and his co-workers, the f.ps. of the solutions are depressed about 2.5° from that of the pure compounds.[5]

A comparison of the solubility of the cyclic hydrocarbon in the two *n*-paraffins as found, and as calculated on the basis of an ideal solution, is shown in Fig. 3. It also shows that the solubility of the cyclic hydrocarbon in the high molecular *n*-paraffins is very high, but the converse is not so.

[5] S. H. Piper, *et al., Biochem. J.*, **25**, 2074 (1931).

Summary

1. The freezing points of the systems *cis–trans* decahydronaphthalene, dotriacontane–*cis*-decahydronaphthalene and tetracosane–*cis*-decahydronaphthalene have been examined and found to be very close to the ideal state.

2. The results indicate that the *cis* and *trans* isomers of decahydronaphthalene have different spacial configurations.

LOS ANGELES, CALIF. RECEIVED DECEMBER 17, 1949

[CONTRIBUTION NO. 1322 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Spectrophotometric Investigation of the Copper(II)-chloro Complexes in Aqueous Solutions of Unit Ionic Strength[1]

BY HARDEN McCONNELL AND NORMAN DAVIDSON

The marked influence of chloride ion on the formal extinction coefficient $\bar{\epsilon}$, of copper(II) in aqueous solutions, as illustrated in Fig. 1 for the 230–400 mμ wave length range, is generally attributed to strongly absorbing chloro-complexes of copper(II). One may therefore consider the equilibria represented in equation (1).

$$\left.\begin{array}{l} \mathrm{CuCl}_{n-1}^{3-n} + \mathrm{Cl}^- = \mathrm{CuCl}_n^{2-n} \\ (\mathrm{CuCl}_n^{2-n})/(\mathrm{CuCl}_{n-1}^{3-n})(\mathrm{Cl}^-) = K_n \end{array}\right\} n = 1,2,3,4 \quad (1)$$

The quantities in parentheses in the equations are taken to be concentrations in units of moles/liter, so that the mass action constants, K_n, are functions of the activity coefficients of the various ions. Of the previous investigations of these equilibria,[2,3,4,5,6,6a] the most satisfactory is that by J. Bjerrum.[6] By using spectrophotometric measurements and rough activity approximations, Bjerrum found that only the copper(II)-chloro complexes for $1 \leq n \leq 4$ in (1) are of importance in aqueous solutions of cupric chloride and that the approximate values of the stability constants, K_n^0, at infinite dilution and at 22.5° are

$$K_1^0 \gtrsim 1,\ K_2^0 = 0.1 - 0.4,\ K_3^0 = 0.02 - 0.06,\ K_4^0 = 0.003 - 0.01 \text{ liter/mole}$$

More accurate information about the equilibria of equations (1) was desired for studies of the non-additive light absorption in solutions containing the chloro-complexes of copper(I) and copper(II).[7] In this paper we describe a spectrophotometric study of the equilibria of equation (1) in solutions containing copper(II) perchlorate, hydrochloric acid and perchloric acid and at an ionic strength of unity. The ionic strength was fixed at this value in order to minimize the variation of the activity coefficients of the particular ions as the composition of the solution was varied. The interpretation of the results is based on the assumption that these variations are indeed negligible, so that one can deduce mass action equilibrium constants valid at the ionic strength of the measurements. (Actually the assumption is that the variations of the activity coefficient functions which relate the mass action equilibrium constants to the thermodynamic constants are negligibly small.) It may be said at this point that this assumption has been found to be in accord with the results of the present investigation. Such a simplifying assumption is not applicable for most of the previous investigations of the equilibria (1) which have been carried out at high and varying ionic strengths. On the other hand, because of the ready dissociation of the copper(II)-chlorocomplexes, they cannot readily be studied in much more dilute solutions. Indeed, in the solutions we have studied, only CuCl^+ and CuCl_2 have been present in detectable concentrations.

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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**, 353 (1934).

[3] G. Spacu and J. Murgulescu, *ibid.*, **A170**, 71 (1934).

[4] T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944).

[5] V. Kohlschutter, *Ber.*, **37**, 1160 (1904).

[6] J. Bjerrum, *D. Kgl. Danske Vidensk. Selskab., Mat.-fys. Medd.*, **22**, no. 18 (1946).

