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Optical Interaction between the Chloro-complexes of Copper(I) and Copper(II) in Solutions of Unit Ionic Strength[1]

BY HARDEN MCCONNELL AND NORMAN DAVIDSON

Several investigators have remarked upon the fact that hydrochloric acid solutions containing copper in two states of oxidation, copper(I) and (II), exhibit an optical absorption in the 400–600 mμ wave length range which is markedly greater than that which might be predicted from Beer's law and the absorptions of the individual components.[2,3,4] Similar phenomena have been observed in 6–12 *F* hydrochloric acid solutions containing the mixed oxidation states of other elements[4,5,6]: tin(II) and (IV), antimony(III) and (V), and iron(II) and (III). For each of these three systems, it has been found that the optical interaction absorption, defined as the difference between the optical density ($D = \log_{10} I_0/I$) of the solution containing the mixed oxidation states of the element and the optical density predicted from Beer's law and the absorption of the components, is proportional to the product of the formal concentrations of the two oxidation states of the element. Apparently chloride coördination, or perhaps in general halogen coördination, of either or both of the oxidation states of the element is essential, as no interaction is observed in aqueous solutions free of halogen ion and the interaction absorption has always been observed to increase with increasing chloride ion concentration.[6,7]

We shall take the point of view that the optical interaction in these solutions is due to one or more "interaction complexes," either ions or uncharged species. The above-mentioned facts then indicate that such interaction complexes will contain two atoms of the interacting element, one in each oxidation state, together with a number of coördinating chloride ions.

The chemical formulas of the interaction complexes of a particular element might be established by a determination of the dependence of the optical interaction on the activities of the several complex species of the two oxidation states of this element. At present, the lack of completely quantitative information on the constitutions, concentrations and activity coefficients of each of the chloro-complexes of the two oxidation states of tin, antimony, iron and copper in 6–12 *F* hydrochloric acid solutions, where the intersection is usually observed, prevents a quantitative study of the interaction complexes in any of these solutions.

However, the optical interaction absorption of the copper(I, II)–hydrochloric acid system is sufficiently intense that, by employing a 10.0 cm. light path, it is possible to measure the interaction absorption in relatively dilute solutions ($\mu = 1.0$) in which the formulas and concentrations of the predominant chloro-complexes of copper(I) and (II) are known and where it is reasonable to assume a negligible variation of the activity coefficients of particular ions as the composition of the solution is varied at a constant ionic strength.

In this paper we shall: (a) give the quantitative data used in the determination of the concentrations of the predominant chloro-complexes of copper(I) and copper(II), (b) give the results of a determination of the dependence of the optical interaction absorption on the concentrations of the complex ions of (a), (c) present the conclusions that we have drawn from (b). It is to be emphasized that all of the solutions used for the studies (a) and (b) were maintained at a fixed total ionic strength of 1.0 with perchloric acid and that the conclusions of (c) are based on the assumption that the activity coefficients of individual ions are constant in such solutions.

The studies of Noyes and Chow[8] and Chang and Cha,[9] as well as others[10,11] indicate that only two copper(I) chloro-complexes, $CuCl_2^-$ and $CuCl_3^=$ are present in 0.2–0.8 *F* hydrochloric acid solutions saturated with cuprous chloride. If k_1 and k_2 are the mass action equilibrium constants for the reactions

$$CuCl(s) + Cl^- = CuCl_2^-$$
$$CuCl(s) + 2Cl^- = CuCl_3^=$$

then the formal solubility, *S*, of copper(I) chloride in solutions containing a free chloride concentration, (Cl^-), is given by the equation

$$S = k_1(Cl^-) + k_2(Cl^-)^2 \qquad (1)$$

Our determinations of the solubility of cuprous chloride in solutions containing varying amounts

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[1] Presented at the Atlantic City Meeting of the American Chemical Society, September 20, 1949.

[2] E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **A171**, 371 (1934).

[3] M. v. Stackelberg, *Z. Elektrochem.*, **46**, 125 (1940).

[4] C. I. Browne, Master's Thesis, California Institute of Technology, 1948.

[5] J. Whitney and N. Davidson, THIS JOURNAL, **69**, 2076 (1947); **71**, 3809 (1949).

[6] H. McConnell and N. Davidson, manuscript submitted to THIS JOURNAL.

[7] Experiments by Mr. J. Ibers of this Institute show that there is no optical interaction between the amine complexes of copper(I) and copper(II), or between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$.

