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A Spectrophotometric Study of Copper(I) Chloro-Complexes in Aqueous 5 M Na(Cl, ClO$_4$) Solutions

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The complex formation of copper(I) ions in aqueous 5 M Na(Cl, ClO$_4$) solutions was studied by spectrophotometry covering a pH range from acidic to alkaline. Over the range of the chloride concentration of 0.05—5 M in acidic solutions, the complexes $CuCl_2^-$ and $CuCl_3^{2-}$ were found. The molar extinction coefficients of the complexes were determined at various wavelengths from 220 to 320 nm. The equilibrium constant for the reaction $CuCl_2^- + Cl^- = CuCl_3^{2-}$ was determined to be 1.95. Chloro-hydroxo mixed complexes of copper(I), such as $CuClOH^-$, $CuCl_2OH^{2-}$, and $CuCl(OH)_2^{2-}$ were formed in alkaline solutions and the molar extinction coefficients of these species were estimated. The formation constants $\beta_{pq} = [CuCl_{2+p}(OH)^q]/[CuCl_2][Cl]^p[OH]^q$ of the complexes were evaluated to be as follows: $\beta_{-11} = (1.1 \pm 0.1) \times 10^4$, $\beta_{01} = (4.1 \pm 0.3) \times 10^3$, and $\beta_{-12} = (3.8 \pm 0.7) \times 10^6$. No polynuclear complex was formed in the solutions.

It is known that the color of copper(I) oxide changes from yellow to red depending upon the conditions of preparation. Red copper(I) oxide is usually prepared by the electrolysis of a concentrated sodium chloride solution using copper electrodes, while yellow copper(I) oxide is precipitated by the hydrolysis of copper(I) chloride in dilute sodium chloride solutions, the former being used for ship bottom paint for antifouling.

As reported in previous publications[1,2] a search was made for favorable conditions for the preparation of red copper(I) oxide. The present study was undertaken as a continuation of this series of studies.

Since the solubility of copper(I) chloride in water is low, reliable results for the formation of copper(I) chloro-complexes have hitherto scarcely been obtained. The oxidation of copper(I) ions causes another difficulty for the experimental procedures of the study. We first note an investigation by Bodländer and Storbeck[3] who interpreted their results of the solubility measurements of copper(I) chloride in sodium chloride solutions by postulating the formation of the complexes $CuCl_2^-$ and $CuCl_3^{2-}$. More than a quarter century after Bodländer's pioneering work, Fromherz and Menshik[4] showed that the absorption maximum of copper(I) chloro-complexes appeared at 272 nm in a concentrated solution of potassium chloride. Glasner and Avinur[5] found an absorption maximum at 273 nm together with a shoulder at 234 nm in an acidic copper(I) solution containing potassium chloride. The formation of the $CuCl_2^-$ complex in a concentrated hydrochloric acid solution was confirmed by an extraction method and Raman spectrophotometry.[6] The formation constants of copper(I) chloro-complexes have been reported to be $[CuCl_2^-]/[Cu^+][Cl^-]^2 = (1.00 \pm 0.05) \times 10^6$, $[CuCl_3^{2-}]/[Cu^+][Cl^-]^3 = (0.97 \pm 0.05) \times 10^6$, and hence $[CuCl_3^{2-}]/[CuCl_2^-][Cl^-] = 0.97$ by the solubility method.[7]

In all previous studies of copper(I) complexes in chloride solutions, measurements were carried out in acidic solutions.[3-8] It is a well-known fact that an increase in the pH of a copper(I) chloride solution results in precipitates which dissolves with a further increase of pH.[9] Nevertheless, no quantitative investigation has yet been made of alkaline solutions of copper(I) chloride. The aim of the present work is to elucidate the reaction equilibria of copper(I) ions in aqueous chloride solutions over a wide pH range.

Experimental

Reagents. Reagent grade copper(I) chloride was recrystallized from hydrochloric acid and dried at 130 °C in a nitrogen atmosphere after washing the crystals with acetic acid.[10] Copper(I) chloride crystals were dissolved into a 0.5 M sodium chloride solution containing sufficient amounts of sodium perchlorate and perchloric acid in order to maintain the ionic strength and pH at 5 and 1, respectively. Sample solutions were prepared by diluting the stock solution by the addition of sodium chloride and sodium hydroxide solutions. Pure copper wire (99.99% purity) was added to the stock solution for reducing a trace amount of copper(II) ions. The amount of copper(II) ions in the stock solution was calculated not to exceed 4.4×10^{-8} M by using the equilibrium constant of the disproportionation reaction[11] and the formation constants[11] of copper(I) and (II) chloro-complexes reported in the literature. Sodium chloride and sodium perchlorate solutions were prepared from reagent grade chemicals by dissolving them in oxygen free water. All the experimental procedures were carried out in an atmosphere of nitrogen.

