Complex Constants and Ultraviolet Absorption Spectra for CuCl–Cl⁻ Complexes in 1 M HClO$_4$

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The complex formation between Cu(I)Cl and Cl$^-$ was investigated in a 1 M HClO$_4$ ionic medium at 22 °C. In saturated CuCl(s)–Cl$^-$-solutions over the concentration range 0–0.25 M Cl$^-$ the only complexes observed are CuCl$_2^-$ and CuCl$_3^{2-}$. The complex constants for the formation of these complexes are $\log \beta_{11} = -1.31$ and $\log \beta_{12} = -1.6$ respectively. The UV-absorption spectra of CuCl$_2^-$ and CuCl$_3^{2-}$ were determined in the wavelength region 220–370 nm. The absorption of CuCl$_2^-$ is characterized by a strong band $\lambda_{\max} < 200$ nm ($\varepsilon > 2.7 \cdot 10^3$) together with a weak band having $\lambda_{\max} = 230$ nm ($\varepsilon = 0.7 \cdot 10^3$). The spectrum of CuCl$_3^{2-}$ is composed of two bands with $\lambda_{\max} = 230$ nm ($\varepsilon = 4.7 \cdot 10^3$) and $\lambda_{\max} = 276$ nm ($\varepsilon = 6.1 \cdot 10^3$).

Introduction

An aqueous suspension of Cu(I)-chloride forms a very labile heterogeneous system. It is defined by several complex and redox equilibria. The system is photosensitive and exhibits photochromism. In the photochromic reaction Cu$^+$ disproportionates into Cu^{2+} and Cu^0. The kinetics of this process depends strongly on the Cl$^-$ concentration of the solution, which in turn is related to the formation of complexes between CuCl and Cl$^-$.

Equilibrium data and absorption spectra for these complexes are therefore needed in order to properly understand the photochromic reactions. Several investigations concerning these complexes have been carried out in various laboratories [1–7]. However, the studies were never designed to yield the information needed for a study of the photochromic phenomena and therefore important pieces of information are lacking. Furthermore the results of these studies are somewhat inconsistent.

Despite the number of studies carried out concerning the CuCl–Cl$^-$ equilibria no systematic study of the light absorption of these complexes has been reported. The work by Sukhova et al. indicates, however, that absorption maxima should be expected at about 200, 235 and 273 nm together with broad bands at 300–400 nm and 1200 to 2000 nm [8]. The maximum at 273 nm showed a concentration dependence which indicated the existence of a CuCl$_3^{2-}$ complex. They also concluded that the broad bands at 300–400 nm are due to polynuclear complexes.

General Considerations

Cu(I)-chloride forms complexes with chloride ions which schematically may be written as CuCl_{n+1}^{-n}. Previous investigations on such complexes have shown that the predominating complexes are CuCl$_2^-$ and CuCl$_3^{2-}$ when the Cl$^-$-concentration is kept below 1 M [1–5]. The equilibria involved are thus:

$$\mathrm{CuCl(s)} + \mathrm{Cl}^- \rightleftarrows \mathrm{CuCl_2}^- \quad K_{s_2}, \qquad (1)$$

$$\mathrm{CuCl_2}^- + \mathrm{Cl}^- \rightleftarrows \mathrm{CuCl_3}^{2-} \quad K_3. \qquad (2)$$

From the equilibria (1) and (2) the following gross complex constants may be defined:

$$\beta_{11} = \frac{[\mathrm{CuCl_2}^-]}{[\mathrm{Cl}^-]}\,; \quad \beta_{12} = \frac{[\mathrm{CuCl_3}^{2-}]}{[\mathrm{Cl}^-]^2}\,. \qquad (3)$$

The total concentration (C_0) of the CuCl–Cl$^-$ complexes is thus:

$$C_0 = \beta_{11}[\mathrm{Cl}^-] + \beta_{12}[\mathrm{Cl}^-]^2\,. \qquad (4)$$

Applying the Lambert-Beer law the light absorption by CuCl$_2^-$ and CuCl$_3^{2-}$ at a certain wavelength may be written

$$A = \varepsilon_{11}\,\beta_{11}[\mathrm{Cl}^-] + \varepsilon_{12}\,\beta_{12}[\mathrm{Cl}^-]^2\,. \qquad (5)$$

An experimental determination of the dependence of C_0 and A on the chloride ion concentration may be used to obtain the constants of Eqs. (4) and (5) through a simple linear regression analysis. The experiments are preferentially carried out at constant ionic strength to keep the activity factors constant. In the present case 1 M HClO$_4$ was used as the ionic medium.

