[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF THE TULANE UNIVERSITY OF LOUISIANA]

Inorganic Complex Compounds Containing Polydentate Groups. I. The Complex Ions Formed Between Copper(II) Ions and Ethylenediamine[1,2]

BY HANS B. JONASSEN AND T. H. DEXTER[3]

Upon addition of an alcoholic[4] or aqueous solution[5] of ethylenediamine to a solution containing copper(II) chloride two different compounds may be obtained. In the presence of excess copper (II) chloride a blue precipitate is isolated which has the composition $CuenCl_2$; if, however, the solution contains excess amine a violet compound with the empirical formula $Cu(en)_2Cl_2 \cdot H_2O$ is obtained. Chattaway and Drew[5] propose that in solutions only one complex ion is formed between the copper(II) ions and ethylenediamine, the $[Cu(en)_2]^{+2}$ ion. For the blue compound formed in the presence of excess copper(II) ions this would necessitate the assumption of a dimeric substance–$[Cu(en)_2]CuCl_4$. These authors claim to substantiate this postulate by preparing the same chloroplatinite from the blue and the violet copper(II) ethylenediamine complex compounds. This proposed structure is in accord with the data reported by Job[6] who investigated this system at a wave length of 615 mμ by the method of continuous variation and found proof for the existence of only the $[Cu(en)_2]^{+2}$ ion.

Mandal,[7] however, was unable to confirm the results obtained by Chattaway and Drew[5] and casts doubt upon the validity of their postulate. Carlson, McReynolds and Verhoek[8] implicitly accept the existence of the $[Cu(en)_2]^{+2}$ and $[Cuen]^{+2}$ ions and report formation constants for both these complex compounds.

This paper reports the results of further studies of the complex ions formed between the copper (II) ions and ethylenediamine. These data indicate that in solutions both the $[Cu(en)_2]^{+2}$ and the $[Cu(en)]^{+2}$ ions exist.

Spectrophotometric Studies

Experimental.—All absorption measurements were obtained with the Beckman Spectrophotometer, cell depth 1.0 cm. The ethylenediamine was purified by fractional distillation, a solution was prepared and standardized against hydrochloric acid using brom phenol blue as an indicator. This solution was then diluted to 0.200 *M*. A standard solution of copper(II) chloride was prepared by dissolving about 0.05 mole of copper chloride in 1000 ml. of water. To this solution excess potassium iodide was added and the liberated iodine was titrated with a standard solution of sodium thiosulfate to the starch endpoint. This solution was then diluted to 0.020 *M*. Two drops of 6 *N* hydrochloric acid were added to repress hydrolysis.

Optical density measurements were made over the range from 400 to 800 mμ for solutions 0.01 *M* in copper(II) ions with varying concentrations of ethylenediamine (0.005, 0.01, 0.02 and 0.03 *M*). These solutions correspond to mole ratios of copper(II) ions to amine of 1:0.5; 1:1; 1:2; 1:3. The observed absorption spectra are shown in Fig. 1. The absorption spectrum obtained for the 1:3 solution is not shown; it is almost identical with that for the 1:2 mixture.

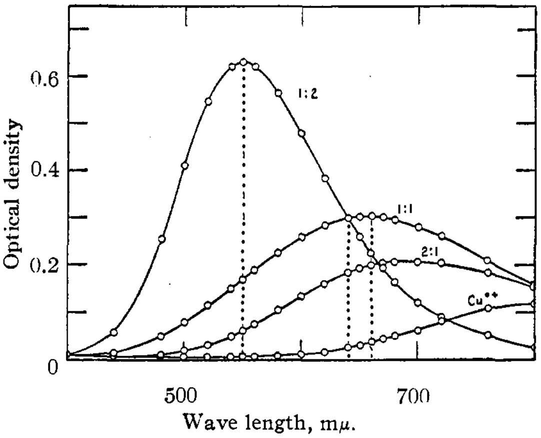

Fig. 1.—Absorption spectra of solutions containing 0.01 mole of cupric chloride and 0.005, 0.01 and 0.02 mole of ethylenediamine per liter.

Further absorption measurements were then made at wave lengths of 550, 640 and 660 mμ according to the method of continuous variation as extended by Vosburgh and Cooper.[9] The solutions had a total solute concentration of 0.02 *M* with varying proportions of copper(II) ions and ethylenediamine. Figure 2 shows the plot of *x* (solute fraction of ethylenediamine) against *y* (the difference between the observed extinction of the complex and that calculated for no reaction).