[8] A. A. Noyes and M. Chow, THIS JOURNAL, **40**, 746 (1918).

[9] K. Chang and Y. Cha, *J. Chinese Chem. Soc.*, **2**, 293 (1934).

[10] G. Bodlander and O. Storbeck, *Z. anorg. Chem.*, **31**, 1, 458 (1902).

[11] Náráy-Szabó and Z. Szabó, *Z. physik. Chem.*, **A166**, 230 (1933).

of chloride ion, copper(II) and copper(I) chloro-complexes, hydrogen ion, and perchlorate ion and adjusted to an ionic strength of 1.0, are represented by the above equation with $k_1 = 0.075$ and $k_2 = 0.034$ liter/mole. This is illustrated in Fig. 1 where $0.075\ (Cl^-) + 0.034\ (Cl^-)^2$ is plotted, together with the observed values of S, against the calculated concentration of free chloride ion. Consequently, for solutions saturated with cuprous chloride, we take $0.075\ (Cl^-)$ as the concentration of $CuCl_2^-$ and $0.034\ (Cl^-)^2$ as the concentration of $CuCl_3^=$. Our values of k_1 and k_2 determined at 25.1° are in fair agreement with Noyes' value of $k_1 = 0.066$ and Chang's value of $k_2 = 0.034$, determined at 25.0° from the solubility of cuprous chloride in pure hydrochloric acid. The applicability of the last two constants to our solutions of ionic strength 1.0 is not certain however.

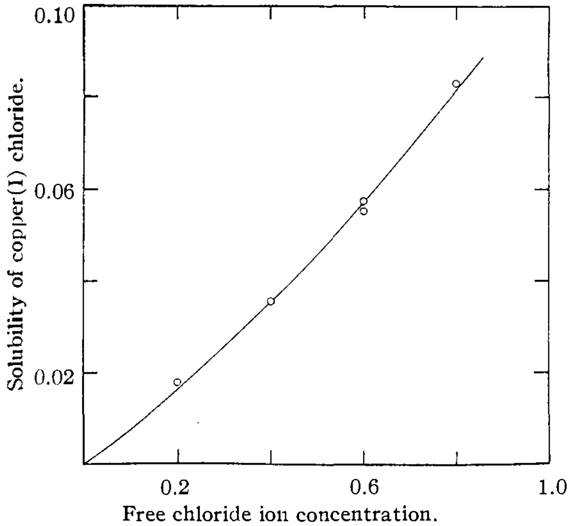

Fig. 1.—O, Experimentally measured solubilities of CuCl in chloride containing solutions of unit ionic strength. Curve is drawn from equation (1), $S = 0.075(Cl^-) + 0.034(Cl^-)^2$. Units are moles/liter.

The concentrations of the predominate copper(II) chloro-complexes and the concentration of free chloride ion present in solutions of 0.080–0.300 F copper(II) and 0.80–0.20 M free chloride ion and maintained at unit iónic strength, were calculated from the mass action stability constants K_1 and K_2 for the equilibria:[12]

$$Cu^{++} + Cl^- = CuCl^-$$

$$(CuCl^+)/(Cu^{++})(Cl^-) = K_1, K_1 = 1.30 \pm 0.03 \text{ liter/mole} \quad (2)$$

$$CuCl^+ + Cl^- = CuCl_2$$

$$(CuCl_2)/(CuCl^+)(Cl^-) = K_2, K_2 = 0.23 \pm 0.15 \text{ liter/mole}$$

Figure 2 shows the calculated distribution of copper(II) among the species Cu^{++}, $CuCl^+$ and $CuCl_2$ as a function of the free chloride ion concentration, using the above values of K_1 and K_2.

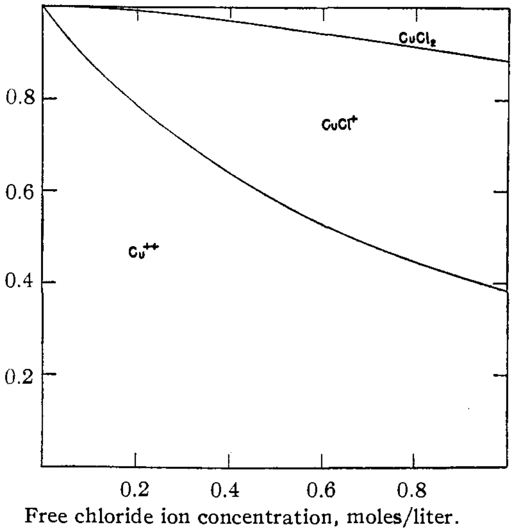

Fig. 2.—Fractional distribution of Cu(II) among Cu^{++}, $CuCl^+$ and $CuCl_2$ in chloride containing solutions at unit ionic strength.