As mentioned above the redox equilibria between Cu^{2+}, Cu^0 and Cu$^+$ must be considered in a study of the complex formation with Cl^- of Cu^+. They are

$$Cu^{2+} + 2\,e^- \rightleftarrows Cu^0(s) \quad (\log K = 11.383)\ ^*, \quad (6)$$

$$Cu^+ + e^- \rightleftarrows Cu^0(s) \quad (\log K = 8.796)\ ^*, \quad (7)$$

$$CuCl(s) \rightleftarrows Cu^+ + Cl^- \quad (\log K = -6.73)\ ^{**}. \quad (8)$$

Combining (6) – (8) yields:

$$2\,Cu^+ \rightleftarrows Cu^{2+} + Cu^0(s) \quad (\log K = 6.209)\,, \quad (9)$$

$$2\,CuCl \rightleftarrows Cu^{2+} + Cu^0(s) + 2\,Cl^- \quad (\log K = -7.25)\,. \quad (10)$$

The constants given above refer to zero ionic strength but were used to estimate the Cu^{2+}-concentration also in the present case. This gives a maximal Cu^{2+}-concentration of $2 \cdot 10^{-5}$-M. (0.050-M. Cl^-). In other words, if the value of K_{10} given above is valid, the Cu^{2+}-concentration can be ignored. At higher Cl^--concentration the Cu^{2+}-concentration decreases rapidly ($6 \cdot 10^{-6}$-M. at 0.1-M. Cl^-).

Experimental

The basic principles for the elucidation of the complex constants and the UV-absorption spectra are as follows: At various Cl^--concentrations the light absorption of saturated $CuCl(s) - Cl^-$ solutions was determined. In order to obtain C_0 the complexes were oxidized. The Cu(I)-concentration was then spectrophotometrically determined as Cu^{2+}.

Preparation of Saturated CuCl(s) – Cl⁻ Solutions

Solutions with 0.05 M $CuCl_2$ in *n*-M. HCl and (1-*n*)-M. $HClO_4$ were prepared, *n* varying from 0.05 to 0.25. Metallic copper was added and the solutions were kept in the dark at 22 °C. The light absorption was measured after three weeks. No change in light absorption was observed after an additional week and it was concluded that equilibrium was reached. The entire procedure was carried out in a nitrogen atmosphere to prevent oxidation of Cu(I). It is furthermore concluded that the activity factors of the solutions are essentially constant as maximally 25% of $HClO_4$ was changed by HCl.

Determination of Absorption Spectra

The light absorption was recorded on a Shimadzu MPS 50L spectrophotometer over the wavelength region 210 – 350 nm. An optical path length of 0.1 cm was used. All measurements were carried out at 22 °C. Absorption spectra were taken of all saturated $CuCl(s) - Cl^-$ solutions before, during and after oxidation.

The oxidation was carried out in air. This made it possible to follow the oxidation spectrophotometrically and to check that a stoichiometric reaction occurred as the $Cu^{2+} - Cl^-$ absorption is known [9]. During the oxidation there were no spectral changes which could be attributed to the occurrence of complexes between Cu(II) and Cu(I).

Results

Determination of Cl⁻-concentration

The determination of $[Cl^-]$ proved critical for accurate evaluation of the complex constants. The best estimate of $[Cl^-]$ was obtained from the absorption spectra as follows. For $\lambda > 280$ nm the absorbance was found to be quadratically dependent on $[Cl^-]$ in agreement with the observation of Sukhova et al. [8] *.

