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Studies on the Preparation of Cuprous Oxide. VIII. A Spectrophotometric Study of Halogenocopper(I) Complexes in Aqueous 5 M Na(ClO$_4$) Solutions

Kazuhiko Sugasaka* and Ayako Fujii

Government Industrial Research Institute, Shikoku, Hananomiya-cho 2-3-3, Takamatsu 761

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The complex formation of copper(I) with bromide and iodide ions in aqueous 5 M (1 M=1 mol dm^{-3}) Na(ClO$_4$) solutions was studied spectrophotometrically over a pH range from acidic to alkaline. Over the concentration range of 0.05—5 M bromide ions in acidic solutions, the $CuBr_2^-$ and $CuBr_3^{2-}$ complexes were found. On the other hand, in the iodide system the CuI_2^-, CuI_3^{2-} complexes and a higher complex were found under the same experimental conditions, although the composition and the formation constant of the last complex could not be determined in this study. The equilibrium constants for the reactions, $CuX_2^- + X^- = CuX_3^{2-}$, were 13 and 1.6 for the bromide and iodide complexes respectively. A hydrolyzed species of copper(I), $Cu(OH)_2^-$, was found in an alkaline solution of the two systems. The formation constants, $\beta_{-22}=[Cu(OH)_2^-][X^-]^2/[CuX_2^-][OH^-]^2$, were evaluated as follows: $\beta_{-22}=(10.0\pm0.7)\times10^7$ ($[Br^-]<2$ M), $(2.6\pm0.7)\times10^7$ ($[Br^-]=3$ M), $(1.7\pm0.7)\times10^7$ ($[Br^-]=4$ M) in the bromide solutions, $(4.0\pm0.4)\times10^3$ ($[I^-]<2$ M), $(2.5\pm0.4)\times10^3$ ($[I^-]=3$ M), $(2.2\pm0.4)\times10^3$ ($[I^-]=4$ M) in the iodide solutions.

During the course of an investigation of copper(I) oxide by the hydrolysis of copper(I) halides, it was shown that the color of copper(I) oxide changed from yellow to red depending upon the concentration of halide ions in solutions.[1,2] For the precipitation of copper(I) oxide by the hydrolysis of copper(I) iodide crystals, the dissolution of the crystals is the rate-determining step in water, whereas the crystal growth of copper(I) oxide is the rate-determining step in a concentrated sodium iodide solution.[3] Based on these observations, we aimed at studying the equilibria of the formation of copper(I) halide complexes in aqueous solutions in order to obtain information on reactions between copper(I) and halide ions.

Bodländer and Storbeck[4,5] suggested the formation of the CuX_2^- and CuX_3^{2-} complexes (X denotes halide ions) on the basis of solubility measurements of copper(I) halides in sodium halide solutions. Fromherz and Menschick[6] and Doehlemann and Fromherz[7] found that a concentrated lithium bromide solution containing both copper(I) and copper(II) showed absorption maxima at 272, 338, and 512 nm. Sukhova *et al.*[8] reported that a copper(I) chloride solution has λ_{max} at 200, 235, and 273 nm and broad bands at 300—400 and 1200—2000 nm, analogous to the absorption maxima of copper(I) bromide and iodide solutions. The formation constants of copper(I) bromo-[9] and iodo-complexes[10] have been reported in the basis of solubility measurements.

In spite of the existence of many results in the literature, investigations of the complex formation of copper(I) ions with halide ions have been restricted to acidic media.

In a previous paper[11] we dealt with the complex formation of copper(I) in an aqueous 5 M Na(Cl, ClO$_4$) solution and found that $CuCl_2^-$ and $CuCl_3^{2-}$ complexes were formed in acidic media, together with these mixed halogeno–hydroxo complexes, $CuClOH^-$, $CuCl_2OH^{2-}$, and $CuCl(OH)_2^{2-}$, in alkaline media. In this paper we wish to describe the complex formation of copper(I) ions with bromide and iodide ions in 5 M Na(ClO$_4$) aqueous solutions over a wide pH range, the total anionic concentration being kept constant.

Experimental

Reagents. Copper(I) bromide was recrystallized according to a procedure described ealier.[11] Copper(I) iodide was purified in the following way: reagent-grade crystals were dissolved into a saturated sodium iodide solution, and then after filtration, the solution was diluted with water. The precipitates thus formed by dilution were washed with water and then with acetic acid before being dried at 130 °C under a nitrogen atmosphere.[12] The stock solutions of copper(I) bromide and iodide were prepared by dissolving copper(I) bromide and iodide crystals into 0.5 M sodium bromide and sodium iodide solutions respectively, both types of solutions containing sufficient amounts of sodium perchlorate and perchloric acid to maintain the total anionic concentration and pH at 5 M and 1 respectively. Since the stock solutions contained pieces of pure copper wire (99.99% purity) for reducing the trace amount of copper(II) ions, the concentrations of copper(II) ions in the bromide and iodide solutions were estimated to be less than 8×10^{-8} M and 3.6×10^{-11} M respectively; these values were calculated on the basis of the equilibrium constants of copper(I) and (II) bromo- and iodo-complexes reported in the literature.[13] Sample solutions were prepared from the stock solutions; sodium bromide, sodium iodide, and sodium hydroxide solutions. The sodium bromide, sodium iodide, sodium perchlorate, and sodium hydroxide were of a reagent grade. The preparation of sample solutions and measurements were carried out under an atmosphere of nitrogen.

