relatively unquenched hydrogenated configurations of cupric, as well as divalent nickel disalicylaldehyde.[5] Susceptibility measurements are also being made on phthalocyanines in an attempt to determine whether a change in configuration occurs after hydrogenation.

Summary

From magnetic measurements made on the pyridine solutions of cupric disalicylaldehyde, a mechanism of catalytic hydrogenation has been proposed. The green copper disalicylaldehyde is probably planar while in the red reduced form the aldehyde groups have been changed to alcohol groups and the configuration has become probably tetrahedral. The relatively unstable tetrahedral configuration readily reacts, losing hydrogen, and thereby reverts to the more stable planar form, with a corresponding conversion of the alcohol to aldehyde groups. The observed susceptibilities, chemical behavior, and relative stabilities of the configurations are in accord with this proposal.

CLAREMONT, CALIF.
LOS ANGELES, CALIF.

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[5] See J. H. van Vleck's discussion, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Anodic Waves Involving Electroöxidation of Mercury at the Dropping Mercury Electrode

BY I. M. KOLTHOFF AND C. S. MILLER[1]

In the present study anodic waves due to electroöxidation of mercury have been investigated. Depending on the anodic reactions in the presence of various depolarizers the equations describing the anodic waves may be different. The experiments were carried out with the manual apparatus used in most previous investigations[2] at 25.00 ± 0.05°. The drop time in general was three to four seconds.

The Anodic Wave in the Absence of Depolarizers.—When a mercury electrode is in equilibrium with the surrounding liquid its potential π is given by the expression

$$\pi = C + \frac{RT}{2F} \ln [Hg_2^{++}]_0 = C' + \frac{RT}{2F} \ln [Hg^{++}]_0 \quad (1)$$

in which the subscript zero denotes the concentration (actually the activity) of the mercurous and mercuric ions at the interface of mercury and solution. Upon electroöxidation of mercury in the absence of a depolarizer the metal enters into solution practically entirely in the form of mercurous ions, the mercuric ion concentration being about one-hundredth that of the mercurous ion. The mercurous ion concentration at the surface of the dropping electrode is proportional to the current i, and hence in this case we can write instead of equation (1)

$$\pi = \pi_0 + \frac{RT}{2F} \ln i \quad (2)$$

Since nitrate ions do not depolarize a mercury electrode, the anodic dissolution of the metal was investigated in 0.1 N potassium nitrate solutions. Slightly different results may be expected in acid medium in which the hydrolysis of the mercurous ions is suppressed. The "free dissolution" wave of mercury was found to start at a potential of +0.4 to +0.45 v. (*vs.* S. C. E.). Plotting the values of the potential π against log i yielded a straight line with a slope of 0.032 in good agreement with the theoretical slope of 0.030 according to equation (2). The latter equation, therefore, describes the wave of the free dissolution of mercury. It is also evident that the mercurous ions are divalent; if they were univalent a slope of 0.060 instead of 0.030 would have been found.

The Anodic Wave in the Presence of Depolarizers which Form Slightly Dissociated Soluble Compounds with Mercuric Mercury. A. Thiosulfate as Depolarizer.—The free dissolution wave of mercury starting at a potential of about +0.4 v. marks the end of the application of the dropping electrode in the positive potential region. This wave is shifted to more negative potentials in the presence of substances which have a great affinity for mercurous or mercuric ions or for both. In the presence of such depolarizers well-defined anodic waves are found

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[1] From the experimental part of a thesis submitted by Carl S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the doctor's degree (1940).

