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Inhibition of Dimerization of Copper(II) Carboxylates by Cyclohexane Ring in Extraction of Copper(II) with Cyclohexanecarboxylic Acid

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The extraction of copper(II) with cyclohexanecarboxylic acid in benzene was carried out at 25 °C and at the aqueous ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). The partition constant, $K_{D,HA}$ of cyclohexanecarboxylic acid between benzene and water, and the dimerization constant, $K_{2,HA}$ of cyclohexanecarboxylic acid in benzene were determined: $\log K_{D,HA}=0.90$ and $\log K_{2,HA}=1.54$, respectively. The monomeric and dimeric copper(II) cyclohexanecarboxylates were responsible for the extraction:

$$\mathrm{Cu^{2+}+(HA)_{2,o}} \rightleftharpoons \mathrm{(CuA_2)_o+2H^+}$$

$$\mathrm{Cu^{2+}+2(HA)_{2,o}} \rightleftharpoons \mathrm{(CuA_2(HA)_2)_o+2H^+}$$

$$\mathrm{2Cu^{2+}+2(HA)_{2,o}} \rightleftharpoons \mathrm{(Cu_2A_4)_o+4H^+}$$

$$\mathrm{2Cu^{2+}+3(HA)_{2,o}} \rightleftharpoons \mathrm{(Cu_2A_4(HA)_2)_o+4H^+}$$

with the extraction constants, $\log K_{ex(10)}=-8.34$, $\log K_{ex(12)}=-7.33$, $\log K_{ex(20)}=-12.47$, and $\log K_{ex(22)}=-11.73$, respectively. By comparing the overall formation constant of the dimeric copper(II) cyclohexanecarboxylate, $Cu_2A_4(HA)_2$ in the aqueous phase with that of copper(II) decanoate and lipoate, the cyclohexane ring was found to inhibit the formation of the dimeric copper(II) carboxylate.

The stability of the dimeric copper(II) carboxylate is so high that no appreciable amount of monomer can be detected in most nonsolvating solvents.[1,2] In the extraction of copper(II) with some sterically crowded carboxylic acids such as trimethylacetic acid,[3] cyclohexanecarboxylic acid,[4] and cyclopentylacetic acid,[5] it was suggested that the monomeric copper(II) species is extracted together with the dimer. But, in the first reference[3] presented by Haffenden and Lawson, they didn't mention the composition of the monomeric copper(II) trimethylacetate. And although the other references[4,5] reported by Brzozka and Rozycki will be later described in detail, there are some doubts about their results. In the previous reports, it has been shown that the monomeric and dimeric copper(II) decanoates are in equilibrium in alcohols[6,7] and ketones,[8] and it has been interpreted according to the regular solution theory that the extraction of the monomeric copper(II) decanoates as well as the dimeric ones can be attributed to the stabilization of the monomeric copper(II) species by the extensive solvation of alcohols or ketones molecules.

The present paper deals with the extraction of copper(II) with cyclohexanecarboxylic acid in benzene, and it was found that the cyclohexane ring at 2-position in cyclohexanecarboxylic acid inhibited the formation of the dimeric copper(II) carboxylate.

Experimental

Reagents. Cyclohexanecarboxylic Acid: Commercial cyclohexanecarboxylic acid (purity: over 97%, Aldrich Chemical Company, Inc.) was dissolved in benzene just before its use. Copper(II) perchlorate,[6] sodium perchlorate,[6] and benzene[9] were the same as employed as previously. All other reagents were reagent grade and used without further purification.

Procedure. Partition was carried out in the same manner as was stated in the previous paper.[10] In the partition of cyclohexanecarboxylic acid between benzene and water, the concentration of the acid in the aqueous phase was determined by potentiometric titration.

Apparatus. Taiyo Incubator M-100^{N}(Taiyokagaku-Kogyo Co., Tokyo) was used for mechanical shaking in a thermostat. The pH measurements and potentiometric titrations were performed with a Horiba pH Analyzer F-80 (Horiba Seisakusho Ltd., Kyoto). A swing type centrifuge model CD-50SR (Tomy Seiko Co. Ltd., Tokyo) was used for centrifugation.