Spectrophotometric Measurements. These were run with a Hitachi EPS-3T spectrophotometer. The absorption spectra of the sample solutions were obtained using 1-, 2-, 10-, and 20-mm cells at 25 °C by referring to blank solutions which were the same in composition with the samples except for the copper(I) ions. Since the amount of copper(II) ions in the sample solutions prepared by the dilution of the stock solutions was estimated to be less than 2×10^{-9} M, and since the molar extinction coefficients of the copper (II) bromide complexes were estimated to be about 10^2—10^3 mol^{-1} dm^3 cm^{-1} over the wavelength region of 260—300 nm,[14-16] the influence of copper(II) ions on the measurements in the bromide solutions was neglected. Although no spectrophotometric data for copper(II) iodide complexes have been given in the literature, the absorption due to copper(II)–iodide complexes was also neglected because of the much lower concentration of copper(II) ions in the iodide solutions than in the bromide solutions. When the sample solution came in contact with air, the solution turned yellow within 20 min. Therefore, an effort was made to avoid the contact of the sample with air by the introduction of nitrogen gas into the cells and to finish the measurements within a few minutes.

Determination of Concentrations of Ions in the Solutions. The copper(I) ions in the stock solutions were determined by atomic-absorption spectrometry. The concentration of halide ions was determined by means of argentometric titration. Since the concentration of the halide ions in the samples was in a large excess compared with that of the copper(I) ions, the concentration of the free halide ions [X^-] was assumed to be equal to the total concentration of the sodium halide in the solutions.

Results and Discussion

Spectra of Copper(I) Halide Solutions. Absorption spectra of copper(I) halide solutions containing various amounts of sodium halide and sodium hydroxide are shown in Figs. 1 and 2. In the absorption spectra of copper(I) bromide in acidic solutions, a maximum absorbance appeared at 278 nm (Fig. 1). The absorbance at 278 nm increased as the concentration of bromide ions increased. When the concentration of hydroxide ions increased, the absorbance at 278 nm decreased, while the absorbance at 240 nm increased.

The absorption maximum appeared at 274—285 nm in the copper(I) iodide solutions in acidic media, depending upon the concentration of iodide ions, as is shown in Fig. 2. The absorption at a wavelength shorter than 270 nm was not measured because the intense absorption due to the iodide ions overlapped with that of the complexes at that wavelength. The absorbance at these wavelengths decreased with the concentration of hydroxide ions.

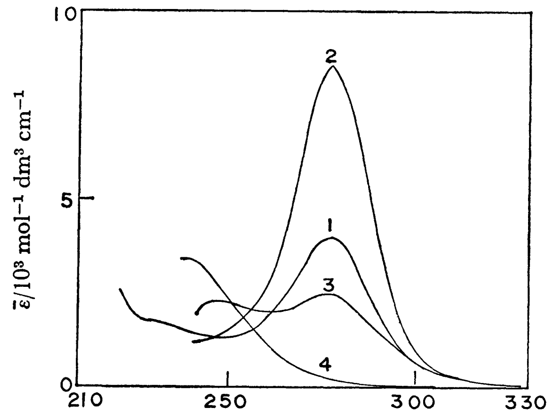

Fig. 1. UV absorption spectra of solution of copper(I) bromide and sodium bromide (at 25 °C).

No.	$[Br^-]_{TOT}$/M	$-\log[OH^-]$	$[Cu(I)]_{TOT}/10^{-4}$ M
1	0.05	11.5	2
2	5	11.5	2
3	4	2.06	0.8
4	4	0.84	0.8

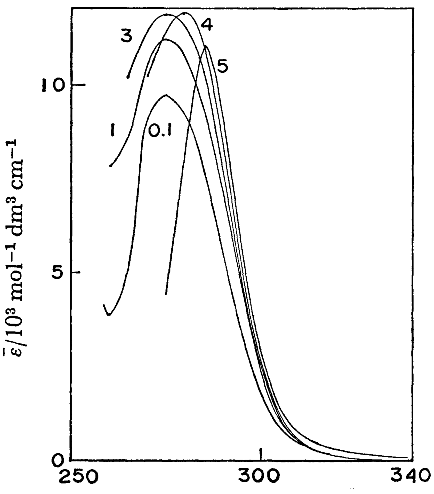

Fig. 2. UV absorption spectra of acidic solutions of copper(I) iodide and sodium iodide (at 25 °C). $-\log[OH^-]=8$—12, $[Cu(I)]_{TOT}/10^{-4}$ M=4.8. Numbers in the figure indicate the total concentration of iodide ions (M).