[6a] NOTE ADDED IN PROOF.—R. Näsänen (*Acta Chem. Scand.*, **4**, 140 (1950)) has recently determined K_1 of equation (1) as a function of ionic strength in hydrochloric acid solutions. His values, ϵ_1 ($\lambda = 272$) = 1478, K_1 ($\mu = 1.0$) = 0.34, differ considerably from those reported by us, ϵ_1 ($\lambda = 272$) = 320, $K_1 = 1.30$. There are indications that most of this discrepancy is not due to differing experimental data: thus for the item in Näsänen's Table I for $\mu^{1/2} = 0.981$ where he obtains $D_{\mathrm{CuCl}^+} = 0.098$, our constants given 0.082. In Table II, for $\mu^{1/2} = 0.939$, our constants give $(\mathrm{CuCl}^+) = 0.00063$, $(\mathrm{CuCl}_2) = 0.00013$, $D_{\mathrm{CuCl}^+} = 0.199$, $D_{\mathrm{CuCl}_2} = 0.266$, $D_{\mathrm{total}} = 0.465$. Näsänen gives $D_{\mathrm{CuCl}^+} = 0.438$, $(\mathrm{CuCl}^+) = 0.00030$. We offer this criticism of his work. Only eleven items of data in Table II have been used to evaluate four constants (his α, B, ϵ, K_1). The formation of CuCl_2 has been neglected, although he indicates that above $(\mathrm{Cl}^-) = 0.25$ (where there are five items of data) this assumption is not too good.

[7] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3168 (1950).

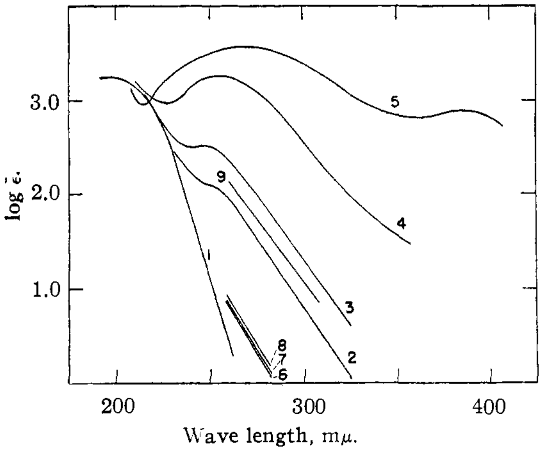

Fig. 1.—Effect of chloride ion on the formal extinction coefficient, $\bar{\epsilon}$, of copper(II): (1) 1.0 *F* $Cu(ClO_4)_2$; (2) 0.047 *F* $CuCl_2$; (3) 0.235 *F* $CuCl_2$; (4) 2.35 *F* $CuCl_2$; (5) 0.47 *F* $CuCl_2$, 4.72 *F* $CaCl_2$; (6) 0.27 *F* $Cu(ClO_4)_2$, 0.007 *F* HCl; (7) 0.20 *F* $Cu(ClO_4)_2$, 0.007 *F* HCl; (8) 0.10 *F* $Cu(ClO_4)_2$, 0.007 *F* HCl; (9) 0.01 *F* $Cu(ClO_4)_2$, 0.15 *F* HCl. (Curves 1–5, Fromherz, ref. 2; curves 6–9, this research, μ = 1.00.)

It is probable that at very high chloride concentrations the complex species $CuCl_4^=$ predominates[3,4,6] and is responsible for the light absorption of curve (5) in Fig. 1. In order to isolate the light absorption due to the first chloro complex, $CuCl^+$, we have observed the optical densities of solutions with a very small chloride concentration, 0.007 *F*, and a much larger Cu(II) concentration, 0.1–0.3 *F*. Representative values of the formal extinction coefficients of Cu(II) in these solutions are displayed in Fig. 1; these show that $CuCl^+$ is much more colored than Cu^{++} in this wave length range. This is not the case at longer wave lengths, 550–1000 mμ, where the formal extinction coefficients of copper(II) are far less sensitive to the concentration of chloride ion.[6]

Thus, if $CuCl^+$ is the only copper(II)-chloro complex present in detectable concentration in solutions having the above cupric perchlorate and hydrochloric acid concentrations,[8] then at a constant ionic strength of 1.00 maintained with perchloric acid and in the 260–280 mμ wave length range, the simple equation

$$\frac{ab}{D - D'} = \frac{a}{(\epsilon_1 - \epsilon_0)} + \frac{1}{(\epsilon_1 - \epsilon_0)K_1} \qquad (2)$$