[2] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

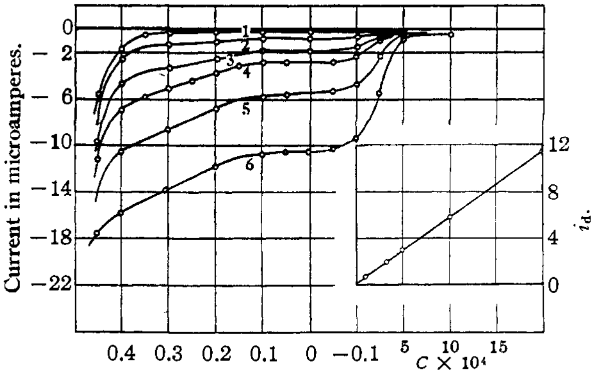

Fig. 1.—Anodic waves of thiosulfate in 0.1 *N* KNO_3–$Na_2S_2O_3$, concns.: Curve 1, 0; 2, 1 × 10^{-4} *M;* 3, 3 × 10^{-4}; 4, 5 × 10^{-4}; 5, 10 × 10^{-4} *M;* 6, 20 × 10^{-4} *M.*

several of which have been mentioned by Revenda,[3] who reported their characteristics from a qualitative point of view. We have investigated the characteristics of the waves more from physicochemical and analytical viewpoints. Upon electroöxidation of mercury in the presence of thiosulfate ions the metal goes into solution in the form of a mercuric complex, as is shown experimentally below. The composition of such a complex can be derived from an analysis of the waves at the dropping electrode. The reaction upon electroöxidation of mercury in the presence of thiosulfate can be written in the general form

$$aS_2O_3^{=} + b\text{Hg} \rightleftharpoons \text{Hg}_b(S_2O_3)_a^{2(a-b)-} + (2b)e \qquad (3)$$

The complex ion dissociates according to

$$\text{Hg}_b(S_2O_3)_a^{2(a-b)-} \rightleftharpoons b\text{Hg}^{++} + aS_2O_3^{=} \qquad (4)$$

and

$$\frac{[\text{Hg}^{++}]^b[S_2O_3^{-}]^a}{[\text{Hg}_b(S_2O_3)_a^{2(a-b)-}]} = K \qquad (5)$$

$$[\text{Hg}^{++}] = \sqrt[b]{K\frac{[\text{Hg}_b(S_2O_3)_a^{2(a-b)-}]}{[S_2O_3^{-}]^a}} \qquad (6)$$

Introducing this relation into equation (1) we find

$$\pi = C'' + \frac{RT}{2F}\frac{1}{b}\ln\frac{[\text{Hg}_b(S_2O_3)_a^{2(a-b)-}]_0}{[S_2O_3^{=}]_0^a} \qquad (7)$$

in which the subscript zero again denotes the concentration at the surface of the dropping mercury. It is easily shown[4] that

$$[S_2O_3^{=}]_0 = \frac{i_d - i}{k'} \text{ and } [\text{Hg}_b(S_2O_3)_a^{2(a-b)-}]_0 = k''i$$

Introducing these relations into expression (7) yields

$$\pi = \pi_0 + \frac{RT}{2F}\frac{1}{b}\ln\frac{i}{(i_d - i)^a} \qquad (8)$$

Plotting log $i/(i_d - i)^a$ against the potential should yield a straight line. Since *a* is a simple whole number, its value is readily found. From the slope of the line the value of *b* is calculated.

A series of current–voltage (c. v.) curves were run in 0.1 *N* potassium nitrate, the concentration of the thiosulfate varying between 0 and 2 × 10^{-3} *M*. The results are given in Fig. 1.

After correction for the residual current of the supporting electrolyte, well-defined diffusion currents were obtained which were strictly proportional to the concentration. Hence, thiosulfate can be determined accurately by polarographic analysis. Revenda[3] states that the wave found with 0.001 *N* thiosulfate starts at −0.26 v. (*vs.* S. C. E.); we found that it starts at about −0.20 v. Assuming that the diffusion coefficient of the thiosulfate ions is the same as that of sulfate ions (1.08 × 10^{-5} cm.^{2} sec.$^{-1}$) we calculated with the aid of the Ilkovic equation[2,5] that one Faraday of electricity is involved in the anodic interaction between 1 mole of thiosulfate and mercury. This gave a strong indication that *b* in equation (3) is equal to 1 and *a* to 2. This conclusion was substantiated by plotting the potential after correction for the *iR* effect against log $i/(i_d - i)^a$. The resistance *R* of the cell was about 300 ohms and the *iR* correction was extremely small. The results of one analysis are given in Fig. 2. A straight line relation was obtained with a value of *a* equal to 2, but a curve