The plots of Fig. 3 are typical examples of the data obtained for the determination of the dependence of the optical interaction on the concentration of the chloro-complexes of copper(I) and copper(II). The optical densities[13] of the solutions containing copper(II) and chloride ion but no copper(I), given in the "b" plots of Fig. 3,

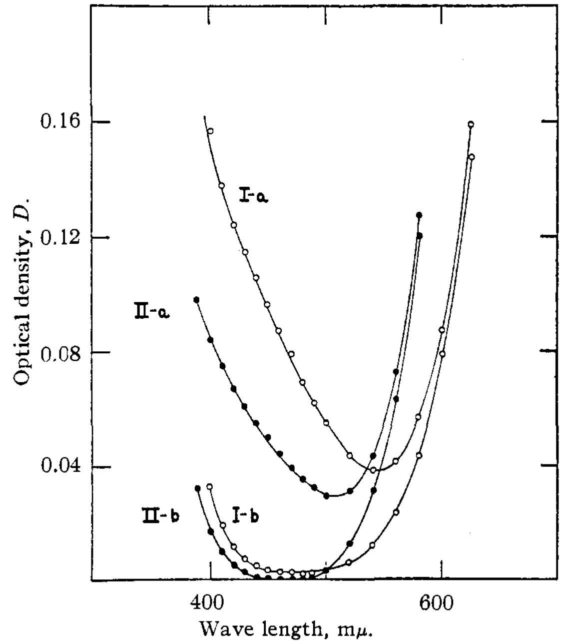

Fig. 3.—Typical data used for the determination of optical interaction absorption: I-a, Cu(II) = 0.080 F, (Cl^-) = 0.80 M, Cu(I) = 0.082 F; I-b, Cu(II) = 0.080 F, (Cl^-) = 0.80 M; II-a, Cu(II) = 0.250 F, (Cl^-) = 0.30 M, Cu(I) = 0.026 F; II-b, Cu(II) = 0.250 F, (Cl^-) = 0.30 M.

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[12] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

[13] All optical densities have been reduced to a light path of 1.00 cm.

are due to the absorption by Cu^{++}, $CuCl^+$ and $CuCl_2$. The "a" plots of Fig. 3 give the optical densities of solutions which contain the same calculated concentrations of Cu^{++}, $CuCl^+$ and $CuCl_2$, as do the corresponding "b" plots, but which in addition are saturated with copper(I) chloride. The corresponding "a" and "b" plots which contain the same formal concentration of copper(II) and the same calculated concentration of free chloride ion, have been designated with the same Roman numeral in Fig. 3. Since the two predominant copper(I) chloro-complexes in these solutions, $CuCl_2^-$ and $CuCl_3^{=}$, are colorless in this wave length range, the optical interaction absorption ΔD, is obtained directly by subtraction of the ordinates of the corresponding "a" and "b" curves.

Several dilution experiments at 0.60 *M* free chloride ion concentration have shown that the optical interaction absorption, ΔD, is within the experimental error, proportional to the product of the formal concentrations of copper(I) and copper(II). As stated previously, this shows that the interaction absorption is due to one or more chloro-complexes, each containing one atom of copper(I) and one atom of copper(II). For solutions which are saturated with copper(I) chloride, the interaction complexes can be considered as being formed according to the equations

$$CuCl(s) + Cu^{++} + nCl^- = Cu_2Cl_{1+n}^{2-n} \qquad (3)$$

with mass action equilibrium constants, L_n.