Discussion

Job[6] investigated the complex ions formed between copper(II) ions and ethylenediamine at the wave length of 615 mμ and found proof for the existence of the $[Cu(en)_2]^{+2}$ ion. A re-investigation of this system over the whole visible range of the spectrum shows that in solutions two complex ions exist—the $[Cu(en)_2]^{+2}$ and the $[Cu(en)]^{+2}$ ion.

As the amine concentration is increased, a shift in the absorption maximum toward shorter wave lengths is observed (Fig. 1). This is accompanied by a sudden change in the shape of the curve after the 1.1 mole ratio has been exceeded; no further change is observed after the 1:2 ratio has been exceeded. This seems to indicate that no colored complex ions containing

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[1] Presented at the Second Regional Meeting of the American Chemical Society at Dallas, Texas, December 13, 1946.

[2] Based on a portion of the M.S. Thesis of T. H. Dexter, 1947.

[3] Department of Chemistry, University of Illinois.

[4] Jonassen, Crumpler and O'Brien, THIS JOURNAL, **67**, 1709 (1945).

[5] Chattaway and Drew, *J. Chem. Soc.*, 947 (1937).

[6] Job, *Ann. Chim.*, [10] **9**, 113 (1928).

[7] Mandal, *Current Science*, **10**, 78 (1941).

[8] Carlson, McReynolds, and Verhoek, THIS JOURNAL, **67**, 1334 (1945).

[9] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

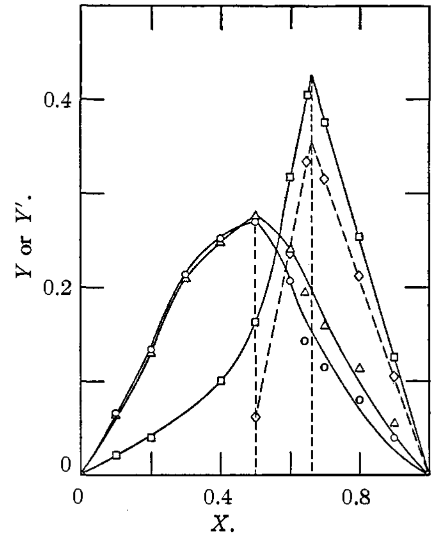

Fig. 2.—Y curves for mixtures of $(1 - X)$ liters of 0.02 M cupric chloride and X liters of 0.02 M ethylenediamine solutions: □, 550; △, 640; and ○, 660 mμ: ◇, Y' curve at 550 mμ.

more than two amine molecules per copper(II) ions are formed. This is in accord with the results obtained by Carlson, McReynolds and Verhoek.[8]

Such a shift in absorption characteristics as the copper(II) ion to ethylenediamine ratio increases is not compatible with Chattaway and Drew's[5] hypothesis of the existence of only the $[Cu(en)_2]^{+2}$ ion in such solutions. It cannot be argued that the decomposition of the yellow $CuCl_4^{-4}$ brings about this change since it has been shown[10] that the concentration of free chloride ion must be greater than 1 molar before the $CuCl_4^{-2}$ shows any measurable light absorption and in these solutions the chloride ion concentration is about 0.01 M.

The continuous variation studies (Fig. 2) show that at the wave length of 640 and 660 mμ the curves go through a maximum at $x = 0.5$ indicating a 1:1 complex ion, $[Cu\,en]^{+2}$. The curve obtained at 550 mμ reaches a maximum at $x = 0.65$ substantiating the existence of the $[Cu(en)_2]^{+2}$ ion. If Chattaway and Drew's[5] postulate were correct only one maximum should have been obtained at $x = 0.65$. The continuous variation studies of Job[6] did not give any indications of the 1:1 complex ion since he only investigated this system at a wave length of 615 mμ. The studies reported here have indicated that only at wave lengths above 635 mμ a maximum is obtained at $x = 0.50$.

Conductometric Titration Studies

Experimental.—One hundred ml. of a solution 0.00961 M in copper(II) ions and 0.00961 M in ethylenediamine was titrated with 0.240 M sodium hydroxide. The specific conductance was determined after the addition of various amounts of sodium hydroxide at 25.5°. In Fig. 3 the specific conductance is plotted against ml. of sodium hydroxide solution; it increases after half the total copper (II) ion has been precipitated. During the titration the color of the solution changes from blue to violet.