Spectrophotometric Measurements were carried out with a Hitachi EPS-3T spectrophotometer. Sample solutions were referred to blank solutions which were identical in composition to the sample solutions except for copper(I) chloride. The influence of copper(II) ions on the measurement of the absorption spectrum was neglected because the amount of copper(II) ions in the sample solution was calculated to not exceed 7.5×10^{-9} M and log ε of the copper(II) chloro-complexes over the wavelength range examined is about 2 to 3.[12] Cells with 1, 2, 10, and 20 mm optical pathlengths were used for the measurements at 25 °C.

Determination of Concentrations of Ions in Solution. The concentration of copper(I) ions in the stock solution was determined by atomic absorption spectrophotometry. The concentration of chloride ions was determined by Mohr's method. Since the concentration of chloride ions was greatly in excess of the copper(I) ions, the concentration of free chloride ions $[Cl^-]$ was equated to the total concentration of sodium chloride in the solution.

pH Measurements. Beckman No. 39013 combination electrodes were used for pH measurements with a Hitachi-Horiba F-5 type expanded-scale pH meter at 25 °C. The electrodes were calibrated against standard solutions of perchloric acid in 5 M Na(Cl, ClO$_4$) media. In an alkaline region, a series of sodium hydroxide solutions at a constant ionic medium of 5 M Na(Cl, ClO$_4$) was used as a series of standard pH buffer solutions. The potentials of the cell obeyed Nernst's equation over the range of the concentration of hydroxide ions from 1×10^{-4} to 3×10^{-2} M to within an uncertainty of ±1 mV.

Results and Discussion

Spectra of Copper(I) Chloride Solutions. Absorption spectra of copper(I) chloride solutions containing various amounts of sodium chloride and sodium hydroxide are shown in Fig. 1. Absorption maxima appeared at 226, 233, and 273 nm depending on the concentrations of chloride and hydroxide ions. In Table 1 are summarized the results of absorption spectra of the solutions. Spectra observed in acidic solutions ($-\log[\mathrm{OH}^-]\simeq12$) are similar to those reported by Froherz4) and Glasner5) and showed two maxima at wavelengths longer than 200 nm. The absorbance at 273 nm decreased as the concentration of chloride ions decreased.

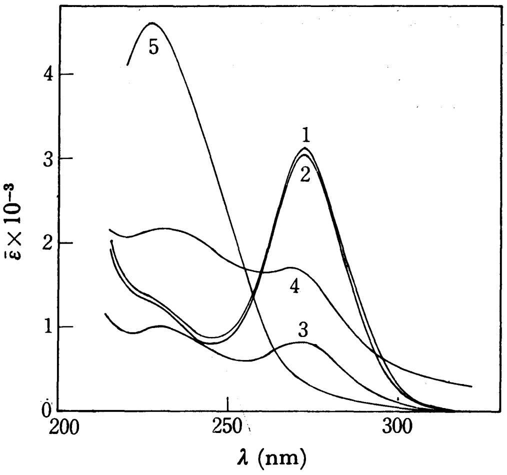

Fig. 1. Spectra of copper(I) chloride aqueous solutions. The compositions of the sample solutions numbered on the curves are shown in Table 1.

The absorption maximum at 226 nm in an alkaline solution has been previously observed.13) The absorbance at this wavelength increased with the concentration of hydroxide ions, whereas the absorbance at 273 nm decreased.

Table 1. Wavelengths of maximum absorption of copper(I) chloride solutions

No	[Cl$^-$] (M)	$-\log[\mathrm{OH}^-]$	$\lambda_{\max}$ (nm)
1	5	~12	233(shoulder), 273(sharp)
2	4	~12	233(shoulder), 273(sharp)
3	0.1	~12	233(broad), 270
4	4	2.5a)	230(broad), 270
5	4	0.25a)	226(sharp)

a) These values were calculated from the analytical concentrations of hydroxide ions.