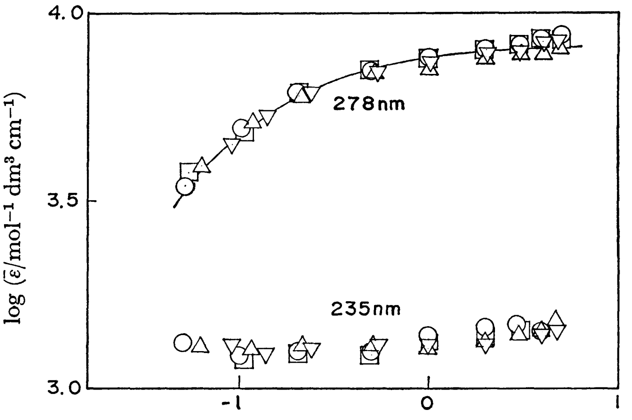

Fig. 3. Relationship between $\bar{\varepsilon}$ at 278 nm and the concentration of bromide ions (at 25 °C). $-\log[OH^-]=8$—12, $[Cu(I)]_{TOT}/10^{-4}$ M=0.2 : ○, 0.7 : □, 2.0 : △, 6.6 : ▽.

Complex Formation in Acidic Media. The apparent molar extinction coefficient, $\bar{\varepsilon}=E/[Cu(I)]_{TOT}$, at 278 nm is shown in Fig. 3, where E denotes the absorbance of a solution for a unit of the optical pathlength. The plot was dependent upon the concentration of bromide ions, but independent of the total copper(I) ions. These results show that no polynuclear complex of copper(I) ions was formed in the solutions. The absorbance at 235 nm remained practically unchanged when the concentrations of both the copper(I) and bromide ions were varied. Therefore, the data were not used for analysis.

Since copper(I) halides hardly dissolve in water, but dissolve only in solutions containing an excess amount of the halide ions, the species in the solution may have the composition of $CuX_m^{(m-1)-}$ (the possibility of the formation of a polynuclear complex is excluded). Therefore, the CuX_2^- complex may be formed in the first stage of complex formation in a halide solution and then higher complexes may be formed by the further addition of halide ions to the CuX_2^- ion:

$$\mathrm{CuX(s)} + \mathrm{X}^- = \mathrm{CuX_2}^- \qquad (1)$$

$$\mathrm{CuX_2}^- + n\mathrm{X}^- = \mathrm{CuX}_{2+n}{}^{(n+1)-}. \qquad (2)$$

Since we used solutions without solid CuX, the equilibrium constant of the first reaction could not be determined though the constants of Reaction 2 were determined.

From the material balance of copper(I) and the absorbance, E, per unit of the path, the following equation is derived:

$$\bar{\varepsilon} = \frac{E}{[\mathrm{Cu(I)_{TOT}}]} = \frac{\varepsilon_0+\sum\limits_n \varepsilon_n\beta_n[\mathrm{X}^-]^n}{1+\sum\limits_n \beta_n[\mathrm{X}^-]^n}, \qquad (3)$$

as long as the ligand shows no absorbance over the entire wavelength range studied or as long as the absorbance due to the ligand has been subtracted as a blank in the measurement of ε. β_n is defined as $\beta_n=[\mathrm{CuX}_{2+n}{}^{(n+1)-}]/[\mathrm{CuX_2}^-][\mathrm{X}^-]^n$. The molar extinction coefficient of the $\mathrm{CuX}_{2+n}{}^{(n+1)-}$ complex is denoted as ε_n. The values of ε_0, ε_n, β_n, and n may be determined by comparing the plots of log ε *vs.* log $[\mathrm{X}^-]$ with a family of the normalized curves, $y=\log\{x^n/(1+x^n)\}=f(\log x)$, because Eq. 3 may be rearranged as:

$$\log(\bar{\varepsilon}-\varepsilon_0) = \log(\varepsilon_n-\varepsilon_0) + \log\frac{\beta_n[\mathrm{X}^-]^n}{1+\beta_n[\mathrm{X}^-]^n}, \qquad (4)$$

by assuming that only one complex, $\mathrm{CuX}_{2+n}{}^{(n+1)-}$, besides the $\mathrm{CuX_2}^-$ complex, is present in the solution. The plots of log $\bar{\varepsilon}$ at 278 nm against log $[\mathrm{Br}^-]$ (Fig. 2) fit a normalized curve, $y=\log\{x/(1+x)\}$; thus, $n=1$, the molar extinction coefficient of the $\mathrm{CuBr_2}^-$ complex, $\varepsilon_0=0$, $\varepsilon_1=8.5\times10^3$, and $\beta_1=13$ were obtained. The values were refined by means of a least-squares calculation with an electronic computer; the values are summarized in Table 1.

