3542 © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *63*, *3542—3549 (1990)* [Vol. 63, No. 12

Effects of Chloro Substituent on Solvent Extraction of Copper(II) with *o*-, *m*-, and *p*-Chlorobenzoic Acids

Hiromichi YAMADA,* Shiho HORIKAWA,† Yukio FUJII,† and Masateru MIZUTA†
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
†Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11

(Received June 29, 1990)

Through the solvent extraction of copper(II) with the three isomeric chlorobenzoic acids in 1-octanol, it has been shown that the entrance of chloro substituent into the three positions in the benzene ring of benzoic acid results in an individuality in the extraction behavior for copper(II). The dimeric copper(II) chlorobenzoates Cu_2A_4 and $Cu_2A_4(HA)_2$ were responsible for the extraction with *m*-chlorobenzoic acid together with the monomer CuA_2, while only the monomeric species CuA_2 was extracted with *o*- and *p*-chlorobenzoic acids. The entrance of chloro group into the ortho position in benzoic acid was found to result in a lowering of both the partition constants of *o*-chlorobenzoic acid itself and its copper(II) compound. That into the para position has led to a significant decrease in the solubilities of the para isomer and its copper(II) compound in both aqueous and octanol phases.

In a series of investigations on the extraction of copper(II) with a variety of aliphatic carboxylic acids,[1-6] it has been shown that the formation of dimeric copper(II) carboxylates is one of important factors in the extraction of copper(II) with carboxylic acids. In the extraction systems with benzoic acid, in which no formation of dimeric copper(II) species was observed to any appreciable extent, it was suggested that the monomeric copper(II) species cannot be extracted into nonsolvating solvents such as benzene, but in solvating solvents such as 1-octanol, the solvation of the monomeric copper(II) species by some solvent molecules makes possible the extraction of copper(II).[7]

In the previous investigation on the extraction of copper(II) with toluic acids, it has been found that the introduction of methyl substituent at the *o*- and *m*-positions in benzoic acid has enable the formation of the dimeric copper(II) species, and leads to the enhancement of the extractability.[8] On the other hand, in the extraction of copper(II) with *p*-toluic acid, the emulsion was observed in the region where the percent extraction of coppper(II) exceeds 30%. This is anticipated to result from the pronounced decrease in the solubility of *p*-toluic acid in both water and 1-octanol.

In this paper, we deal with the extraction of copper(II) with *o*-, *m*-, and *p*-chlorobenzoic acids in 1-octanol.

Experimental

Reagents. *o*-, *m*-, and *p*-Chlorobenzoic Acids: Commercial chlorobenzoic acids(purity: over 99%) were dissolved in purified 1-octanol. Copper(II) perchlorate, sodium perchlorate and 1-octanol were prepared by the same methods as employed previously.[2] All other reagents were reagent grade and used without further purification.

Procedure. Partition was performed at a total copper concentration of 5×10^{-3} mol dm^{-3} and chlorobenzoic acid concentration of 0.3—0.7 mol dm^{-3} for ortho-isomer, 0.3—0.9 mol dm^{-3} for meta-isomer, and 0.05—0.12 mol dm^{-3} for para-isomer, respectively. Partition and pH measurement were carried out in a bath thermostated at 25.0±0.2 °C. Ionic strength of the aqueous phase was adjusted to 0.1 mol dm^{-3} with sodium perchlorate. Shaking for about 1 h was found to be sufficient for complete equilibration. The concentrations of copper(II) and hydrogen ions in the aqueous phase were determined by the same methods as employed previously.[7] The dissociation constants of chlorobenzoic acids were potentiometrically estimated. In the estimation of the partition constants of *o*-, *m*-, and *p*-chlorobenzoic acids between 0.1 mol dm^{-3} perchloric acid and 1-octanol, the individual absorption maxima at 280, 283, and 241 nm corresponding to each acid were used for the determination of the concentrations of the acids in the aqueous phase.

Apparatus. The apparatus for mechanical shaking in a thermostat, centrifugation, pH measurements, and spectrophotometric determinations were the same as employed previously.[7]

Results and Discussion

Partition of Chlorobenzoic Acids. The dissociation constants of *o*-, *m*-, and *p*-chlorobenzoic acids, which were potentiometrically determined at the ionic strength of 0.1 mol dm^{-3} ($NaClO_4$), are summarized in Table 1. These values are in agreement with those in the literature[9] with making activity coefficient corrections.

Through the partition of the chlorobenzoic acids between 1-octanol and 0.1 mol dm^{-3} perchloric acid, in which the dissociation of the chlorobenzoic acids can be neglected, it was recognized that the dimerization of the respective acids in 1-octanol does not occur to any appreciable extent and that the distribution ratio of each acid is equal to its partition constant. The partition constants obtained are listed in Table 1.

In the present extraction systems, the concentration of the monomeric chlorobenzoic acid in 1-octanol phase can be calculated by the following expression:

Table 1. Extraction of Cu(II) with Aromatic Carboxylic Acids

Acids	$\mathrm{p}K_a$	$\log K_{\mathrm{D,HA}}$	$\log K_{\mathrm{ex(10)}}$	$\log K_{\mathrm{ex(20)}}$	$\log K_{\mathrm{ex(22)}}$	$K_{\mathrm{D,HA}}/K_a$
o-Chlorobenzoic acid	2.74	2.07	−6.75			6.5×10^4
m-Chlorobenzoic acid	3.66	2.65	−7.03	−12.20	−12.04	2.0×10^6
p-Chlorobenzoic acid	3.95	2.67	−7.15			4.2×10^6
Benzoic acid[a)]	4.04	1.88	−7.70			9.1×10^5
o-Toluic acid[b)]	3.73	2.21	−7.84	−12.84		8.7×10^5
m-Toluic acid[b)]	4.09	2.41	−7.84	−13.15		3.2×10^6
p-Toluic acid[b)]	4.21	2.33	−7.84			3.5×10^6

