

A Contribution to Our Knowledge of Weak Chloro Complex Formation by Copper(II) in Aqueous Chloride Solutions

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Dedicated to Professor K. A. Jensen on his 70th birthday

The problems involved in obtaining both stability constants and extinction coefficients from spectrophotometric measurements are discussed in relation to a recently published study of the copper(II) chloride system. The results of this latter study do not agree well with those obtained previously by one of the present authors and we have therefore made some supplementary measurements and recalculated the data.

In the case of strong metal ion complex formation with rapid equilibrium adjustment the concentration stability constants can usually be determined with a high degree of accuracy by potentiometric methods when the measurements are performed in the presence of a high concentration of an inert salt and low concentrations of the reacting species. However, these experimental conditions cannot be fulfilled in the case of weak complex formation which takes place first at high concentrations of the complex forming electrolyte. In such cases spectrophotometric methods provide the best means of studying complex formation.

It is usually possible to distinguish between inner- and outer-sphere complex formation when the metal ion complexes in question give rise to ligand-field absorption bands, but on the other hand it is a hard test of the data to try to determine stability constants as well as extinction coefficients in the general case where the absorption is a cumulative property of all the complexes present. This can some-

times be done by separating the determination of the constants and the extinction coefficients, and such separate determination is possible using the Principle of Corresponding Solutions for complexes of average stability by varying both the metal and the ligand concentrations.^{1,2} However, this procedure has been superseded by modern computer techniques. One has a much better chance of obtaining reliable results in those special cases where the optical method permits the direct determination of the concentration of one of the complexes present over a certain range of ligand concentrations. Such data provide a firm basis for calculation, but if the composition of the salt medium is changed by more than about 10 % it is not possible to calculate the concentration stability constants with any high degree of certainty.³ Therefore in cases in which very weak complex formation in aqueous solution is involved it is often preferable to study the system using solutions in which the salt medium is provided by varying concentrations of the complex-forming electrolyte itself, and with the introduction of crude activity corrections under simplifying conditions. Studies of this kind, which give rough information about the activity stability constants have been performed by the present authors⁴⁻⁶ for the case of weak chloro complex formation in aqueous solutions of copper(II) and cobalt(II) ions, where the formation of the tetrachloro complexes is first complete in solutions with chloride concentrations ≥ 10 M.

THE STABILITY CONSTANTS OF THE CHLORO COPPER(II) COMPLEXES

One stimulus for the present study was a recent publication by Schwing-Weill,^{7,8} in which she has calculated stability constants and extinction coefficients for the four chloro copper(II) complexes from spectrophotometric data measured for a 5 M mixed NaCl and NaClO₄ medium.

A complete bibliography of copper(II) chloride stability constants determined up to 1969 is to be found in *Tables of Stability Constants*,⁹ and some of the more reliable spectrophotometric data including recently published results are given in Table 1. Spectrophotometric methods usually give reliable values of the products $K_n \epsilon_n$ of the consecutive constants and corresponding extinction coefficients, but are not well suited to determination of these quantities individually for very strong or very weak complexes. The values for K_1 and ϵ_1 in 1 M HClO₄ given by three different authors¹²⁻¹⁴ (Table 1) show this clearly; it should be noted that the product $K_1 \epsilon_1$ is not far from being constant. Näsänen¹⁰ has determined K_1 in mixed solutions of CuCl₂ and LiClO₄ and corrected to ionic strength zero by the use of Debye-Hückel expressions with two empirically determined parameters. However, subsequent complex formation was not taken into consideration.^{12,13} Libus¹¹ has determined K_1 at ionic strength zero from measurements in mixtures of Cu(ClO₄)₂ and Mg(ClO₄)₂ to which only minute amounts of NaCl are added. Both of these authors' results agree reasonably well with the results of Bjerrum^{4,5} who was able to determine the concentration of CuCl₂²⁻ and approximate values for all of the four consecutive constants by employing simplified assumptions about the activity coefficients in concentrated chloride solutions in which the salt medium is provided by varying concentrations of the complex-forming electrolyte itself. The values given in Table 1 are those corresponding to the use of the activity expression^{4,5} $\log F = -0.5 + B[Cl^-]$, where B was adapted to the experimental data with the following values for the various chloride media: HCl 0.20, LiCl 0.23, MgCl₂ 0.18 and CaCl₂ 0.18. Schwing-Weill^{7,8} has calculated values for the four copper(II) chloride stability constants, as well

