Discussion

Although the authors believe that the proposed theory is a general one capable of explaining the cause of minima in the diffusion plateaus of polarographic waves of highly oxidizing compounds, there are certain other "minima" that do not fall into this category and consequently must have some other mechanism.

A case very similar to the present one, although not involving oxidation of mercury, was reported by Laitinen and Ziegler.[30] The polarographic reduction of tungsten (VI) in the presence of perchloric acid produces a very large catalytic current at potentials corresponding to the reduction of W(VI) to W(V). The catalytic current is due to the perchloric acid which oxidizes W(V) back to the hexavalent state which again is electroreduced to W(V) and so forth. At somewhat more negative potential the current falls off producing a "minimum." Here the electroreduction of W(V) to W(III) starts to interfere with the chemical oxidation of the pentavalent form and the catalytic cycle drops off. The principle is thus identical with the one presented in this paper.

Other cases of polarographic minima do not necessarily fall into a similar category. For example, a minimum in the reduction of hexamminecobalt-(III) ion has been attributed to the formation of a film of cobalt(II) hydroxide.[31] The examples given by Pecsok and Juvet,[11] Kolthoff and Lingane,[3] Konopik and Berger,[10] Filipovic, *et al.*,[12] and Parry and Yakubik[13] merit further investigation.

Acknowledgment.—The authors are grateful to Dr. K. B. Oldham for valuable discussions in connection with this research.

This investigation was carried out under the sponsorship of the Office of Naval Research, contract N6-ori-07136-NR 052-282.

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[30] H. A. Laitinen and W. A. Ziegler, THIS JOURNAL, **75**, 3045 (1953).

[31] H. A. Laitinen, A. J. Frank and P. Kivalo, *ibid.*, **75**, 2865 (1953).

URBANA, ILLINOIS

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

The Anodic Waves of Cysteine at the Convection and Dropping Mercury Electrodes

BY I. M. KOLTHOFF, WALTER STRICKS AND NOBUYUKI TANAKA[1]

RECEIVED JUNE 13, 1955

Current-voltage curves of cysteine at the convection mercury electrode (C.M.E.) were studied over the *p*H range between 1 and 13 at cysteine concentrations from 10^{-4} to 10^{-3} *M* and compared with polarograms observed at the dropping mercury electrode (D.M.E.). Polarograms run from negative to positive potentials at the C.M.E. in cysteine solutions more acid and more alkaline than *p*H 9 exhibit a prewave which is attributed to the formation of a film of mercurous cysteinate on the electrode. The film breaks down at more positive potentials when the "normal" wave corresponding to the formation of mercurous cysteinate at the electrode appears. From the area of cathodic dissolution patterns in polarograms recorded from positive to negative potentials the thickness of the film is calculated to correspond to that of a monomolecular layer of mercurous cysteinate. The film formed at the D.M.E. in solutions of *p*H 5 and of cysteine concentrations larger than 0.00025 *M* was also found to be of monomolecular dimension. Film formation at both electrodes is eliminated at 80° and also at 25° in the presence of sufficient surface active disulfides like dithiodiglycolic acid.

Under proper conditions[2] cysteine gives an anodic wave at the dropping mercury electrode (D.-M.E.) which corresponds to a reversible reaction

$$\mathrm{RSH} + \mathrm{Hg} \rightleftarrows \mathrm{HgRS} + \mathrm{H}^+ + e^- \qquad (1)$$

In solutions with *p*H between 2 and 9 a prewave is observed at cysteine concentrations greater than 0.00025 *M*, the false diffusion current being almost independent of the cysteine concentration. Grubner[3] reports normal waves without a prewave at a temperature of 90°. The false diffusion current at room temperature has been attributed[2,3] to the formation of a film of mercurous cysteinate (HgRS) on the surface of the drop which prevents further electrode reaction with mercury until the potential is made positive enough to cause a breakdown of the film.

In a recent communication[4] the convection mercury electrode(C.M.E.) was found well suited for a study of electro-active films on mercury surfaces.

