ing. The theory also is useful in calculating the dielectric constant due to prerotation in the three shorter bromides. The model required that the transition temperatures should rise nearly linearly with increasing chain length in agreement with experiment. Polarity seems to affect the transition points only slightly. In certain cases it is possible to estimate the additional heat capacity and the dielectric constant due to prerotation given ΔH_T and T_r. The theory does not imply free rotation above the transition point. The theory of rotating molecules presented in this paper, in conjunction with the concept of an equilibrium between metastable phases, seems able to give an account of the gross features of the rotational behavior in long chain molecules.

Acknowledgments.—The authors wish to express their indebtedness to Professor W. J. Kauzmann, Dr. A. D. Franklin and Dr. R. A. Oriani for many helpful conversations.

Summary

The dielectric constants and cooling curves of *n*-hexadecane, *n*-dodecyl, *n*-hexadecyl, *n*-octadecyl and *n*-docosyl bromide have been measured over a large temperature range. Prerotation was found in the bromides even at very low temperatures. On cooling, *n*-docosyl bromide froze at 40° and showed a sharp transition at 30°, and a suitable analysis showed that the molecules rotated about the long molecular axis between the freezing and transition point. No unsharp transitions were found. A theory of molecular rotation has been developed and the dielectric properties of long-chain bromides have been discussed in terms of the results. Heat capacity also has been discussed. Comparisons have been made between the properties of long-chain bromides, alcohols, iodides and paraffins.

PRINCETON, NEW JERSEY RECEIVED JUNE 7, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Polarographic Studies of Metal Complexes. II. The Copper(II) Citrates[1]

BY LOUIS MEITES*

Other papers in this series have dealt with the polarographic characteristics of copper(II) in oxalate[1] and tartrate[2] media. The present paper includes the results of a similar study of the various citrate complexes.

Experimental

The apparatus used will be described elsewhere.[3]

Data and Discussion

Figure 1 shows the variation in the half-wave potential of copper(II) in 0.5 *F* potassium citrate as a function of *p*H. There are four major sections of interest, bounded, at this citrate concentration, by the *p*H limits 2.5–5.5, 5.5–7.4, 7.4–11.8, and 11.8–14.

In the most acid range, as a first approximation, the half-wave potential is related to the *p*H by the equations

$$E_{1/2} = 0.112 - 0.052_3\,p\text{H (0.5 }F\text{ citrate)} \qquad (1)$$

and

$$E_{1/2} = 0.142 - 0.050\,p\text{H (0.05 }F\text{ citrate)} \qquad (2)$$

The working formula for the half-wave potential of a metal complex, neglecting activities, is

$$\Delta E_{1/2} = \frac{0.0591}{n}\log K_{\text{d}} - \frac{0.0591}{n}\,p\log\,[\text{X}] \qquad (3)$$

where $\Delta E_{1/2}$ is the algebraic difference between the half-wave potentials of, here, the citrato- and aquo-copper ions, K_{d} is the dissociation constant of the complex, p is the number of complexing groups attached to one copper atom, n is 2 for reduction to the metallic state, and [X] is the concentration of the citrate species involved in the complex. Laitinen, Onstott, Bailar and Swann[4] have recently rewritten equation (3) in the related form

$$\Delta E_{1/2} = \frac{0.0591}{n}\log K_{\text{d}} - \frac{0.0591}{n}p(p\text{H} - pK + \log\,[\text{HX}]) \qquad (4)$$

where [HX] and K_{a} are the concentration and dissociation constant, respectively, of the acid corresponding to the complexing anion. They state that "from this equation it is apparent that the half-wave potential will be a linear function of *p*H if the dissociation of the acid is small. . . ." This is only true within the accuracy of the measurements when $p\text{H} \leqslant pK_{\text{a}} - 1$, and, as this is not the case here, equations (1) and (2) would not be expected to be as accurate as the data themselves.

The four regions of the graph can hardly indicate anything but the formation of complexes with, successively, the dihydrogen and monohydrogen citrate ions, the citrate ion itself, and, at high *p*H values, with both hydroxyl ion and citrate. In solutions more acid than *p*H about 5, the dihydrogen citrate ion predominates. Its

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* Harvard University Ph.D., 1947.