Table 1. A selection of estimated consecutive stability constants (K_n) and molar extinction coefficients for the monochloro (ϵ_1) and dichloro complex (ϵ_2) in aqueous copper(II) solutions at $\sim 25^\circ\text{C}$.

Medium	K_1	K_2	K_3	K_4	$\epsilon_1(250)$	$\epsilon_1(272)$	$\epsilon_2(250)$	Ref.
0 corr	~ 1	~ 0.4	~ 0.06	~ 0.01	—	—	—	4,5
0 corr	1.11					1478		10
0 corr	1.63 ± 0.15					1115 ± 80		11
1 M H(Cl,ClO ₄)	1.30 ± 0.03	0.23 ± 0.15			~ 1000	~ 316		12
1 M H(Cl,ClO ₄)	0.27				3800			13
1 M H(Cl,ClO ₄)	2.3 ± 0.4	0.72 ± 0.9			530	~ 186	1620	14
5 M Na(Cl,ClO ₄)	4	1.2	0.42	0.12	1042		2424	7,8
4 M Na(Cl,ClO ₄)	1.3 ± 0.1							15
6 M Na(Cl,ClO ₄)	1.85 ± 0.2							15
5 M Na(Cl,ClO ₄)	1.5	0.42	0.14	0.036	2705		2002	This paper

Table 2. Extinction coefficients of copper(II) chloride at 436 nm in weakly acid 5 M NaCl – NaClO₄ solutions at 25 °C.

C_{CuCl_2}	C_{NaCl}	C_{NaClO_4}	$C_{\text{Cl}^-} + C_{\text{ClO}_4^-}$	$[\text{Cl}^-]$	ϵ_{436}	$\alpha_4 = \epsilon_{436}/308$
0.0943	0.943	3.774	5.00	1.043	1.317	0.0043
0.0943	1.887	2.830	5.00	1.944	4.03	0.0131
0.0943	2.830	1.887	5.00	2.859	7.38	0.0239
0.0943	3.774	0.994	5.00	3.780	10.5	0.0336
0.02433	5.00	—	5.05	4.997	15.8	0.0513
0.01218	5.00	—	5.02	4.998	15.6	0.0507

as corresponding extinction coefficients, from spectrophotometric measurements in a salt medium varying from 5 M NaClO₄ to 5 M NaCl. Thus the ionic strength has been kept constant, but this gives no guarantee for proportionality between activity and concentration of the species involved in such strong salt solutions. The estimated stability constants, together with values for ϵ_1 and ϵ_2 at 250 nm, are tabulated in Table 1. Schwing-Weill calculates a suspiciously low value for the extinction coefficient of the tetrachloro complex at 400 nm ($\alpha_4 = 216$). For comparison it can be mentioned that a 0.0008 M CuCl₂ solution in saturated CaCl₂ at 400 nm has $\epsilon = 950$ (see Experimental). It was therefore thought worthwhile to examine whether more detailed information could be obtained when Schwing-Weill's data were employed together with the basis for Bjerrum's^{4,5} determination of the constants, *viz.* that the tetrachloro complex is the only species absorbing at the wavelength of the blue mercury line (436 nm) at chloride concentrations higher than 3 M. The degree of formation of the tetrachloro complex $\alpha_4 = [\text{CuCl}_4^{2-}]/C_{\text{Cu}}$ can then be calculated directly from the expression

$$\alpha_4 = \epsilon_{436}/\epsilon_{436}^\circ$$

where ϵ_{436}° is the limiting extinction coefficient for $[\text{Cl}^-] \geq 12$ M. We have taken ϵ_{436}° to be 308, the value measured for saturated CaCl₂ solutions (see Experimental).