Species of Copper(I) Chloro-complexes in Acidic Solutions Containing Sodium Chloride. The apparent molar extinction coefficient $\bar{\varepsilon}=E/[\mathrm{Cu(I)}]_{\mathrm{TOT}}$ (E denotes the absorbance of a solution for a unit optical length) at 233 and 273 nm varied with the concentration of chloride ions as shown in Fig. 2. $\bar{\varepsilon}$ was independent of the concentration of copper(I) chloride. This result shows that no polynuclear complex of copper(I) was formed in the solution.

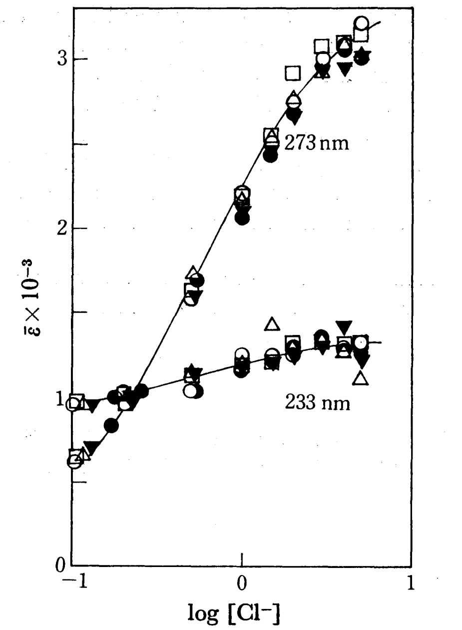

Fig. 2. Plots of $\bar{\varepsilon}$ against log[Cl$^-$] ($\mu=5$, $-\log[\mathrm{OH}^-]=12$, at 25 °C).
[Cu(I)]=○2.4×10^{-4}, □4.7×10^{-4}, △9.4×10^{-4}, ▼1.9×10^{-3}, ●4.7×10^{-3} M.

Copper(I) chloride, which is only slightly soluble in water, becomes soluble in an aqueous solution containing chloride ions to form $\mathrm{CuCl}_m{}^{(m-1)-}$ complexes, where $m\geq2$. Therefore, it may be reasonable to assume that the complex $\mathrm{CuCl_2}^-$ is formed at the first stage of complex formation in a chloride solution and formation reactions of higher complexes in solution may be described by the following equation:

$$\mathrm{CuCl_2}^- + n\mathrm{Cl}^- = \mathrm{CuCl}_{2+n}{}^{(n+1)-}. \tag{1}$$

From the material balance of copper(I), the following equation is derived:

$$[\mathrm{Cu(I)}]_{\mathrm{TOT}} = [\mathrm{CuCl_2}^-] + \sum_n \beta_n[\mathrm{CuCl_2}^-][\mathrm{Cl}^-]^n \tag{2}$$

where $\beta_n=[\mathrm{CuCl}_{2+n}{}^{(n+1)-}]/[\mathrm{CuCl_2}^-][\mathrm{Cl}^-]^n$. Since the ligand shows no absorption over the entire range studied, the absorbance E per unit path is given by

$$E = \varepsilon_0[\mathrm{CuCl_2}^-] + \sum_n \varepsilon_n\beta_n[\mathrm{CuCl_2}^-][\mathrm{Cl}^-]^n. \tag{3}$$

Then, $\bar{\varepsilon}$ is given by

$$\bar{\varepsilon} = \frac{\varepsilon_0+\sum_n \varepsilon_n\beta_n[\mathrm{Cl}^-]^n}{1+\sum_n \beta_n[\mathrm{Cl}^-]^n}. \tag{4}$$

The plots of $\bar{\varepsilon}$ *vs.* log[Cl$^-$] were fitted to a normalized curve, $y=\log\{a/(1+x)\}$, by choosing a suitable value of a. From this it was found that $n=1$, and thus Eq. (4) is rewritten as

$$\bar{\varepsilon} = \frac{\varepsilon_0+\varepsilon_1\beta_1[\mathrm{Cl}^-]}{1+\beta_1[\mathrm{Cl}^-]} = \varepsilon_1 + \frac{\varepsilon_0-\varepsilon_1}{1+\beta_1[\mathrm{Cl}^-]}. \tag{5}$$

From the best fit to the $\bar{\varepsilon}$ curves at 233 and 273 nm, the following values were obtained: at 273 nm ε_0 (*i.e.*, the molar extinction coefficient of the $CuCl_2^-$ complex) $=0$, $\varepsilon_1=3.5\times10^3$, $\beta_1=1.95$ and at 233 nm $\varepsilon_0=0.9\times10^3$, $\varepsilon_1=1.4\times10^3$ and $\beta_1=1.80$. The formation constant β_1 and the values of ε_0 and ε_1 at 273 and 233 nm were refined with the aid of an electronic computer by means of least squares calculations as shown in Table 2.