will hold in the approximation that the concentration of $CuCl^+$ is small compared to the concentration of Cu^{++} and the activity coefficients of Cu^{++}, $CuCl^+$ and Cl^- are constant at the constant ionic strength. In equation (2) D (= $\log_{10} I_0/I$) is the optical density of a solution containing a concentration *a* formal of cupric perchlorate, *b* formal of hydrochloric acid and sufficient perchloric acid to bring the ionic strength to 1.00. The quantities ϵ_0 and ϵ_1 are the molar extinction coefficients of Cu^{++} and $CuCl^+$, respectively, and D' is the optical density of a solution *a* formal in cupric perchlorate at unit ionic strength. Equation (2) may be derived from the simple expressions, $D = \epsilon_0(Cu^{++}) + \epsilon_1(CuCl^+)$; $D' = a\epsilon_0$; $a = (Cu^{++}) + (CuCl^+) \simeq (Cu^{++})$; $b = (CuCl^+) + (Cl^-)$ and the equilibrium equation involving K_1 in (1).

The experimental values of $ab/(D - D')$ are plotted against *a* in Fig. 2 for three wave lengths and two temperatures. The plots are straight lines within the experimental errors, as predicted by equation (2). According to this equation the ratio of the *y* intercept to the slope gives K_1 and the reciprocal of the slope gives $\epsilon_1 - \epsilon_0$. (For the wave lengths used, 260–280 mμ, ϵ_0 is negligibly small in comparison to ϵ_1.) The results of a least squares treatment of these data, giving the most probable values of K_1 together with the probable errors, are given in Table I. The linear character of the plots in Fig. 2 and the concordant values of K_1 obtained at different wave lengths establish the validity of the assumptions made in deriving equation (2), namely, that the absorbing copper(II)-chloro complex present in these solutions is $CuCl^+$ rather than say, Cu_2Cl^{+++} or $CuCl_2$, and that the variations of the activity coefficients are negligible for the range of concentrations used.

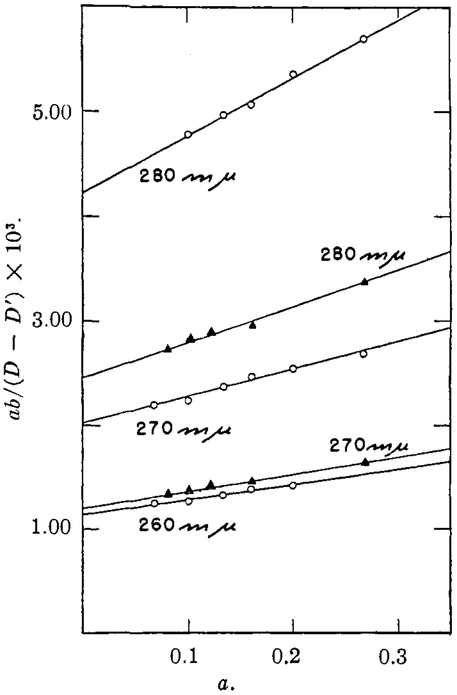

Fig. 2.—Determination of K_1 at two temperatures (see equation 2): ○, 25.2°; ▲, 46.9°.

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[8] That there is no detectable hydrolysis of Cu^{++} to $Cu(OH)^+$ in the solutions used is shown by the fact that the extinction coefficients of Cu^{++} ion in perchloric acid observed in the present research agree with the literature values for neutral copper perchlorate solutions.[2]

TABLE I

DETERMINATIONS OF THE EQUILIBRIUM CONSTANTS K_1 AND K_2

Temp., °C.	Wave length, mμ	Most probable K_1, liter/mole
25.2	260	1.29 ± 0.10
25.2	270	1.30 ± 0.06
25.2	280	1.30 ± 0.04
	Average K_1	1.30 ± 0.03
46.9	270	1.39 ± 0.05
46.9	280	1.395 ± 0.11
	Average K_1	1.39 ± 0.05
		Best value K_2, liter/mole
25.2	280	0.11 ± 0.02
25.2	290	0.29 ± 0.04
25.2	300	0.18 ± 0.11
	Average K_2	0.23 ± 0.15

Back calculations using the values of K_1 and ϵ_1 and the values of K_2 and ϵ_2 determined subsequently, show that the numerical approximations used in formulating equation (2) introduce no appreciable error in the evaluation of K_1 and ϵ_1.

The approximate value 600 ± 350 cal. for the enthalpy of formation of $CuCl^+$ from Cu^{++} and Cl^-, ΔH at unit ionic strength, is obtained from the data of Table I giving K_1 at two temperatures by neglecting any variation of ΔH with temperature. The corresponding entropy change is $\Delta S = 2.5 \pm 1.2$ cal./deg. Our value of ΔH is in agreement with Bjerrum's "order of magnitude" estimate of this quantity, 1.2 kcal./mole.