In order to obtain more insight into the properties and formation of the mercurous cysteinate film the anodic waves of cysteine at the convection mercury electrode were studied in detail. Current-voltage curves observed at the convection mercury electrode in cysteine solutions of *p*H lower than 9 and also in 0.1 *M* sodium hydroxide exhibit similar characteristics as those found at the dropping mercury electrode as indicator electrode. Current-voltage curves were recorded from positive to negative potentials and *vice versa*. The polarograms indicate that the resistance exhibited by the film is greater when the potential is varied from negative to positive values than *vice versa*.

From the area of the cathodic dissolution patterns observed in polarograms recorded from positive to negative potentials the thickness of the film was found to be independent of the cysteine concentration, length of time of anodic polarization and to have the dimensions of a monomolecular layer. A film of monomolecular thickness was also postulated to be formed at the dropping mercury electrode.

Experimental

The experimental setup of the convection electrode was the same as described previously.[5] The effective area of

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[1] Department of Chemistry, Tohoku University, Sendai, Japan.

[2] I. M. Kolthoff and C. Barnum, THIS JOURNAL, **62**, 306 (1940).

[3] O. Grubner, *Collection Czechoslov. Chem. Communs.*, **19**, 444 (1954).

[4] I. M. Kolthoff and J. Jordan, THIS JOURNAL, **77**, 3215 (1955).

[5] I. M. Kolthoff, J. Jordan and S. Prager, *ibid.*, **76**, 5221 (1954).

TABLE I

APPARENT HALF-WAVE POTENTIALS, $E_{1/2}$ AND LIMITING CURRENTS i OF CYSTEINE AT C.M.E. AT 25°

$\longrightarrow$ Recorded from positive to negative potentials.
$\longleftarrow$ Recorded from negative to positive potentials.

pH	Concn. RSH × 10^4, M	$\overrightarrow{E_{1/2}}$ v. *vs.* S.C.E.	$\overleftarrow{E_{1/2}}$[a] v. *vs.* S.C.E.	$\overrightarrow{i,\ \mu a.}$	$\overrightarrow{i/c}$[b]	$\overleftarrow{i,\ \mu a.}$	$\overleftarrow{i/c}$[b]
13.0	1.67	−0.36	−0.20	at −0.33 v. 1.70	10.2	at −0.15 v. 3.4	20.2
13.0	9.80	−0.42	−0.20	at −0.33 v. 15.2	15.5	poorly defined	...
9.2	5.0	−0.51	−0.51	at −0.35 v. 8.0	16.0	at −0.35 v. 8.1	16.2
7.0	1.67	−0.15	−0.11	at −0.1 v. 2.7	16.2	at −0.05 v. 3.0	17.9
5.2	1.67	−0.12	−0.03	at −0.02 v. 3.4	20.4	at 0.0 v. 3.1	18.6
5.2[c]	1.65	−0.14	−0.04	at −0.03 v. 3.2	19.4	at 0.0 v. 3.2	19.4
5.0[d]	1.65	−0.23	...	at −0.1 v. 3.6	21.8	...	...
5.2	5.00	−0.15	−0.04	at −0.02 v. 10.4	20.8	at 0.0 v. 9.0	18.0
5.2[e]	1.67	−0.24	−0.24	at −0.05 v. 11.3	68.0	at −0.05 v. 10.8	65.0
5.2[e]	9.70	...	−0.24	...	...	61.0	63.0
1.0	1.68	−0.01	+0.14	at +0.1 v. 2.8	16.7	at +0.15 v. 3.00	17.8
1.0	5.0	+0.015	*f*	at +0.1 v. 8.3	16.6	*f*	...
1.0	9.8	−0.01	*f*	at +0.1 v. 16.2	16.5	*f*	...