TABLE 2. THE MOLAR EXTINCTION COEFFICIENTS AND THE FORMATION CONSTANT OF THE COMPLEXES

λ_{max} (nm)	ε_0	ε_1	β_1
233	$(0.80\pm0.02)\times10^3$	$(1.45\pm0.01)\times10^3$	1.95
273	$(0.00\pm0.08)\times10^3$	$(3.33\pm0.05)\times10^3$	

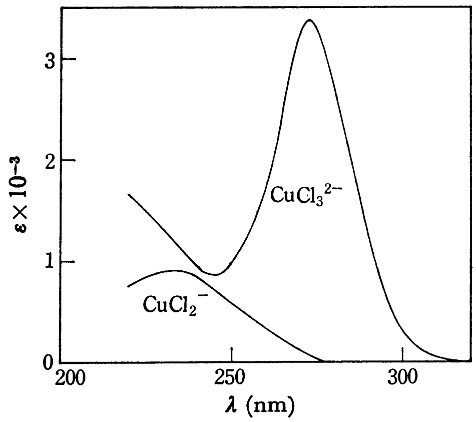

Fig. 3. Calculated spectra for the species of $CuCl_2^-$ and $CuCl_3^{2-}$ in acidic solution.

Figure 3 shows the spectra of the $CuCl_2^-$ and $CuCl_3^{2-}$ complexes calculated from spectrophotometric data at various wavelengths using the constants given in Table 2.

Copper(I) Chloro-complexes in Alkaline Solutions. As shown in Fig. 1, $\bar{\varepsilon}$ at 226 nm increases with the hydroxide ion concentration, whereas $\bar{\varepsilon}$ at 273 nm decreased. Typical examples of the change in $\bar{\varepsilon}$ at 273 and 226 nm with the hydroxide ion concentration are shown in Figs. 4 and 5. $\bar{\varepsilon}$ at 273 and 226 nm also changed with the chloride ion concentration. Therefore, both chloride and hydroxide ions must be taken into consideration in the reaction equilibria of copper(I) chloro-complexes in alkaline solutions. It is obvious that the formation of any polynuclear complex is ruled out because $\bar{\varepsilon}$ was independent of the concentration of copper(I) ions. From the fact that $\bar{\varepsilon}$ at 226 nm at the highest hydroxide ion concentration decreased as the concentration of chloride ions increased, it can be concluded that some $CuCl_{2+p}(OH)_q$ complexes with $p<0$ are formed in the alkaline solution, thus

$$CuCl_2^- + pCl^- + qOH^- = CuCl_{2+p}(OH)_q^{(p+q+1)-}. \quad (6)$$

The material balance for copper(I) ions can be represented by

$$[Cu(I)]_{TOT} = [CuCl_2^-] + \beta_1[CuCl_2][Cl^-] + \sum_p\sum_q\beta_{pq}[CuCl_2^-][Cl^-]^p[OH^-]^q, \quad (7)$$

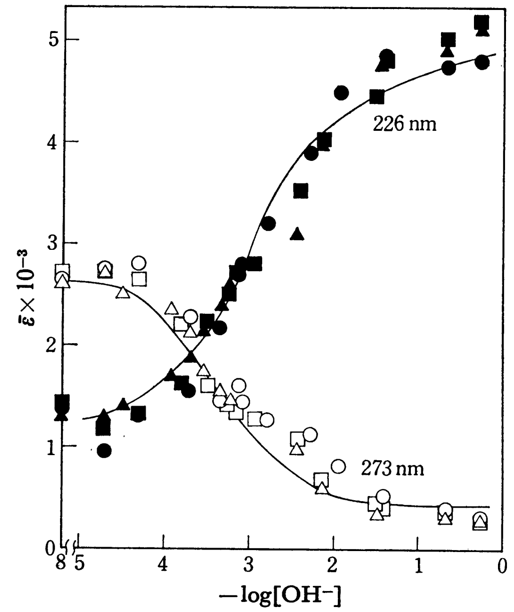

Fig. 4. Plots of $\bar{\varepsilon}$ against the concentration of hydroxide ion.
$[Cu(I)]=$○2.4×10^{-4}, □4.6×10^{-4}, △9.4×10^{-4} M, $[Cl^-]=2$ M.