Solvent: 1-Octanol. *o*-Chlorobenzoic acid: $\log\beta_1=0.76$ and $\log\beta_2=1.88$ in the aqueous phase.
a): Ref. 7. b): Ref. 8.

$$[\mathrm{HA}]_o=\frac{K_{\mathrm{D,HA}}C_{\mathrm{HA}}}{K_{\mathrm{D,HA}}+1+\dfrac{K_a}{[\mathrm{H}^+]}}, \tag{1}$$

where K_a, $K_{\mathrm{D,HA}}$, $[\mathrm{HA}]_o$, and C_{HA} denote the dissociation constant, the partition constant, the monomer concentration in the organic phase, and the total concentration of each acid, respectively. From the results for *m*-, and *p*-chlorobenzoic acids shown in Table 1, it has been found that the concentration of the monomeric acid in 1-octanol phase can be approximated by the total concentration of the respective acids under the present extraction conditions: $C_{\mathrm{HA}}=0.3\ \mathrm{mol\,dm^{-3}}$ ($-\log[\mathrm{H}^+]=3.7$—4.3), 0.5 (3.4—3.7), 0.6 (3.4—3.8), 0.7 (3.3—3.8), and 0.9 (3.2—3.6) for *m*-chlorobenzoic acid, and 0.05 (4.0—4.6), 0.063 (4.0—4.5), 0.1 (3.7—4.3), and 0.125 (3.8—4.3) for *p*-chlorobenzoic acid. On the other hand, as shown in Table 1, the dissociation constant of *o*-chlorobenzoic acid in the aqueous solution is much greater than that of the other isomers, and the partition constant of the former is lower than that of the latter. According to Eq. 1, the concentration of the monomeric *o*-chlorobenzoic acid in 1-octanol phase has been found to vary with the hydrogen ion concentration in the aqueous phase under the present extraction conditions: $C_{\mathrm{HA}}=0.3\ \mathrm{mol\,dm^{-3}}$ ($-\log[\mathrm{H}^+]=3.7$—4.5), 0.5 (3.5—4.2), and 0.7 (3.3—4.0).

Extraction of Copper(II) with Chlorobenzoic Acids. Analysis of Extraction Equilibrium: If the *j*-merized copper(II) species $\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a$ is presumed to be extracted as an extracted species, the following equilibrium is set up between the organic and aqueous phases:

$$j\mathrm{Cu}^{2+}+(2j+a)(\mathrm{HA})_o \rightleftharpoons (\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a)_o+2j\mathrm{H}^+,$$

with the extraction constant:

$$K_{\mathrm{ex}(ja)}=\frac{[\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a]_o[\mathrm{H}^+]^{2j}}{[\mathrm{Cu}^{2+}]^j[\mathrm{HA}]_o^{(2j+a)}}, \tag{2}$$

and the total concentration of copper(II) in the organic phase can be represented as Eq. 3:

$$C_{\mathrm{Cu,o}}=\sum_j\sum_a jK_{\mathrm{ex}(ja)}[\mathrm{Cu}^{2+}]^j[\mathrm{H}^+]^{-2j}[\mathrm{HA}]_o^{(2j+a)}, \tag{3}$$

where $j\geqq1$, $a\geqq0$, both j and a are integers, and the subscript o refers to the organic phase.

The total concentration of copper(II) in the aqueous phase can be expressed as: $C_{\mathrm{Cu,w}}=[\mathrm{Cu}^{2+}]\alpha_{\mathrm{Cu}}$, where α_{Cu} denotes the side-reaction coefficient of copper(II) in the aqueous phase.

Suppose that only $\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a$ is responsible for the extraction, the following expression can be obtained from Eq. 3:

$$\begin{aligned}\log C_{\mathrm{Cu,o}}&=j(\log C_{\mathrm{Cu,w}}-2\log[\mathrm{H}^+]-\log\alpha_{\mathrm{Cu}})\\&\quad+(2j+a)\log[\mathrm{HA}]_o+\log j+\log K_{\mathrm{ex}(ja)}.\end{aligned} \tag{4}$$

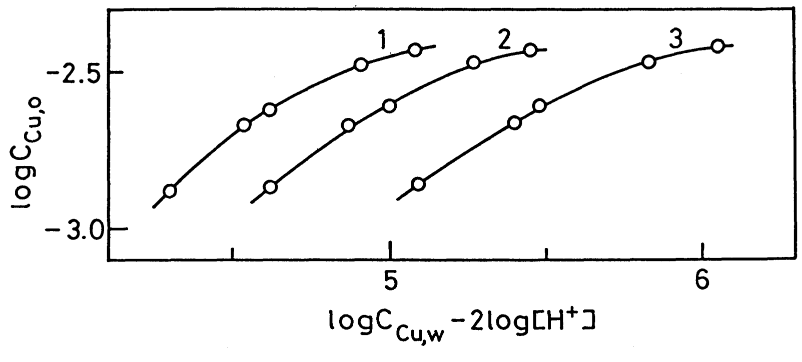

Fig. 1. Determination of the degree of polymerization of the extracted species.
HA: *o*-chlorobenzoic acid. C_{HA}; No. 1 : 0.7, No. 2 : 0.5, and No. 3 : 0.3 $\mathrm{mol\,dm^{-3}}$.