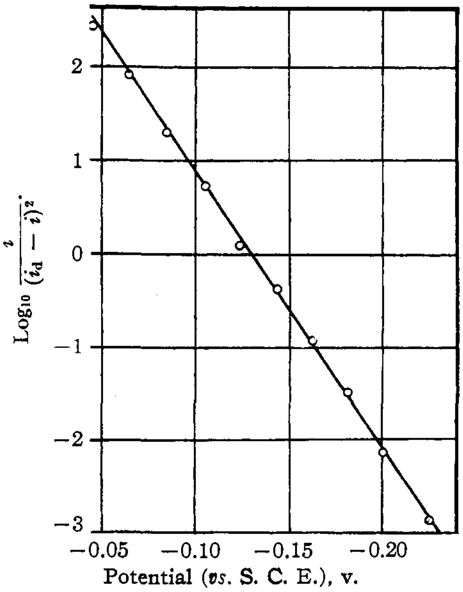

Fig. 2.—Analysis of thiosulfate wave.

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[3] J. Revenda, *Collection Czechoslov. Chem. Commun.*, **6**, 453 (1934).

[4] See ref. 2, and especially J. Heyrovsky and D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **7**, 198 (1935).

[5] D. Ilkovic, *ibid.*, **6**, 498 (1934).

was found when a was taken equal to 1. The slope of the straight line was equal to 0.033 in good agreement with the theoretical slope of 0.030 when b is equal to 1. Thus, the equation of the wave is given by

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^2} \qquad (9)$$

Equation (9) shows that the *half wave potential of thiosulfate is not* a constant. Heyrovsky and Ilkovic[4] report a half wave potential of −0.19 v. (*vs.* S. C. E.), but this value is not constant and changes with the concentration of thiosulfate or with i_d according to

$$\pi_{1/2} = \pi_0' - \frac{RT}{2F} \ln i_d \qquad (10)$$

In 0.002 M thiosulfate we observed a diffusion current of 10.2 microamperes and a half wave potential of −0.152 v. (*vs.* S. C. E.). The half wave potentials at smaller thiosulfate concentrations calculated with the aid of equation (10) agreed well with the observed values as shown by the following data: $i_d = 5.2$; $\pi_{1/2\,\text{obsd.}} = -0.145$; (calcd. −0.141); $i_d = 2.5$; $\pi_{1/2\,\text{obsd.}} = -0.134$; (calcd. −0.133); $i_d = 1.6$; $\pi_{1/2\,\text{obsd.}} = -0.127$; (calcd. −0.127).

All the results obtained so far indicate that the anodic reaction is given by

$$2S_2O_3^{=} + Hg \rightleftharpoons Hg(S_2O_3)_2^{=} + 2e \qquad (11)$$

It should be pointed out that the oxidation of thiosulfate to tetrathionate

$$2S_2O_3^{=} \longrightarrow S_4O_6^{=} + 2e \qquad (12)$$

also might account for the phenomena even though this reaction is irreversible. Conclusive evidence that the reaction occurs according to equation (11) was obtained by an electrolysis experiment at a quiet mercury electrode. A solution containing exactly one millimole of thiosulfate in about 25 ml. of 0.1 N potassium nitrate was electrolyzed in the polarographic cell using a large pool of mercury at the bottom as the anode, and an outside saturated calomel electrode as the cathode. During the electrolysis the anode potential was maintained at 0.00 v. (*vs.* S. C. E.) and the amount of electricity which passed was measured with the aid of a hydrogen coulometer connected in series with the cell. In order to prevent air oxidation of the mercury a stream of nitrogen was passed through during the electrolysis. After a current equivalent to 0.384 micro-faraday had passed, the electrolysis was discontinued and the solution analyzed with the aid of the dropping electrode. The results showed that the anodic reaction does not occur according to eq. (12). The ratio of the cathodic to the sum of the cathodic and anodic diffusion currents was 8.7/22.9 = 0.38 which, again, is equal to the number of micro-faradays passed during the electrolysis. The results obtained agree quantitatively with a reaction according to equation (11). That no tetrathionate was formed during the electrolysis was finally shown by adding an excess of potassium iodide to the solution after electrolysis and titrating with iodine. The same amount of iodine was used as before electrolysis.