For the iodide system, on the other hand, the apparent molar extinction coefficient, $\bar{\varepsilon}$, at 274 nm first increased and then sharply decreased with an increase in the concentration of iodide ions (Fig. 4). This fact obviously showed that at least two complexes, one with a larger value and the other with a much smaller value of ε than ε_0, must exist in the solution. Since the ε's at both 274 and 285 nm were independent of the concentration of the copper(I) ions, the formation of any polynuclear complex of copper(I) ions was ruled out.

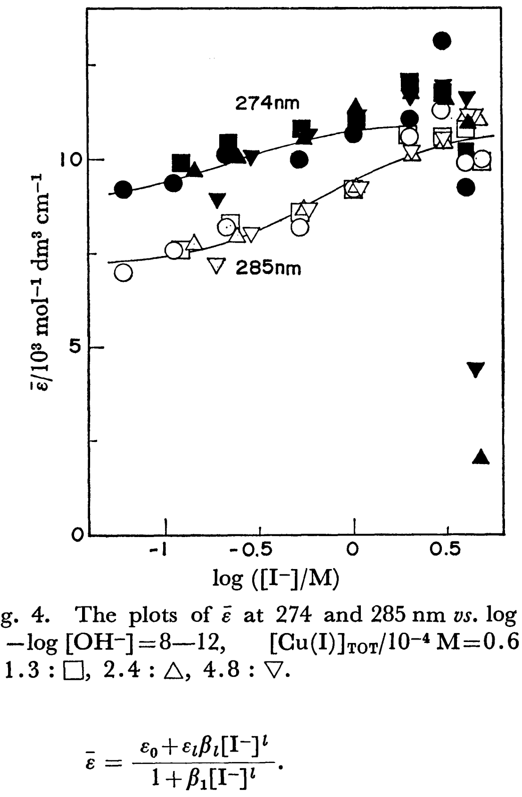

Fig. 4. The plots of $\bar{\varepsilon}$ at 274 and 285 nm *vs.* log $[\mathrm{I}^-]$. $-\log[\mathrm{OH}^-]=8$—12, $[\mathrm{Cu(I)}]_{\mathrm{TOT}}/10^{-4}\,\mathrm{M}=0.6$: ○, 1.3 : □, 2.4 : △, 4.8 : ▽.

At first, the formation of two complexes, $\mathrm{CuI}_{2+l}{}^{(l+1)-}$ and $\mathrm{CuI}_{2+l+m}{}^{(l+m-1)-}$, besides the $\mathrm{CuI_2}^-$ complex, was assumed. The apparent molar extinction coefficient, $\bar{\varepsilon}$, of the solution may thus be given by Eq. 5:

$$\bar{\varepsilon} = \frac{\varepsilon_0+\varepsilon_l\beta_l[\mathrm{I}^-]^l+\varepsilon_{l+m}\beta_{l+m}[\mathrm{I}^-]^{l+m}}{1+\beta_l[\mathrm{I}^-]^l+\beta_{l+m}[\mathrm{I}^-]^{l+m}}. \qquad (5)$$

Since the $\bar{\varepsilon}$ values at 274 nm steeply decreased at about $[\mathrm{I}^-]\simeq 3$ M, we assume that the second species may be formed in a solution of $[\mathrm{I}^-]\gtrsim 3$ M, and that, in the concentration region of $[\mathrm{I}^-]$ lower than 3 M, the equilibrium between $\mathrm{CuI_2}^-$ and the first complex, $\mathrm{CuI}_{2+l}{}^{(l+1)-}$ may be established, where the molar extinction coefficient of the solution may approximately be given as follows:

$$\bar{\varepsilon} = \frac{\varepsilon_0+\varepsilon_l\beta_l[\mathrm{I}^-]^l}{1+\beta_l[\mathrm{I}^-]^l}. \qquad (6)$$

A curve-fitting method may be applied to the plot of log $\bar{\varepsilon}$ *vs.* log $[\mathrm{I}^-]$ in order to determine ε_0, ε_l, and β_l, as well as l, by comparing the plots with the normalized curve, $y=\log\{x^n/(1+x^n)\}$, at various n's, or by comparing $\bar{\varepsilon}$ *vs.* log $[\mathrm{I}^-]$ with a family of normalized curves, $u=\log\{a/(1+v^n)\}$, with various sets of a and n. In both the curve-fitting procedures, the data fit the curve of $n=1$; thus, the value of l was determined to be unity. The values estimated by the curve-fitting method were as follows: at 274 nm, $\varepsilon_0=9.4\times10^3$, $\varepsilon_1=1.3\times10^4$, and log $\beta_1=0.22$ ($\beta_1=1.7$); at 285 nm, $\varepsilon_0=7.0\times10^3$, $\varepsilon_1=1.1\times10^4$, and log $\beta_1=0.18$ ($\beta_1=1.5$).