Figure 1 shows the absorbance at $\lambda = 290$ nm vs. $[Cl^-]^{1/2}$ and this graph was used for further deter-

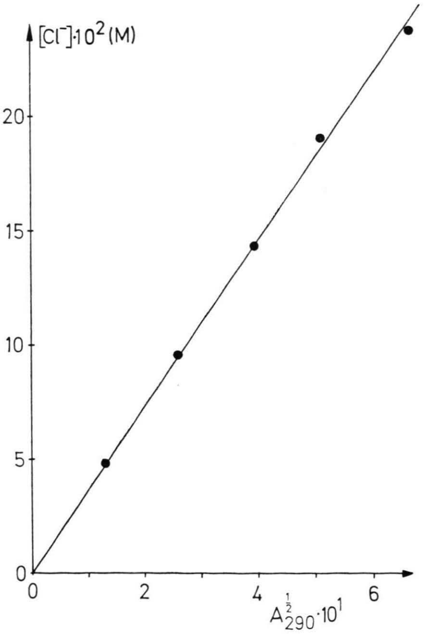

Fig. 1. Determination of the free Cl^- concentration. Plot showing the quadratic relation between the absorption at 290 nm and the free Cl^--concentration.

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* From "Handbook of Chemistry and Physics", 45th ed. 1964 – 65 (Publ. by The Chemical Rubber Co.).

** From Ref. 3.

* $[Cl^-]$ was calculated as the total amount of HCl added minus the concentration of the complexes. The error in $[Cl^-]$ thus obtained is <1%.

minations of [Cl$^-$]. This method of determining [Cl$^-$] through the absorption measurements at $\lambda = 290$ nm should improve the precision by a factor two ($\sqrt{n-1}$, $n=5$) as the error involved in the absorption measurements can be neglected.

Determination of the Complex Constants

From Eq. (4) it is apparant that β_{11} and β_{12} can be determined as the intercept and slope respectively from a plot of $C_0/[\mathrm{Cl}^-]$ vs. $[\mathrm{Cl}^-]$. This gives $\beta_{11} = 0.0486 \pm 0.0004$ and $\beta_{12} = 0.025 \pm 0.002$.

As C_0 was set equal to [Cu^{2+}] after oxidation the disproportionation Eq. (10) may introduce an error in C_0 of $K_{10} \cdot [\mathrm{Cl}^-]^{-3}$. However, the deviation from a linear relationship is not significant enough to markedly affect the values obtained for β_{11} and β_{12} in agreement with the obtained estimates of [Cu^{2+}] obtained at $I=0$, zero ionic strength (cf. above).

From the values of β_{11} and β_{12} obtained in this investigation, equilibrium constants for reaction 11 and 12 may be calculated:

$$\mathrm{CuCl(s)} = \mathrm{Cl} \rightleftarrows \mathrm{CuCl_2^-}; \qquad (11)$$

$$\log K_{s_2} = -1.313 \pm 0.004\,,$$

$$\mathrm{CuCl_2} + \mathrm{Cl^-} \rightleftarrows \mathrm{CuCl_3^{2-}}; \qquad (12)$$

$$\log K_3 = 0.29 \pm 0.04\,.$$

Absorption Spectra of $CuCl_2^-$ and $CuCl_3^{2-}$

From plots of $A/[\mathrm{Cl}^-]$ vs. $[\mathrm{Cl}^-]$, the values of $\varepsilon_{11}\beta_{11}$ and $\varepsilon_{12}\beta_{12}$ were calculated [Equation (5)]. These values together with the values evaluated above for β_{11} and β_{12} yielded absorption spectra for CuCl$_2^-$ and CuCl$_3^{2-}$ as shown in Figs. 2 and 3. In particular for CuCl$_3^{2-}$ there is a notable uncertainty in the absolute value of ε_{12} as β_{12} is determined with fairly low precision.