Inspection of Fig. 1 shows that when the potential is increased the diffusion current of thiosulfate no longer remains constant but that a second drawn out wave between +0.15 and +0.4 v. is obtained which coincides with the "free dissolution" wave of mercury before the second diffusion current is reached. The appearance of the second wave corresponds to that of an irreversible reaction. If on the second wave mercury went into solution with formation of mercuric thiosulfate HgS_2O_3 the reaction would be expected to be reversible and the slope of the wave would be much steeper. Neither is it possible that the thiosulfate in the complex $Hg(S_2O_3)_2^{=}$ ion formed on the first wave is oxidized to tetrathionate with the liberation of mercuric ions, since the latter would be reduced to mercury at potentials on the second wave. Hence the number of electrons liberated due to oxidation of the thiosulfate according to equation (12) would be equal to that taken up by the mercuric ions. The net anodic current would not increase after the first diffusion current of thiosulfate. Therefore, it seems most probable that the thiosulfate on the second wave is oxidized to sulfite[6] according to the equation

$$3H_2O + S_2O_3^{=} \longrightarrow H_2SO_3 + 2H^+ + 4e \qquad (13)$$

B. Sulfite as Depolarizer.—The waves start at about −0.10 v. (*vs.* S. C. E.). The diffusion current after correction for the residual current is proportional to the sulfite concentration. Only one wave is obtained in a mixture of thiosulfate and sulfite. The sulfite waves were analyzed in a way similar to those of thiosulfate, and it was shown that the anodic reaction is given by the equation

$$2SO_3^{=} + Hg \longrightarrow Hg(SO_3)_2^{=} + 2e \qquad (14)$$

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[6] *Cf.* W. M. Latimer, "Oxidation Potentials," Prentice-Hall Co., Inc., New York, N. Y., 1938.

The equation of the wave is given quantitatively by expression (9). Again, the half wave potential is not found constant, but it shifts with i_d in the same way as that of thiosulfate (equation 10). In 2×10^{-3} M sulfite solution in 0.1 N potassium nitrate $\pi^1{}_{1/2}$ was found equal to -0.015 v. (*vs.* S. C. E.); in 10^{-3} M solution -0.007 v. (calcd. -0.008 v.); in 5×10^{-4} M solution $+ 0.006$ v. (calcd. $+ 0.003$ v.).

C. **Hydroxide as Depolarizer.**—The diffusion currents of hydroxyl ions are much greater than those of equinormal solutions of sulfite or thiosulfate, as the diffusion coefficient of the hydroxyl ions is so much greater than those of the other two anions. Analysis of the current voltage curves showed that the anodic reaction is given by the equation

$$2OH^- + Hg \rightleftarrows Hg(OH)_2 + 2e \qquad (15)$$

The mercuric hydroxide remained in solution when the hydroxyl ion concentration was smaller than about 0.001 N. At higher concentrations a solid film of mercuric hydroxide is formed at the surface of the dropping mercury. The equation of the wave, again, is given by the expression (9) at hydroxyl ion concentrations at which mercuric hydroxide does not separate at the surface of the mercury. The shift of the half wave potential with i_d is given by expression (10). In 0.001 N sodium hydroxide solution we found a half wave potential of $+0.080$ v. (*vs.* S. C. E.) and in 0.0005 N solution of $+0.091$ v. (calcd. $+0.091$ v.). The concentration of hydroxyl ions can be determined polarographically if the solution is well protected from carbon dioxide from the air. In agreement with Revenda,[3] we found that the hydroxyl wave starts at a potential of about 0.00 v.

