assumed but unproved explanation of the allomerization of chlorophyll.[29] A preliminary experiment, performed with allomerized chlorophyll, indicates that fluorescence activation occurs equally well with allomerized and normal chlorophyll, which is contrary to predictions based upon the detailed hypotheses which have been used to explain allomerization and fluorescence activation, respectively. The available evidence is not sufficient to permit a definite decision which, if either, of these detailed, incompatible mechanisms is correct. There is no conflict between the experimental facts or between the general explanation of allomerization and of fluorescence activation.

Acknowledgment.—The authors wish to acknowledge the many valuable suggestions, chiefly in regard to structural considerations, of Dr. R. Arnold and Dr. W. Lipscomb, of this department.

Summary

Chlorophyll dissolved in pure dry hydrocarbons is practically non-fluorescent. The addition to such a solution of 0.01% or more of water, or certain alcohols or amines, raises the intensity of the fluorescence to the value which is characteristic of chlorophyll dissolved in alcohols or similar solvents. The absorption spectrum of chlorophylls in dry hydrocarbons differs from the spectrum of chlorophyll in hydrocarbon solvents containing a trace of water or other "activator." Moreover the spectrum in the presence of a small amount of activator is independent of the chemical nature of the activator and bears no resemblance to the spectrum of chlorophyll dissolved in the pure activator.

For all activators studied, the intensity of fluorescence, I_f, fits a relation of the form

$$\frac{I_{f,\,\max.}}{I_f} = \frac{1}{K_1(\mathrm{HA})} + 1$$

where $I_{f,\,\max.}$ is the upper limiting value of the fluorescence, (HA) is the concentration of the activator, and K_1 is an adjustable constant which is a measure of the efficiency of the activator.

These results are consistent with the postulate that a molecule of chlorophyll and one of the activator form an addition compound which is the fluorescent entity, and that the simple chlorophyll molecule in an inert solvent is non-fluorescent. This postulate has been interpreted in terms of hydrogen bonding, probably involving a keto oxygen on ring V of the chlorophyll molecule.

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[29] Compare Rabinowitch, "Photosynthesis," Vol. I, 1945, pp. 459-462 and 492-493.

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Polarography of Copper Complexes. I. Ethylenediamine, Propylenediamine, Diethylenetriamine and Glycine Complexes

By H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and Sherlock Swann, Jr.

Several complex ions of copper were studied by means of the dropping mercury electrode in order to determine the effect of specific coördinating agents on the stability of the cuprous and cupric oxidation states. Results on complexes of ethylenediamine, propylenediamine, diethylenetriamine, and glycine are reported in this paper.

The stability and composition of the ethylenediamine and propylenediamine complexes of copper have been determined by Carlson, McReynolds and Verhoek,[1] who used the method of Bjerrum.[2] Job and Brigando[3] and Haendler[4] have employed the method of continuous variations for the study of the diethylenetriamine complex of copper. Keefer[5] previously has studied the glycine complex using the dropping mercury electrode, but it was desired to extend the range of his investigation to lower pH values by using suitable buffer solutions.

All of these complexes are reduced directly to the amalgam, in contrast to the cupric complexes of ammonia,[6,7] pyridine,[8] thiocyanate ion,[9] and chloride ion,[10] which are reduced first to the respective cuprous complexes before being further reduced to the amalgam.

Experimental

Reagent grade chemicals were used without further purification except for the glycine which was once recrystallized. Solutions of the amines, obtained from the Carbide and Carbon Chemicals Corporation, were standardized potentiometrically with hydrochloric acid using a Beckman pH meter. A solution of cupric nitrate was standardized iodometrically.

The solutions for analysis were made up from stock solutions of the reagents. Potassium nitrate was used as indifferent electrolyte for the amine complexes, and for the glycine complex the buffer of potassium dihydrogen phosphate plus sodium hydroxide was used as indifferent electrolyte. Gelatin and methyl cellulose were found to be

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[1] Carlson, McReynolds and Verhoek, This Journal, **67**, 1334 (1945).