To determine K_2 we have measured the optical densities of solutions in which the ratio of the chloride to copper formal concentrations (b/a) was increased over that used in the above experiments until solutions were obtained in which the Cu(II) was largely present as Cu^{++} and $CuCl^+$, along with smaller concentrations of $CuCl_2$. Assuming Cu(II) to be present only in these three forms, one may write equation 3 for the wave length range 250–300 mμ by taking the activity coefficients of Cu^{++}, $CuCl^+$, $CuCl_2$ and Cl^- to be constant at the constant ionic strength.

$$\frac{a}{D_c} = \frac{F}{\epsilon_2 K_1 K_2} + \frac{1}{\epsilon_2}, \text{ where}$$

$$F = \frac{\epsilon_1 K_1}{(Cl^-)^2}\left[\frac{1}{\epsilon_1 K_1} + \frac{(Cl^-)}{\epsilon_1} - \frac{a(Cl^-)}{D_c}\right] \qquad (3)$$

In this relation, ϵ_2 is the molar extinction coefficient of $CuCl_2$, (Cl^-) is the concentration of free chloride ion and D_c is the contribution to the optical density by $CuCl^+$ and $CuCl_2$. The quantities a, b, D, D' and ϵ_1 are defined as in equation (2). Equation (3) may be derived from the equation of copper conservation

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

the equation for the contribution to the total optical density by the complexes $CuCl^+$ and $CuCl_2$

$$D_c = \epsilon_1(CuCl^+) + \epsilon_2(CuCl_2)$$

and the equations involving K_1 and K_2 in (1).

Working in the concentration range, a = 0.002–0.10 F, b = 0.1–0.8 F, we have used the first approximation that $(Cl^-) = b$ and that $D_c = D - D'$. A numerical and graphical analysis of the data using equation (3) then yielded values of $\epsilon_2 K_2$ and ϵ_2 at six wave lengths in the range 250–300 mμ and values of $\epsilon_1 K_1$ at wave lengths 250, 290 and 300 mμ. (Calculations at 260, 270 and 280 mμ were considerably simplified by using values of $\epsilon_1 K_1$ found in the determination of K_1.) The fact that practically all of the data fitted the form of equation (3) indicates that, within the experimental errors, the assumptions used in formulating (3) are justified. In particular, the linear character of the plots of a/D_c *vs.* F as shown in Fig. (3) shows that there is no detectable contribution of $CuCl_3^-$ to the color of these solutions.

For a second approximation to the solution of equation (3), the deviation between b and (Cl^-) has been calculated using the first approximation to K_2. The chloride correction is small, ~1%, and only slightly different values of K_2 are obtained in the second approximation.

Our evaluation of K_2 appears to suffer from two serious sources of error. At the shorter wave lengths of the 250–300 mμ range, the scatter of the experimental points in the plot of a/D_c *vs.* F results in considerable uncertainty in the value of the small intercept, $1/\epsilon_2$, and thus in the value of K_2 given by $(1/K_1)$ times the ratio of the intercept to the slope. Values of K_2 ranging from 0.15 to 0.54 liter/mole were obtained at the wave lengths 250, 260 and 270 mμ. At the longer wave lengths, 280, 290 and 300 mμ, the principal known source of error is the uncertainty as to the exact dependence of D' on the concentration of Cu^{++}. As the uncertainties due to experimental scatter are smaller at these longer wave lengths and as the extreme limits of K_2 due to the uncertainty as to D' may be accurately determined (D' may be taken proportional to the Cu^{++} concentration, or it may be taken as constant, this uncertainty usually amounting to ± 0.005 in D_c), we consider the experimental values of K_2 determined at these three wave lengths to be the most reliable. In Table I, the margin of error given for K_2 at each wave length was calculated solely from the uncertainty in D'. It is evident from Table I that there are systematic sources of error in K_2 which are greater than those due to the uncertainty in D' alone. The sources of these errors are unknown. By weighting the determinations at the longer wave lengths most heavily, we select for K_2 the value 0.23 liter per mole with a safe margin of error, ± 0.15.