D. **Thiocyanate as Depolarizer.**—Anodic thiocyanate waves start at potentials of about $+0.14$ v. (S. C. E.). The diffusion current (after correction for the residual current) was found proportional to the thiocyanate concentration. The net anodic reaction can be given by the equation

$$2CNS^- + Hg \rightleftarrows Hg(CNS)_2 + 2e$$

Plotting the potential π against log $i/(i_d - i)^2$ yielded a straight line with a slope of 0.038 instead of the theoretical slope of 0.030. This deviation undoubtedly is due to the fact that various complex ions, such as $Hg(CNS)_4^{=}$, $Hg(CNS)_3^-$, $Hg(CNS)^+$, in addition to $Hg(CNS)_2$, are present on the surface of the dropping mercury at various points of the wave. An exact analysis of the wave requires a knowledge of the various complex constants and becomes very involved. The half wave potential was found to shift with i_d according to equation (10). In 0.001 M thiocyanate solution it was found equal to $+0.18$ v.

E. **Cyanide.**—In order to prevent the hydrolysis of cyanide ions and loss of hydrogen cyanide, cyanide is best determined in dilute (0.01 to 0.1 N) solutions of sodium hydroxide. In 0.0005 M cyanide solution the wave was found to start at about -0.45 v., and the diffusion current was found proportional to the cyanide concentration. The net anodic reaction is given by: $2CN^- + Hg \rightleftarrows Hg(CN)_2 + 2e$. A well-defined diffusion current is found before the hydroxyl wave starts.

The Anodic Wave in the Presence of Depolarizers which Form Slightly Soluble Mercurous Compounds.—If a slightly soluble mercurous compound, say mercurous chloride, separates on the surface of the dropping mercury during the electrolysis, and the film does not interfere with the latter, (v. i.) it is easily derived from expression (1) that the equation of the anodic wave is given by

$$\pi = C + \frac{RT}{2F} \ln\,[Hg_2{}^{++}]_0 = C + \frac{RT}{2F} \ln \frac{S_{Hg_2Cl_2}}{[Cl^-]_0} =$$
$$C' - \frac{RT}{F} \ln\,[Cl^-]_0 = \pi_0'''' - \frac{RT}{F} \ln\,(i_d - i) \qquad (16)$$

in which $S_{Hg_2Cl_2}$ represents the solubility product of mercurous chloride. If a slightly soluble mercuric compound separates, the same expression should hold.

Revenda[3] has shown already that chloride, bromide, iodide and sulfide yield anodic waves at the dropping electrode. In some cases he observed abnormal slopes of the current–voltage curves the cause of which has been studied in the present paper.

A. **Chloride.**—Current–voltage curves of chloride were determined in 0.1 N potassium nitrate solutions. In agreement with Revenda[3] it was found that the waves start at a potential of about $+ 0.2$ v. (*vs.* S. C. E.), this potential shifting to more negative values with increasing chloride concentration. At chloride concentration between 10^{-4} and 2×10^{-3} N the diffusion current, after correction for the residual current, was found exactly proportional to the concentration. At chloride concentration greater than 10^{-3} N the waves at higher values of the current have a somewhat abnormal appearance which is caused by a film of calomel around the mercury drop. As soon as this interference occurs, equation (16) no longer determines the slope of the wave. Neither does this equation determine the slope at the very beginning of the wave because a definite current must flow through before calomel separates in the solid form. Thus equation (16) has a limited application only. Plotting the values of the potential against log (i_d − i) we found in 5 × 10^{-4} N chloride solutions at potentials between 0.26 and 0.34 v. a straight line with a slope of 0.054, the latter being in fair agreement with the theoretical value of 0.060.

From equation (16) it is seen that the half wave potential is not constant, but varies with i_d; $\pi_{1/2} = \pi_0'''' - \frac{RT}{F} \ln i_d$. At chloride concentration smaller than 1.5 × 10^{-3} N, we actually found the half wave potential to change according to this expression. For example we found at [Cl^-] = 1.5 × 10^{-3} N, $\pi_{1/2}$ = +0.243 v; [Cl^-] = 10^{-3} N, $\pi_{1/2}$ = +0.254 v. (calcd. 0.252); [Cl^-] = 5 × 10^{-4} N, $\pi_{1/2}$ = +0.267 v. (calcd. 0.269).