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

[3] Job and Brigando, *Compt. rend.*, **210**, 438 (1940).

[4] Haendler, This Journal, **64**, 686 (1942).

[5] Keefer, *ibid.*, **68**, 2329 (1946).

[6] Stäckelberg and Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[7] Lingane, *Chem. Rev.*, **29**, 1 (1941).

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

[9] Kolthoff and Lingane "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

[10] Lingane, *Ind. Eng. Chem.. Anal. Ed.*, **15**, 583 (1943).

effective maximum suppressors. Gelatin tended to suppress the height of the polarographic wave, while with methyl cellulose the values of the slopes from the logarithmic plots tended to be higher than with gelatin, indicating a greater deviation from reversible behavior. Drop times were somewhat greater with methyl cellulose than with gelatin. No maximum suppressor was needed for the glycine complex.

Polarograms were recorded with a Sargent model XI polarograph, both by automatic and by manual operation of the instrument. Potential measurements were made with a Leeds and Northrup student type potentiometer. An H-type cell with a temporary plug of 3% agar in 0.1 *N* potassium nitrate and the bulb type saturated calomel electrode were used. A Beckman *p*H meter was used for *p*H measurements.

Oxygen was removed from the solutions for analysis with a stream of oxygen-free nitrogen. The temperature was kept at 25 ± 0.1°.

Reversibility of the electrode reactions was tested by determining the slopes of plots of log $(i_d - i)/i$ *vs.* E. Corrections were made for residual current. Values for the half-wave potentials were taken from the logarithmic plots. Data for these plots were taken by manual operation of the polarograph, since by automatic operation the lag of the galvanometer introduced an error of a few millivolts in the half-wave potentials. Half-wave potentials were generally reproducible to ±2 mv.

Discussion

The reduction of a cupric complex directly to the amalgam may be represented by

$$\mathrm{CuX_p}^{(2+\mathrm{p}b)+} + 2\mathrm{e}^- \longrightarrow \mathrm{Cu(Hg)}_x + \mathrm{pX}^b$$

The equation relating the half-wave potentials of the simple and complex ions is[7]

$$(E_{1/2})_c - (E_{1/2})_s = 0.0296 \text{ kog } K_d(f_c/f_s)(D_s/D_c)^{1/2} - \mathrm{p}0.0296 \log C_x f_x \quad \text{(A)}$$

where K_d represents the dissociation constant of the complex, f the activity coefficients of the ions, C_x the concentration of the complexing agent, and D the diffusion coefficients of the ions. The c and s subscripts refer to the complex and simple ions, and the x subscript refers to the complexing agent. The number of groups attached to each cupric ion is represented by p. As a first approximation, the activity coefficients may be assumed to be unity, and in most cases D_s and D_c are nearly equal so that their ratio may also be assumed to be unity.

Equation (A) may be more specifically applied to the case of α-amino acid complexes where the concentration of complexing agent is dependent on *p*H. From the expression for the dissociation constant of the α-amino acid, $K_a = C_{A^-} \cdot C_{H^+}/C_{AH}$, it follows that $\log C_{A^-} = p\mathrm{H} - p\mathrm{K_a} + \log C_{AH}$. Substituting this expression in C_{A^-} for C_x in equation (A) and setting the activity coefficients and the ratio of diffusion coefficients equal to unity, the following equation is derived

$$(E_{1/2})_c - (E_{1/2})_s = 0.0296 \log K_d - \mathrm{p}0.0296(p\mathrm{H} - pK_a) - \mathrm{p}0.0296 \log C_{AH} \quad \text{(B)}$$

From this equation it is apparent that the half-wave potential of the complex ion will be a linear function of *p*H if the dissociation of the acid is small and the concentration of complexing agent at the electrode surface remains equal to that in the bulk of the solution. A buffer must therefore be used in order to prevent depletion of the hydrogen ion concentration at the electrode surface. The reaction between hydrogen ions and acid anions must also be assumed to be rapid and reversible.

