

TABLE III

DEVELOPING AGENT ($5 \times 10^{-4} M$) IN DIETHYLEGLICINE
BUFFER AT pH 10.0Developing agent $E_{1/2}$ vs. S. C. E. (mv.) $\Delta E_{1/2}$ (mv.)

CASE I		
	$(C_2H_5)_2$	-14
	$N(C_2H_5)_2$	+17
	$N(C_2H_5)_2$	+37
CASE II		
	$N(C_2H_5)_2$	-14
	$N(C_2H_5)_2$	+32
	$N(C_2H_5)_2$	+73

CASE III		
	$N(C_2H_5)_2$	-14
	$N(C_2H_5)_2$	-29
	$CH_2CH_2NHSO_2CH_3$	-15

Acknowledgments.—The authors wish to acknowledge the efforts of A. Weissberger, of the Synthetic Organic Research Department of these Laboratories, in the selection and preparation of the developing agents, and of E. E. Jelley, of these Laboratories, for his interest and cooperation in the development of this method.

Summary

An application of stationary microelectrodes of platinum to the polarographic determination of half-wave potentials has been described. Examples of the anodic oxidation of several phenylenediamines have been given to illustrate the usefulness of the method. The application of the potentials obtained to studies of the effects of variations in the structure of developing agents has been illustrated.

ROCHESTER 4, N. Y.

RECEIVED MARCH 1, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography of Copper Complexes. II. Dipyridyl, Orthophenanthroline and Thiourea Complexes. A Double Complex System¹

BY E. I. ONSTOTT² AND H. A. LAITINEN

In this second paper are presented the results of polarographic studies of α, α' -dipyridyl, orthophenanthroline and thiourea, and the combination of ethylenediamine and thiourea as complexing agents for copper(II) and copper(I). Results on ethylenediamine, propylenediamine, diethylenethiamine, and glycine were reported previously.¹

The copper(II) complexes of dipyridyl and orthophenanthroline are reduced in two steps. In the first step the cupric complex is reduced to the cuprous complex, and in the second step the cuprous complex is further reduced to the amalgam. Other copper(II) complexes which show similar behavior are the ammonia^{3,4} pyridine,⁵ thiocyanate ion⁶ and chloride ion⁷ as well as various copper(II) chelates.⁸

Copper(II) complexes of thiourea do not exist; only copper(I) complexes are stable.^{9a,b,c,d,e} Hence, a single polarographic wave corresponding to the reduction of a copper(I) complex of thiourea to the amalgam is observed.

Bis-(ethylenediamine)-copper(II) ion in the presence of excess ethylenediamine alone is reduced directly to the amalgam.¹ However, in the presence of a large excess of both ethylenediamine and thiourea, it is reduced first to copper(I) before being further reduced to the amalgam.

Experimental

For the most part, the solutions for analysis were composed from stock solutions of reagent grade chemicals. α, α' -Dipyridyl and orthophenanthroline, obtained from the G. F. Smith Chemical Company, were weighed for each solution prepared, as was the thiourea for solutions requiring a high concentration of this constituent. A stock solution of cupric nitrate was used as the source of copper, except that solutions of the thiourea complex were prepared from a stock solution of cuprous chloride in 0.1 *M* thiourea. The indifferent electrolyte was 0.1 *N* potassium nitrate.

Because of the low solubility of dipyridyl and ortho-

(1) Paper I, Laitinen, Onstott, Bailar and Swann, *THIS JOURNAL*, **71**, 1550 (1949).

(2) Abstracted from the Doctorate Thesis of E. I. Onstott, 1950.

(3) Stackelberg and Freybold, *Z. Elektrochem.*, **46**, 120 (1940).

(4) Lingane, *Chem. Rev.*, **29**, 1 (1941).

(5) Lingane and Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941).

(6) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

(7) Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(8) Calvin and Bailes, *THIS JOURNAL*, **68**, 949 (1946).

(9) (a) Kohlschütter, *Ber.*, **36**, 1151 (1903); (b) Kohlschütter and Brittlebank, *Ann.*, **349**, 232 (1906); (c) Rathke, *Ber.*, **17**, 297 (1884); (d) Rosenheim and Loewenstamm, *Z. anorg. Chem.*, **34**, 62 (1903); (e) Walter and Storf, *Monatsh.*, **65**, 21 (1934).

phenanthroline in water, several solutions supersaturated with these complexing agents were prepared in order to extend the range of the polarographic measurements. Polarograms were recorded immediately after making the supersaturated solutions so that the effect of crystallization of the excess amines from solution would be eliminated. Supersaturated solutions containing up to four times the saturated concentration of dipyrldyl or orthophenanthroline were stable in most cases for periods of several days.