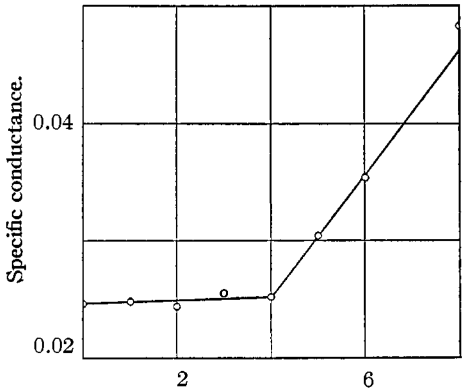

Fig. 3.—Conductometric titration of Cu en^{++} with sodium hydroxide.

The optical density of the solutions obtained after the addition of various amounts of sodium hydroxide was measured at 520 and 700 mμ. These wave lengths were selected because of the large difference in absorption between the solutions containing the 1:1 and 1:2 mole ratios of copper(II) ions to amine. In Fig. 4 (solid lines) the optical density is plotted against ml. of sodium hydroxide at the two wave lengths.

For comparison, absorption spectra were then measured at the same wave lengths for solutions 0.00961 M in ethylenediamine containing copper(II) ions concentrations equivalent to those present at the various steps in the titration. The broken lines in Fig. 4 represent these data.

Discussion

Calculations based upon the formation constants for the system copper(II) ions and ethylenediamine[8] and upon the $K_{s.p.}$ of copper hydroxide determined by Feitknecht[11] show that in solutions containing copper(II) ions and ethylenediamine molecules the bis-ethylenediamine copper(II) complex ions alone are not destroyed by hydroxide ions. The $K_{s.p.}$ of copper hydroxide will be exceeded only if hydrated copper(II) ions or mono-ethylenediamine copper(II) ions are present in the solution.[12]

The data obtained from the conductometric titration of the solution containing copper(II) ions and ethylenediamine in a 1:1 mole ratio show that the conductivity of the solution increases after half the total copper(II) ion concentration has been removed by sodium hydroxide (Fig. 3). During the titration copper hydroxide is precipitated and the color of the solution changes from deep blue to violet, which seems to indicate

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(10) Bjerrum, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **22**, no. 18 (1946).

(11) Feitknecht, *Helv. Chim. Acta*, **27**, 771 (1944).

(12) Since the values for the formation constants for the $[Cu(en)_2]^2$ ion determined by Carlson and Job varied (Carlson's $pK_N = 19.6$; Job's = 5.9), this constant was redetermined by the pH and the polarographic method. The values obtained for pK_N, pK_1 and pK_2 checked with those reported by Carlson $pK_N = 19.5$; $pK_1 = 10.5$; $pK_2 = 9.0$.

the formation of a new complex ion. A different complex ion can be formed only if ethylenediamine is liberated. During the reaction ethylenediamine, however, can be liberated only if the original complex ion is the mono-ethylenediamine copper (II) ion. This seems to indicate that during the precipitation of half the total copper ions an equivalent amount of ethylenediamine is liberated. This reacts with the remaining mono-ethylenediamine copper(II) ions to form bis-ethylenediamine copper(II) ions.

If the above reactions occur, the absorption at 700 mμ should decrease and the absorption at 520 mμ increase. This is borne out by the experimental results given in Fig. 4. The optical density values for these solutions are somewhat lower than those of the standard solutions (broken lines in Fig. 4) indicating depletion of the solute concentration through adsorption on the copper hydroxide precipitate.[13] Theoretically, the spectral absorption should become constant after half the copper ions have been removed; however, because of the formation of a slight precipitate it increased at 700 mμ and decreased at 520 mμ. A slight Tyndall effect was also observed in these solutions after 5 ml. of sodium hydroxide had been added.

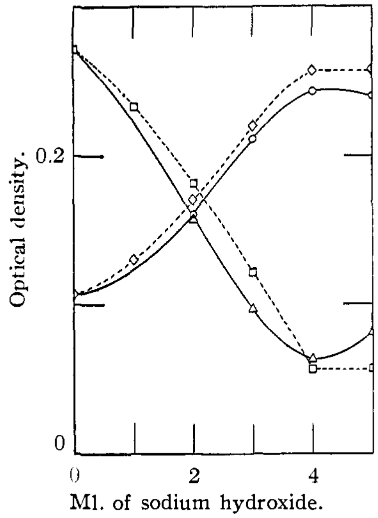

Fig. 4.—Comparison of optical density between solutions from conductimetric titrations (solid lines) and standard solutions containing constant ethylenediamine concentration and varying concentration of copper(II) ion (broken lines): ⊙, ◇, 520 mμ; △, ◻, 700 mμ.