B. **Bromide.**—Some typical bromide waves are shown in Fig. 3. It is seen that at bromide concentrations larger than 10^{-3} N the c. v. curve shows two distinct waves. If the diffusion current corresponding to the horizontal portion of the second wave after correction for the residual current is plotted against the concentration a straight line is found. Hence, bromide can be determined polarographically.

The appearance of two waves in some bromide solutions has been noticed already by Revenda.[3] He attributes the phenomenon to the simultaneous formation of mercurous and mercuric bromide; however, this explanation cannot account for the facts observed. We obtained conclusive evidence that the abnormality is due to the formation of a film of mercurous bromide around the mercury drop which interferes with the further electrolysis. Regardless of the concentration, we always found, using the same capillary, the end of the first wave in the neighborhood of 6 microamp. By mounting a microscope with proper illumination before the drop we could not observe a film at this current, but a distinct yellow film of mercurous bromide around the drop was seen when the current was 25 microamp. or greater. With Majer[7] we conclude that when solid electrolysis products are formed as films on the surface of the dropping electrode, the apparent resistance may increase by very large amounts. If the resistance suddenly would become 25,000 ohms when the current is equal to 6 microamp., the iR drop would correspond to a shift of the wave of 0.15 v. to more positive potentials. This is the order of magnitude which was actually found (Fig. 3). In agreement with this interpretation is the observation that the location of the first wave remained unchanged when the potassium nitrate concentration was increased from 0.1 to 2 N, while the second wave continuously came closer to the first wave with increasing salt concentration. Very striking and of importance from a quantitative point of view is the effect of a trace of gelatin. As shown in Fig. 4, the first apparent diffusion current is completely eliminated when 0.01% of gelatin is added to a 0.002 N bromide solution in 0.1 N potassium nitrate. In the polarographic determination of bromide it is recommended to add a trace of gelatin to the solution. Under these conditions a smooth wave with a well-defined diffusion current is obtained. Apparently, the gelatin prevents the formation of a coherent film of mercurous bromide at the surface of the drop.

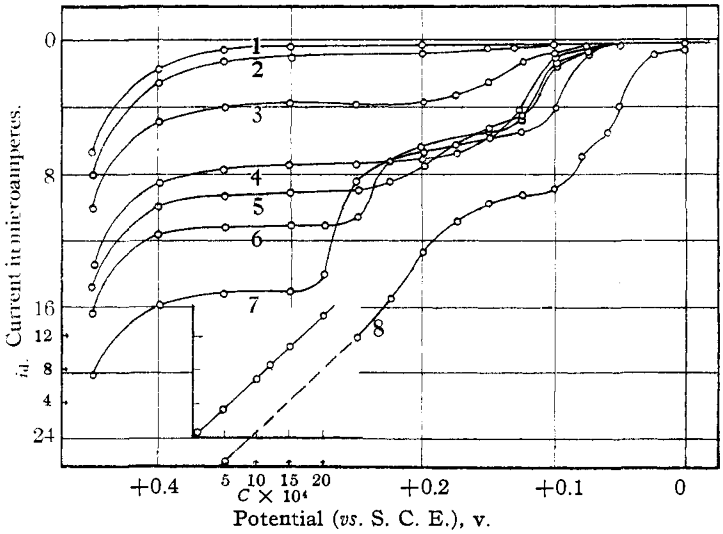

Fig. 3.—Anodic bromide waves in 0.1 N KNO_3; bromide concentration: Curve 1, 0; 2, 1 × 10^{-4} M; 3, 5 × 10^{-4}; 4, 10 × 10^{-4}; 5, 12 × 10^{-4}; 6, 15 × 10^{-4}; 7, 20 × 10^{-4}; 8, 10^{-2} M.

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(7) V. Majer, *Collection Czechoslov. Chem. Commun.*, **7**, 146, 215 (1935); **9**, 360 (1937).