The concentration of copper in solutions containing dipyrldyl or orthophenanthroline was kept low so that at least a fiftyfold excess of the complexing agent would be present. Consequently, the accuracy of the diffusion current data is not as great as would be expected if higher concentrations of the reducible ion were used.

In preparing the solutions containing bis-(ethylenediamine)-copper(II) ion and excess ethylenediamine and thiourea, care was taken to add the ethylenediamine to the copper solutions before adding the thiourea. This precaution was necessary in order to prevent the irreversible reduction of the aquo copper complex by thiourea.

Gelatin (0.01%) was found to be suitable as a maximum suppressor. However, the maximum occurring at the second wave (copper(I) to amalgam reduction) in the reduction of the dipyrldyl or orthophenanthroline complex was not completely suppressed by gelatin if the concentration of copper was greater than 0.1 millimolar.

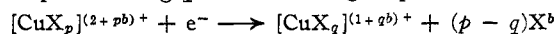
An H-cell with a temporary plug of 3% agar in 0.1 *N* potassium nitrate was used. The capillary used had an *m* value of 1.467 mg. sec.⁻¹ for a mercury column height of 69.8 cm. Oxygen was removed from the solutions for analysis with oxygen-free nitrogen.

Polarograms were recorded automatically with a Sargent Model XXI polarograph. Maximum currents, corrected for residual current, were used for calculating the values of $\log(i_d - i)/i$ for the plots to test the reversibility of the electrode reactions. However, the diffusion currents were measured at a constant potential with maximum damping of the Brown recorder to obtain average diffusion current data. Potentials were measured to the nearest millivolt with a Leeds and Northrup potentiometer. All measurements were made at 25 ± 0.1°.

Values of the half-wave potentials were taken from the plots of $\log(i_d - i)/i$ vs. the potential. Half-wave potentials determined from maximum current data were generally one or two millivolts more positive than those determined from average current data.

Discussion

For the reduction of a cupric complex having *p* coördinated groups of charge *b* to a cuprous complex having *q* coördinated groups

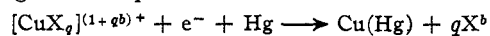


the equation relating the half-wave potentials of the simple and complex ion reductions is⁵ for 25°

$$(E_{1/2})_0 - (E_{1/2})_s = 0.05915 \log K_{d_{ic}}/K_{d_{ous}} - (p-q) \cdot 0.05915 \log C_x f_x \quad (1)$$

In this equation the ratio of diffusion coefficients and the ratio of activity coefficients of the cupric and cuprous complex ions do not appear as they are assumed to be unity. The *c* subscript refers to the complex ion, the *s* subscript refers to the simple ion, and the *x* subscript refers to the complexing agent. $K_{d_{ic}}$ is the symbol for the dissociation constant of the cupric complex, and $K_{d_{ous}}$ that of the cuprous complex. The concentration of complexing agent is expressed by C_x and f_x designates the activity coefficient of the complexing agent.

For the reduction of the cuprous complex to the amalgam an equation similar to that for the re-



duction of a cupric complex directly to the amalgam is valid⁵

$$(E_{1/2})_0 - (E_{1/2})_s = 0.05915 \log K_{d_{ous}} - q \cdot 0.05915 \log C_x f_x \quad (2)$$

This equation is not exact, as the diffusion coefficients of the simple and complex ions are assumed to be equal and the ratio of the activity coefficients of the simple and complex ions is assumed to be unity. However, as a first approximation, it is sufficiently accurate so that it can be used in this form. Symbols are the same as those defined for equation (1).

Dipyrldyl Complexes.—Values of the slopes of the plots of $\log(i_d - i/i)$ vs. *E* (Table I) show that both electrode reactions are reversible and one electron is added in each reduction process. Further evidence for the one electron additions is apparent from the values of the diffusion current constant $i_d/Cm^{3/2}t^{1/2}$, which are in satisfactory agreement considering the small concentrations of copper necessitated by the limited solubility of dipyrldyl.

TABLE I

DIPYRIDYL COMPLEXES

Diffusion current measured at -0.35 volt for first wave, at -0.80 volt for second wave.

