$, where k_d is the dissociation rate constant. Since the rate of formation of weak acids is, in general, controlled by diffusion, the rate constant may be estimated as 10^{11} s mol^{-1} dm^3 [20]. Then v_1 becomes 3×10^{-5} mol s^{-1} by use of the formation constant of HS$^-$, 10^{14} mol^{-1} dm^3. On the other hand, the rate of the surface reaction, v_2, is equal to I/F, by eqn. (11) and is $< 2 \times 10^{-8}$ mol s^{-1}. Comparison of v_2 with v_1 thus makes it unlikely that kinetics of dissociation of HS$^-$ participate in the overall reaction.

CONCLUSION

Formation of silver sulfide from silver and sulfide can be separated formally into two reactions, (II) and (III). We cannot differentiate whether or not reactions (II) and (III) really take place stepwise. Since the known kinetic equations are for charge transfer reaction (II) or chemical reaction (III), combining the former with the latter allows us to discuss the overall reaction quantitatively.

If reactions (II) and (III) are in equilibrium, the current is expressed by eqn. (6), resulting in the calculated curve b of Fig. 1. The wave form controlled by the charge-transfer step in the chemical equilibrium is given by curve c. Both curves are different from the experimental curve a in overall morphology. It was found in Fig. 2 that the stoichiometric number of reaction (III) was 2, indicating the surface-chemical reaction. The surface-chemical reaction rate constant was obtained in Fig. 3. This permitted the calculation of the $I-E$ curve of curve d, Fig. 1. These considerations, plus consideration of the kinetics of reaction (II) results in curve e, which is consistent with the experimentally obtained curve a. It seems to us that the above procedures should play a vital role in the analysis of anodic dissolution waves for any other systems.

The significant results of examining the $I-E$ curves are that reaction (III) occurs on the electrode surface and that the charge-transfer coefficient is equal to unity. This not only accounts for features (a)–(e) of the $I-E$ curves described in the Introduction, but also provides us with a profile of the activation potential energy for reaction (I).

ACKNOWLEDGEMENT

REFERENCES

1 T. Erdey-Grúz, Kinetics of Electrode Processes, Wiley-Interscience, New York, 1972, p. 304.
2 T. Erdey-Grúz, Kinetics of Electrode Processes, Wiley-Interscience, New York, 1972, Ch.7.
3 R.D. Armstrong and G.M. Bulman, J. Electroanal. Chem., 25 (1970) 121.
4 J.O'M. Bockris, Z. Nagy and A. Damjanovic, J. Electrochem. Soc., 119 (1972) 285.
5 R.D. Armstrong, J.D. Milewski, W.P. Race and H.R. Thirsk, J. Electroanal. Chem., 21 (1969) 517.
6 N.A. Hampson and R.J. Latham, J. Electroanal. Chem., 32 (1971) 337.
7 A. Damjanovic and A.T. Ward in J.O'M. Bockris (Ed.), International Review of Science, Physical Chemistry Series Two, Vol. 6, Butterworths, London–Boston, 1976, Ch. 3.
8 R.D. Armstrong and M.F. Bell, Specialist Periodical Report, Electrochemistry, No. 4, The Chemical Society, London, 1974, Ch. 1.
9 R.D. Armstrong, K. Edmondson and G.D. West, Specialist Periodical Report, Electrochemistry, No. 4, The chemical Society, London, 1974, Ch. 2.
10 K. Shimizu, K. Aoki and R.A. Osteryoung, J. Electroanal. Chem., 129 (1981) 159.
11 J. Heyrovský and J. Kůta, Principles of Polarography, Academic Press, New York, 1966, p. 172.
12 Yu.V. Pleskov and V.Yu. Filinovskii, The Rotating Disk Electrode, Studies in Soviet Science, Moscow, 1976.

13 J. Bjerrum, G. Schwarzenbach and L.G. Sillen, Stability Constants of Metal–ion Complexes, The Chemical Society, London, 1958.

14 V.G. Schwarzenbach and W. Widmer, Hel. Chem. Acta, 49 (1966) 111.

15 N.A. Shumilova and G.V. Zhutaeva in A.J. Bard (Ed.), Encyclopedia of Electrochemistry of Elements, Vol. 8, Marcel Dekker, New York, 1978, p. 5.

16 J.O'M. Bockris, M.A.V. Devanathan and A.K.N. Reddy, Proc. R. Soc., A279 (1964) 327.

17 R. Tamamushi, Kinetics of Electrode Reactions of Metallic Compounds, Butterworths, Boston, (1975).

18 W. Mehl and J.O'M. Bockris, J. Chem. Phys., 27 (1957) 818.

19 R.J. Brodd, J. Res. Nat. Bur. Stand., 65A (1961) 275.

20 T. Erdey-Grúz, Kinetics of Electrode Processes, Wiley-Interscience, New York, 1972, p. 43.

21 J. Heyrovský and J. Kůta, Principles of Polarography, Academic Press, New York, 1966, p. 365.