The absorption spectra of the two CuCl – Cl$^-$ complexes differ greatly. CuCl$_2^-$ shows a weak absorption maximum at about 230 nm close to a strong absorption band with $\lambda_{\max}$ below 210 nm (cf. peak reported at 200 nm by Sukhova et al.[8]), CuCl$_3^{2-}$ yields a stronger absorption at longer wavelengths with two well separated absorption maxima at 230 and 276 nm.

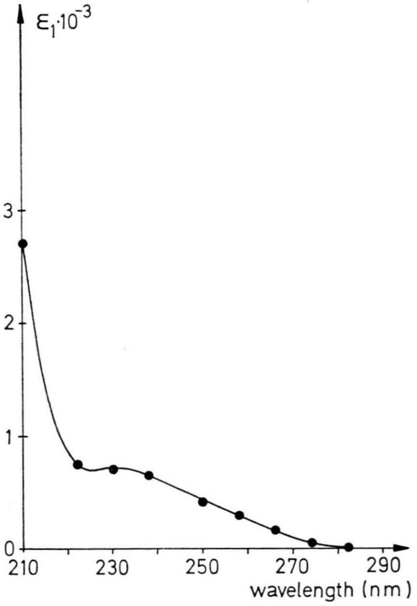

Fig. 2. Evaluated absorption spectrum for CuCl$_2^-$ (ε values in M^{-1} cm^{-1}).

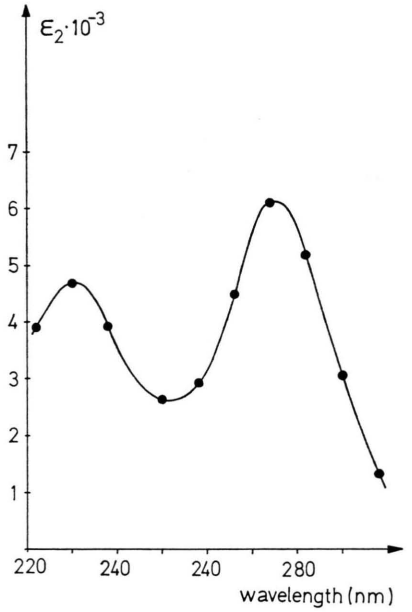

Fig. 3. Evaluated absorption spectrum for CuCl$_3^{2-}$ (ε values in M^{-1} cm^{-1}).

Discussion

Almost all previous investigations concerning complex formation between CuCl and Cl$^-$ are entirely based on solubility data. The general conclusion is that the predominating complexes at moderate Cl$^-$-concentrations (<1-M.) are CuCl$_2^-$ and CuCl$_3^{2-}$. This interpretation is strongly supported by the results of the present investigation since solubility data as well as spectrophotometric data are in full agreement with the above assumptions.

Complex Constants

As mentioned in the introduction, literature data are somewhat inconsistent concerning the reported values of the complex constants. Table 1 lists equilibrium data obtained in the different investigations.

Table 1. Literature data for the complex constants for the formation of Cu(I) — Cl^- complexes.

Temp.	Ionic medium	log K_{S2}	log K_3	log K_4	Ref.
22 °C	1 M $HClO_4$	−1.31	−0.29	—	This work [0]
25 °C	4 M $HClO_4$	−1.36	−0.04 **	—	[1]
25 °C	1 M $HClO_4$	−1.12	−0.34	—	[2]
25 °C	HCl var	−1.18	—	—	[3]
25 °C	O corr	—	−0.89	—	[4]
25 °C	O corr	−1.18 *	−0.51	—	[5]
16 °C	KCl var	−1.31	—	—	[6]
25 °C	1 M $HClO_4$	−1.23	−0.34	−0.32	[7] ***

* This value of K_{S2} was obtained from Ref. 3 and was used in the calculation of K_3.
** Complex constant expressed in m^{-1}.
*** From the investigation by Hikita et al., only the results from 25 °C and 1 M $HClO_4$ are included in the table.