Cu ⁺⁺ milli- molar	Dipyrldyl milli- molar	Slope of log plot	- <i>E</i> _{1/2} vs. S. C. E.	<i>i</i> _d , μamp.	<i>i</i> _d / <i>Cm</i> ^{3/2} <i>t</i> ^{1/2}
Cu(II) to Cu(I) reduction					
0.103	4.7	0.072	0.164	0.255 ^b	1.50
.051	5.0	.072	.168	.115 ^b	1.35
.103	7.9	.067	.180	.230 ^b	1.35
.103	9.7	.065	.186	.231 ^b	1.36
.205	19.4 ^a	.065	.201	.472	1.39
.103	19.7 ^a	.064	.203	.237	1.39
.103	19.7 ^a	.060	.200	.237	1.39
.205	39.4 ^a	.060	.210	.450	1.32
.103	39.6 ^a	.061	.210	.230	1.35
.103	39.6 ^a	.061	.211	.223	1.31
Cu(I) to amalgam reduction					
.103	4.7	.068	.425	.213	1.26
.051	5.0	.066	.436	.103	1.22
.103	7.9	.069	.450	.205	1.21
.103	9.7	.067	.458	.215	1.27
.205	19.4 ^a460	1.36
.103	19.7 ^a	.065	.499	.218	1.29
.103	19.7 ^a	.065	.499	.225	1.33
.205	39.4 ^a445	1.31
.103	39.6 ^a	.063	.536	.215	1.27
.103	39.6 ^a	.061	.538	.212	1.25

^a Supersaturated with dipyrldyl. ^b *i*_d measured at -0.32 volt.

The number of groups coördinated to cuprous ion is found by determining the slope of a plot of the logarithm of the concentration of complexing agent versus the half-wave potential of the

complex ion, the variables in equation (2). Knowing this number, then the number of groups coordinated to cupric ion is obtained by making a similar plot of the variables in equation (1). Data for the dipyriddy complexes, which are recorded in Table I are plotted in Fig. 1. The reciprocal slope of 0.122 for the plot of the data for the cuprous complex ion reduction, as compared with the theoretical value of 0.118, is good evidence for two dipyriddy molecules being coordinated, and the reciprocal slope of 0.049 for the second plot shows that in the predominant species of cupric complex one additional molecule is coordinated to a cupric ion. While a reciprocal slope of 0.059 would theoretically be expected, a slope of zero would be required to indicate that only two groups are coordinated to a cupric ion. This finding that two dipyriddy molecules are coordinated to cuprous ion and three are coordinated to cupric ion is not out of line with chemical evidence, as a compound of copper(I) containing two coordinated orthophenanthroline molecules were prepared by Tartarini¹⁰ and a compound of copper(II) containing three coordinated dipyriddy molecules was prepared by Jaeger and van Dijk.¹¹

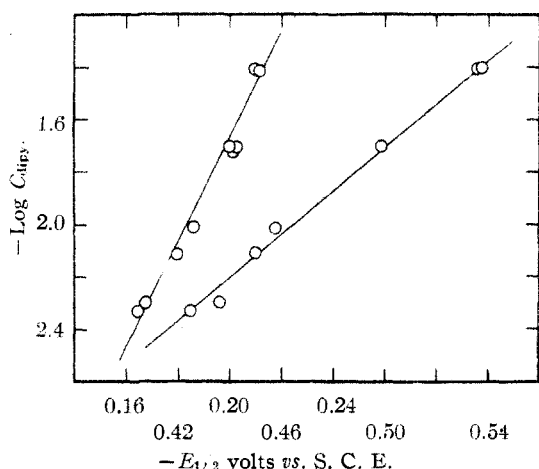


Fig. 1.—Upper scale cupric reduction; lower scale cuprous reduction.

Knowledge of the half-wave potentials for both simple ion reductions is necessary before the dissociation constants of the dipyriddy complex ions can be calculated. The half-wave potential for the reduction of simple cupric ion to cuprous ion should be the same as the standard potential,⁵ so the value of -0.079 volt (*vs.* S.C.E.) will be used.¹² An experimental value for the half-wave potential of the simple cuprous ion reduction cannot be obtained, but a hypothetical value can be calculated from equation (2) with the aid of the

(10) Tartarini, *Gazz. chim. ital.*, **63**, 579 (1933).

(11) Jaeger and van Dijk, *Proc. Acad. Sci., Amsterdam*, **37**, 618 (1934).