[a] Reversible half-wave potentials at 25° at pH 9.2, 7, 5.2 and 1.0 are −0.52, −0.39, −0.28 and −0.036 volt *vs.* S.C.E., respectively. [b] i/c is current of 10^{-3} M cysteine solution. [c] Acetate buffer was 0.2 M in total acetate. [d] In the presence of 1.63×10^{-4} M cystine. [e] Temperature of solution was 80°. [f] No convection current plateau was observed.

the indicator electrode was 0.02 sq. cm. and the sensitivity[6] 21.0 μa. meq./l. for thallous ion in 0.1 M potassium chloride at a rate of stirring of 900 r.p.m. Current–voltage curves were recorded with a Leeds and Northrup Chemograph Type E. The rate of change of applied potential, $\Delta v/\Delta t$, was 3.33 mv./sec. in all experiments. The capacity of the electrolysis cell was 250 ml. and the volume of the solution was 150 ml. in experiments with the C.M.E. After each recording of a polarogram the cuvet of the cell was cleaned with hot concentrated nitric acid and refilled with freshly distilled mercury.

The characteristics of the dropping mercury electrode were m = 2.02 mg. sec.$^{-1}$, t = 3.83 sec. at open circuit. Current–voltage curves at the dropping electrode were recorded with a Heyrovsky Type Sargent polarograph, Model XII ($\Delta v/\Delta t$ = 2.85 mv./sec.).

The potentials were measured against the saturated calomel electrode (S.C.E.). All experiments were carried out at 25 ± 0.1° unless stated otherwise.

Cysteine (RSH) stock solutions were prepared by dissolving cysteine hydrochloride (Pfanstiehl) in air-free distilled water and kept in bottles closed with caps which were provided with self-sealing rubber gaskets. The solution was withdrawn by means of a syringe. Thioglycolic acid (TSH), dithiodiglycolic acid (TSST) and oxidized glutathione were prepared in the same way as described previously.[7,8]

Borax (0.05 M borax, 0.1 M KCl, pH 9.2), phosphate (0.1 M total phosphate, 0.1 M KCl, pH 7), acetate (0.1 M total acetate, pH 5.2) buffers, 0.1 M perchloric acid and 0.1 M sodium hydroxide were used as supporting electrolytes.

Experiments with the Convection Mercury Electrode

Current–voltage curves were run of solutions of varying cysteine concentrations (1.7 to 9.8 × 10^{-4} M) in a pH range of 1 to 13; some illustrations are given in Fig. 1. Apparent half-wave potentials and limiting currents are listed in Table I. All polarograms were recorded from positive to negative potentials and *vice versa*.

In a borax solution of pH 9.2 the shape of the anodic convection wave was similar to that observed in the same medium at the D.M.E.[2] The wave had the characteristics of a reversible one electron wave with a half-wave potential of −0.51 volt as compared to −0.52 volt at the D.M.E. The half-wave potential of the convection wave was found to be the same no matter whether the polarogram was run from positive to negative potentials or *vice versa* and the limiting current at a given potential was proportional to the cysteine concentration.

In media of pH less than 9 and in 0.1 M sodium hydroxide the shape of the c–v curves at the C.M.E. exhibited irregularities and was different when recorded from positive to negative or *vice versa*. For example a 1.7 × 10^{-4} M cysteine solution at pH 1 gave a wave of normal appearance when recorded from positive to negative potentials while the polarogram of the same solution, recorded in the opposite direction exhibited a small prewave followed by a very steep wave at more positive potentials (compare curves A and A_1 in Fig. 1). In curve A the convection current remained constant over a potential range of 0.1 volt, while in curve A_1 it extended over a range of only 0.03 volt. The potential region in which the convection current was constant became shorter with increasing cysteine concentration, but the convection current remained proportional to the concentration. The half-wave potential of wave A is about 0.026 volt more positive than the thermodynamic value. On the other hand the half-wave potential of the prewave in curve A_1 (−0.04 volt) agrees satisfactorily with the theoretical value of −0.036 volt. The prewave extends up to a potential of about +0.12 volt when the true convection current can develop. With increasing pH (but less than pH 9) all the waves became ill defined, immaterial whether run from positive to negative potentials or *vice versa* and the half-wave potentials were considerably more positive than those corresponding to

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(6) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3893 (1954).

(7) D. L. Leussing and I. M. Kolthoff, *J. Electrochem. Soc.*, **100**, 334 (1953).

(8) W. Stricks and I. M. Kolthoff, THIS JOURNAL, **74**, 4646 (1952).