$$L_n = (Cu_2Cl_{1+n}^{2-n})/(Cu^{++})(Cl^-)^n \qquad (4)$$

We shall assume that the L_n's are sufficiently small so that the total formal concentration of the interaction complexes is small compared to the formal concentrations of copper(I) and copper(II). (This assumption is in accordance with the results of investigations of interaction absorption in systems containing other elements.[4,5,6]) Then the concentration of free cupric ion, (Cu^{++}), appearing in (4) is related to the total formal concentration of copper(II), $(Cu(II))$, by the equation

$$(Cu(II)) = (Cu^{++})(1 + K_1(Cl^-) + K_1K_2(Cl^-)^2)$$

The free chloride ion concentration, (Cl^-), can be calculated from the total formal concentration of chloride and the amount of chloride bound in copper(I) and copper(II) complexes. Then if E_n is the extinction coefficient of $Cu_2Cl_{1+n}^{2-n}$, $\Delta D = \Sigma_n E_n(Cu_2Cl_{1+n}^{2-n})$. A suitable function for graphical analysis is Q, given by the equation

$$Q = \Delta D(1 + K_1(Cl^-) + K_1K_2(Cl^-)^2)/(Cu(II)) \qquad (5)$$

$$= \sum_{n=0}^{\infty} L_nE_n(Cl^-)^n$$

The results of the present investigation are that for solutions containing 0.2, 0.3 and 0.4 *M* calculated free chloride ion concentration and 0.30, 0.25 and 0.20 *F* copper(II) the function Q is proportional, within the experimental error of 4–6%, to the square of the chloride ion concentration; that is, the third term in the summation of equation (5) is most important in these solutions. This dependence on the chloride ion concentration is found to hold for all wave lengths in the range 425–600 mμ. Representative data at two wave lengths are given in Fig. 4. For these solutions, the uncertainties in Q and in the calculated free chloride ion concentrations due to the uncertainty in K_2, are less than the 4–6% experimental error.

This quadratic dependence on the chloride ion concentration implies the existence of a strongly colored uncharged interaction complex, Cu_2Cl_3, and practically no contribution to the interaction absorption by the complexes Cu_2Cl^{++} and $Cu_2Cl_2^+$.

Plots of $Q/(Cl^-)^2$ *vs.* wave length are given in Fig. 5 for the calculated chloride concentrations 0.2, 0.3 and 0.4 *M*. Since Cu_2Cl_3 is the complex primarily responsible for the interaction absorption in these solutions, the vertical coördinates of Fig. 5 are proportional to the extinction coefficients, E_2, of this complex, the proportionality factor being L_2. The fact that the extinction coefficients rise rapidly with decreasing wave length suggests that the absorption spectrum of this complex is a case of the "electron transfer" spectra which have been discussed by Rabinowitch.[14] (As the concentration of the interaction complex in these solutions is not known, no quantitative comparison can be drawn between the extinction coefficients of the interaction complex and the large extinction coefficients characteristic of electron transfer spectra.)

To elaborate: The strong absorption band of Cu^{++} in the 200–260 mμ wave length range is attributed, in the electron transfer picture, to a photochemical act in which an electron is transferred from the aqueous solvent to a Cu^{++} ion, producing Cu^+. Increasing chloride coördination of the copper(II) produces a marked shift of the electron transfer band to longer wave lengths (*cf.* Fig. 4, of ref. 12). Thus the energy required to transfer an electron from a chloride ion to a cupric ion is less than the energy required to transfer an electron from a water molecule to a cupric ion. Furthermore, for values of $n > 1$ in the photochemical process of equation (6), there is the possibility of electron exchange between chloride ions and a chlorine atom in the photochemically excited state, that is, the coordination sphere in the excited state is not to be considered as consisting of one chlorine atom and $n - 1$ chloride ions, but of n chlorines with a charge of $-n + 1$. This electron exchange would probably cause an increase in the transition

$$Cu^{++}(Cl^-)_n^{-n} \xrightarrow{h\nu} Cu^+(Cl)_n^{-n+1} \qquad (6)$$

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(14) E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942).