The variation in $\bar{\varepsilon}$ at 274 nm in the $[\mathrm{I}^-]>3$ M region was so steep that no reasonable assumption to explain the data was given; the $l+m$ value must, though, be very large ($l+m\gg2$). However, since the data at 285 nm showed no clear indication for the formation of such a high complex, we concluded that the $l+m$ value was not so large, but that the ionic-medium principle to keep constant the activity coefficients of all reacting species did not hold in the region of $[\mathrm{I}^-]>$ 3—5 M. Therefore, we did not use these data for the determination of the formation constant of the second complex, $\mathrm{CuI}_{2+l+m}{}^{(l+m-1)-}$. The $l+m$ value was also not determined for this complex.

The formation constant, β_1, and the molar extinction coefficients, ε_0 and ε_1, at 274 and 285 nm were refined by means of a least-squares calculation with the aid of an electronic computer. The final results are summarized in Table 1 together with the results for the copper(I) chloro complexes.11)

Halogenocopper(I) Complexes in Alkaline Solutions. The absorbance of a copper(I) bromide solution at 278 nm decreased when sodium hydroxide was added to the solution (see Fig. 1). Typical examples of the change in $\bar{\varepsilon}$ at 278 nm of copper(I) bromide solutions with the concentration of the hydroxide ions are shown in Fig. 5. Patterns similar to those of bromide system were obtained for the iodide system at 285 nm; they are shown in Fig. 6. It is obvious from the plots that no polynuclear complex was formed, because $\bar{\varepsilon}$ was independent of the concentration of the copper(I) ions in both the bromide and iodide solutions. Since the curves depend on the concentration of the halide ions, we assumed the formation of complexes with the general formula of $\mathrm{CuX}_{2+p}(\mathrm{OH})_q^{(p+q-1)-}$ in the alkaline solutions. The formation constant, β_{pq}, of the complex is defined as follows:

Table 1. The molar extinction coefficients and the formation constants of the copper(I) halide complexes

Species	$\lambda_{\max}$ (nm)	ε (mol^{-1} dm^3 cm^{-1})	β
$\mathrm{CuBr_2^-}$	278	0.0	—
$\mathrm{CuBr_3^{2-}}$	278	$(8.3\pm0.1)\times10^3$	13.0 ± 0.4
$\mathrm{CnI_2^-}$	274 285	$(9.0\pm0.4)\times10^3$ $(7.0\pm0.1)\times10^3$	—
$\mathrm{CuI_3^{2-}}$	274 285	$(1.2\pm0.1)\times10^4$ $(10.0\pm0.2)\times10^3$	1.6 ± 0.1
$\mathrm{CuCl_2^-}$	233	$(1.45\pm0.1)\times10^3$	—[11]
$\mathrm{CuCl_3^{2-}}$	273	$(3.33\pm0.1)\times10^3$	1.95[11]

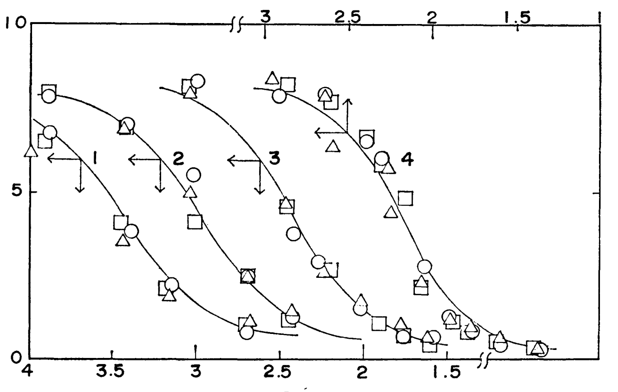

Fig. 5. Relationships between $\bar{\varepsilon}$ at 278 nm and the concentration of hydroxide ion for bromide solutions. Numbers indicated in the figure show the total concentrations of bromide ions (M).
$[\mathrm{Cu(I)}]_{\mathrm{TOT}}/10^{-4}\,\mathrm{M}=0.2$: ○, 0.4 : □, 0.8 : △.

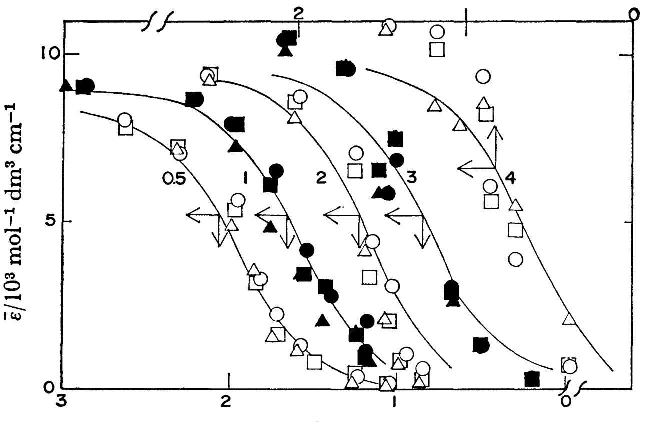

Fig. 6. Relationships between $\bar{\varepsilon}$ at 285 nm and the concentration of hydroxide ion for iodide solutions. Numbers indicated in the figure show the total concentrations of iodide ions (M).
$[\mathrm{Cu(I)}]_{\mathrm{TOT}}/10^{-4}=0.3$: ○, 0.7 : □, 1.3 : △.