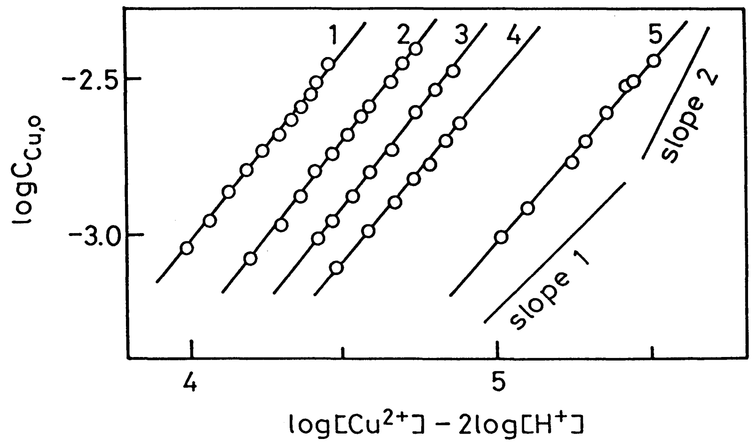

Fig. 2. Determination of the degree of polymerization of the extracted species.
HA: *m*-chlorobenzoic acid. C_{HA}; No. 1 : 0.9, No. 2 : 0.7, No. 3 : 0.6, No. 4 : 0.5, and No. 5 : 0.3 mol dm^{-3}.

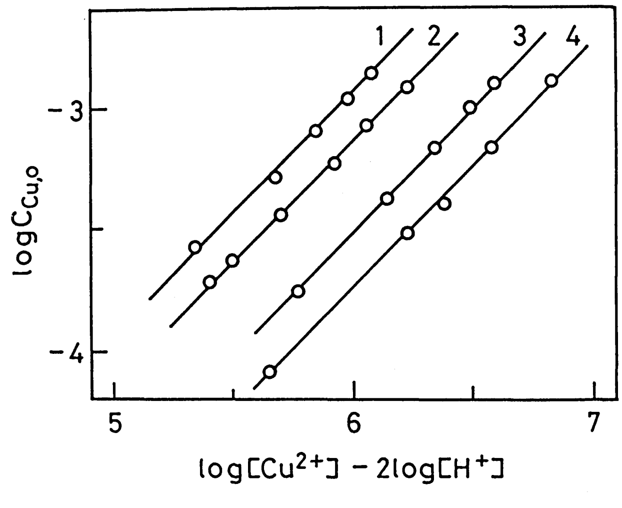

Fig. 3. Determination of the degree of polymerization of the extracted species.
HA: *p*-chlorobenzoic acid. C_{HA}; No. 1 : 0.125, No. 2 : 0.1, No. 3 : 0.063, and No. 4 : 0.05 mol dm^{-3}. Solid lines are the straight ones with slope of 1.0.

If the concentration in the aqueous phase occupied by the copper(II) species other than Cu^{2+} ion can be neglected compared with copper(II) ion concentration, that is, $\alpha_{Cu}=1$, the degree of polymerization of the extracted species can be found from the slope of the plot of $\log C_{Cu,o}$ against ($\log C_{Cu,w}-2\log[H^+]$) at constant $[HA]_o$. The results are represented in Figs. 1, 2, and 3 for *o*-, *m*-, and *p*-chlorobenzoic acids, respectively. In Fig. 2, the slope of the plots shows the values ranging from 1.1 to 1.3. It is sugggested that the polymeric copper(II) species is responsible for the extraction with *m*-chlorobenzoic acid together with the monomeric one. The plots in Fig. 3 fall on a straight line with slope of 1.0. Then, only the monomeric copper(II) species was expected to be responsible for the extraction with *p*-chlorobenzoic acid. In contrast with the plots in Figs. 2 and 3, those in Fig. 1 draw convex arcs. As stated above, the concentration of the monomeric *o*-chlorobenzoic acid in 1-octanol phase varies with the hydrogen ion concentration in the aqueous phase under the present extraction conditions. Therefore, in this case it is convenient to introduce the following expression instead of Eq. 4:

$$\log C_{Cu,o}-a\log[HA]_o=j(\log C_{Cu,w}-2\log[H^+]+2\log[HA]_o) + \log j+\log K_{ex(ja)}-j\log \alpha_{Cu}. \qquad (5)$$

Judging from the coordination number of copper, the value of "a" can be expected to be 0, 1, or 2. Figure 4 illustrates the plots of ($\log C_{Cu,o}-a\log[HA]_o$ for $a=0$, 1, and 2) vs. ($\log C_{Cu,w}-2\log[H^+]+2\log[HA]_o$) on the basis of Eq. 5 under the conditions: $C_{HA}=0.3$, 0.5, and 0.7 mol dm^{-3}. As shown in Fig. 4, the relation based on Eq. 5 can be set up only in the case of $a=0$, irrespective of the total concentration of *o*-chlorobenzoic acid, and the plots are found to be the curve with slope of less than unity. These informations suggest that the monomeric species CuA_2 can be estimated as an extracted species, that is, $a=0$ and $j=1$, and the side-reaction of copper(II) ion with *o*-chlorobenzoate anion in the aqueous phase influences the extraction equilibrium on this extraction system. Then, the side-reaction coefficient of copper(II) ion with *o*-chlorobenzoate anion in the aqueous phase can be represented as follows:

$$\alpha_{Cu(A^-)}=1+\beta_1[A^-]+\beta_2[A^-]^2, \qquad (6)$$

where β_1, β_2, and A^- denote the over-all formation constants ($\beta_1=[CuA^+]/[Cu^{2+}][A^-]$ and $\beta_2=[CuA_2]/[Cu^{2+}][A^-]^2$) and *o*-chlorobenzoate anion in the aqueous phase. Judging from the results obtained, the following expression can be derived from Eqs. 5 and 6:

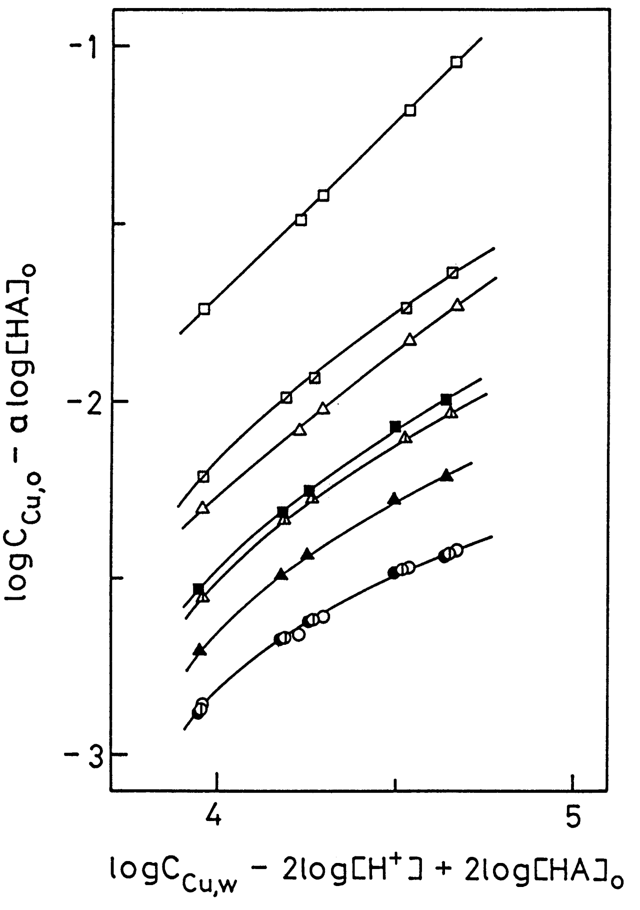

Fig. 4. Determination of the degree of polymerization and the number of *o*-chlorobenzoic acid molecules involved in the extracted species.
Symbols are as follows: circles: a=0, C_{HA}; ○: 0.3, ⦶: 0.5, and ●: 0.7 mol dm^{-3}, triangles: a=1, C_{HA}; △: 0.3, ◭: 0.5, and ▲: 0.7 mol dm^{-3}, and squares: a=2, C_{HA}; □: 0.3, ▨: 0.5, and ■: 0.7 mol dm^{-3}, respectively.

$$C_{Cu,o}^{-1}C_{Cu,w}[H^+]^{-2}[HA]_o^2 = K_{ex(10)}^{-1} + \beta_1 K_{ex(10)}^{-1}[A^-] + \beta_2 K_{ex(10)}^{-1}[A^-]^2, \quad (7)$$

where $K_{ex(10)}$ denotes the extraction constant of CuA_2. The values of the left-hand side of Eq. 7 are related to the second order with respect to $[A^-]$. Then, we can evaluate the constants, $K_{ex(10)}$, β_1, and β_2 by adjusting to obtain the best fit between the observed values and the calculated curve on the basis of Eq. 7. The results are demonstrated in Fig. 5, and the extraction and over-all formation constants were calculated by the least-squares method as follows: $\log K_{ex(10)}=-6.75$, $\log\beta_1=0.76$, and $\log\beta_2=1.88$, respectively. According to the resulting informations for *o*-chlorobenzoic acid, the following equation can be derived from Eq. 5:

$$\log C_{Cu,o} - 2\log[HA]_o = \log C_{Cu,w} - 2\log[H^+] - \log\alpha_{Cu(A^-)} + \log K_{ex(10)}. \quad (8)$$

Consequently, the plots of $(\log C_{Cu,o} - 2\log[HA]_o)$

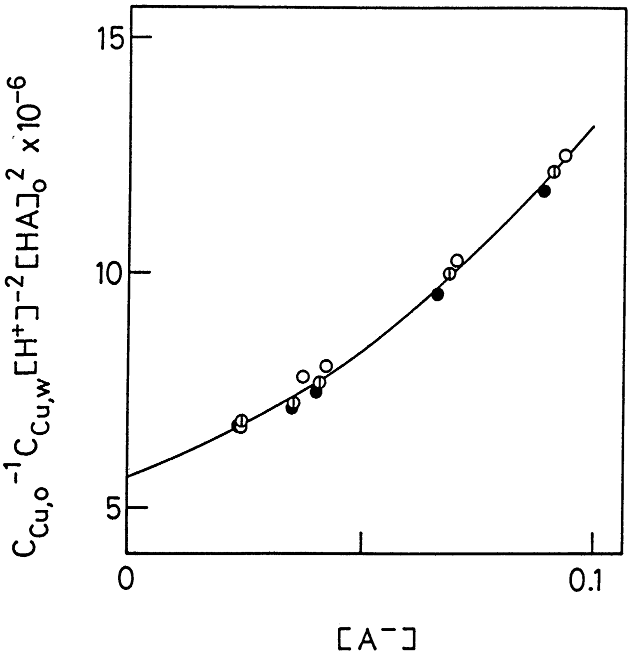

Fig. 5. Estimation of the extraction and over-all formation constants in the *o*-chlorobenzoic acid systems.
Solid line is the calculated curve of the second order with respect to $[A^-]$, and is illustrated as smooth as possible to find the values of $K_{ex(10)}$, β_1, and β_2 by the least-squares method. Symbols are the same as in Fig. 4.