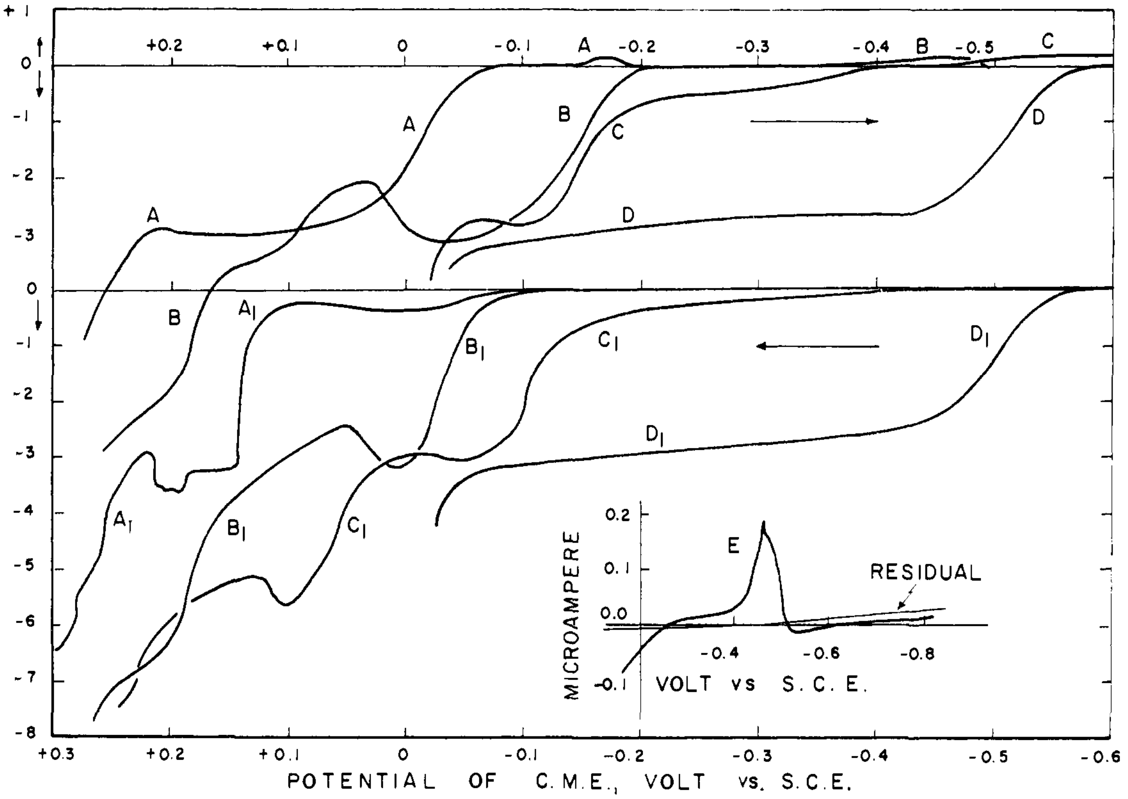
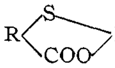


Fig. 1.—Current-voltage curves at C.M.E. of 1.67×10^{-4} *M* cysteine in: A, A_1, 0.1 *M* $HClO_4$ (*p*H 1); B, B_1, E (dissolution pattern) acetate buffer (0.2 *M* total acetate, *p*H 5.2); C, C_1, phosphate buffer (0.1 *M* total phosphate, *p*H 7.0); D, D_1, 0.05 *M* borax, 0.1 *M* KCl (*p*H 9.2). Curves A, B, C, D, E are recorded from positive to negative potentials. Curves A_1, B_1, C_1, D_1, are recorded from negative to positive potentials.

reversible reaction 1. Thus at *p*H 5 and 7 the potentials on curves B and C of Fig. 1 are 0.164 and 0.240 volt more positive than the true values. Some of the curves, like B and B_1 showed a second ill-defined anodic wave of approximately the same height as that of the main wave. Similar waves also have been observed in polarograms at the D.M.E. both in solutions of cysteine and of glutathione.[8] The second wave might be attributed to further oxidation of mercurous cysteinate to a compound to the type



The behavior of cysteine in strongly alkaline solutions (0.1 *M* NaOH) at the C.M.E. was similar to that observed in the *p*H range less than 9. From the data in Table I it is seen that the half-wave potential at *p*H 13 is considerably more positive than at *p*H 9.2, the shift to the positive side being greater in polarograms run from negative to positive potentials than *vice versa*.