[1] L. Meites, THIS JOURNAL, **71**, 184 (1949).

[2] L. Meites, *ibid.*, **71**, 13269 (1949).

[3] L. Meites and T. Meites, to be submitted.

[4] H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann, Jr., THIS JOURNAL, **71**, 1550 (1949).

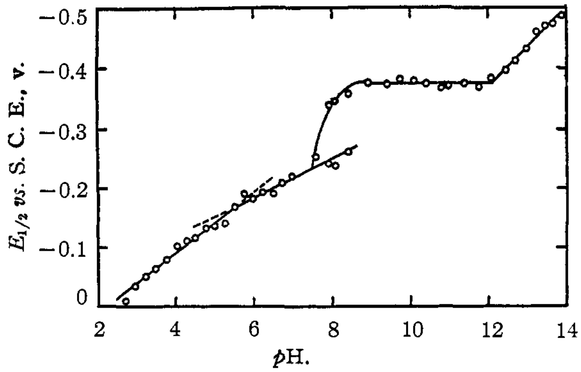

Fig. 1.—Effect of pH on the half-wave potential of copper(II) in *ca.* 0.5 F potassium citrate.

concentration is related to the concentration of hydrogen ion by the equation

$$[H_2Cit^-] = \frac{K_1C[H^+]^2}{[H^+]^3 - K_1[H^+]^2 - K_1K_2[H^+] - K_1K_2K_3} \quad (5)$$

where C is the formal concentration of citrate and the K_1 are the dissociation constants of citric acid. Using the recent values of Bates and Pinching[5] for the latter, one computes from equation (5) that the dihydrogen citrate concentration in 0.5 F citrate is 0.19 M at pH 3, 0.38 M at pH 4, and 0.18 M at pH 5. One would, therefore, expect the half-wave potentials to be nearly equal at pH 3 and 5, and to be somewhat more negative than this at pH 4. This is evidently not the case, although the values predicted by equation (1) are somewhat too positive at pH values near 4 and become slightly too negative as the pH departs from this in either direction. Therefore the hydrogen ion concentration must affect the half-wave potential by some other mechanism which is independent of its effect of the dihydrogen citrate concentration. It should be noted here that plots of $-E_{d.e.}$ against log $i/(i_d - i)$ at all pH values have slopes ranging from 29 to 33.5 mv., in good agreement with the expected value, 29.6 mv., for a thermodynamically reversible two-electron reduction, and therefore that all of these waves correspond to the reversible reduction of the complexes to the metal.

At any given pH in this acid range, the concentration of the dihydrogen citrate ion in 0.5 F citrate is, obviously, ten times that in 0.05 F citrate, and, by equations (1) and (2), this difference corresponds to a difference in the half-wave potential of roughly 30 mv. This is the effect calculated from equation (3) for $n = 2$ and $p = 1$, so that stoichiometrically we must write

$$\text{(complex)} + 2e \longrightarrow \text{Cu(Hg)} + H_2Cit^- + \ ? \quad (6)$$

Now the effect of the hydrogen ion concentration is very close to that expected for $p = -n$ in equation (3), so that equation (6) becomes

$$\text{(complex)} + 2H^+ + 2e \longrightarrow \text{Cu(Hg)} + H_2Cit^- \quad (7)$$

Figure 2 shows the agreement between the observed half-wave potentials and those calculated from equations (3) and (7), taking the measured half-wave potential in 0.5 F citrate at pH 3.5 as the reference point for the calculations.

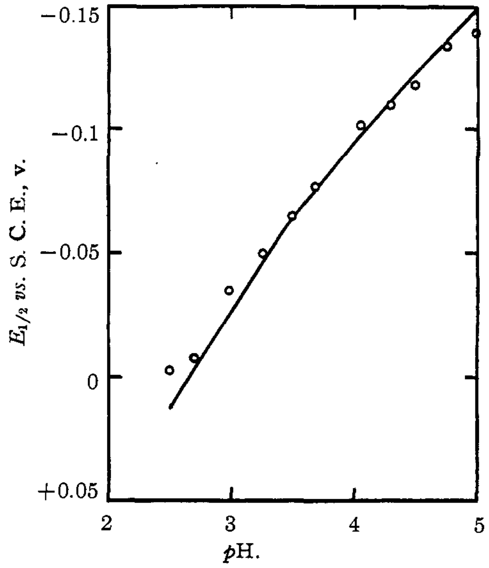

Fig. 2.—Variation of $E_{1/2}$ of the dihydrogen citrato copper(II) complex with pH. The curve represents the values calculated from equations (3) and (7).