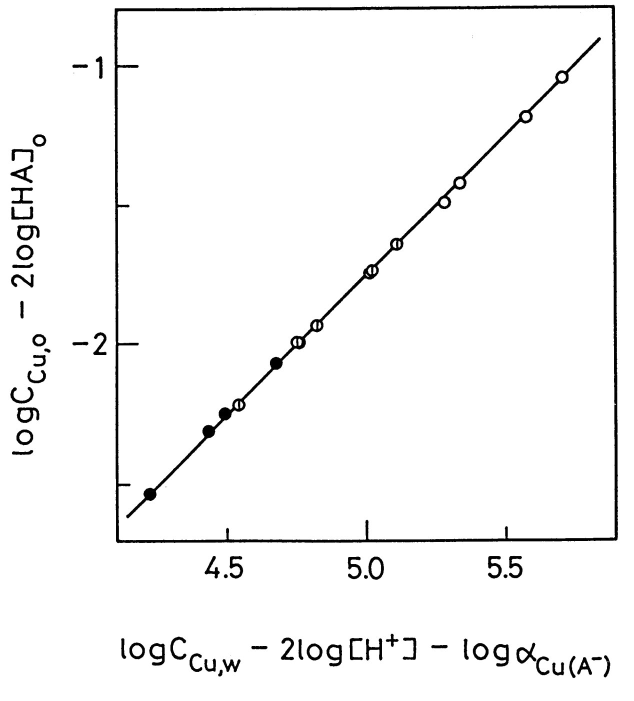

Fig. 6. The validity of the corrections by cosidering the side-reaction coefficient on the basis of Eq. 8 in the *o*-chlorobenzoic acid systems.
Solid line is the straight one with slope of 1.0 and intercept of $\log K_{ex(10)}$ (−6.75). Symbols are the same as in Fig. 4.

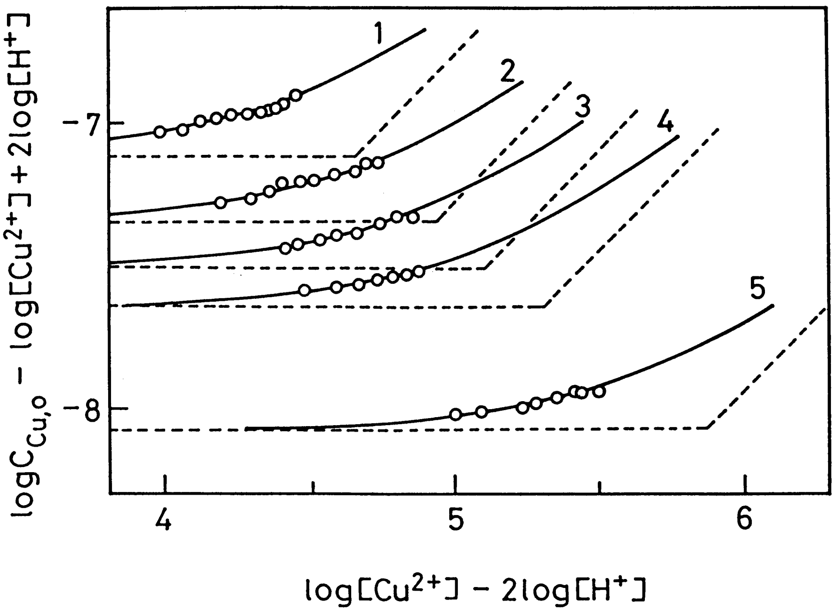

Fig. 7. The identification of the degree of polymerization of copper(II) *m*-chlorobenzoates.
Curves are the normalized ones, log(1+X) vs. log$X$. Dotted straight lines are the asymptotes of the respective normalized curves. Numbers are the same as in Fig. 2.

against ($\log C_{\mathrm{Cu,w}}-2\log[\mathrm{H^+}]-\log \alpha_{\mathrm{Cu(A^-)}}$) should fall on the straight line with slope of unity and intercept of $\log K_{\mathrm{ex(10)}}=-6.75$. As expected, the calculated line according to Eq. 8 has proved to be in good agreement with the observed values (Fig. 6).

In the extraction system with *m*-chlorobenzoic acid, both the monomeric and dimeric copper(II) species have been suggested to be extracted, as shown in Fig. 2. The following expression can be obtained on the assumption that $\mathrm{CuA_2(HA)}_a$ and $\mathrm{Cu_2A_4(HA)}_b$ are responsible for the extraction:

$$\log C_{\mathrm{Cu,o}}-\log[\mathrm{Cu^{2+}}]+2\log[\mathrm{H^+}]=(2+a)\log[\mathrm{HA}]_{\mathrm{o}} + \log K_{\mathrm{ex}(1a)}+\log\left(1+\frac{2K_{\mathrm{ex}(2b)}}{K_{\mathrm{ex}(1a)}}[\mathrm{HA}]_{\mathrm{o}}^{(2+b-a)}[\mathrm{Cu^{2+}}][\mathrm{H^+}]^{-2}\right), \tag{9}$$

where $K_{\mathrm{ex}(1a)}$ and $K_{\mathrm{ex}(2b)}$ represent the extraction constants of the monomer and dimer, respectively. As reported previously,[2,3,8] it was confirmed that the monomeric and dimeric copper(II) species were responsible for the extraction with *m*-chlorobenzoic acid, by fitting the plots of ($\log C_{\mathrm{Cu,o}}-\log[\mathrm{Cu^{2+}}]+2\log[\mathrm{H^+}]$) vs. ($\log[\mathrm{Cu^{2+}}]-2\log[\mathrm{H^+}]$) at constant $[\mathrm{HA}]_{\mathrm{o}}$ to the normalized curve, log(1+X) vs. logX. As shown in Fig. 7, both the monomer and dimer copper(II) species were found to be extracted by *m*-chlorobenzoic acid under the present extraction conditions.