Polarograms of cysteine at the D.M.E. at the extreme ends of the *p*H scale had a normal appearance[2] and thus differed markedly from those observed at the C.M.E. in the same media.

All polarograms at the C.M.E. at *p*H other than 9, when recorded from positive to negative potentials exhibited a small characteristic cathodic dissolution pattern. One such pattern is illustrated at great galvanometer sensitivity (recorded with a Sargent Model XII polarograph) in Fig. 1E. Since the rate of change of applied potential was constant in our experiments, the abscissas in Fig. 1 may represent potential as well as time. Therefore, the quantity of electricity corresponding to the cathodic dissolution area could be calculated readily. The area of the dissolution patterns was measured for solutions at *p*H 5.2 at various cysteine concentrations after prepolarization at −0.1 volt for various periods of time. The data in Table II show that the area of the dissolution pattern is unaffected by the cysteine concentration and by the length of time of electrolysis.

At a temperature of 80° cysteine solutions of *p*H 5 gave perfectly normal convection waves, no matter whether recorded from positive to negative potentials or *vice versa*. The temperature coefficient of the convection current was found to be about 4% per degree between 25 and 80°. The difference $E_{3/4} - E_{1/4}$ at 80° for 1.67×10^{-4} and 9.7×10^{-4} *M* cysteine solutions was found to be 54 and 57 mv., respectively, after correction for the *IR* drop. These values compare favorably with the calculated value of 65.5 mv. for a reversible one electron transfer at 80°. No dissolution patterns were observed at 80°. The remarkable change in the characteristics of the convection wave at higher temperature is analogous to that reported for the diffusion controlled cysteine wave at the D.M.E. in an acetate buffer.[3]

Table II

Quantity of Electricity Corresponding to Area of Dissolution Patterns at C.M.E. in Cysteine Solutions at *p*H 5.2 after Prepolarization at −0.1 Volt

Concn. RSH × 10^4, *M*	Time of prepolarization, min.	Quantity of electricity, µcoulomb
1.67	1	3.8
1.67	10	3.5
10.00	1	3.6
10.00	10	3.9
	av.	3.7

The prewave and the small cathodic dissolution pattern are attributed to a film of mercury cysteinate. It appeared of interest to study the effect of capillary active substances on the film formation in cysteine solutions of *p*H 5. Among the substances studied cystine (RSSR) and dithiodiglycolic acid (TSST) were found to be effective in preventing film formation and to give rise to cysteine waves with a normal appearance and the expected half wave potentials (see Table I for an example of a cysteine-cystine mixture).

Not included in Table I are mixtures of cysteine and

TSST which gave normal cysteine waves with a well-defined convection current plateau. As an example, the anodic wave of a 2 × 10^{-4} *M* cysteine solution (*p*H 5), 10^{-4} *M* in TSST was found to have a half-wave potential of −0.21 volt and a limiting current of 3.34 μa. The difference $E_{3/4} - E_{1/4}$ for this wave was 0.070 volt which compares favorably with the theoretical value of 0.059 volt at 25°. No dissolution patterns were found in the presence of RSSR or TSST.

Considering that thioglycolic acid (TSH) in contrast to cysteine gives normal *c-v* curves throughout the entire *p*H range at the D.M.E.,[7] it was of interest to study the behavior of this acid at the convection mercury electrode. A polarogram of a solution of 4 × 10^{-4} *M* TSH in 0.2 *M* total acetate (*p*H 5.0), recorded from positive to negative potentials, consisted of a single wave with a half-wave potential (−0.25 volt) which was practically equal to the thermodynamic value. No dissolution pattern was observed. When recorded from negative to positive the wave, although of similar appearance, was shifted by about 0.05 volt to more positive potentials. The *i/c* value for both waves, measured at +0.13 volt, was found to be only 16.5.