Using equations (3) and (5), one calculates that, in 1 M hydrogen ion and 1 M dihydrogen citrate, $E_{1/2}$ = +0.124 v. (*vs.* S.C.E.). Kolthoff and Lingane[6] gave E^0 = +0.033 v. for the reaction

$$Cu^{++} + 2e \longrightarrow \text{Cu(Hg)}$$

and therefore, by equation (3)

$$E_{1/2} = 0.124 - 0.033 = 0.0296 \log K_d$$

whence

$$K_d = \frac{[H_2Cit^-][Cu^{++}]}{[H^+]^2[\text{complex}]} = 1.19 \times 10^3 \quad (8)$$

and, using the value of E^0 quoted by Lewis and Randall[7] for the standard potential of the copper–cupric ion couple

$$Cu \longrightarrow Cu^{++} + 2e;\ E^0 = -0.3448 \text{ v. (N. H. E.)}$$

we find

$$Cu + H_2Cit^- \longrightarrow \text{(complex)} + 2H^+ + 2e;\quad E^0 = -0.44 \text{ v. (N. H. E.)} \quad (9)$$

Equation (8) further gives

$$Cu^{++} + H_2Cit^- \longrightarrow \text{(complex)} + 2H^+;\quad \Delta F^0 = +4.16 \text{ kcal.} \quad (10)$$

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[5] R. G. Bates and G. D. Pinching, THIS JOURNAL, **71**, 1274 (1949).

[6] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 176.

[7] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 433.

In the second *p*H region, that between *p*H 5.5 and 7.4, the data of Fig. 1 are represented, fairly closely, by the equation

$$E_{1/2} = -0.027 - 0.026p\text{H} \qquad (11)$$

the *p*H dependency indicating that the reaction is

$$\text{(complex)} + \text{H}^+ + 2\text{e} \longrightarrow \text{Cu(Hg)} + b\text{HCit}^= \qquad (12)$$

Comparing the half-wave potentials in 0.5 *F* citrate with those in 0.05 *F* citrate in this region (whose boundaries are much narrower in the more dilute solution, so that it is difficult to establish an equation like equation (11)), the former are found to be from 25 to 37 mv. more negative. Therefore $b = 1$ in equation (12) and the reaction is

$$\text{(complex)} + \text{H}^+ + 2\text{e} \longrightarrow \text{Cu(Hg)} + \text{HCit}^= \qquad (13)$$

By the procedure outlined above, the following values are deduced

$$K = [\text{HCit}^=][\text{Cu}^{++}]/[\text{H}^+][\text{complex}] = 2.4_0 \times 10^{-3} \qquad (14)$$

$$\text{Cu} + \text{HCit}^= \longrightarrow \text{(complex)} + \text{H}^+ + 2\text{e};\quad E^0 = -0.24 \text{ v. (N. H. E.)} \qquad (15)$$

$$\text{Cu}^{++} + \text{HCit}^= \longrightarrow \text{(complex)} + \text{H}^+;\quad \Delta F^0 = -4.82_5 \text{ kcal.} \qquad (16)$$

As the *p*H is increased above 7.4, the concentration of the monohydrogen citrate ion decreases rapidly, and this complex is accordingly converted into a normal citrate complex, whose half-wave potential is independent of *p*H above about 8.5: the shift toward more negative potentials at lower *p*H values is related to the increase in the citrate concentration with *p*H. Only in the range of *p*H in which both of these complexes exist at substantial concentrations are two waves observed: this shows that the rate of interconversion of these complexes at the drop surface is very slow, contrasted to the probably nearly instantaneous attainment of equilibrium at other transition *p*H values.