In the region where the monomer prevails, that is, in the region on the straight line asymptotes with slope of zero in Fig. 7, the following relation can be obtained from Eq. 3:

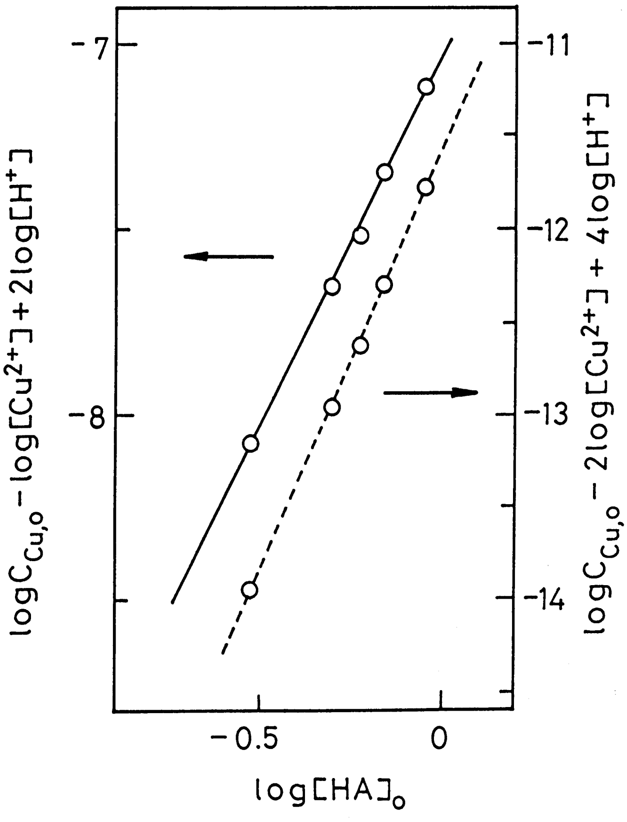

Fig. 8. Determination of the number of *m*-chlorobenzoic acid molecules involved in the monomeric and dimeric copper(II) species, respectively.
Solid and dotted lines are the straight ones with slope of 2.0 and 4.5, respectively.

$$\log C_{\mathrm{Cu,o}} - \log[\mathrm{Cu}^{2+}] + 2\log[\mathrm{H}^+] = \log\sum_a (K_{\mathrm{ex}(1a)}[\mathrm{HA}]_{\mathrm{o}}^{(2+a)}). \qquad (10)$$

According to this equation, the number of the acid molecules involved in the monomeric copper(II) species can be estimated from the slope of the plots of ($\log C_{\mathrm{Cu,o}}$$-$$\log[\mathrm{Cu}^{2+}]$$+$$2\log[\mathrm{H}^+]$) vs. $\log[\mathrm{HA}]_{\mathrm{o}}$. As can be seen from Fig. 8, the plots fall on a straight line with slope of 2.0, that is, a=0. Then, the monomer is found to be $\mathrm{CuA_2}$. In addition, the extraction constant of $\mathrm{CuA_2}$ can be estimated from the intercept of the plots: $\log K_{\mathrm{ex}(10)}$=$-$7.03.

In the region where the plots in Fig. 7 fall on the straight line asymptotes with slope of unity, that is, $[\mathrm{CuA_2}]_{\mathrm{o}} \ll 2\sum_b[\mathrm{Cu_2A_4(HA)}_b]_{\mathrm{o}}$, the following expression can be derived from Eq. 3:

$$\log C_{\mathrm{Cu,o}} - 2(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]) = \log 2\sum_b (K_{\mathrm{ex}(2b)}[\mathrm{HA}]_{\mathrm{o}}^{(4+b)}). \qquad (11)$$

We can determine the number of the acid molecules involved in the dimer from the slope of the plots of the values of left-hand side of Eq. 11 against $\log[\mathrm{HA}]_{\mathrm{o}}$. The results in Fig. 8 suggest that two dimeric copper(II) species are at least responsible for the extraction and one of them is certainly $\mathrm{Cu_2A_4}$(b=0). If the other is $\mathrm{Cu_2A_4(HA)}_b$ ($b \geqslant 1$), the following expression can be obtained:

$$\log C_{\mathrm{Cu,o}} - 2(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]) - 4\log[\mathrm{HA}]_{\mathrm{o}} = \log\left(1 + \frac{K_{\mathrm{ex}(2b)}}{K_{\mathrm{ex}(20)}}[\mathrm{HA}]_{\mathrm{o}}^{b}\right) + \log 2 + \log K_{\mathrm{ex}(20)}. \qquad (12)$$

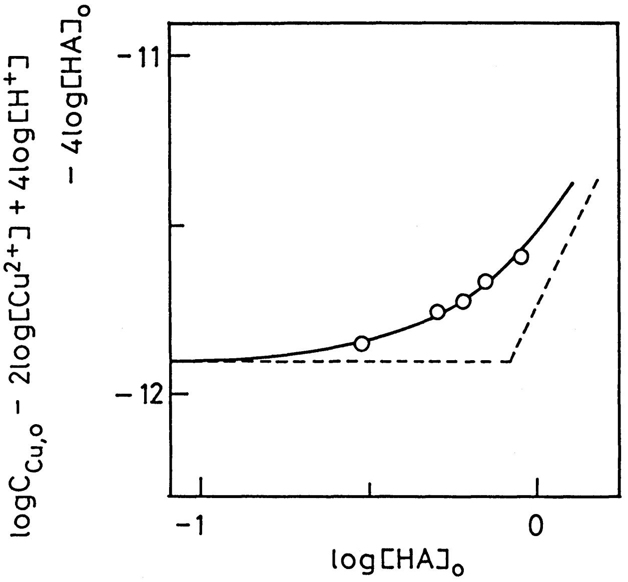

Fig. 9. Determination of the number of *m*-chlorobenzoic acid molecules involved in the dimeric copper(II) *m*-chlorobenzoates by the curve-fitting method.
Solid curve is the normalized one, $\log(1+X^2)$ vs. $\log X$. Dotted lines are the asymptotes of the normalized curve.