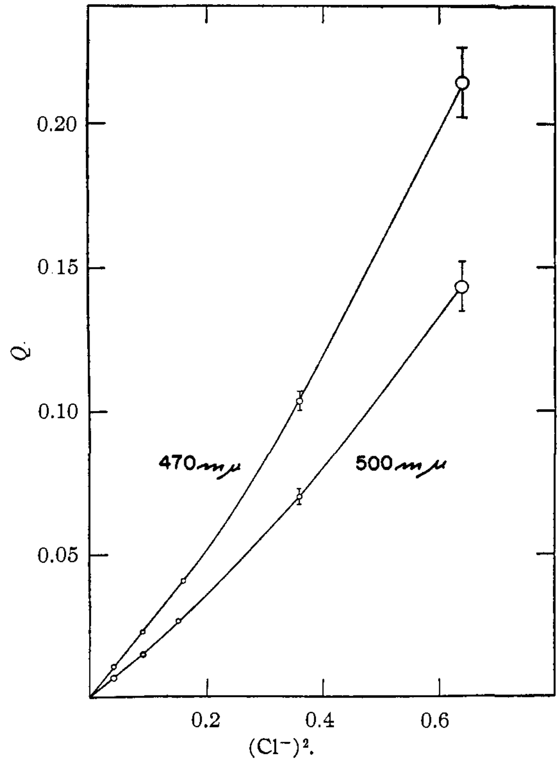

Fig. 4.—Typical plots used for the determination of the relative magnitudes of the first terms in the power series of equation (3) for solutions of low free chloride ion concentrations.

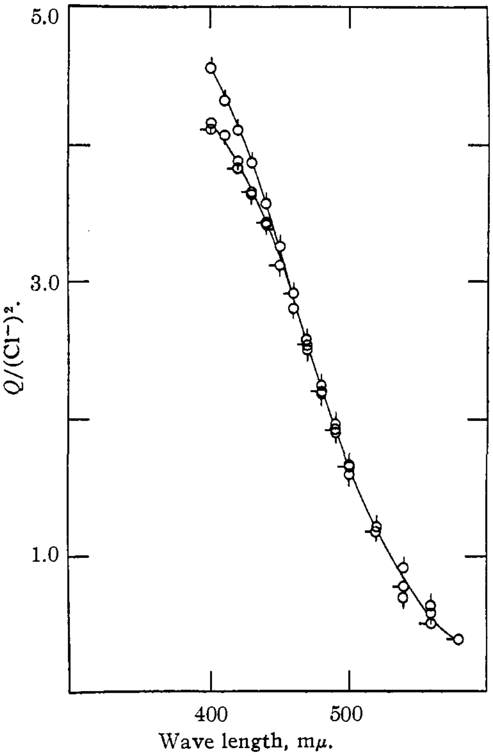

Fig. 5.—Relative absorption spectrum of the postulated interaction complex, Cu_2Cl_3. The vertical coördinate is proportional to the extinction coefficient of this complex, E_2; calculated free chloride ion concentration, (Cl^-): ȯ, 0.20 *M*; ọ, 0.30 *M*; -o, 0.40 *M*.

probabilities or a decrease in the energy of excitation, or both, and such effects explain the shifts in the absorption spectrum to longer wave lengths with increasing *n*. The fact that chloride coördination has much less influence on the absorption of copper(II) at longer wave lengths, 550–700 mμ, is at least one reason for believing that the absorption process at these wave lengths is not one of photochemical electron transfer, but rather an internal electronic excitation of a *d* electron of the copper(II) atom.

We propose that the strongly colored complex, Cu_2Cl_3, has the symmetrical structure Cl–Cu–Cl–Cu–Cl, and that its absorption spectrum may be regarded as due to an electron transfer process. In the ground state of Cu_2Cl_3 the two Cu atoms may or may not be distinguishable. Even if Cu_2Cl_3 is completely symmetrical with equivalent Cu atoms, probably the wave function of the extra valence electron has large maxima around the two Cu^{++} cores with very little overlap in the region of the bridging chlorine atom. This corresponds to a small exchange stabilization of this complex, in agreement with the fact that it does not form to a major extent in solution. In the excited state, one may think that this electron vibrates back and forth between the two Cu^{++} cores much more readily; that is, the wave function of the optically excited electron is spread over both copper atoms and the intervening bridging chlorine atom. Such an electron exchange interaction in the optically excited state may be more marked in the proposed symmetrical structure than in other possible structures of lower symmetry.

For most of the cases of the optical interaction between oxidation states in solution, there seems to be only a weak binding of the atoms of the two oxidation states in the ground state of the dimeric interaction complex. *We propose that in general the optical interaction is principally due to a strong exchange interaction in the optically excited state.*[15]

The analogy between the absorption spectra of Cu^{++}, $CuCl_n^{2-n}$ and Cu_2Cl_3 may be completed with the remark that at still longer wave lengths, >600 mμ, little or no optical interaction is observed, as may be seen from Fig. 4. Thus the electronic transition is again localized to a *d* electron of copper(II) in the complex Cu_2Cl_3.