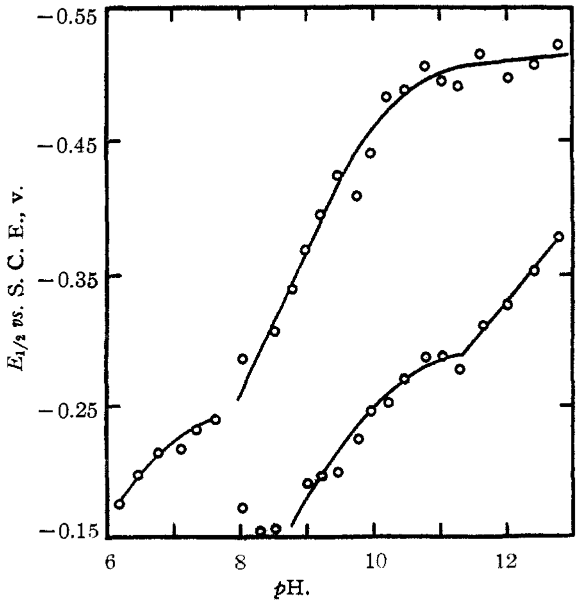

Fig. 3.—Effect of *p*H on the half-wave potential(s) for the reduction of copper(II) from *ca.* 0.5 *F* "ammonium citrate."

In 0.395 *M* citrate the half-wave potential for the reduction of the normal citrate complex is −0.372 ± 0.005 v., and in 0.0472 *M* citrate it is − 0.351 ± 0.002 v. The expected difference if one citrate is coördinated with one copper is 27 mv., in good agreement with the observed 21 mv. Therefore, as above

$$K = [\text{Cu}^{++}][\text{Cit}^{\equiv}]/[\text{CuCit}^-] = 6.2 \times 10^{-15} \qquad (17)$$

$$\text{Cu} + \text{Cit}^{\equiv} \longrightarrow \text{CuCit}^- + 2\text{e};\quad E^0 = +0.07_5 \text{ v. (N. H. E.)} \qquad (18)$$

$$\text{Cu}^{++} + \text{Cit}^{\equiv} \longrightarrow \text{CuCit}^-;\quad \Delta F^0 = -19.3_9 \text{ kcal.} \qquad (19)$$

In more strongly alkaline solutions, the wave shifts to more negative potentials: the half-wave potentials are defined by the equations

$$E_{1/2} = 0.450 - 0.067_9p\text{H} \text{ (0.39 } F \text{ citrate)} \qquad (20)$$

and

$$E_{1/2} = 0.491 - 0.068_7p\text{H} \text{ (0.046 } F \text{ citrate)} \qquad (21)$$

The effect of *p*H is close to that expected if two hydroxyl ions are coördinated with one copper, while the difference between the numerical constants in these equations indicates that one copper combines with two citrate ions. Therefore, correcting to 1 *M* citrate and 1 *M* hydroxyl, we write

$$\text{Cu} + 2\text{Cit}^{\equiv} + 2\text{OH}^- \longrightarrow \text{Cu(OH)}_2\text{(Cit)}_2^{-6} + 2\text{e};\quad E^0 = +0.23 \text{ v. (N. H. E.)} \qquad (22)$$

The complex is identical in type with that formed in strongly alkaline tartrate solutions.[2] In the extrapolation leading to the E^0 value quoted in equation (22), the figure derived from the measurements in the more dilute citrate solutions is about 25 mv. more positive than the other, which is in the expected direction if the activity coefficient of the citrate ion is smaller in the more concentrated solutions. The mean of the individual values is the one given. One also calculates

$$K = \frac{[\text{Cu}^{++}][\text{OH}^-]^2[\text{Cit}^{\equiv}]^2}{[\text{Cu(OH)}_2\text{(Cit)}_2^{-6}]} = 5 \times 10^{-20} \qquad (23)$$

and

$$\text{Cu}^{++} + 2\text{OH}^- + 2\text{Cit}^{\equiv} \longrightarrow \text{Cu(OH)}_2\text{(Cit)}_2^{-6};\quad \Delta F^0 = -26.4 \text{ kcal.} \qquad (24)$$