Results and Discussion

Partition of Cyclohexanecarboxylic Acid. The following equilibria on cyclohexanecarboxylic acid (HA) should be considered: (a) The dissociation of HA in the aqueous phase ($K_a=[H^+][A^-]/[HA]$), (b) the partition of HA into benzene ($K_{D,HA}=[HA]_o/[HA]$), and (c) the dimerization of HA in the organic phase ($K_{2,HA}=[(HA)_2]_o/[HA]_o^2$), where the subscript o refers to the organic phase and $[(HA)_2]_o$ denotes the concentration of the dimeric acid in the organic phase. Then, the distribution ratio of the acid between benzene and water can be written as:

$$\begin{aligned} D &= C_{HA,o}/C_{HA,w} \\ &= K_{D,HA}(1+2K_{2,HA}K_{D,HA}[HA])/(1+K_a[H^+]^{-1}). \end{aligned} \qquad (1)$$

In the lower pH region where the dissociation of the acid in the aqueous phase can be neglected, that is, $1 \gg K_a[H^+]^{-1}$, the following equation can be obtained:

$$\log D = \log K_{D,HA} + \log (1+2K_{2,HA}K_{D,HA}[HA]). \qquad (2)$$

According to Eq. 2, by comparing the plots of log D against log [HA] with the normalized curve, log $(1+X)$ vs. log X, the dimerization constant in the organic phase and the partition constant can be determined. Benzene solutions of cyclohexanecarboxylic acid ranging from 0.024 to 0.96 mol dm^{-3} were equilibrated with 0.01 mol dm^{-3} perchloric acid solution (ionic strength: 0.1 mol dm^{-3} H, $NaClO_4$). From the plots shown in Fig. 1, the following constants of cyclohexanecarboxylic acid were determined by the curve-fitting method: log $K_{D,HA}=0.90$ and log $K_{2,HA}=1.54$, respectively.

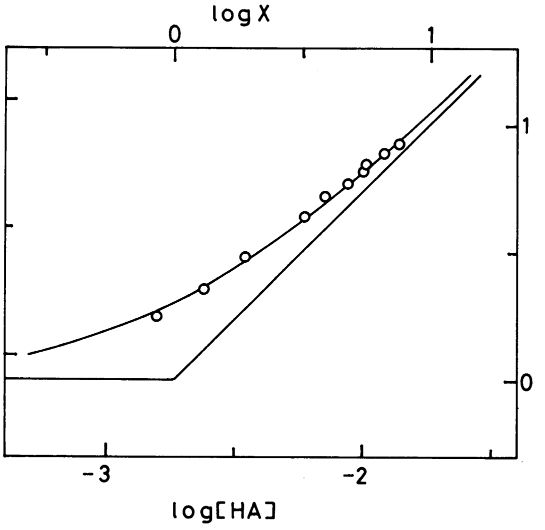

Fig. 1. Determination of the dimerization constant in benzene and the partition constant between benzene and water of cyclohexanecarboxylic acid. Solid curve is the normalized curve, log$(1+X)$ vs. log$X$. Solid lines are the asymptotes of the normalized curve.

Under the present experimental conditions, the dissociation of cyclohexanecarboxylic acid in the aqueous phase can being neglected, the concentration of the dimeric acid in the organic phase can be written as follows:

$$[(HA)_2]_o = 0.5\,(C_{HA} - [HA]_o - [HA]) \qquad (3)$$

where C_{HA} denotes the total concentration of the acid. Then, the concentration of the dimeric cyclohexanecarboxylic acid in the organic phase was calculated by substituting the dimerization and partition constants of the acid in Eq. 3.

Extraction of Copper(II) with Cyclohexanecarboxylic Acid. If a j-merized copper(II) carboxylate, $Cu_jA_{2j}(HA)_a$ is extracted, the following equilibrium is relevant to the extraction:

$$jCu^{2+} + 0.5\,(2j+a)\,(HA)_{2,o} \rightleftharpoons (Cu_jA_{2j}\,(HA)_a)_o + 2jH^+$$

with

$$K_{ex(ja)} = [Cu_jA_{2j}(HA)_a]_o[H^+]^{2j}[Cu^{2+}]^{-j}[(HA)_2]_o{}^{-0.5(2j+a)}. \qquad (4)$$

The following relation can hold for the total concentration of copper in the organic phase, $C_{Cu,o}$:

$$\log C_{Cu,o} = \log \sum_j \sum_a \{jK_{ex(ja)}([Cu^{2+}][H^+]^{-2})^j[(HA)_2]_o{}^{0.5(2j+a)}\}. \qquad (5)$$