The reported values are with one exception determined from solubility measurements. In Ref. [4] the method employed was EMK-measurements and only one complex is considered. The investigated concentration range was 1 – 4-M. KCl and a complex constant for $CuCl_3^{2-}$ was estimated from rough activity approximations. The methods employed in the other investigations were essentially the same. At different Cl^--concentrations the total complex concentration was estimated from redox titrations on dissolved Cu(I). It should be noted, however, that the activity factors were not kept constant in the earlier investigations [3, 5, 6] i. e. the ionic strength varied. Among these the determination of K_{s_2} by Noyes and Cha [3] is often referred to in the literature but it suffers from the fact that only one complex, $CuCl_2^-$, is considered. K_{s_2} is simply calculated as the mean value for the complex concentrations at 0.3, 0.2 and 0.1 M. Cl^- despite thef act that a systematic decrease in K_{s_2} was experimentally obtained. The determination of K_3 by Chang and Chen [5] is based on this K_{s_2} value and is furthermore related to extremely concentrated HCl concentrations involving some considerable approximations of the activities of the species involved.

The more recent investigations [0, 1, 2, 7] are all carried out in $HClO_4$ and under conditions where the ionic strength is kept constant. As K_{s_2}, to a first approximation, ought to be independent of ionic strength it was first difficult to understand why different values of this constant were obtained [1, 2]. However, after the completion of this work, recent investigations by Hikita et al. [7] have shown that K_{s_2} is in fact dependent on the concentration of the ionic medium ($HClO_4$). Hikita et al. reported the determination of the complex constants for the formation of $CuCl_2^-$, $CuCl_3^{2-}$ and $CuCl_4^{3-}$ at 15, 25 and 35 °C and at various $HClO_4$ concentrations ranging from 0.5 to 6.5 M. They obtained a marked decrease in K_{s_2} with increasing concentration of $HClO_4$. Using the ΔH value reported by Hikita et al. the K_{s_2} value for the present investigation is calculated to be 0.053 at 25 °C in good agreement with their values $K_{s_2} = 0.059$. In fact, if the values of K_{s_2} of the various investigations [0–3, 6, 7] are plotted vs. the $HClO_4$ concentrations all results with the exception of the value reported by McConnel and Davidson [2] closely agree with the observed ionic strength dependence mentioned above [7]. A possible explanation for this ionic strength dependence is ion pair interaction. This would imply that the interaction between H^+ and Cl^- is markedly different from the interaction between H^+ and $CuCl_2^-$ *. Noteworthy is the good agreement between the K_3 values [2, 7] as K_3 is determined by a homogeneous equilibrium in contrast to the heterogeneous equilibrium determining K_{s_2}. Hikita et al. also assume the existence of the $CuCl_4^{3-}$ complex. In the concentration range used here (0 to 0.25 M) the influence from this complex is negligible.

The Absorption Spectra

The spectra of $CuCl_2^-$ and $CuCl_3^{2-}$ are quite different, which indicates different electronic structures. According to Webb [10] very little is known about the existing coordination number of inorganic Cu(I) complexes in solution, but in general Cu(I) as well

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* Ion pair interaction is taken into account by adding to the common Debye-Hückel expression $-\log \gamma = A\sqrt{I}/(1+B\sqrt{I})$ a term $K \cdot I$. The constant K is primarily determined from interaction between ions with opposite charges.

as Ag(I) and Au(I) form either two collinear (sp) bonds or four tetrahedral (sp^3) bonds. In the compound K_2CuCl_3 4-covalent Cu(I) exists and tetrahedral $CuCl_4$ groups share two corners to form infinite chain ions $(CuCl_3)_n^{2n-}$. The corresponding $CuCl_2^-$ salts have not, as far as we know, been studied. However, one 1:1 compound of cuprous chloride and o-phenylene bisdimethylarsine has been formulated as a salt [Cu(diarsine)$_2$] ($CuCl_2$) which indicates the existence of 2-covalent Cu(I) in $CuCl_2^-$. From this and the observed differences in the absorption spectra of $CuCl_2^-$ and $CuCl_3^{2-}$ it appears quite possible that in solution, 2-covalent Cu(I) is present in $CuCl_2^-$ but 4-covalent Cu(I) in $CuCl_3^{2-}$.

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