(12) Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

dissociation constant of diamine copper(I) ion which has been measured by Bjerrum,¹³ and the half-wave potential of this complex ion. Using the value of -0.500 volt (*vs.* S.C.E.) for the half-wave potential for an ammonia concentration of one molar^{4,5} and the value of 1.35×10^{-11} for the dissociation constant, assuming the activity coefficient of ammonia to be unity, a value of 0.143 volt (*vs.* S.C.E.) is calculated. Since Bjerrum's measurement of the dissociation constant was made at 18° , this calculation will contain the small error inherent from the difference in the value of the dissociation constant at 18 and 25° .

Dissociation constants for the dipyriddy complex ions were calculated from the data in Table I, using equations (1) and (2) and the values for the half-wave potentials of the simple ion reductions given above. The activity coefficient for dipyriddy was assumed to be unity. The dissociation constant for bis-(dipyriddy)-copper(I) ion was found to be 6.3×10^{-15} , and for tris-(dipyriddy)-copper(II) ion, a value of 1.4×10^{-18} was calculated.

Orthophenanthroline Complexes.—Accurate data for the orthophenanthroline complexes could not be obtained, as the current of the reduction processes did not appear to be entirely diffusion controlled. An unusual current-time relationship, apparently caused by an adsorption phenomenon, was observed. As was mentioned above, the reduction proceeds in two steps, the half-wave potential of the first reduction process being approximately -0.2 volt (*vs.* S.C.E.), and that of the second process being about -0.8 volt for 10 millimolar excess orthophenanthroline. Orthophenanthroline itself is reduced at about -1.0 volt.

Thiourea Complex.—That a reversible one electron addition occurs in the reduction of the thiourea complex is apparent from the values of the slopes of the plots of $\log(i_d - i)/i$ *vs.* E recorded in Table II. The values of the diffusion current constant $i_d/Cm^{2/3}t^{1/6}$, also show that one electron is added in the electrode reaction. The variations in diffusion current constant at high thiourea

TABLE II

THIOUREA COMPLEX

Solutions contained one millimolar CuCl; i_d measured at -1.0 volt.

Thiourea molar	Slope of log plot	$-E_{1/2}$ vs. S. C. E.	i_d , μ amp.	$i_d/Cm^{2/3}t^{1/6}$
1.596	0.062	0.814	2.58	1.56
1.580	.061	.811	2.49 ^a	1.53
0.816	.062	.745	2.59	1.57
.416	.062	.677	2.66	1.61
.028	.063	.611	2.67	1.61
.100	.064	.540	2.69	1.63
.048	.066	.484	2.69	1.62

^a 0.99 millimolar CuCl.

(13) Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941; *C. A.*, **35**, 6527 (1941).

concentration may be ascribed to changes in solution viscosity.

By plotting the variables of equation (2), the number of thiourea groups coordinated to cuprous ion can be determined. In Fig. 2 is plotted the half-wave potential of the complex ion reduction versus the logarithm of the thiourea concentration. The reciprocal slope of 0.277 is sufficiently close to the theoretical value of 0.237 for four coordinated groups to show that the predominant species of complex ion contain four coordinated thiourea molecules. This finding is not verified by investigators who have prepared solid complex compounds of thiourea and copper(I),^{9a,b,c,d,e} although the observations of Kohlschütter and Brittlebank^{9b} indicate that tetrathiourea copper(I) ion exists. They found that thiourea is more soluble in a solution of trithiourea-copper(I) chloride than it is in water alone, and the solid complex compound dissolves more easily in a solution of thiourea than it does in pure water. Morgan and Burstall¹⁴ found that ethylene thio-carbamide, a complexing agent quite similar to thiourea, combines with cuprous ion to form a compound in which four molecules of ethylene thio-carbamide are associated with each cuprous ion.

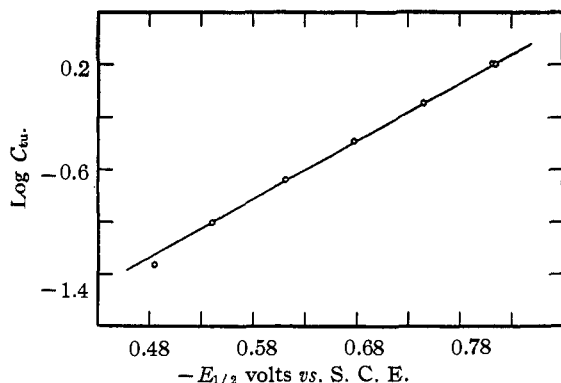


Fig. 2.