Figure 3 shows the variation with *p*H of the half-wave potentials for the reduction of copper(II) from a solution containing 0.5 *F* potassium citrate and 1.5 *F* ammonium nitrate. The double wave, which first appears at *p*H 8.0 in 0.5 *F* "ammonium citrate" and at *p*H 7.4 in 1 *F* "ammonium citrate," is well defined except for a small maximum in the second wave which is suppressed by increasing *p*H (Fig. 4) and by increasing salt concentration. Since the two waves appear to be nearly equal in height, the reduction must, as is common in ammoniacal solutions,[1,2]

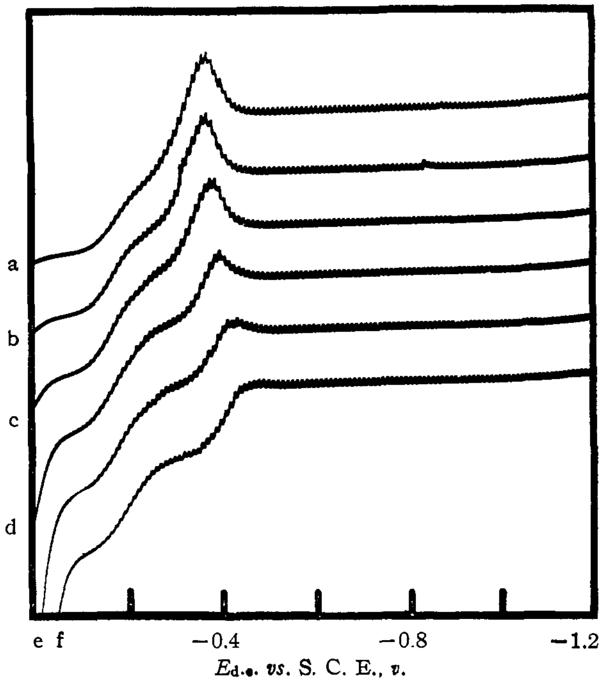

Fig. 4.—Polarograms of 3.2 millimolar copper(II) in *ca.* 0.5 *F* "ammonium citrate" at *p*H (a) 8.04, (b) 8.30, (c) 8.52, (d) 8.80, (e) 9.00, and (f) 9.22.

proceed *via* the +1 state. For each of the waves $E_{3/4} - E_{1/4}$ is about − 63 mv., compared to the −58 mv. expected[8] for a thermodynamically reversible one-electron reduction.

Figure 5 shows the effect of the concentration of ammonia on these half-wave potentials in 0.5 *F* citrate. At low concentrations of ammonia $\Delta E_{1/2}/\Delta \log [NH_3]$ is about − 165 mv. for each wave: this would indicate that 2.8 molecules of ammonia are liberated in each step for each copper atom reduced, and thus the complexes formed are $Cu(NH_3)_6(Cit)_a^{2-3a}$ and $Cu(NH_3)_3(Cit)_b^{1-3b}$.

Taking 1 *M* ammonia as a point for comparison, one finds for the first wave $E_{1/2} = -0.223$ v. in 0.5 *F* citrate and −0.187 v. in 1.0 *F* citrate: this gives $\Delta E_{1/2}/\Delta \log [Cit^{\equiv}] = +119$ mv., so that $(a - b)$ is −2. For the second wave, at the same concentration of ammonia, $E_{1/2}$ is −0.416 v. in 0.5 *F* citrate and −0.381 v. in 1.0 *F* citrate, which gives $b = -2$. The writer has no plausible explanation to offer for this absurdity.

At high concentrations of ammonia, the half-wave potentials are much more negative than would be predicted from the formulas of the complexes given above.

In strongly alkaline solutions the half-wave potential of the first wave shifts to more negative potentials: in 0.5 *F* ammonium citrate $E_{1/2} = 0.374 - 0.0585\ pH$ at $pH \geqslant 11.5$. This indicates that, as with the complex copper(II) ammino-oxalate,[1] one hydroxyl ion is liberated in the reduction to the +1 state. In this *p*H range, however, the half-wave potential is about 32 mv. more *positive* in 1 *F* citrate than in 0.5 *F* citrate. The copper ammino-citrates are badly in need of study by other methods.