It may be noted that the slopes of the lines of Fig. 3 give values of $1/(K_1K_2\epsilon_2)$ which are much more accurate than the separate values of K_2 and ϵ_2. The absorption spectrum of $CuCl_2$, given in Fig. 4 together with those of $CuCl^+$

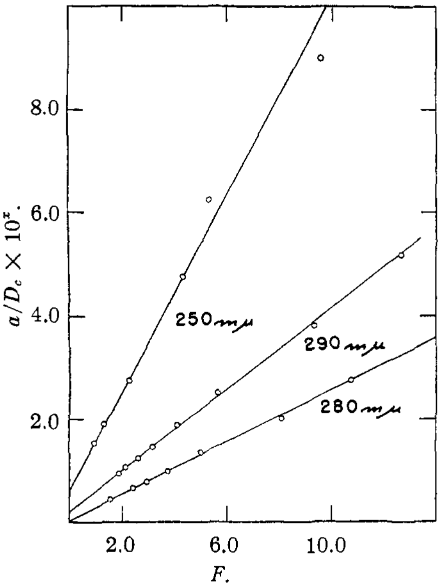

Fig. 3.—Determination of K_2 (see equation 3). For wave lengths 280 and 290 mμ, $x = 2$; for 250 mμ, $x = 3$.

and Cu^{++}, has been calculated from the values of $\epsilon_2 K_2$ assuming the value of K_2 to be 0.23 liter/mole. The apparent extinction coefficients of Cu(II) in 4.7 *F* calcium chloride are also included for comparison.[2] This curve is usually assumed to be due principally to $CuCl_4^=$. The apparent shift of the "electron transfer" spectrum of Cu(II) to longer wave lengths with increasing chloride coördination is similar to that which has been observed for several other systems of cation–anion complexes.[9]

Experimental Part

Materials.—A stock solution of cupric perchlorate was prepared by adding an excess of basic cupric carbonate, $CuCO_3 \cdot Cu(OH)_2$, to a solution of perchloric acid, removing the excess solid by centrifugation and then adding a slight excess, 0.005 *F*, of perchloric acid. The Cu(II) concentration in this solution was determined using three independent analytical procedures: (a) iodometry with a standard thiosulfate solution, (b) the silver reductor method of Birnbaum and Edmonds,[10] and (c) spectrophotometric determination using the extinction coefficients of copper(II) in cupric perchlorate solutions given in the literature[2] and assuming Beer's law to hold for these solutions. The agreement between the results of (a), (b) and (c) was excellent.

Hydrochloric and perchloric acid concentrations were determined acidimetrically.

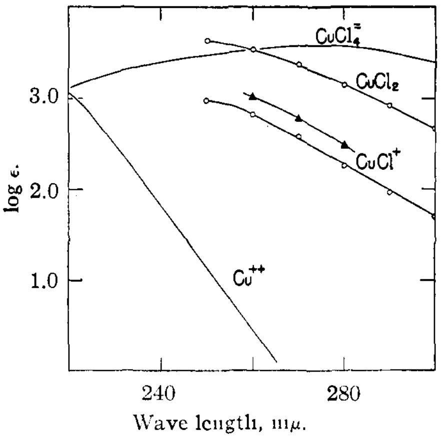

Fig. 4.—Absorption spectra of Cu^{++}, $CuCl^+$, $CuCl_2$ and the supposed absorption spectrum of $CuCl_4^=$: ○, 25.2°; ▲, 46.9° ($CuCl_4^=$ curve, curve 5 of Fig. 1.)

Apparatus.—Measurements of optical density were made with a Model DU Beckmann Spectrophotometer, using a hydrogen lamp and rectangular right prism quartz cells of 1.00-cm. path length. The cells were maintained at constant temperature, 25.2 ± 0.05° or 46.9 ± 0.1°, by means of a specially constructed cell compartment having a jacket through which thermostated water was circulated. The cell compartment was provided with quartz windows.

As solutions placed in the cell compartment required more than one hour to come to thermal equilibrium at the higher temperature, glass stoppered quartz cells were used to minimize evaporation.

Acknowledgments.—This research has been supported by the Office of Naval Research. We are indebted to Messrs. W. Schuelke and S. Hart of the machine shop not only for the construction of the thermostated cell compartment but for excellent advice as to its design. We are indebted to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer.

Summary

The absorption spectra of mixed solutions of copper(II) perchlorate, perchloric acid and hydrochloric acid at a constant ionic strength of 1.00 in the wave length range 250–300 mμ are interpreted in terms of the equilibria $Cu^{++} + Cl^- = CuCl^+$, $K_1(25.2°) = 1.30 \pm 0.03$; $K_1(46.9°) = 1.39 \pm 0.05$ liters/mole. $CuCl^+ + Cl^- = CuCl_2$, $K_2(25.2°) = 0.23 \pm 0.15$ liter/mole. The absorption spectra of $CuCl^+$ and $CuCl_2$ have been determined in the given wave length range.

PASADENA, CALIF. RECEIVED OCTOBER 20, 1949

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

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