Data obtained in this investigation are given in Tables I, II, III, and IV. The electrode reaction for all four complexes undoubtedly involves two electrons, as is shown by the values of the slopes of the plots of log $(i_d - i)/i$ against the potential, and diffusion current constants $i_d/Cm^{2/3}t^{1/6}$. Only single waves were observed in all cases.

TABLE I

ETHYLENEDIAMINE COMPLEX

Indifferent electrolyte 0.1 *N* $\mathrm{KNO_3}$; 5.14×10^{-4} *M* $\mathrm{Cu(NO_3)_2}$; 0.01% gelatin maximum suppressor; mercury column 69.8 cm.; m = 1.467 mg. sec.$^{-1}$; $m^{2/3}t^{1/6}$ = 1.66 mg.$^{2/3}$sec.$^{-1/2}$; i_d measured at −0.7 volt.

Concn. en molar	$-E_{1/2}$ *vs.* S. C. E.	i_d μamp.	Slope of log plot	Diffusion current constant
1.02	0.568	2.72	0.034	3.19
0.409	.544	2.91	.034	3.42
.204	.526	2.97	.035	3.48
.102	.506	3.03	.033	3.56
.041	.482	3.04	.035	3.57
0.020	.463	3.06	.036	3.59
	− .016	..	...	..

TABLE II

PROPYLENEDIAMINE COMPLEX

Conditions were the same as those described in Table I except that 0.01% methyl cellulose was used as maximum suppressor.

Concn. pn molar	$-E_{1/2}$ *vs.* S. C. E.	i_d μamp.	Slope of log plot	Diffusion current constant
1.06	0.583	2.47	0.036	2.90
0.422	.554	2.74	.035	3.22
.211	.541	2.82	.038	3.31
.211	.538	2.73	.034	3.22[a]
.106	.518	2.89	.035	3.38
.042	.493	2.90	.036	3.39
.021	.481	2.69	.038	3.16[a]

[a] These solutions contained 0.01% gelatin maximum suppressor.

TABLE III

DIETHYLENETRIAMINE COMPLEX

Conditions were the same as those given in Table I except for these changes: $m^{2/3}t^{1/6}$ = 1.65 mg.$^{2/3}$sec.$^{-1/2}$; i_d measured at −0.75 volt for the two solutions most concentrated in dien, at −0.70 volt for others.

Concn. dien molar	$-E_{1/2}$ *vs.* S. C. E.	i_d amp.	Slope of log plot	Diffusion current constant
1.00	0.602	2.10	0.034	2.48
0.400	.575	2.41	.034	2.84
.200	.559	2.50	.035	2.95[a]
.100	.542	2.63	.036	3.10
.040	.520	2.71	.040	3.20
.020	.504	2.66	.036	3.14

[a] This solution contained 0.01% methyl cellulose maximum suppressor.

TABLE IV

Indifferent electrolyte 0.05 M KH_2PO_4 plus NaOH; no maximum suppressor; 1.027 × 10^{-3} M $Cu(NO_3)_2$; 1 M glycine put into solutions; mercury column 69.8 cm.; m = 1.467 mg. sec.$^{-1}$; $m^{2/3}t^{1/6}$ = 1.67 mg.$^{2/3}$sec.$^{-1/2}$; i_d measured at −0.50 volt.

pH	$-E_{1/2}$ vs. S. C. E.	i_d μamp.	Slope of log plot	Diffusion current constant
7.90	0.325	5.49	0.033	3.20
7.61	.309	5.41	.033	3.16
7.27	.290	5.30	.035	3.09
7.08	.278	5.35	.034	3.12
6.72	.257	5.35	.035	3.12
6.60	.244	5.49	.034	3.20
6.31[a]	.238	5.18	.036	3.02

[a] This solution contained 0.075 M KH_2PO_4.

The number of groups coördinated to each cupric ion is obtained from the slope of the plots of equations A and B, shown in Fig. 1 and Fig. 2.