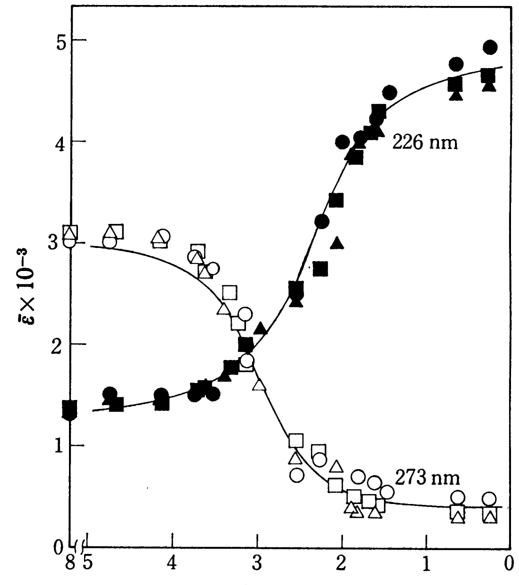

Fig. 5. Plots of $\bar{\varepsilon}$ against the concentration of hydroxide ion.
$[Cu(I)]=$○2.4×10^{-4}, □4.6×10^{-4}, △9.4×10^{-4} M $[Cl^-]=4$ M.

where p is either positive, zero or negative, and q is zero or a positive integer. The apparent molar extinction coefficient $\bar{\varepsilon}$ may be written as follows:

$$\bar{\varepsilon} = \frac{\varepsilon_0+\varepsilon_1\beta_1[Cl^-]+\sum_p\sum_q\varepsilon_{pq}\beta_{pq}[Cl^-]^p[OH^-]^q}{1+\beta_1[Cl^-]+\sum_p\sum_q\beta_{pq}[Cl^-]^p[OH^-]^q}. \quad (8)$$

By comparing the family of normalized curves, $y=\log\{a/(1+x^b)\}=f(\log x)$, having various values of a and b with the $\bar{\varepsilon}$ *vs.* $\log[OH^-]$ curves at constant $[Cl^-]$, q in the $CuCl_{2+p}(OH)_q^{(p+q+1)-}$ complex can be roughly estimated. The normalized curve with $b=1$ is less steep and that with $b=2$ is steeper than the experimental ones. These facts suggest that complexes with $q=1$ and 2 are formed in the solution.

In the first approach, the formation of $CuCl_{2+p}OH^{(p+2)-}$ complexes with varying p in the region of relatively low [OH$^-$] concentration ($-\log[OH^-]\gtrsim 3$) was assumed. With this assumption, Eq. (8) may be rewritten as

$$\bar{\varepsilon} = \frac{\varepsilon_0+\varepsilon_1\beta_1[Cl^-]+\sum_p \varepsilon_{p1}\beta_{p1}[Cl^-]^p[OH^-]}{1+\beta_1[Cl^-]+\sum_p \beta_{p1}[Cl^-]^p[OH^-]}. \tag{9}$$

By rearranging this equation, the following is obtained:

$$\begin{aligned} F &\equiv \{\bar{\varepsilon}(1+\beta_1[Cl^-])-(\varepsilon_0+\varepsilon_1\beta_1[Cl^-])\}[OH^-]^{-1} \\ &= \sum_p \varepsilon_{p1}\beta_{p1}[Cl^-]^p - \bar{\varepsilon}\sum_p \beta_{p1}[Cl^-]^p. \end{aligned} \tag{10}$$

The plots of F vs. $\bar{\varepsilon}$ are shown in Fig. 6 in which three straight lines are seen. The values of $\sum_p \beta_{p1}[Cl^-]^p$ and $\sum_p \varepsilon_{p1}\beta_{p1}[Cl^-]^p$ were obtained from the slopes and intercepts, respectively, of the lines. If it is simply assumed that only one complex is formed, *i.e.*, $p=P$, the values of $\beta_{P1}[Cl^-]^P$ and $\varepsilon_{P1}\beta_{P1}[Cl^-]^P$ are obtained.