These data prove that the mono-ethylenediamine copper(II) ion exists in a solution of a 1:1 mole ratio of ethylenediamine and copper(II) ion.

Saturation Studies

Discussion.—If the optical density obtained at a certain wave length for varying ratios of copper(II) ions to ethylenediamine is plotted against the value of x (see Fig. 2), the curve goes through a maximum or breaks and becomes horizontal after a certain amine to copper(II) ion ratio has been reached (Fig. 5). This is in accord with the theoretical considerations reported by Ruff.[14] The optical density curves at 640, 660 and 700 mμ show maxima or breaks at a 1:1 mole ratio, whereas those at 520 and 550 mμ break at a 1:2 mole ratio of copper(II) ions to ethylenediamine.

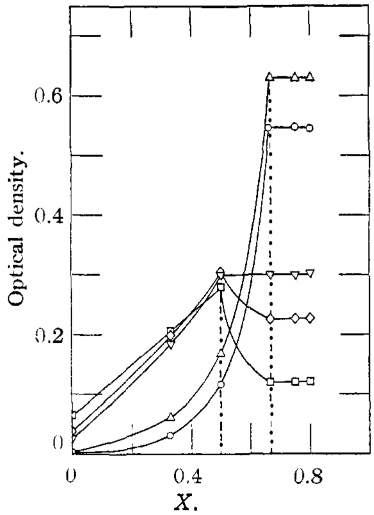

Fig. 5.—The connection between optical density and x for the copper(II)-ethylenediamine system at wave lengths: ⊙, 520; △, 550; ▽, 640; ◇, 660; and ◻, 700 mμ.

Absorption Spectra of Solutions Prepared from the Solid Complex Compounds

Experimental.—The complex compounds $Cu\,enCl_2$ and $Cu(en)_2Cl_2\cdot H_2O$ were prepared according to the procedure given by Chattaway and Drew,[5] and absorption spectra were measured for 0.01 M solutions of each of these complex compounds.

Discussion

The spectrum for the mono-ethylenediamine copper(II) complex compound coincided with that for the solution containing the two constituents in the 1:1 ratio; that of the bis-ethylenediamine copper(II) ion was identical with that of the solution containing the 1:2 mole ratio of copper(II) ion to amine given in Fig. 1.

All the above data indicate that in solutions over the concentration range studied two colored complex ions are formed between copper(II) ions and ethylenediamine: mono- and bis-ethylenediamine copper(II) ions. Even the crystalline complex compounds dissolved in water show the absorption characteristics of solutions containing the 1:1 or 1:2 mole ratios, respectively.

Summary

1. The complex ions formed in solution be-

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(13) Mehrortra and Dhar, *J. Phys. Chem.*, **33**, 216 (1929).

(14) Ruff, *Z. physik. Chem.*, **76**, 21 (1911).

tween copper(II) ions and ethylenediamine have been re-investigated over the visible range of the spectrum by the method of continuous variations and other physical methods.

2. In solutions over the concentration range studied it has been shown that both mono-ethylenediamine and bis-ethylenediamine copper(II) ions are present.

3. Water solutions of the crystalline complex compounds $CuenCl_2$ and $Cu(en)_2Cl_2 \cdot H_2O$ show marked difference in absorption characteristics.

NEW ORLEANS, LOUISIANA RECEIVED DECEMBER 2, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Investigations on the Mechanism of Hydrogen Overvoltage. The Salt Effect[1]

BY ANDRÉ J. DE BÉTHUNE[2]