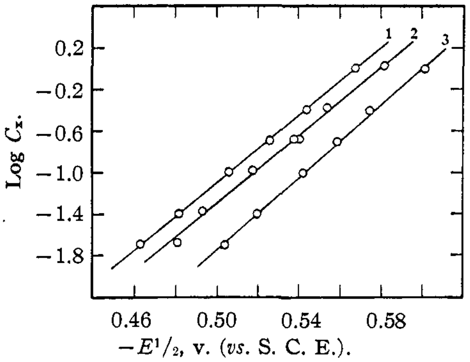

Fig. 1.—Variation of half-wave potential with concentration of complexing agent: 1, ethylenediamine; 2, propylenediamine; 3, diethylenetriamine.

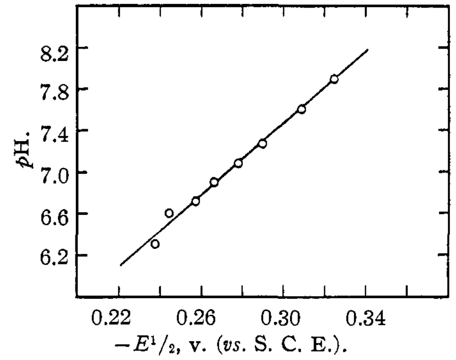

Fig. 2.—Variation of half-wave potential of glycine complex with pH.

The reciprocal slope of the plot for the ethylenediamine complex is 0.061, for the propylenediamine complex 0.061, for the diethylenetriamine complex 0.058, and for the glycine complex it is 0.059, indicating that two groups are coördinated in each case. This finding verifies the work of other investigators[1,4,5] although Haendler[4] has reported a diethylenetriamine complex containing one molecule of the amine, and Gould and Vosburgh[11] have reported a glycine complex containing one coördinated glycinate ion. However, both of these complexes exist in solutions containing a low concentration of the complexing agent. Job and Brigando[3] have reported the existence of a tetrakis-(diethylenetriamine)-tricopper(II) ion, but it is probable that their formulation is in error in view of Haendler's findings and the results obtained in this investigation.

The diethylenetriamine complex is of interest in that in it cupric ion may show the coördination number of six, whereas its usual coördination number is four. Such an effect of chelation in changing the usual coördination number of an ion has been previously observed in bis-(α,β,γ-triaminopropane)-platinum(II) iodide.[12]

Dissociation constants, which were calculated after making the simplifying assumptions previously described, are given in Table V. For the glycine complex, Keefer's value[5] of 9.69 for pK_a was used. Values of dissociation constants calculated from the data of Carlson, McReynolds and Verhoek,[1] and the value reported by Keefer[5] are included for reference.

TABLE V

Complex	K_d calcd.	K_d previously reported[a]
Ethylenediamine	1.9 × 10^{-20}	2.5 × 10^{-20}
Propylenediamine	6.8 × 10^{-21}	2.2 × 10^{-20}
Diethylenetriamine	1.4 × 10^{-21}	....
Glycine	7.9 × 10^{-16}	7.4 × 10^{-16}

[a] See references 1 and 5.

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Summary

1. Polarographic measurements show that cupric ion coördinates two molecules of ethylenediamine, propylenediamine, or diethylenetriamine in solutions containing forty to two thousandfold excess of the respective complexing agent. In buffered solutions containing one to tenfold excess of glycinate ion, cupric ion coördinates two glycinate ions.

2. The half-wave potential of the glycine complex is a linear function of pH in the useful range of phosphate buffer.

3. Dissociation constants for the complex ions studied have been evaluated. There is a good agreement between the method of Bjerrum and the polarographic method.

4. Because of the relative stability of the diethylenetriamine complex, it is probable that in it copper shows the coördination number of six.

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[11] Gould and Vosburgh, THIS JOURNAL, **64**, 1630 (1942).

[12] Mann, *J. Chem. Soc.*, 890 (1928).