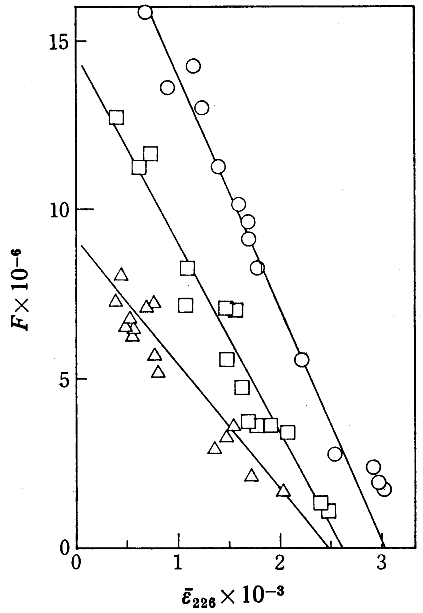

Fig. 6. Plots of F against $\bar{\varepsilon}_{226}$.
[Cl$^-$]=○2, □3, △4 M.

These values are almost inversely proportional to [Cl$^-$]. However, both β_{P1} and $\varepsilon_{P1}\beta_{P1}$ calculated assuming $P=-1$ were not constant but decreased slightly with [Cl$^-$]. Therefore, it is concluded that the $CuCl_2OH^{2-}$ complex must be taken into consideration, in addition to the main product of $CuClOH^-$. On the assumption of the formation of complexes with $P=0$ and -1, β_{-11}, β_{01}, ε_{-11} and ε_{01} were obtained by the simultaneous solution of Eq. (10) at various chloride and hydroxide ion concentrations. At high hydroxide ion concentrations $CuCl_{2+p'}(OH)_2{}^{(p'+3)-}$ may be formed. Taking into consideration the formation of dihydroxo-complexes, Eq. (8) can be rewritten as

$$\bar{\varepsilon} = \frac{\begin{gathered}\varepsilon_0+\varepsilon_1\beta_1[Cl^-]+\varepsilon_{-11}\beta_{-11}[Cl^-]^{-1}[OH^-]+\varepsilon_{01}\beta_{01}[OH^-] \\ +\sum_{p'}\varepsilon_{p'2}\beta_{p'2}[Cl^-]^{p'}[OH^-]^2\end{gathered}}{\begin{gathered}1+\beta_1[Cl^-]+\beta_{-11}[Cl^-]^{-1}[OH^-]+\beta_{01}[OH^-] \\ +\sum_{p'}\beta_{p'2}[Cl^-]^{p'}[OH^-]^2\end{gathered}}. \tag{11}$$

Rearrangement of Eq. (11) leads to

$$\begin{aligned} F' &\equiv \{\bar{\varepsilon}(1+\beta_1[Cl^-]+(\beta_{-11}[Cl^-]^{-1}+\beta_{01})[OH^-]) \\ &\quad -(\varepsilon_0+\varepsilon_1\beta_1[Cl^-]+(\varepsilon_{-11}\beta_{-11}[Cl^-]^{-1} \\ &\quad +\varepsilon_{01}\beta_{01})[OH^-])\}[OH^-]^{-2} \\ &= \sum_{p'}\varepsilon_{p'2}\beta_{p'2}[Cl^-]^{p'} - \bar{\varepsilon}\sum_{p'}\beta_{p'2}[Cl^-]^{p'}. \end{aligned} \tag{12}$$

The left-hand side of Eq. (12), F', can be calculated from the experimental data by the insertion of the values ε_{-11}, ε_{01}, β_{-11} and β_{01} determined in the previous section. The plots of $F'\times[Cl^-]$ vs. $\bar{\varepsilon}$ are shown in Fig. 7. The points fall on a single straight line, the spread of the points being probably due to experimental uncertainties. From the plot, it can be seen that the values of $F'\times[Cl^-]$ are independent of the chloride ion concentration, and thus $p'=-1$, *i.e.*, $CuCl(OH)_2{}^{2-}$. From the slope and intercept of the line, the values of β_{-12} and ε_{-12} were obtained.