Equation (2) was employed to calculate the dissociation constant of the thiourea complex ion. Using the value of -0.767 volt (*vs.* S.C.E.) for the half-wave potential of the complex ion reduction at a thiourea concentration of one molar, and the value of 0.143 volt (*vs.* S.C.E.) for the half-wave potential of the simple cuprous ion reduction (calculated above), and assuming the activity coefficient of thiourea to be unity, a value of 4.1×10^{-16} was calculated.

Double Complex System.—Two distinct waves are shown by the polarographic reduction of bis-(ethylenediamine)-copper(II) ion in the presence of excess ethylenediamine and thiourea. In Fig. 3 is reproduced a typical polarogram obtained in this investigation.

Diffusion current data for both reduction processes are given in Table III. Values for the

(14) Morgan and Burstall, *J. Chem. Soc. (London)*, 1943 (1928).

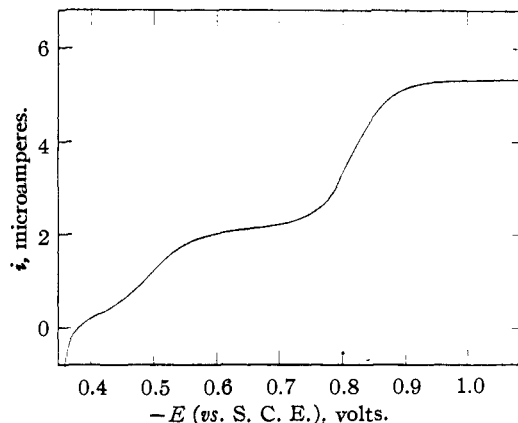


Fig. 3.—Polarogram of 10^{-3} $\text{Cu}(\text{en})_2^{++}$ in $0.1 M$ ethylenediamine, $1.6 M$ thiourea, $0.1 M$ KNO_3 , with 0.01% gelatin.

reduction process occurring at the more positive potential are somewhat lower than those for the second reduction process, but the differences are small enough so that it can be concluded with certainty that one electron is involved in each electrode reaction. A small amount of the cuprous complex in the solutions could account for the differences in the magnitude of the diffusion current for each reduction process.

TABLE III

DOUBLE COMPLEX SYSTEM

Solutions contained 1.027 millimolar cupric ion; i_d of first wave measured at about -0.6 volt, second wave at -1.0 volt.

Thiourea, molar	en, molar	Cu(II) to Cu(I) reduction		Cu(I) to amalgam reduction	
		i_d , $\mu\text{amp.}$	$i_d/\text{cm.}^2/\text{s}^{1/2}$	i_d , $\mu\text{amp.}$	$i_d/\text{Cm}^2/\text{s}^{1/2}$
1.60	0.10	1.97	1.17	2.59	1.54
0.80	.10	2.44	1.45	2.70	1.60
.40	.10	2.51	1.49	2.85	1.69
.80	.20	2.41	1.43	2.67	1.58
.64	.41	2.36	1.40	2.80	1.66
1.00	.41	2.21	1.31	2.67	1.58

Reduction of the cuprous complex to the amalgam takes place reversibly when the concentration of excess ethylenediamine and thiourea are such that the waves are completely separated. Values for the slopes for the plots of $\log(i_d - i)/i$ vs. E are close to the theoretical value for a

TABLE IV

DOUBLE COMPLEX SYSTEM

Thiourea, molar	en, molar	Cu(II) to Cu(I) reduction		Cu(I) to amalgam reduction	
		$-E_{1/2}$ vs. S. C. E.	$-E_{1/2}$ calcd.	Slope of log plot	$-E_{1/2}$ vs. S. C. E.
1.60	0.10	0.47^a	0.168	0.060	0.815
0.80	.10	.48 ^b	.229	.061	.744
.40	.10	.51 ^b	.311	.047	.693
.80	.20	.48 ^b	.265	.059	.735
.64	.41	.46 ^b	.335	.060	.727
1.00	.41	.44 ^b	.295	.061	.768

^a Slope of plot of $\log(i_d - i)/i$ vs. E was 0.088 . ^b Approximated from polarographic wave.

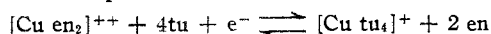
one electron reduction (Table IV). The one low value of 0.047 was taken from a polarogram in which the two waves blended. Probably in this case the electrode reaction was a mixed process, the reduction of the cupric complex not taking place completely before further reduction to the amalgam occurred.