When the electrolysis of aqueous solutions of electrolytes is conducted in such a manner that hydrogen is evolved at the cathode, the electromotive force (with its sign[3]) of the cell

cathode | solution | reversible hydrogen electrode (1)

is known as *the hydrogen overvoltage* η *of the cathode.* It is also convenient to define the cathode potential V as the e. m. f. (with its sign) of the cell

constant reference electrode || solution | cathode (2)

where the constant reference electrode may be, *e. g.*, a calomel electrode or a standard hydrogen electrode, and the liquid junction potential is eliminated as well as possible.[4] The relation between cathode potential and overvoltage is

$$V = V_e - \eta \qquad (3)$$

where V_e is the equilibrium cathode potential (*i. e.*, the cathode potential at zero current, provided the electrochemical reaction remains the same in the measurement of V_e as in the measurement of V). The measured overvoltage defined above always includes a fraction of the Ohmic potential drop in the solution. This must be suitably eliminated or corrected for to obtain the "true" overvoltage. Overvoltage measurements can have meaning only within the current density range in which a single reaction occurs at the cathode (except at a dropping cathode). When several reactions occur at once, not only do the observed overvoltages and currents become very unsteady but they become difficult to interpret.

The overvoltage may be considered as an e. m. f. localized at or near the cathode surface, and needed to drive the chemical reaction at the cathode at a finite rate. The overvoltage vanishes at zero current, and is, in general, a monotonously increasing function of the current density I (in amperes cm.$^{-2}$). On several metals and in moderately acid solutions, the overvoltage can be represented over a fairly wide range of current densities by the Tafel equation

$$\eta = b \log I/I_0 \qquad (4)$$

where b and I_0 are empirical constants.[5] At low overvoltages, this equation breaks down since η and I must approach zero together. The constant b is proportional[6,7] to the absolute temperature T, and at 25° often has the value 0.12 volt, which is 2 (ln 10)kT/e, where k is the Boltzmann constant and e the electronic charge. This value of b has been confirmed by numerous workers and observed on different metals.[8] The constant I_0 is very dependent on the metal used; its temperature dependence is given by the Arrhenius equation (with an energy of activation of 18 kcal. on mercury in 0.2 N sulfuric acid.[6])

The dependence of I_0 on the composition of the solution has been investigated by Bowden,[9] Frumkin and co-workers[10] and Béthune and Kimball,[11] who all used mercury cathodes. Bowden discovered that, in dilute acids and in buffers containing 0.1 M potassium chloride, I_0 is constant throughout the entire pH range covered (from 0.8 to 6.6) ($\log I_0 = -11.5 \pm 0.2$ at 18°). This result was confirmed by the Russian workers for dilute solutions of *pure acids.* Béthune and Kimball extended Bowden's work to more concentrated acids and found that I_0 remains constant in sulfuric acid up to a concentration of 3 M. Above 3 M, there is a gradual decrease in overvoltage as the acid concentration is increased. In acid solutions containing salts, the Russian measurements seemed to indicate a salt effect, which, in the case of sulfates, raised the overvoltage (*i. e.*, lowered

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[1] Presented before the symposium on Galvanic Cells and Batteries, at the 113th National Meeting of the American Chemical Society, in Chicago, Ill., in April, 1948.

[2] National Research Fellow in Chemistry 1945–1947. Present address: Boston College, Chestnut Hill, Massachusetts.

[3] We are here adhering to the Lewis and Randall convention which makes the e. m. f. E of a cell positive when the + terminal is on the right.

[4] As here defined, the cathode potential is usually a negative quantity, while the overvoltage is always positive.

(5) J. Tafel, *Z. physik. Chem.*, **50**, 641 (1905).

(6) F. P. Bowden, *Proc. Roy. Soc. (London)*, **A126**, 107 (1929).

(7) A. Frumkin, *Acta physico-chimica U.R.S.S.*, **18**, 45 (1943).

(8) S. Glasstone, *Ann. Reports Chem. Soc.*, **34**, 107 (1937); F. P. Bowden and J. N. Agar, *ibid.*, **35**, 90 (1938); K. Wirtz, *Z. Elektrochem.*, **44**, 303 (1938); S. Glasstone, "Introduction to Electrochemistry," Chapter XIII, Van Nostrand Co., Inc., New York, N. Y., 1942.

(9) F. P. Bowden, *Trans. Faraday Soc.*, **24**, 473 (1928).

(10) Papers by A. Frumkin, S. Levina, W. Sarinsky, S. Jofa, B. Kabanov, E. Kuchinski and F. Chistiakov, *Acta physico-chimica U. R. S. S.*, **6**, 491 (1937); **7**, 485 (1937); **10**, 317, 903 (1939); **18**, 23, 183 (1943).

(11) A. J. de Béthune and G. E. Kimball, *J. Chem. Phys.* **13**, 53 (1945).