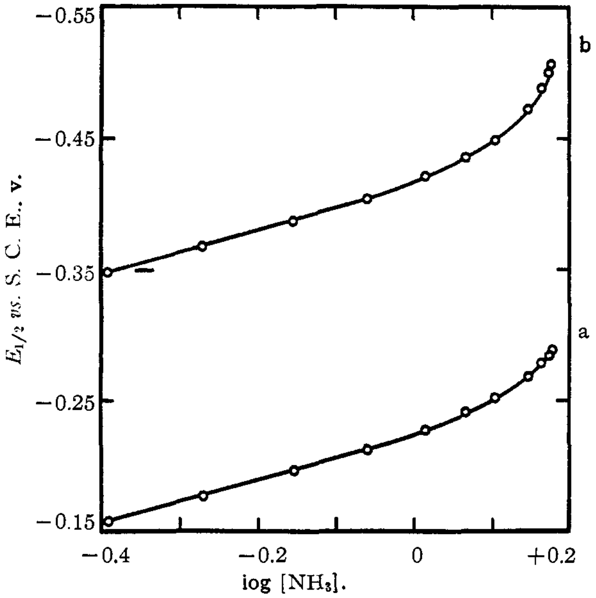

Fig. 5.—Effect of ammonia concentration on the half-wave potentials of the (a) first and (b) second wave for the reduction of copper(II) from 0.5 *F* "ammonium citrate."

Summary

The following new thermodynamic constants have been derived from polarographic data: (a) For the dihydrogen citrato copper(II) complex

$$(\text{Complex}) + 2H^+ \longrightarrow Cu^{++} + H_2Cit^-;$$
$$K = 1.19 \times 10^3;\quad \Delta F^0 = -4.16 \text{ kcal}$$
$$Cu + H_2Cit^- \longrightarrow (\text{Complex}) + 2H^+ + 2e;$$
$$E^0 = -0.44 \text{ v.}$$

(b) For the monohydrogen citrato copper(II) complex

$$(\text{Complex}) + H^+ \longrightarrow Cu^{++} + HCit^{=};$$
$$K = 2.4_0 \times 10^{-3};\quad \Delta F^0 = +4.82_5 \text{ kcal.}$$
$$Cu + HCit^{=} \longrightarrow (\text{Complex}) + H^+ + 2e;$$
$$E^0 = -0.24 \text{ v.}$$

(c) For the normal citrato copper(II) complex

$$CuCit^- \longrightarrow Cu^{++} + Cit^{\equiv};\ K = 6.2 \times 10^{-15};$$
$$\Delta F^0 = +19.3_9 \text{ kcal.}$$
$$Cu + Cit^{\equiv} \longrightarrow CuCit^- + 2e;\ E^0 = +0.07_5 \text{ v.}$$

(d) For the hydroxycitrato copper(II) complex

$$Cu(OH)_2(Cit)_2^{-6} \longrightarrow Cu^{++} + 2OH^- + 2Cit^{\equiv};$$
$$K = 4._8 \times 10^{-20};\quad \Delta F^0 = +26.4 \text{ kcal.}$$
$$Cu + 2OH^- + 2Cit^{\equiv} \longrightarrow Cu(OH)_2(Cit)_2^{-6} + 2e;$$
$$E^0 = +0.23 \text{ v.}$$

The data secured on the polarographic characteristics of the reversible copper(II) and copper(I) waves in ammoniacal ammonium citrate solutions

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(8) Ref. 6, pp. 177–178.

are not susceptible to chemical or thermodynamic interpretation in the absence of confirmatory information secured from other sources.

NEW HAVEN, CONN. RECEIVED JUNE 2, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Polarographic Studies of Metal Complexes. III. The Copper(II) Oxalates and Carbonates

BY LOUIS MEITES*

The present paper is a continuation of a series whose earlier members have been devoted to the tartrate[1] and citrate[2] complexes of +2 copper.

Experimental

The experimental apparatus and techniques were essentially identical with those used previously.[1,2]

Data and Discussion

Polarography of Cu(II) in Oxalate Media.—Figure 1 shows the relationship between the half-wave potential of copper(II) in 0.09 *F* potassium oxalate and the *p*H of the solution between 0.8 and 11. The waves are well defined at all *p*H values, but in solutions more acidic than *p*H 2 a maximum develops whose height is greatly increased by decreasing oxalate concentration.