The symmetrical complex, Cu_2Cl_3, may be considered as being formed in a bimolecular collison between $CuCl_2^-$ and $CuCl^+$ in which the positions of the chloride ligands are not shifted with respect to the original copper cores.

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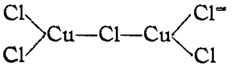
(15) This idea has been briefly discussed previously, *cf.* J. Whitney, C. I. Browne, H. McConnell, N. Davidson, "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven Conference Report, Upton, N. Y., Dec., 1948, p. 196 and also ref. (6).

It may be seen from Fig. 4 that at higher concentrations of free chloride ion, 0.6 and 0.8 *F*, *Q* increases somewhat more rapidly than the square of the free chloride concentration. However, the uncertainties in *Q* in this concentration range, 7–11%, due to the uncertainty in K_2 ($K_2 = 0.23 \pm 0.15$) and due to experimental errors, do not allow a determination of the relative magnitudes of the higher terms in equation (8), especially the relative values of the coefficients of the $(Cl^-)^3$ and $(Cl^-)^4$ terms. The proposed structure above for the complex Cu_2Cl_3 with a single halogen bridge between the atoms of Cu(I) and Cu(II) (rather than a square double halogen bridge) would suggest the next strongly colored symmetrical interaction complex to be



corresponding to the $(Cl^-)^4$ term in equation (5). The evidence for contribution of higher (than quadratic) terms to the interaction absorption is in accord with earlier observations of much greater interaction in more concentrated hydrochloric acid solutions. For example, Fig. 6 shows an absorption curve similar to those of Fig. 3, giving the interaction absorption between copper(I) and (II) in 6 *F* hydrochloric acid.[4]

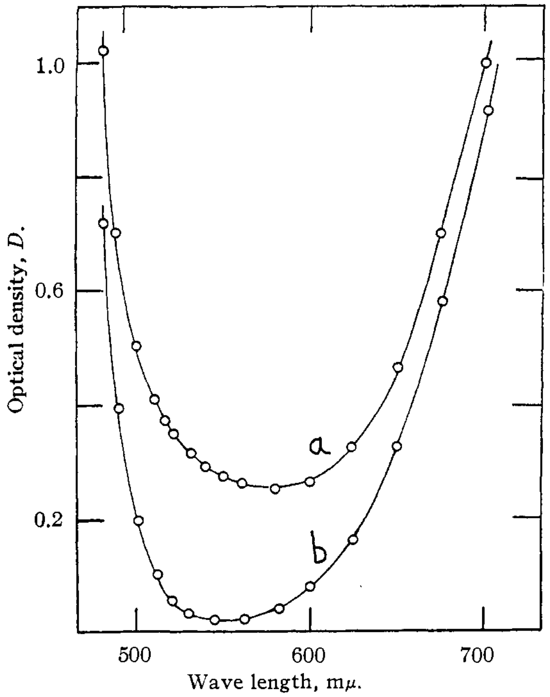


Fig. 6.—Optical interaction in 6 *F* hydrochloric acid solutions: *a*, Cu(II) = 0.025 *F*, (Cl⁻) = 6.0 *F*, Cu(I) = 0.05 *F*; *b*, Cu(II) = 0.025 *F*, (Cl⁻) = 6.0 *F* (data of C. I. Browne and Rollie J. Myers).

Experimental

Materials and Procedures.—A stock solution of cupric perchlorate was prepared as described previously.[12] Solutions of cupric perchlorate and cupric chloride were analyzed for copper(II) by the silver reductor method of Birnbaum and Edmonds,[16] using pure copper metal as a primary standard. This involves the analysis of a copper(I) solution by treatment with excess iron(III) and titration with cerium(IV) to an *o*-phenanthroline end-point; the same procedure was used for the determination of copper(I) in the interaction mixtures. This method of analysis for copper(II) was checked with the usual iodometric analysis, employing a standard thiosulfate solution. Perchloric and hydrochloric acid solutions were standardized acidimetrically.

In general, a copper(I,II) (or "interaction") solution was prepared by shaking an excess of reagent grade copper(I) chloride with a copper(II) solution contained in a centrifuge bottle placed in a thermostat at 25.1°. The solid copper(I) chloride was washed several times with portions of the copper(II) solution before the final saturation in order to remove any copper(II) present with the solid due to air oxidation. The washing was carried out under a carbon dioxide atmosphere. The composition of the copper(II) solution, which was prepared from standard solutions of cupric perchlorate, cupric chloride, hydrochloric and perchloric acids, was calculated to be such that the resulting copper(I,II) solution had the desired free chloride ion concentration and an ionic strength of 1.0. The change in volume on solution of copper(I) chloride was assumed negligible. The uncertainty in the calculated free chloride ion concentration in these solutions, due to the uncertainty in K_2, was never greater than 2.5%.