$$\mathrm{CuX_2^-} + p\mathrm{X^-} + q\mathrm{OH^-} = \mathrm{CuX}_{2+p}(\mathrm{OH})_q^{(p+q-1)-} \tag{7}$$

$$\beta_{pq} = [\mathrm{CuX}_{2+p}(\mathrm{OH})_q^{(p+q-1)-}]/[\mathrm{CuX_2^-}][\mathrm{X^-}]^p[\mathrm{OH^-}]^q. \tag{8}$$

The material balance for copper(I) ions may be represented by the following equation:

$$[\mathrm{Cu(I)}]_{\mathrm{TOT}} = [\mathrm{CuX_2^-}] + \sum_n \beta_n[\mathrm{CuX_2^-}][\mathrm{X^-}]^n + \sum_p\sum_q \beta_{pq}[\mathrm{CuX_2^-}][\mathrm{X^-}]^p[\mathrm{OH^-}]^q, \tag{9}$$

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

$$\bar{\varepsilon} = \frac{\varepsilon_0 + \sum_n \varepsilon_n\beta_n[\mathrm{X^-}]^n + \sum_p\sum_q \varepsilon_{pq}\beta_{pq}[\mathrm{X^-}]^p[\mathrm{OH^-}]^q}{1+\sum_n\beta_n[\mathrm{X^-}]^n + \sum_p\sum_q \beta_{pq}[\mathrm{X^-}]^p[\mathrm{OH^-}]^q}. \tag{10}$$

$^*\beta_{pq}$ symbolizes a conditional constant, $\beta_{pq}[\mathrm{X^-}]^p$, at a constant $[\mathrm{X^-}]$; here $[\mathrm{X^-}]$ is approximated to $[\mathrm{X^-}]_{\mathrm{TOT}}$. By inserting $^*\beta_{pq}$ into Eq. 10 and rearranging it, we obtain:

$$\frac{\bar{\varepsilon}(1+\sum_n {}^*\beta_n) - (\varepsilon_0 + \sum_n \varepsilon_n {}^*\beta_n)}{\varepsilon_{pq} - \bar{\varepsilon}} = {}^*\beta_{pq}[\mathrm{OH^-}]^q. \tag{11}$$

Since $\bar{\varepsilon}$ decreased with the increase in the concentration of hydroxide ions and approached zero, ε_{pq} may be assumed to be zero as a first approximation.

One function, F_1 is defined as follows:

$$F_1 = \log\left\{\frac{(\varepsilon_0 - \sum_n \varepsilon_n {}^*\beta_n) - \bar{\varepsilon}(1+\sum_n {}^*\beta_n)}{\bar{\varepsilon}}\right\} = \log {}^*\beta_{pq} + q\log[\mathrm{OH^-}]. \tag{12}$$

The plots of F_1 *vs.* log $[\mathrm{OH^-}]$ are shown in Figs. 7 and 8 for the bromide and iodide systems respectively. Both plots gave straight lines with a slope of 2: thus, $q=2$ was estimated for both the bromide and iodide solutions. Therefore, Eq. 10 is rewritten as follows:

$$\bar{\varepsilon} = \frac{\varepsilon_0 + \sum_n \varepsilon_n {}^*\beta_n + \sum_p \varepsilon_{p2} {}^*\beta_{p2}[\mathrm{OH^-}]^2}{1+\sum_n {}^*\beta_n + \sum_p {}^*\beta_{p2}[\mathrm{OH^-}]^2}. \tag{13}$$

Another function, F_2 is defined, after the rearrangement of Eq. 13, as follows:

$$F_2 = \{\bar{\varepsilon}(1+\sum_n {}^*\beta_n) - (\varepsilon_0 + \sum_n \varepsilon_n {}^*\beta_n)\}[\mathrm{OH^-}]^2 = \sum_p \varepsilon_{p2} {}^*\beta_{p2} - \bar{\varepsilon}_p {}^*\beta'_{p2}. \tag{14}$$

Since F_2 is experimentally determinable at a given $[\mathrm{X^-}]$, F_2 can be plotted against $\bar{\varepsilon}$. The plots are shown in Figs. 9 and 10 for the bromide and iodide systems respectively. Although the data are scattered to some extent, straight lines may be drawn through the points, as may be seen in the figures. In both plots, the lines pass a point near the original point of the coordinate: therefore, ε_{p2} may be zero or small compared with ε_0 and ε_n. The slopes of the lines,