On the basis of this equation, by fitting the plots of the left-hand side of Eq. 12 vs. $\log[\mathrm{HA}]_{\mathrm{o}}$ to the normalized curves, $\log(1+X^n)$ vs. $\log X$, we can evaluated the composition of the other dimer and the extraction constants of the two dimers. As shown in Fig. 9, the plots fit well with the normalized curve with n=2. Then, the other dimer is found to be $\mathrm{Cu_2A_4(HA)_2}$, that is, b=2, and both the extraction constants of $\mathrm{Cu_2A_4}$ and $\mathrm{Cu_2A_4(HA)_2}$ were obtained as listed in Table 1.

In the extraction with *p*-chlorobenzoic acid, the extraction equilibrium was evaluated under the conditions where the emulsion does not appear. In Fig. 3, only the monomeric copper(II) species was shown to be extracted in this system. Then, the composition and extraction constant of the monomer can be estimated from the slope and intercept of the plots of ($\log C_{\mathrm{Cu,o}}$$-$$\log[\mathrm{Cu}^{2+}]$$+$$2\log[\mathrm{H}^+]$) against $\log[\mathrm{HA}]_{\mathrm{o}}$. From Fig. 10, the monomeric species was found to be $\mathrm{CuA_2}$ with $\log K_{\mathrm{ex}(10)}$=$-$7.15.

Consequently, the extraction equilibria for the chlorobenzoic acids systems can be summarized as follows:

-*o*-chlorobenzoic acid-

$$\mathrm{Cu}^{2+} + 2(\mathrm{HA})_{\mathrm{o}} \overset{K_{\mathrm{ex}(10)}}{\rightleftharpoons} (\mathrm{CuA_2})_{\mathrm{o}} + 2\mathrm{H}^+$$

In this extraction system, the concentration of CuA^+

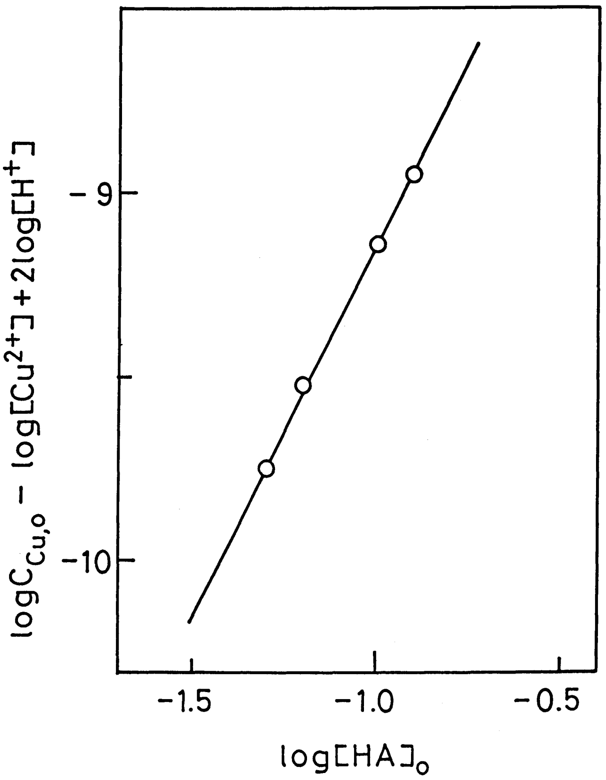

Fig. 10. Determination of the number of *p*-chlorobenzoic acid molecules involved in the monomeric copper(II) species.
Solid line is the straight one with slope of 2.0.

and CuA_2 species in the aqueous phase cannot be neglected compared with the concentration of Cu^{2+} ion in the aqueous phase. Then, the partition ratio of copper(II) is expressed as follows:

$$\begin{aligned} D &= [CuA_2]_o/([Cu^{2+}]+[CuA^+]+[CuA_2]_w) \\ &= K_{ex(10)}[HA]_o^2[H^+]^{-2}\alpha_{Cu(A^-)}{}^{-1}. \end{aligned} \tag{13}$$

-*m*-chlorobenzoic acid-

$$Cu^{2+} + 2(HA)_o \xrightleftharpoons{K_{ex(10)}} (CuA_2)_o + 2H^+$$

$$2Cu^{2+} + 4(HA)_o \xrightleftharpoons{K_{ex(20)}} (Cu_2A_4)_o + 4H^+$$

$$2Cu^{2+} + 6(HA)_o \xrightleftharpoons{K_{ex(22)}} (Cu_2A_4(HA)_2)_o + 4H^+$$

-*p*-chlorobenzoic acid-

$$Cu^{2+} + 2(HA)_o \xrightleftharpoons{K_{ex(10)}} (CuA_2)_o + 2H^+.$$

The emulsion appeared in the region where the percent extraction of copper(II) exceeds about 3.0%, as well as in *p*-toluic acid system.

Extraction Constant and Four Equilibrium Constants: Each of the three positions of substitution in the benzene ring was found to have a clear individuality.

An anomalous extraction behavior of copper(II) *o*-chlorobenzoate shown in Fig. 1 can be attributed to an abnormally low partition constant of the monomeric Cu(II)-*o*-chlorobenzoate, CuA_2, which can be estimated in the manner described below.