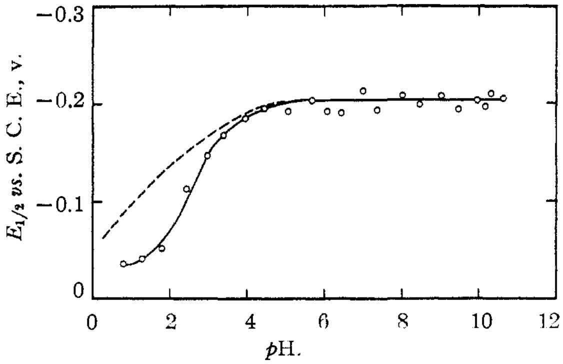

Fig. 1.—Half-wave potentials of 3.2 millimolar copper(II) in 0.09 *F* potassium oxalate: the dashed line represents the theoretical values if no hydrogen oxalate complex is formed.

Above *p*H 5.7, where substantially all of the oxalate has been converted into the C_2O ion, no change in half-wave potential is observed. As in this *p*H range, the concentrations of all other anions in the solution are small compared to the copper concentration (usually 3m*M*), the greenish-blue complex must be of the type $Cu(C_2O_4)_x^{2-2x}$. For the reversible $(\Delta(-E_{d.e.})/\Delta \log (i/(i_d - i)$ = 28–31 mv.[3]) reduction of this complex to the metal, the half-wave potential is −0.204 ± 0.006 v. (*vs.* S.C.E.) in 0.090 *F* oxalate and −0.271 ± 0.006 v. in 0.95 *F* oxalate. Then, from the general equation[8] for the half-wave potential of a reversible *n*-electron reduction, we have

$$\frac{\Delta E_{1/2}}{\Delta \log [C_2O_4^=]} = \frac{-0.067}{1.024} = -\frac{0.0591}{n}x \qquad (1)$$

whence, since $n = 2$, $x = 2.2$. Therefore the complex must be $Cu(C_2O_4)_2^=$.

From equation (1) and the measured half-wave potentials in 0.95 *F* oxalate, the half-wave potential for the reduction of the $Cu(C_2O_4)_2^=$ ion from 1.00 *F* oxalate should be −0.272 v. For the reduction of the aquo-copper(II) ion at the dropping electrode, Kolthoff and Lingane[4] give $E^0 = +\ 0.033$ v. The difference between this and the above figure is related to the dissociation constant of the complex by the expression[3]

$$-0.272 - 0.033 = (0.0591/n) \log K \qquad (2)$$

whence

$$K = [Cu^{++}][C_2O_4^=]^2/[Cu(C_2O_4)_2^=] = 4.8 \times 10^{-11} \qquad (3)$$

and, using the standard free energies of the cupric and oxalate ions computed by Latimer,[5] F°-$Cu(C_2O_4)_2^=$ = −315.5 kcal.

For the reaction $Cu \rightarrow Cu^{++} + 2e$, Lewis and Randall[6] give E^0 = −0.3448 v. (*vs.* N.H.E.). Then from equation (3) we deduce

$$Cu + 2\ C_2O_4^= \longrightarrow Cu(C_2O_4)_2^= + 2e; \quad E^0 = -0.04\ v.\ (N.\ H.\ E.) \qquad (4)$$

The dashed line in Fig. 1 corresponds to the half-wave potentials in 0.094 *F* oxalate calculated from equation (1) on the assumption that no hydrogen oxalate complex is formed. The line is coincident with the experimental points down to a *p*H of about 3, but in more acidic solutions the deviation is appreciable. This *p*H corresponds quite closely to that at which, from the values of K_1 and K_2 for oxalic acid quoted by

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* Harvard University Ph.D., 1947.

[1] L. Meites, THIS JOURNAL, **71**, 3269 (1949).

[2] L. Meites, *ibid.*, **72**, 180 (1950).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 161–164.

[4] Ref. 3, p. 176.

[5] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938.

[6] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.