Cystine itself, at *p*H 5 gives a drawn-out cathodic convection wave starting at about −0.9 volt and attaining a plateau at −1.4 volt. The cathodic convection current was found to be 6.90 μa. for a 1.63 × 10^{-4} *M* cystine solution (1.65 × 10^{-4} *M* in cysteine) corresponding to an *i/c* value of 21.05 μa./meq./l., which compares favorably with the value of 21.8 for the anodic current of cysteine in the presence of cystine (see Table I). Dithiodiglycolic acid did not give a reduction wave at the C.M.E.

Experiments with the Dropping Mercury Electrode

For a better comparison of the abnormalities of cysteine waves at the convection- and dropping electrodes, a few polarograms of cysteine at the D.M.E. are illustrated in Fig. 2. Curves A, B and C all clearly show the prewave. Curve A (*p*H 3) exhibits a peak which has the appearance of a polarographic maximum. Similar breaks in the curves are observed at *p*H 5 and 7 (see I in Fig. 2), but also a second break (indicated by II in Fig. 2) occurs. The relatively poorly defined current at this second break corresponds to the true diffusion current. From the average value of i_d/c in a concentration range between 10^{-3} and 10^{-4} *M*, a value of the diffusion coefficient of cysteine at *p*H 5 and 7 was calculated to be 8.2 × 10^{-6} cm.^{2} sec.$^{-1}$ as compared to 7.0 × 10^{-6} in 0.1 *M* perchloric acid.[2]

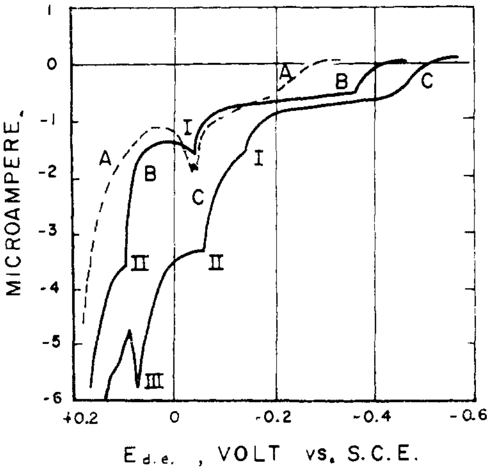


Fig. 2.—Current-voltage curves at the D.M.E. of 9.17 × 10^{-4} *M* cysteine at: A, *p*H 2.83; B, *p*H 4.95; C, *p*H 6.95.

Since RSSR and TSST had been found able to eliminate the film formation at the C.M.E., the effect of these disulfides and also of oxidized glutathione was studied on *c-v* curves of cysteine at the D.M.E. Experiments with cystine in the *p*H range from 7 to 3 were limited to concentrations not higher than 10^{-3} *M* RSSR which is approximately the solubility of cystine in this *p*H range. At *p*H 7 and 5 cystine had no effect on the height and appearance of the anodic cysteine wave in the solutions of 10^{-4} to 10^{-3} *M* cysteine. At *p*H 3 the sharp maximum of the cysteine wave became rounded and its height was found to attain the value of the true diffusion current in a 5 × 10^{-4} *M* cysteine solution in the presence of 5 × 10^{-4} to 10^{-3} *M* cystine.

Considering the TSST and oxidized glutathione are freely soluble at *p*H 3 to 7 these substances were conveniently used for studies of the effect of disulfides on the cysteine wave. The change in the appearance of waves upon the addition of increasing amounts of TSST to a cysteine solution of *p*H 5 is illustrated in Fig. 3. The current at break I increased markedly (compare curves A and B in Fig. 3), and the break disappeared when the concentration of TSST is 5 × 10^{-3} *M* (curve C). With further addition of TSST (see curve D, Fig. 3) the true diffusion current of cysteine was measured within a potential region of +0.1 to −0.1 volt in a concentration range of 10^{-4} to 10^{-3} *M* cysteine and the half-wave potentials of the waves were independent of the concentration (−0.272 volt) and equal to the thermodynamic value. Curve D has the characteristics of a wave corresponding to a one-electron reversible reaction. Oxidized glutathione had qualitatively the same effect on the RSH-wave as TSST but larger concentrations of the peptide were required in order to obtain a normal cysteine wave. For example, a 4 × 10^{-4} *M* RSH solution (*p*H 5) 8 × 10^{-3} *M* in TSST gave a fully developed wave with an i_d/c value of 3.4, while in the presence of the same concentration of the peptide the anodic cysteine wave was still poorly defined and gave an apparent i_d/c value of 2.9 as measured at a potential of −0.1 volt.