According to Eq. 5, the degree of polymerization of the extracted species can be found from the slope of the plot of log $C_{Cu,o}$ against (log$[Cu^{2+}]-2\log[H^+]$) at constant $[(HA)_2]_o$. If two or more species with different degree of polymerization are responsible for the extraction, the plot should give rise to a curve. The results are shown in Fig. 2. The slope lies between unity and two, and tends to approach to two with increasing copper concentration in the organic phase. Therefore, it is expected that the monomeric and dimeric copper(II) carboxylates are responsible for the extraction. Then, the total concentration of copper(II) in the organic phase is expressed as follows:

$$C_{Cu,o} = [CuA_2(HA)_a]_o + 2[Cu_2A_4(HA)_b]_o. \qquad (6)$$

By substituting the extraction constants $K_{ex(1a)}$ and $K_{ex(2b)}$ in Eq. 6, the following expression can be derived:

$$\log C_{Cu,o} - \log[Cu^{2+}] + 2\log[H^+] = 0.5\,(2+a)\log[(HA)_2]_o + \log K_{ex(1a)} + \log\left(1+\frac{2K_{ex(2b)}}{K_{ex(1a)}}[(HA)_2]_o{}^{0.5(2+b-a)}[Cu^{2+}][H^+]^{-2}\right). \qquad (7)$$

According to Eq. 7, by comparing the plots of the left-hand side of Eq. 7 against (log$[Cu^{2+}]-2\log[H^+]$) at constant $[(HA)_2]_o$ with the normalized curve, log $(1+X)$ vs. log X, the degree of polymerization of cop-

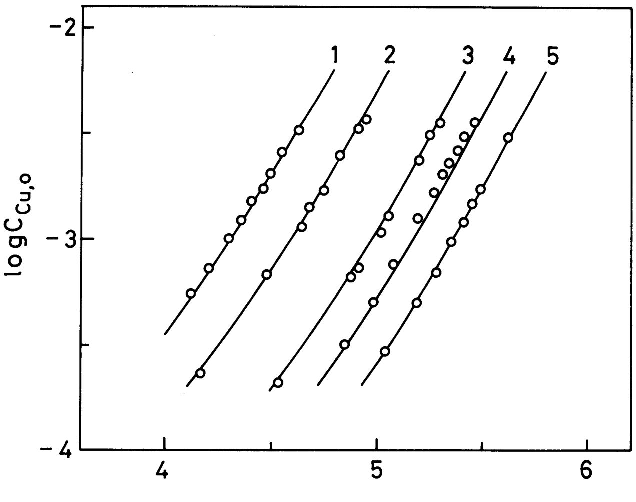

Fig. 2. Determination of the degree of polymerization of copper(II) carboxylate. C_{HA}; 1: 1.47, 2: 0.98, 3: 0.55, 4: 0.40, 5: 0.29 mol dm^{-3}. Solid lines are calculated curves based on the results obtained in this work.

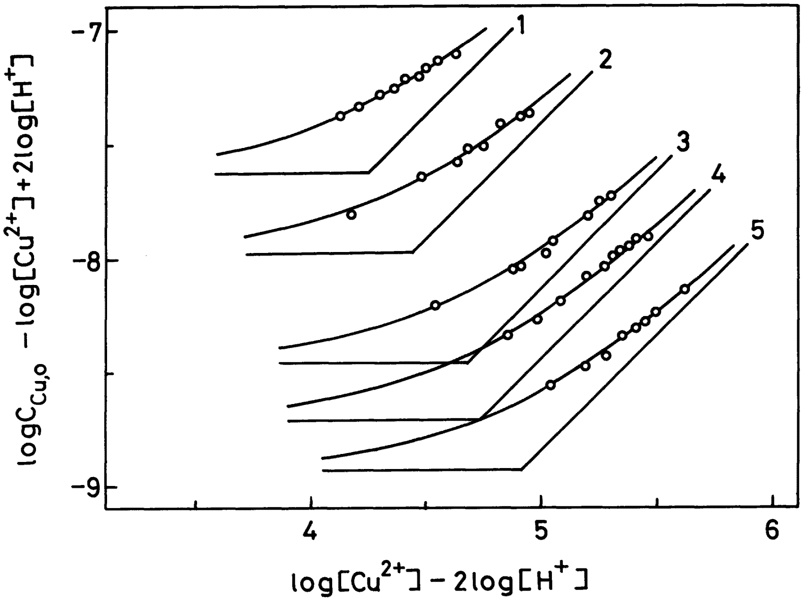

Fig. 3. Identification of the degree of polymerization of copper(II) carboxylate. Solid curves are the normalized curves, $\log(1+X)$ vs. $\log X$. Solid lines are the asymptotes of the normalized curves. Numbers are the same as in Fig. 2.

per(II) species can be identified. As shown in Fig. 3, the plots fit well the normalized curve. Therefore, it was proved that both the dimeric and monomeric copper(II) carboxylates are responsible for the extraction.