The potential of the copper(I) to copper amalgam reduction process is determined by tetrathiourea-copper(I) ion. The half-wave potential varies with the thiourea concentration (Table III) in the same manner that the half-wave potential of tetrathiourea-copper(I) ion varies (Table II), but it is independent of the ethylenediamine concentration. Although the potential is determined by tetrathiourea-copper(I) ion, the current is controlled by the diffusion of bis-(ethylenediamine)-copper(II) ion to the electrode.

Since tetrathiourea-copper(I) ion determines the potential of the copper(I) to copper amalgam reduction process, it apparently is formed when bis-(ethylenediamine)-copper(II) ion is reduced at the more positive potential. Thus, for the copper(II) to copper(I) reduction process to proceed reversibly, the ethylenediamine groups must be rapidly and reversibly replaced by thiourea groups simultaneously as the electron is added. A test of the reversibility of the electrode reaction was made by finding the slope of a plot of $\log(i_d - i)/i$ vs. E for the solution first listed in Table IV. A slope of 0.088 was found, showing that the process is irreversible. Other solutions containing varying amounts of ethylenediamine and thiourea were not tested for the reversibility of the electrode reaction, as the waves appeared to be too drawn-out to show reversible behavior.

A further test of the reversibility of the reduction of bis-(ethylenediamine)-copper(II) ion to tetrathiourea-copper(I) ion can be made by considering the shift in the half-wave potential with a change in the concentration of thiourea and/or ethylenediamine. An equation relating these variables was derived in much the same manner that Lingane⁵ has derived a general equation which describes the change in the half-wave potential of the reduction of one complex ion to another complex ion in a lower oxidation state with a change in the concentration of a single complexing agent.

For the reduction of the cupric complex to the cuprous complex



the half-wave potential for 25° is defined by the equation

$$(E_{1/2})_c = (E_{1/2})_s + 0.05915 \log K_{d_{1c}}/K_{d_{01c}} + 0.2366 \log \frac{C_{\text{tu}}}{C_{\text{en}}} - 0.1183 \log C_{\text{en}} \quad (3)$$

Knowing the dissociation constants of the cupric and cuprous complexes, the half-wave

potential of the simple ion reduction, and the concentrations of thiourea and ethylenediamine, then the half-wave potential of the complex ion reduction can be calculated and compared to the value obtained experimentally.

In Table IV are recorded data for the half-wave potentials of the complex ion reduction which were approximated from the polarographic waves. Theoretical half-wave potentials calculated from equation (3) also are included. In calculating the theoretical values, the half-wave potential of the simple ion reduction was taken to be -0.079 volt (*vs.* S.C.E.)⁶ The value of 1.9×10^{-20} for the dissociation constant of bis-(ethylenediamine)-copper(II) ion¹ was used, and for the dissociation constant of tetrathiourea-copper(I) the value of 4.1×10^{-16} calculated above was used. The experimental values of the half-wave potentials differ from the calculated values by a considerable amount, showing that the electrode reaction is irreversible. A high concentration of ethylenediamine seems to favor a decrease in the overvoltage.

When a dropping mercury electrode reaction is irreversible, usually one or more steps in the reaction is slow. In the irreversible reduction of bis-(ethylenediamine)-copper(II) ion to tetrathiourea-copper(I) ion, the slow step probably is the replacement of ethylenediamine molecules with thiourea molecules. This replacement reaction must be fairly rapid, however, as a diffusion current region is reached before further reduction of bis-(ethylenediamine)-copper(II) ion to copper amalgam occurs.

Acknowledgment.—The helpful suggestions and criticisms of Professor John C. Bailar are gratefully acknowledged. Funds for preliminary work were provided by the Burgess Battery Company and Graham, Crowley and Associates.

Summary

1. In solutions containing fifty to two hundredfold excess dipyriddy, cupric ion coordinates three molecules of dipyriddy. Under the same conditions, cuprous ion coordinates two dipyriddy molecules. Four thiourea molecules are coordinated to cuprous ion in solutions containing fifty to sixteen hundredfold excess thiourea.

2. In the presence of excess ethylenediamine and thiourea, bis-(ethylenediamine)-copper(II) ion is reduced at the dropping mercury electrode in two steps. In the first step the cupric complex ion is reduced irreversibly to the tetrathiourea-copper(I) ion. Further reduction to the amalgam takes place reversibly.

3. Dissociation constants for tris-(dipyriddy)-copper(II) ion, bis-(dipyriddy)-copper(I) ion, and tetrathiourea-copper(I) ion were calculated from polarographic data.

URBANA, ILLINOIS

RECEIVED MARCH 8, 1950