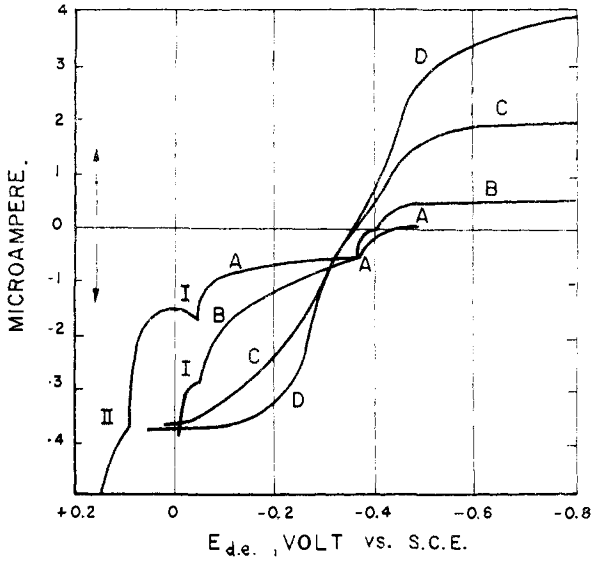


Fig. 3.—Current-voltage curves at the D.M.E. of 9.5 × 10^{-4} *M* cysteine at *p*H 4.9 (0.1 *M* total acetate) in the presence of dithiodiglycolic acid at concentrations of: A, zero; B, 10^{-3} *M*; C, 4.8 × 10^{-3} *M*; D, 9.2 × 10^{-3} *M*.

Experiments with cysteine solutions at *p*H 5 in the presence of 10^{-3} *M* thioglycolic acid (TSH) revealed that the polarographic behavior of cysteine is entirely changed in the presence of TSH, the anodic wave being well-defined and its height proportional to the cysteine concentration in the range between 2 × 10^{-4} to 1.6 × 10^{-3} *M* (i_d/c = 3.4). The effect of thioglycolic acid is analogous to that of reduced glutathione reported previously[9] for mixtures with cysteine.

Discussion

A comparison of Figs. 1 and 2 reveals that prewaves of cysteine are observed both at the C.M.E. and D.M.E. in a certain *p*H region. The cathodic dissolution pattern observed at the C.M.E. (see curve E, Fig. 1) strongly suggests that the prewave must be due to a film of mercury cysteinate. This film prevents further electrode reaction according to

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(9) W. Stricks and I. M. Kolthoff, *Anal. Chem.*, **25**, 1030 (1953).

equation 1. From the fact that the main wave yielding the normal limiting current appears at both types of electrode at considerably more positive potentials than the prewave, it is evident that the film must break down at these more positive potentials. It is of interest to note (Fig. 2) that this breakdown potential is more positive at *p*H 5 than at *p*H 7, the reversible electrode reaction also occurring at more negative potentials with increasing *p*H. The breakdown potential, especially at *p*H less than 5, is more positive when the polarogram is run from negative to positive potentials than in the opposite direction indicating that the structure of the film is affected by conditions of its formation.[4] Cysteine and its mercury compounds are dipolar and oriented at the electrode. The adherence of the film to the mercury surface therefore may depend on the charge of the electrode and on the *p*H of the solution. Film formation is decreased by increasing temperature. No film formation and waves corresponding to a reversible one electron reaction are observed at 80° both at C.M.E. and the D.M.E. RSSR and TSST when present at high enough concentrations appear to be stronger adsorbed on mercury than HgRS and eliminate the prewave at room temperature. Apparently the adsorbed layer of disulfide is permeable to cysteine.