In the region, where the plots in Fig. 3 fall along the horizontal asymptotes, the predominant extracted species is the monomer. Then the total concentration of copper(II) in the organic phase can be written as:

$$\log C_{\mathrm{Cu,o}} = \log \sum_{a} (K_{\mathrm{ex}(1a)}[\mathrm{Cu}^{2+}][\mathrm{H}^+]^{-2}[(\mathrm{HA})_2]_{\mathrm{o}}^{0.5(2+a)}). \tag{8}$$

According to Eq. 8, the number of cyclohexanecarboxylic acid molecules involved in the monomeric copper(II) species can be obtained from the slope of the plot of ($\log C_{\mathrm{Cu,o}} - \log[\mathrm{Cu}^{2+}] + 2\log[\mathrm{H}^+]$) against $\log [(\mathrm{HA})_2]_{\mathrm{o}}$. As shown in Fig. 4, the plot deviates upward from the straight line with a slope of two with decreasing $[(\mathrm{HA})_2]_{\mathrm{o}}$. This fact suggests that the two monomeric species are responsible for the extraction in the lower concentration of copper in the organic phase: One of them is $\mathrm{CuA_2(HA)_2}$ and the other $\mathrm{CuA_2(HA)}_a (a<2)$. Under these conditions the total copper concentration in the organic phase can be written as follows:

$$\log C_{\mathrm{Cu,o}} - \log[\mathrm{Cu}^{2+}] + 2\log[\mathrm{H}^+] - 2\log[(\mathrm{HA})_2]_{\mathrm{o}}$$

$$= \log\left(1 + \frac{K_{\mathrm{ex}(1a)}}{K_{\mathrm{ex}(12)}} [(\mathrm{HA})_2]_{\mathrm{o}}^{-0.5(2-a)}\right) + \log K_{\mathrm{ex}(12)}. \tag{9}$$

Comparing the plot of the left-hand side of Eq. 9 against $-\log [(\mathrm{HA})_2]_{\mathrm{o}}$ with the normalized curves, $\log (1+X^n)$ vs. $\log X$, another monomeric species can be determined. As evident from Fig. 5, the plot fits well the normalized curve with $n=1$, $\log (1+X)$ vs. $\log X$, that is, $0.5 (2-a)=1$ or $a=0$. Then the monomeric species are $\mathrm{CuA_2}$ and $\mathrm{CuA_2(HA)_2}$. By the curve-fitting method from Fig. 5, the respective extraction constants $K_{\mathrm{ex}(10)}$ and $K_{\mathrm{ex}(12)}$ can be determined: $\log K_{\mathrm{ex}(10)} = -8.34 \pm 0.03$, $\log K_{\mathrm{ex}(12)} = -7.33 \pm 0.03$, respectively.

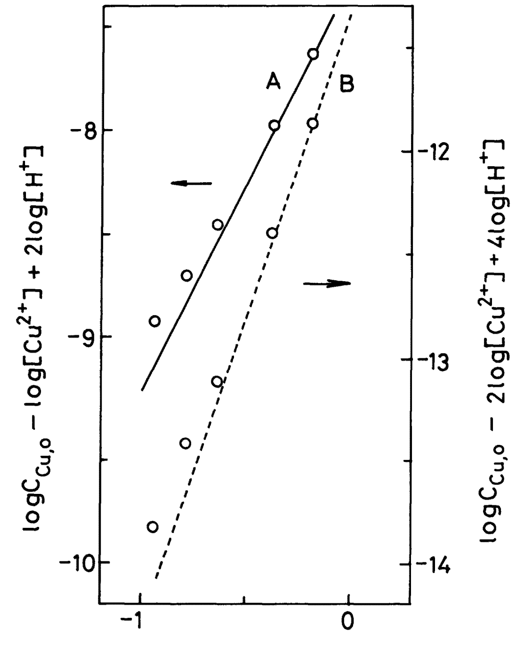

Fig. 4. Determination of the number of carboxylic acid molecules involved in the monomeric and dimeric copper(II) species. A: Monomeric copper(II) carboxylate. B: Dimeric copper(II) carboxylate. Solid and dotted lines are the straight lines with a slope of 2.0 and 3.0, respectively.