It was found necessary to centrifuge carefully (2500 g.) each copper(I,II) solution in order to remove suspended particles of solid copper(I) chloride which were otherwise responsible for considerable scattered light. After centrifugation, the solution was replaced in the thermostat for one-half to one hour and then transferred under a carbon dioxide atmosphere to a glass stoppered quartz spectrophotometer cell of 10.0-cm. light path. The absorption spectrum was then measured as rapidly as possible (15–20 min.) using the Model DU Beckman Spectrophotometer. As the room temperature was always within 3° of 25° (usually 25 ± 1°) and as the volume of the solution contained in the cell was about 30 ml., it is probable that little change in the temperature of the solutions occurred during the time required for the spectrophotometric measurements.

The cell solution was then immediately analyzed for copper(I) and for total copper by the method outlined above.[16] In this fashion the solubilities of copper(I) chloride were measured and a constant check was maintained to insure the absence of any air oxidation of copper(I). No such oxidation was observed within the accuracy of the analyses for total copper, *ca.* ± 0.0015 *F*.

An example of the method of making up the solutions and an indication of (a) the reliability of the equilibrium constants K_1, K_2, k_1 and k_2, (b) the reproducibility of the solubility determinations and (c) the accuracy of the assumption of constant activity coefficients, is given by the following experiments: A solution containing 0.150 *F* $CuCl_2$, 0.445 *F* HCl and 0.251 *F* $HClO_4$ was saturated with CuCl. The calculated concentrations (in moles/liter) of the various components of this solution are: $(Cu^{++}) = 0.0794$, $(CuCl^+) = 0.062$, $(CuCl_2) = 0.0086$, $(CuCl^-_2) = 0.045$, $(CuCl_3^-) = 0.012$, $(H^+) = 0.696$, $(ClO_4^-) = 0.251$ and $(Cl^-) = 0.597$. The calculated ionic strength of this solution is 1.01. The experimentally observed solubility of CuCl in this solution was 0.057 *F*.

A second solution was prepared containing 0.075 *F* $CuCl_2$, 0.561 *F* HCl and 0.280 *F* $HClO_4$ and was saturated with CuCl. The calculated composition of this solution is: $(Cu^{++}) = 0.0397$, $(CuCl^+) = 0.031$, $(CuCl_2) = 0.0043$, $(CuCl_2^-) = 0.045$, $(CuCl_3^-) = 0.012$, $(H^+) = 0.841$, $(ClO_4^-) = 0.280$ and $(Cl^-) = 0.602$. The ionic strength is 1.00. The experimentally observed solubility was 0.058 *F*.

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[16] N. Birnbaum and E. Edmonds, *Ind. Eng. Chem., Anal. Ed.*, **12**, 155 (1940).

In general, the uncertainties of the calculated total ionic strengths of these solutions, due to the probable errors in the stability constants of the chloro-complexes of copper(I) and copper(II) are estimated to be 5% or less.

Acknowledgments.—This research has been supported by the Office of Naval Research. We are indebted to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer. Professor W. H. Stockmayer, as a referee, contributed a valuable suggestion concerning the presentation of equation (4).

Summary

The non-additive light absorption in the 400–600 mμ wave length range of solutions maintained at unit ionic strength with perchloric acid and which contain copper(I), copper(II), and low concentrations of chloride ion, has been interpreted in terms of an "interaction" complex, Cu_2Cl_3. The symmetry of the structure Cl–Cu–Cl–Cu–Cl may be important for the large contribution of this complex to the interaction absorption. At higher chloride ion concentrations of the same ionic strength, interaction complexes of higher chloride coördination (but still containing only one copper(I) and one copper(II) in each complex) are important.