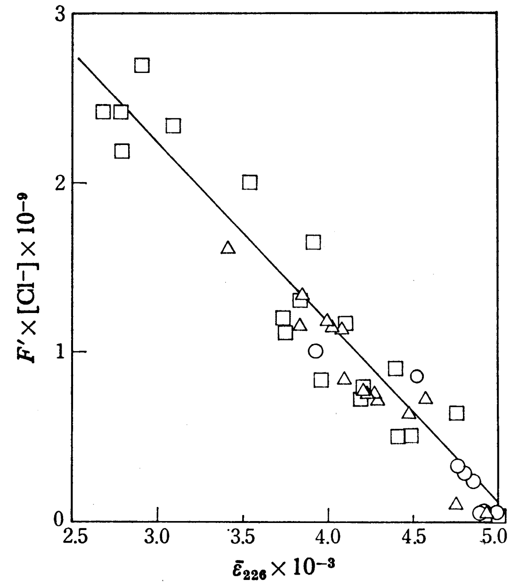

Fig. 7. Plots of $F'\times$[Cl$^-$] against $\bar{\varepsilon}_{226}$.
[Cl$^-$]=○2, □3, △4 M.

Finally the formation constants and the molar extinction coefficients of the complexes proposed were refined with the aid of an electronic computer and the results are summarized in Table 3.

TABLE 3. THE MOLAR EXTINCTION COEFFICIENTS AND FORMATION CONSTANTS OF COPPER(I) CHLORO-HYDROXO-COMPLEXES

Species	ε_{pq}(cm^{-1}·M^{-1}) 226 nm	ε_{pq}(cm^{-1}·M^{-1}) 273 nm	β_{pq}
$CuClOH^-$	5080	300	$(1.1\pm0.1)\times10^4$
$CuCl_2OH^{2-}$	0	0	$(4.1\pm0.3)\times10^3$
$CuCl(OH)_2{}^{2-}$	4760	500	$(3.8\pm0.7)\times10^6$

The solid lines in Figs. 4 and 5 show the curves calculated using the constants finally obtained. Although slightly systematic deviations were found in the plots of $\bar{\varepsilon}$ *vs.* $-\log[\mathrm{OH}^-]$ at 273 nm, it is expected that better results cannot be obtained assuming additional complexes because of the relatively large uncertainties in the pH measurements and the reproducibility of the data for the alkaline solutions.

The distribution of the complexes in 2 and 4 M chloride solutions at an ionic strength of 5 over the $-\log[\mathrm{OH}^-]$ range from 5 to 0 is shown in Fig. 8.

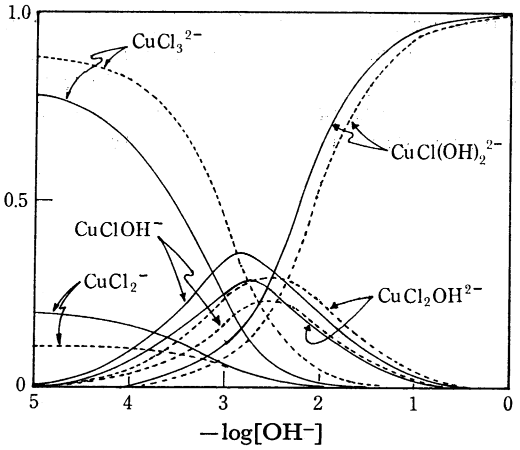

Fig. 8. Distribution of the species of copper(I).
[Cl⁻]=—2, ---4 M.

The following equilibrium constants were also obtained from the results in Table 3.

$$\mathrm{CuCl_2^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{CuClOH^-} + \mathrm{Cl^-}$$
$$K_{-11} = \beta_{-11} = (1.1\pm0.1)\times10^4 \quad (13)$$

$$\mathrm{CuCl_2^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{CuCl_2OH^{2-}}$$
$$K_{01} = \beta_{01} = (4.1\pm0.3)\times10^3 \quad (14)$$

$$\mathrm{CuCl_3^{2-}} + \mathrm{OH^-} \rightleftharpoons \mathrm{CuCl_2OH^{2-}} + \mathrm{Cl^-}$$
$$K_{01}' = \beta_{01}/\beta_1 = (2.1\pm0.2)\times10^3 \quad (15)$$

$$\mathrm{CuClOH^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{CuCl(OH)_2^{2-}}$$
$$K_{-12} = \beta_{-12}/\beta_{-11} = (3.5\pm1.0)\times10^2 \quad (16)$$

$$\mathrm{CuCl_2OH^{2-}} + \mathrm{OH^-} \rightleftharpoons \mathrm{CuCl(OH)_2^{2-}} + \mathrm{Cl^-}$$
$$K_{-12}' = \beta_{-12}/\beta_{01} = (0.9\pm0.2)\times10^3 \quad (17)$$

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