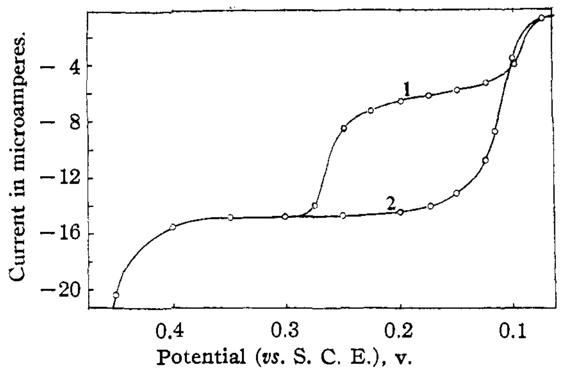

Fig. 4.—Effect of gelatin on the bromide waves in 0.1 *N* KNO_3: Curve 1, KBr 2 × 10^{-3} *M*; 2, the same with 0.01% gelatin.

Figure 5 gives c. v. curves of the medium (0.1 *N* nitrate) and of 0.002 *N* bromide in the same medium together with parts of the corresponding electrocapillary curves. The latter were determined by measuring the drop time at various potentials as indicated by circles in the figure. Going from the isoelectric point (about −0.55 v.) to more positive potentials, the mercury becomes more and more capillary active. At a potential at which the anodic wave starts the electrode becomes depolarized and the surface tension changes very slightly until a potential is reached at which the second wave yields a diffusion current. From this point on the two electrocapillary curves coincide. The electrocapillary behavior harmonizes with the view that the film causes a large resistance around the drop and that the film resistance breaks down at potentials where the second wave starts.

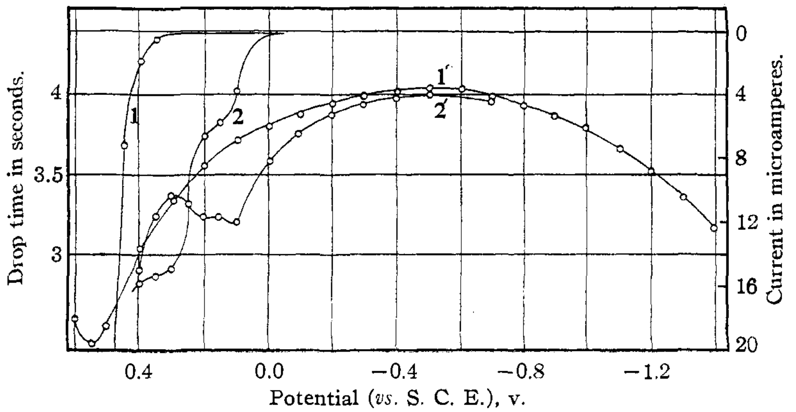

Fig. 5.—1, Current-voltage curve of 0.1 *N* KNO_3; 2, as 1, with 2 × 10^{-3} *M* KBr; 1', electrocapillary curve of 1; 2', electrocapillary curve of 2.

C. Iodide.—The characteristics of anodic iodide waves have not been discussed by Revenda.[3] Some iodide waves, which start at a potential of about −0.1 v., are shown in Fig. 6. The waves have a normal appearance until the diffusion current is reached. When the latter is equal to or greater than 10 microamp. (drop time four seconds), the i_d is ill-defined and changes in a highly irregular way with increasing positive potential. From the characteristics of the capillary we calculated that the film of mercurous iodide around the drop at a current of 10 microamp. has a thickness of 7 to 8 molecules. Microscopically, the film was invisible, but with the proper illumination a yellow film of mercurous iodide could be seen when the current was equal to about 25 microamp. At the point where the first abnormalities in the c. v. curve appeared the growth of the drop was seen to be irregular and the drop pulsated. It is remarkable that the abnormalities always appear near and at the diffusion current region, when the interfacial iodide concentration is very small. The properties of the mercurous iodide film must be quite different from those of the mercurous bromide film. The latter caused two distinct waves on the c. v. curve of bromide, while in the case of iodide the wave keeps a normal appearance until the diffusion current is reached (see Curve IV in Fig. 5). In the case of bromide the film caused a definite polarization of the drop while in the case of iodide the film seems to give rise to irregular stirring around