Schwing-Weill has made no measurements at 436 nm and we have therefore made some supplementary measurements with the 5 M salt medium at this wavelength. The results are shown in Table 2. In Table 3 $\epsilon_{436}/\epsilon_{436}^\circ$ (interpolated to "round-number" chloride ion concentrations) is compared with the values of

α_4 and \bar{n} one calculates from the stability constants presented in Table 1. The quantity $\epsilon_{436}/\epsilon_{436}^\circ$ is seen to be much smaller than α_4 calculated with Schwing-Weill's stability constants, in spite of the fact that owing to absorption of the lower complexes it must be larger than the latter. The set of constants proposed by us in Table 1, with K_1 chosen to be 1.5 M⁻¹, is selected as giving more reasonable values for α_4 with the tacit assumption that the system has a characteristic coordination number 4 and a nearly constant ligand effect, although this cannot be regarded as certain.¹⁸ The ligand effect¹⁸ is defined as follows:

$$L_{n,n+1} = \log (K_n/K_{n+1}) - S_{n,n+1}$$

where $S_{n,n+1} = \log \{(4-n+1)(n+1)/(4-n)n\}$ is the statistical effect in the case of characteristic coordination number four and monodentate ligands. Our set has been chosen to have $L_{1,2} = L_{2,3} = 0.13$ and $L_{3,4} = 0.15$. The values of α_4 and \bar{n} corresponding to these constants are shown in Table 3, and it is obvious that this set of constants is adapted to fulfill the condition that $\epsilon_{436}/\epsilon_{436}^\circ$ is equal to α_4 in 4–5 M chloride

Table 3. Comparison of the values of $\epsilon_{436}/\epsilon_{436}^\circ$ in 5 M Na(Cl,ClO₄) with values of α_4 and \bar{n} calculated from the sets of stability constants given in Table 1.

$[\text{Cl}^-]$	$\epsilon_{436}/\epsilon_{436}^\circ$	Schwing-Weill ^{7,8}		This paper	
		α_4	\bar{n}	α_4	\bar{n}
1	0.0040	0.0195	1.69	0.00098	0.94
2	0.0137	0.078	2.28	0.0070	1.42
3	0.0254	0.147	2.60	0.0186	1.74
4	0.0360	0.213	2.81	0.0345	1.97
5	0.0510	0.272	2.97	0.0532	2.14

Table 4. Calculated molar extinction coefficients for the intermediate chloro copper(II) complexes.

$\lambda(\text{nm})$	ϵ_1	ϵ_2	ϵ_3
230	1241 ± 7	1257 ± 35	2372 ± 66
250	2705 ± 7	2002 ± 34	2810 ± 71
280	563 ± 2	3150 ± 23	1636 ± 60
360	0.3 ± 0.4	116 ± 4	54 ± 12
380	-0.4 ± 0.3	53 ± 3	81 ± 14
756	23.6 ± 0.1	34.6 ± 0.3	32.4 ± 0.6

solutions. It is also in agreement with what should be expected^{4,5} that $\epsilon_{436}/\epsilon_{436}^\circ$ gives too high values for α_4 for solutions with chloride concentrations smaller than ~ 3 M, for which the absorption of the lower complexes cannot be neglected. The \bar{n} -values, which are considerably smaller than those calculated from Schwing-Weill's constants, have been used to correct the total chloride concentrations to concentrations of free chloride in the cases where such a correction is necessary.

THE EXTINCTION COEFFICIENTS OF THE CHLORO COPPER(II) COMPLEXES

From the spectrophotometric data reported by Schwing-Weill^{7,8} we have calculated the extinction coefficients ϵ_1 , ϵ_2 and ϵ_3 of the intermediate chloro complexes. The calculation using the modified stability constants makes use of values of the extinction coefficients for the tetrachloro complex which have been equated with those given in Table 5 for copper(II) chloride in 6–7 M calcium chloride solution. This calculation of the extinction coefficients for the three intermediate chloro complexes from chosen values for the stability constants entails the solution of linear equations and was carried out by the method of least squares. The results are given in Table 4. The rather low uncertainty assigned to the extinction coefficients calculated in this way merely reflects the fact that the uncertainties in the stability constants in this case have not been taken into account.