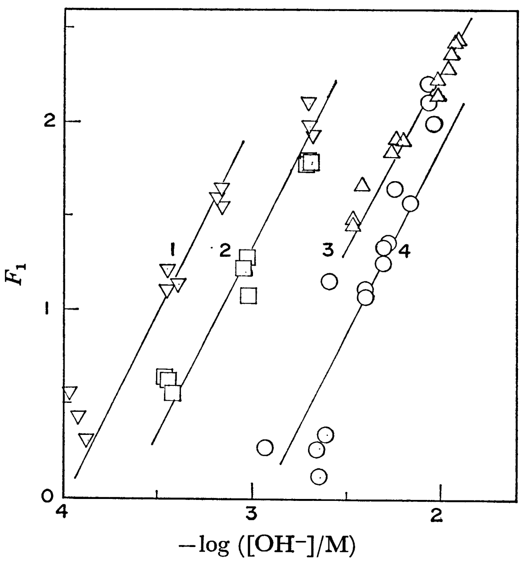

Fig. 7. Relationship between F_1 and $\log[OH^-]$ for bromide solutions.
Numbers in the figure show the total concentrations of bromide ions (M).

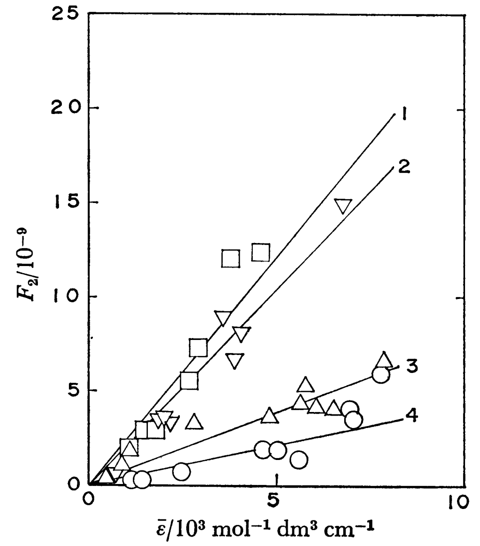

Fig. 9. Relationship between F_2 and $\bar{\varepsilon}$ at 278 nm for bromide solutions.
Numbers in the figure show the total concentrations of bromide ions (M).

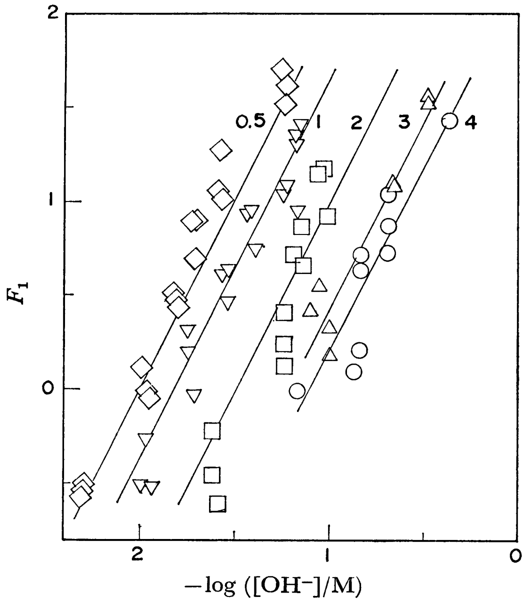

Fig. 8. Relationship between F_1 and $\log[OH^-]$ for iodide solutions.
Numbers in the figure show the total concentrations of iodide ions (M).

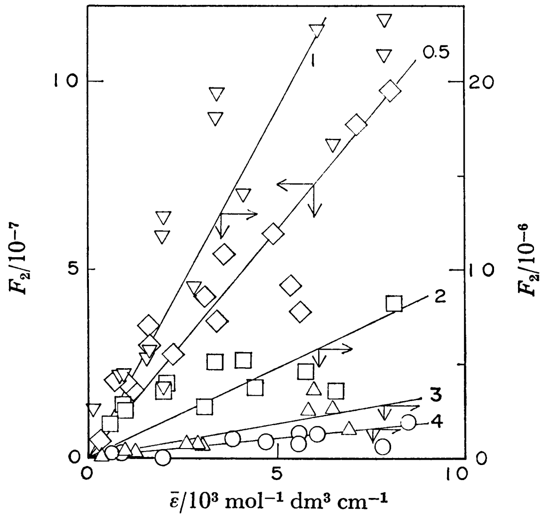

Fig. 10. Relationship between F_2 and $\bar{\varepsilon}$ at 285 nm for iodide solutions.
Numbers in the figure show the total concentrations of iodide ions (M).

TABLE 2. THE FORMATION CONSTANTS OF THE DIHYROXOCOPPER(I) COMPLEX, $Cu(OH)_2^-$

Solution	$[X^-]_{TOT}$ (M)	β_{pq}
Bromide	4	$(1.7\pm0.1)\times10^7$
	3	$(2.6\pm0.1)\times10^7$
	2−1	$(10.0\pm0.1)\times10^7$
Iodide	4	$(2.2\pm0.2)\times10^3$
	3	$(2.5\pm0.2)\times10^3$
	2−0.5	$(4.0\pm0.1)\times10^3$
Chloride[11]	$CuClOH^-$	$(1.1\pm0.1)\times10^4$
	$CuCl_2OH^{2-}$	$(4.1\pm0.3)\times10^3$
	$CuCl(OH)_2^{2-}$	$(3.8\pm0.1)\times10^6$

$\sum_p {}^*\beta_{p2}$, thus obtained are plotted against $\log[X^-]$ in Fig. 11. For both the bromide and iodide systems, $p=-2$ was found. Therefore, we concluded that, in the bromide and iodide solutions, $Cu(OH)_2^-$ was produced in alkaline solutions.