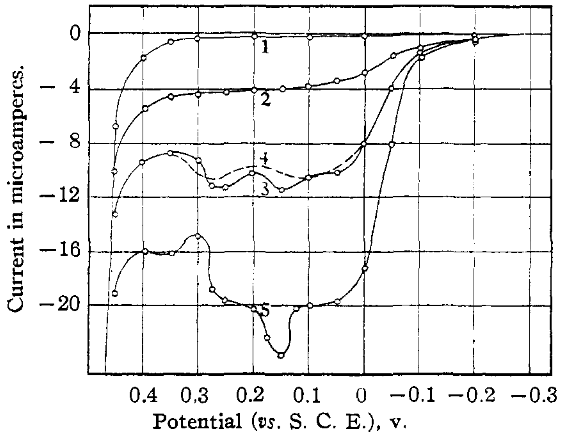

Fig. 6.—Anodic iodide waves in 0.1 *N* KNO_3; iodide concentration: Curve 1, 0; 2, 5 × 10^{-4} *M*; 3, 10 × 10^{-4}; 4, 10 × 10^{-4} and methyl red 10^{-4} *M*; 5, 20 × 10^{-4} *M*.

the drop on the diffusion current region. At present, it is not possible to account for the difference in properties of the films of mercurous bromide and iodide at the dropping electrode.

The presence of gelatin was found to improve the shape of the diffusion current line. In the quantitative polarographic determination of iodide it is recommended to use a 0.05% solution of gelatin in 0.1 N potassium nitrate as a supporting electrolyte. The diffusion current is then found proportional to the concentration of iodide when the latter is equal to or smaller than 1.5×10^{-3} N ($t = 4$ sec.). When the drop time is decreased this limiting concentration becomes larger.

D. Sulfide.—In agreement with Revenda[3] we found that sulfide waves at concentrations of the order of 10^{-3} M start at a potential of about −0.6 v. (*vs.* S. C. E.). At the start the waves were found to have a fairly steep slope but at currents greater than about 2 microamp. the waves became flattened out. At the beginning of the wave the mercuric sulfide formed undoubtedly remains in solution in the form of the complex ion $HgS_2^{=}$. At larger currents the mercuric sulfide deposits at the surface of the electrode, causing the wave to deviate from its theoretical slope. The diffusion currents were well defined and found to be proportional to the concentration in the investigated range between 5×10^{-4} and 3×10^{-3} M. These waves were determined in air-free solutions using 0.1 N sodium hydroxide as a supporting electrolyte.

Summary

1. The equation of the anodic waves of thiosulfate, sulfite, hydroxide and thiocyanate ions is given by

$$\pi = \pi_0' + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^2}$$

It has been shown that the waves of thiosulfate and sulfite correspond to the formation of a complex ion: $S_2O_3^{=} + Hg \rightleftarrows Hg(S_2O_3)_2^{=} + 2e$. The waves of hydroxyl and thiocyanate correspond to the formation of undissociated mercuric hydroxide and thiocyanate.

2. Thiosulfate yields a second wave due to an irreversible oxidation.

3. The half wave potentials of the above four waves change with the diffusion current according to: $\pi_{1/2} = \pi_0'' - (RT/2F) \ln i_d$. In 0.001 N solutions the following half wave potentials (*vs.* S. C. E.) were measured: thiosulfate −0.145 v.; sulfite −0.007 v.; hydroxide +0.080 v.; thiocyanate +0.18 v.

4. Chloride, bromide and iodide yield the corresponding mercurous salts on the anodic waves. Films of the insoluble mercurous compounds may interfere with the course of the current–voltage curves. When the film has attained a certain thickness in the case of bromide the drop becomes polarized and a second wave appears. The film effect is eliminated in the case of bromide by addition of a trace of gelatin. The film of mercurous iodide exerts properties at the electrode different from those of the bromide. The effect of the films upon the electrocapillary behavior of mercury has been determined.

5. All of the above anions and also sulfide and cyanide can be determined polarographically under the proper conditions.

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