Fig. 1 shows the directly measured spectrum for the tetrachloro complex and the estimated spectra for the mono-, di- and trichloro com-

plexes; the latter have been drawn through the few calculated points with a considerable degree of uncertainty. The spectra are very similar and therefore difficult to resolve, and it is clear that the best wavelength range in which to study the formation of the tetrachloro complex is that used earlier by Bjerrum^{4,5} close to 400 nm where the absorption of the other chloro complexes is negligible.

The UV absorption bands of the chloro copper(II) complexes are of the electron transfer type and as such are more sensitive to the environment¹⁷ than is the case with ligand field bands. Thus it is characteristic that the molar extinction coefficient at 436 nm has the following limiting values: 308 in 6.5 M CaCl_2 , 308 in 5 M MgCl_2 , 416 in 12 M LiCl and 537 in 13 M HCl .⁵ This pronounced medium effect renders the choice of correct values of the extinction coefficients for the tetrachloro complex in 5 M NaCl somewhat uncertain, but we believe that only a relatively small error is introduced by equating them with the nearly constant values for CaCl_2 solutions with chloride concentrations between 12 and 14 M. The weak ligand-field band in infrared is less influenced by changes in the salt medium, but chloro complex formation causes such

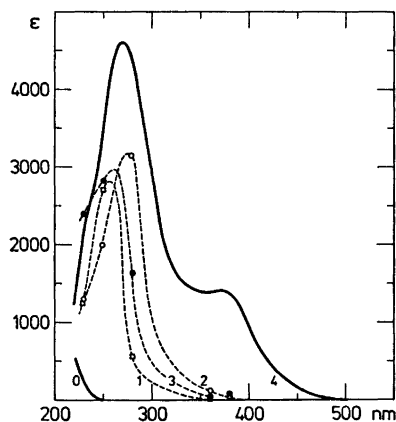


Fig. 1. The UV spectra of the four chloro-copper(II) complexes. The numbers on the curves indicate the number of Cl^- per Cu(II) ion. The full curve 4 represents the directly measured absorption curve for a 6.5 M CaCl_2 solution, and the curve 0 for that of the aqua copper(II) ion. The points marked on the dashed curves correspond to the values of ϵ_1 (\square), ϵ_2 (\circ), and ϵ_3 (\bullet) in Table 4.

Table 5. Molar extinction coefficients for CuCl_4^{2-} in 6.2 M CaCl_2 .

nm	ϵ	nm	ϵ
230	2188	560	0.25
250	3488	600	0.95
270	4613	660	5.7
280	4356	700	16.2
300	2906	740	33.5
320	1750	756	42.4
340	1456	780	57.6
360	1394	820	83.4
380	1394	860	105.2
400	950	900	119
436	308	940	125
460	99	960	126
500	7.85		

small changes in this band that it is hardly possible to use it as a basis for a calculation of the stability constants. Estimated values for the extinction coefficients of the intermediate chloro complexes at 756 nm are shown in Table 4 and data for the absorption of the tetrachloro complex are quoted in Table 5.

The conclusion of this paper is that attempts to obtain quantitative results in studies of consecutive weak complex formation in solution necessitate the use of many approximations, and studies of such systems can therefore be expected to give only semiquantitative results.

EXPERIMENTAL

The solutions used for spectrophotometric measurements were prepared from analyzed stock solutions. The water used was doubly-distilled, and all chemicals were of analytical grade.

Spectrophotometric measurements were made on a Zeiss DMR 21 recording spectrophotometer with a cell-holder thermostated at 25 °C. Extinction coefficients quoted are corrected for the absorption of the medium. Quartz cells (1 cm and 5 cm) were used and the concentrations of CuCl_2 varied from 0.0002 M to 0.1 M, depending on the magnitude of the absorption. The values obtained for the molar extinction coefficients of CuCl_4^{2-} in 6.2 M CaCl_2 are given in Table 5.

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