The thickness of the film of mercurous cysteinate at the C.M.E. can be found from the dissolution pattern. The number of HgRS molecules reduced (see equation 1) from right to left can be calculated from the quantity of electricity corresponding to the area of the dissolution patterns (Table II). From the known area of the electrode surface this number was calculated to be 11.6×10^{14} molecules HgRS per cm.^{2} of electrode surface and the area occupied by one HgRS molecule is therefore 8.6 Å.^{2}. From the density of mercury, the effective area of the electrode and the assumption of cubic structure of mercury the number of mercury atoms on the surface of the electrode at 25° is calculated to be also 11.7×10^{14} atoms per cm.^{2}, *i.e.*, one atom occupies 8.5 Å.^{2}. These results clearly indicate that the film at the C.M.E. is composed of a monomolecular layer of HgRS.

Attributing the prewave observed at the D.M.E. also to an adsorbed film of HgRS, its thickness can be calculated from the Brdicka[10] relation

$$i = nFZ\Delta q$$

where i is the current determined by the amount of adsorbed substance, F the faraday, Z the maximum number of adsorbed moles per cm.^{2} and Δq the average increase of the electrode surface per second. Expressing the characteristics of the dropping electrode m in g. per sec. and t in sec., Δq is given by

$$\Delta q = 0.85 m^{2/3} t^{-1/3} \text{ cm.}^2\text{/sec.}$$

Taking for i the value of the false diffusion current (0.62 μa. at -0.2 volt, see Fig. 2B) measured in a solution of a cysteine concentration greater than 2.5×10^{-4} M at *p*H 5.0 the value for Z was calculated to be 7.4×10^{-10} mole per cm.^{2} or 4.4×10^{14} adsorbed molecules per cm.^{2}, a value which is of the same order of magnitude as that (11×10^{14}) calculated for the film at the C.M.E. The agreement between these figures is rather striking, considering that the hydrodynamic conditions around the mercury are so different with both types of electrodes. It is reasonable, then, to conclude that the film at both electrodes is composed of a monomolecular layer of mercurous cysteinate which becomes the seat of a high electrical resistance.

Acknowledgment.—This investigation was supported by research grants from the National Cancer Institute, U. S. Public Health Service (C-721, C_6) and from the National Science Foundation. Experiments with the dropping mercury electrode have been carried out with the assistance of Dr. R. C. Kapoor.

(10) R. Brdicka, *Z. Elektrochem.*, **48**, 278 (1942).

MINNEAPOLIS, MINNESOTA

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

Polarographic Reduction of Cystine and of Dithiodiglycolic Acid in the Presence of Iron

BY I. M. KOLTHOFF, W. STRICKS AND NOBUYUKI TANAKA[1]

RECEIVED MAY 27, 1955

In alkaline medium (*p*H 9.2) iron has a great effect on the polarographic reduction of cystine. In the presence of sufficient iron only one wave of cystine is observed at fairly positive potentials which yields the normal diffusion current while in the absence of iron a relatively small prewave followed by a drawn out reduction wave is found. The potentials of the iron-catalyzed wave correspond to a reversible one-electron reaction, although the over-all reduction involves two electrons. The catalysis is explained by the reaction: $\text{RSSR} + \text{Fe(II)} \rightarrow \text{Fe(III)} + \text{RS}^{\cdot} + \text{RS}^{-}$ which is rapid and is followed by polarographic reduction of RS$^{\cdot}$ and Fe(III), of which the iron reduction is potential determining. An alternate mechanism accounts equally for the experimental facts. The iron catalysis is eliminated by Versene and much pyrophosphate, but tartrate has no effect. The oxidation potential measured at the dropping mercury electrode of the cystine–cysteine system in the presence of iron does no longer correspond to the reaction $\text{RSSR} + 2\text{H}^+ + 2\text{e}^- \rightleftarrows 2\text{RSH}$.

In studies of iron–cysteine–cystine systems[2] it was observed that iron increases the polarographic prewave of cystine. This effect has been studied in greater detail and the results are reported in the present paper. The first (prewave) of the double wave of cystine at the dropping mercury electrode in a *p*H range of 3 to 9 was found to be kinetic in

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(1) Tohoku University, Sendai, Japan.

(2) N. Tanaka, I. M. Kolthoff and W. Stricks, THIS JOURNAL, **77**, 1980, 1996 (1955).