PASADENA 4, CAL. RECEIVED OCTOBER 20, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Pure Magnesium Sulfide and its Use as a Base Material for Infrared Phosphors[1]

BY E. BANKS, V. J. RUSSO AND R. WARD

Phosphors having the property of storage of energy and energy release under infrared stimulation have been described by Urbach,[2] Ward[3,4,5] and others. Earlier work by Tiede[6] and co-workers, had shown that magnesium sulfide yields efficient phosphors when singly activated, exhibiting normal fluorescence and phosphorescence when excited with ultraviolet light. Urbach and his co-workers[7] prepared infrared sensitive phosphors with magnesium sulfide using the activator pairs Ce–Sm and Eu–Sm. The stimulation peaks for these phosphors were identical, confirming Urbach's opinion that the trapping centers are associated with the samarium ions. The magnesium sulfide was prepared by passing a stream of dry nitrogen saturated with carbon disulfide over magnesium sulfate.[8] The phosphors were not nearly so sensitive as the corresponding strontium sulfide phosphors and it was suspected that this may be due to the presence of impurities such as magnesium oxide.

The present work was initiated in order to determine whether brighter phosphors could be prepared using a highly-purified oxide-free base material. Phosphors prepared from this material were used in an investigation into the factors involved in the dependence of brightness on activator concentration.

Experimental

I. Preparation of Pure Magnesium Sulfide.—Pure magnesium sulfate was obtained by heating purified magnesium ammonium chloride in a stream of hydrogen sulfide according to the method of Sarge.[9] It was found necessary to keep the temperature below the melting point of magnesium chloride for about an hour and to raise the temperature gradually to 1000° over a period of an hour and one-half. The product was a white to cream-colored powder containing 43.32% magnesium, 57.35% sulfur, and a trace of chloride.

II. Magnesium Sulfide Phosphors.—The activator ions were incorporated mainly by the addition of solutions containing small amounts of the chloride or nitrate to a supposedly inactive flux and evaporating to dryness. The flux and activator mixture was then mixed with an appropriate proportion of magnesium sulfide and the mixture was heated above the melting point of the flux. Several fluxes such as LiF, $MgCl_2$, KCl, NaCl, and mixtures $MgCl_2$ + NaCl, MgF_2 + NaCl, were used. The most effective appeared to be sodium chloride, which could be used in proportions up to 50 mole per cent.

The elements tried as activators were Pb, Ag, Mn, Sb, Ce, Sm and Eu. The infrared response was very poor with all except the rare earth pairs Eu–Sm and Ce–Sm. The latter gave the brightest phosphors, having a green emission similar to the corresponding strontium sulfide phosphor (Standard VII). Under the best conditions found, however, the brightness of this phosphor was less than one-tenth that of Standard VII.

Attempts to obtain some rational explanation for the poor performance of this phosphor by investigating the MgS–NaCl system have not been successful. There is no solid solution of sodium chloride in magnesium sulfide that could be detected by precision lattice constant measurements.[10] The solubility of magnesium sulfide in molten sodium chloride at 1000° is about 1 mole per cent.[11]

The low solubility of magnesium sulfide in sodium chloride at about 800° is also indicated by the small freezing

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(1) This work was carried out under Contracts Nobs-28370 and Nobsr-39045 between the Polytechnic Institute of Brooklyn and the Bureau of Ships.

(2) F. Urbach, D. Pearlman and H. Hemmendinger, *J. Opt. Soc. Am.*, **36**, 372 (1946).

(3) A. L. Smith, R. D. Rosenstein and R. Ward, THIS JOURNAL, **69**, 1725 (1947).

(4) K. F. Stripp and R. Ward, *ibid.*, **70**, 401 (1948).

(5) "Preparation and Characteristics of Solid Luminescent Materials," John Wiley and Sons, Inc., New York, N. Y., 1948.

(6) (a) E. Tiede and A. Schleede, *Centr. Mineral. Geol.*, 154–158 (1921); (b) E. Tiede and A. Schleede, *Ann. d. Physik*, **67**, 573–580 (1922); (c) E. Tiede and W. Schikore, *Ber.*, **75B**, 586–590 (1932).

(7) University of Rochester Report No. 16.5-125 on Contract OEMsr-81, dated September 24, 1945.

(8) E. Tiede and F. Richter, *Ber.*, **55**, 69 (1922).

(9) T. W. Sarge, U. S. Patent 2,358,661, Sept. 19, 1944.

(10) W. Primak, H. Kaufman and R. Ward, THIS JOURNAL, **70**, 2043 (1948).

(11) R. W. Mason, Dissertation, Polytechnic Institute of Brooklyn, 1948.