The formation constant of the complex proposed here was refined by means of a least-squares calculation: the final results are tabulated in Table 2, as are the values for the copper(I) chloro–hydroxo mixed complexes.[11] The solid lines in Figs. 5 and 6 show the curves calculated by using the constants finally obtained. In the solutions containing halide ions larger than 3 M, the formation constants obtained were slightly different from those found in the solutions with concentrations of the halide ions lower than 3 M;

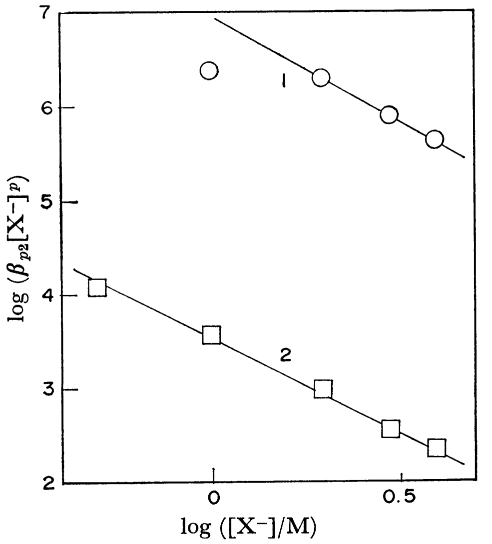

Fig. 11. Relationship between $\log(\beta_{p2}[X^-]^p)$ and $\log[X^-]$.
1 : Bromide solutions, 2: iodide solutions.

this was due to the change in the property of the ionic media by the introduction of a large amount of the halide ions to the sodium perchlorate medium.

We have already reported in a previous paper[11] that the mixed halogeno–hydroxo complexes of copper(I) were found in alkaline solutions of the chloride system, whereas the dihydroxocopper(I) complex was not so found. In the bromide and iodide systems, the mixed halogeno–hydroxo complexes were not found, only the dihydroxocopper(I) complex was found in alkaline media.

The following formation constants of the $CuX_n^{(n-1)-}$ complexes have been reported in the literatures: for the chloride system, $CuCl_2^- + Cl^- = CuCl_3^{2-}$: $\log K_3 = 0.29 \pm 0.04$ by spectrophotometry;[17] for the bromide system, $CuBr_2^- + Br^- = CuBr_3^{2-}$: $K_3 = 10.2 \times 0.9\ M^{-1}$,[9] and for the iodide system, $[CuI_2^-]/[I^-] = (0.91—1.13) \times 10^{-3}$, $[CuI_3^{2-}]/[I^-]^2 = (4.32—5.9) \times 10^{-3}$. The results obtained in our experiments for the chloride and bromide systems are the same or nearly the same as the values in literature, but for the iodide system ones is smaller than the value in the literature.

The formation constant of the CuX_3^{2-} complex is smaller in the iodide system than in the bromide system. At a glance, this trend seems to be in the direction opposite to that expected from the hard-and-soft acid-and-bases concept. However, these results may be well explained on the HSAB basis as follows: a very soft acid the Cu^+ ion, may combine with a very soft base, I^-, to form the fairly stable CuI_2^- complex, which may have a linear structure; hence, the CuI_2^- complex may not be deformed by the insertion of the next iodide ion into the complex. On the other hand, the $CuBr_2^-$ complex may be less than the CuI_2^- complex, thus allowing for the addition of the third bromide ion to the complex to form the $CuBr_3^{2-}$ complex.

The much smaller formation constant of the $Cu(OH)_2^-$ complex in the iodide system than in the bromide system may be interpreted much like the fact that the stable CuI_3^{2-} complex (the overall formation constant of the CuI_3^{2-} may be large than that of the $CuBr_3^{2-}$, according to the HSAB concept) is not easily decomposed to form the $Cu(OH)_2^-$ complex with hydroxide ions by releasing the iodide ions within the complex.

It is thought that the difference in the behavior of the complex formation of copper(I) among the three halides may be related to the precipitation process of copper(I) oxide by the hydrolysis of copper(I) halide. In the precipitation of the less-soluble salt, the size of the nucleus depends on the ratio of the concentration of the supersaturation to the saturation of the solute.[18] As the halogeno complexes of copper(I) are stable in a concentrated solution of sodium halide and are much more stable in an iodide solution than in other halide solutions, the ratio of the concentration of the supersaturation to the saturation of copper(I) oxide is kept low: that is, large crystals of copper(I) oxide are easily precipitated in a concentrated solution of sodium halide, especially in an iodide solution.

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