The extraction constant of CuA_2 can be formulated by the four equilibrium constants as follows:

$$K_{ex(10)} = K_{D,CuA_2}K_{D,HA}{}^{-2}\beta_2K_a{}^2, \tag{14}$$

where K_{D,CuA_2} denotes the partition constant of CuA_2 between water and 1-octanol. By substituting the values of $K_{D,HA}$, β_2, and K_a, which were obtained in the present study, into Eq. 14, the partition constant of CuA_2 was calculated as: $\log K_{D,CuA_2}=0.99$. This value is much smaller than that approximated by the relation between the partition constants of the extracting agent and extracted compound as follows: $K_{D,MA_n}=K_{D,HA}{}^n$.[10] It is satisfactory to consider that a lowering of the partition constant of CuA_2 can be caused by the hydration of the extracted copper(II) species, CuA_2.

This can be attributable to the steric characteristic of *o*-chlorobenzoic acid, in which the chloro-group is adjacent to the carboxyl-one. Judging from Eq. 14, the extraction constant becomes greater as K_{D,CuA_2}, β_2, and K_a become greater and $K_{D,HA}$ becomes smaller. But, in generall the value of K_{D,CuA_2} varies in proportion to $K_{D,HA}$ and the value of $\beta_2(=K_1K_2)$ can be expected to become smaller as K_a becomes greater by the linear free energy relationship (LFER). That is to say, the two sets of these constants in Eq. 14 have proved to be compensated each other. Then, it is impossible to assess the extractability of the extracting agent from only the individual values of these constants.

In the useful extraction system, the concentration of an extracting agent in the organic phase, $[HA]_o$ can be generally approximated to its total concentration, C_{HA} under the appropriate extraction conditions. Then, under these conditions, $[A^-]$ is shown to be negligibly low compared with the total concentration, C_{HA}. An increase in $[A^-]$ should be essentially favorable for extracting a metal ion, since it facilitates the formation of the extracted species. On the other hand, it results in an increase in $\alpha_{M(A^-)}$ and leads to a lowering of the partition ratio of copper(II), as can be seen from Eqs. 6 and 13. Therefore, the extracting agent anion is required to a concentration low enough to avoid this lowering of the partition ratio of copper(II). In the present extraction systems, the concentration of chlorobenzoate anion, $[A^-]$ can be calculated by Eq. 15, provided the concentration of chlorobenzoic acid is much higher than the copper(II) concentration.

$$[A^-] = \frac{C_{HA}}{1+\dfrac{[H^+]}{K_a}(K_{D,HA}+1)}. \tag{15}$$

According to Eq 15, the value of $K_{D,HA}/K_a$ must be sufficiently large in order that the concentration of A^- anion, though dependent on a hydrogen ion concentration in the aqueous phase, can be maintained at a low enough. The values of $K_{D,HA}/K_a$ for mono-substituted benzoic acids are given in Table 1 together with the other constants. The value of *o*-chlorobenzoic acid is significantly small compared with the other acids. This is expected to result in a lowering of the extractability of *o*-chlorobenzoic acid. As expected, the results are shown in Fig. 1. Then, the value of $K_{D,HA}/K_a$ for an extracting agent is anticipated to be one of guides to its extractability.

Irrespective of the large $K_{D,HA}/K_a$ value, the application of *p*-chlorobenzoic acid to solvent extraction of copper(II) should be restricted to the lower range of copper(II) concentration, owing to the poor solubility of *p*-chlorobenzoic acid and its copper compound in both the aqueous and 1-octanol phases as well as in the systems of *p*-toluic acid.

In addition to the value of $K_{D,HA}/K_a$, the dimerization of the extracted species is also an important factor for the extraction of copper(II) carboxylates. In the present extraction systems, the dimeric copper(II) chlorobenzoates were found to be extracted only in the *m*-chlorobenzoic acid system. The extractability for this extraction system is also enhanced by the formation of another dimer involving two molecules of *m*-chlorobenzoic acid.

The similarity of the extraction behavior in the chlorobenzoic acid systems to that in the toluic acid systems for meta and para isomers can be attributed the fact that both the chloro and methyl substituents have the same positive mesomeric effects on the benzene ring, though opposite in the inductive effects, where the former is negative and the latter positive. On the other hand, the remarkable differences in the extraction equilibrium between *o*-chloro- and *o*-methyl-isomers can be reduced to the fact that in the former the chloro-group just adjacent to the carboxyl-one has the coordinating ability, though the methyl-group has not, through a lone pair of electrons.

References

1) H. Yamada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **38**, 1501 (1976).

2) H. Yamada, S. Suzuki, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **43**, 1873 (1981).

3) H. Yamada, R. Kitazaki, and I. Kakimi, *Bull. Chem. Soc. Jpn.*, **56**, 3302 (1983).

4) H. Yamada, K. Takahashi, Y. Fujii, and M. Mizuta, *Bull. Chem. Soc. Jpn.*, **57**, 2847 (1984).

5) H. Yamada, T. Okuda, Y. Fujii, M. Mizuta, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **59**, 3855 (1986).

6) H. Yamada, M. Ito, and M. Mizuta, *Bull. Chem. Soc. Jpn.*, **60**, 3557 (1987).

7) H. Yamada, K. Adachi, Y. Fujii, and M. Mizuta, *Solvent Extr. Ion Exch.*, **4**, 1109 (1986).

8) H. Yamada, S. Horikawa, Y. Fujii, and M. Mizuta, *Bull. Chem. Soc. Jpn.*, **61**, 835 (1988).

9) "CRC Handbook of Chemistry and Physics," 70th ed (1989—1990), ed by C. W. Robert and R. L. David, CRC Press Inc., Boca Raton, FL (1989), p. D-163.

10) M. Tanaka, Solvent Extr. Proc. Int. Solvent Extr. Conf., 1971, p. 16.