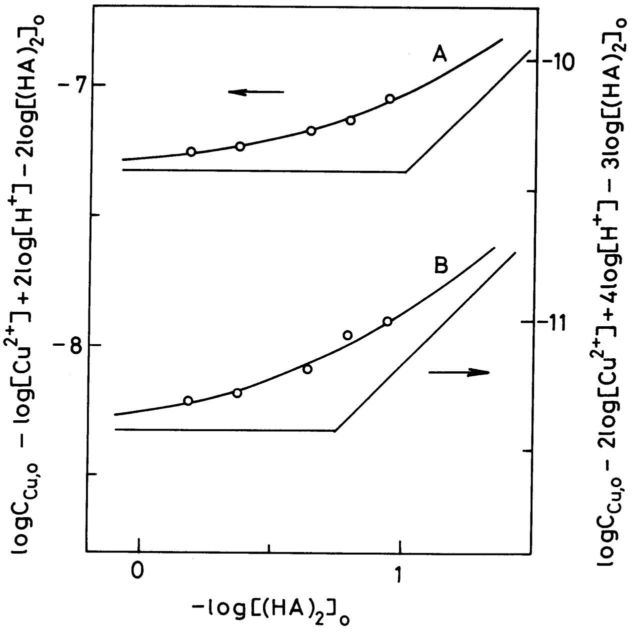

Fig. 5. Determination of the number of carboxylic acid molecules involved in the copper(II) species by curve-fitting method. A and B are the same as in Fig. 4. Solid curves are the normalized curves, $\log(1+X)$ vs. $\log X$. Both solid lines are the asymptotes of the normalized curves.

On the other hand, in the region, where the dimeric copper(II) species is predominant, that is, the plots shown in Fig. 3 fall along the straight line asymptotes with a slope of unity, the total concentration of copper(II) in the organic phase can be represented as:

$$\log C_{\mathrm{Cu,o}} = \log(2[\mathrm{Cu}^{2+}]^2[\mathrm{H}^+]^{-4}) + \log(\sum_b (K_{\mathrm{ex}(2b)}[(\mathrm{HA})_2]_\mathrm{o}^{0.5(4+b)})). \qquad (10)$$

According to Eq. 10, the number of cyclohexanecarboxylic acid molecules involved in the dimer can be obtained from the slope of ($\log C_{\mathrm{Cu,o}} - 2\log[\mathrm{Cu}^{2+}] + 4\log[\mathrm{H}^+]$) against $\log[(\mathrm{HA})_2]_\mathrm{o}$. As shown in Fig. 4, the plot gets to approach the straight line with a slope of 3.0 with increasing the concentration of dimeric cyclohexanecarboxylic acid in the organic phase. As judged from this tendency, the two dimeric species, $\mathrm{Cu_2A_4(HA)_2}$ and $\mathrm{Cu_2A_4(HA)}_b$ ($b<2$) exist in the higher concentration of copper in the organic phase. Therefore, the following relation can be expected to hold for the total concentration of copper in the organic phase:

$$\log C_{\mathrm{Cu,o}} - 2\log[\mathrm{Cu}^{2+}] + 4\log[\mathrm{H}^+] - 3\log[(\mathrm{HA})_2]_\mathrm{o}$$
$$= \log(1 + \frac{K_{\mathrm{ex}(2b)}}{K_{\mathrm{ex}(22)}}[(\mathrm{HA})_2]_\mathrm{o}^{-0.5(2-b)}) + \log 2 + \log K_{\mathrm{ex}(22)}. \qquad (11)$$

In the similar manner as the monomeric species, another dimeric species can be determined. As shown in Fig. 5, the plot of the left-hand side of Eq. 11 against $-\log[(\mathrm{HA})_2]_\mathrm{o}$ fits with the normalized curve, $\log(1+X)$ vs. $\log X$, that is, $0.5(2-b)=1$ or $b=0$. Then, $\mathrm{Cu_2A_4}$ is also involved in the extraction together with $\mathrm{Cu_2A_4(HA)_2}$ under the present conditions. In addition we can determine the extraction constants $K_{\mathrm{ex}(20)}$ and $K_{\mathrm{ex}(22)}$ in the similar manner as the monomer: $\log K_{\mathrm{ex}(20)} = -12.47 \pm 0.03$ and $\log K_{\mathrm{ex}(22)} = -11.73 \pm 0.03$, respectively.

Consequently, in the present extraction system, the corresponding extraction equilibria are described as follows:

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

$$\mathrm{Cu}^{2+} + 2(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(12)}} (\mathrm{CuA_2(HA)_2})_\mathrm{o} + 2\mathrm{H}^+$$

$$2\mathrm{Cu}^{2+} + 2(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(20)}} (\mathrm{Cu_2A_4})_\mathrm{o} + 4\mathrm{H}^+$$

$$2\mathrm{Cu}^{2+} + 3(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(22)}} (\mathrm{Cu_2A_4(HA)_2})_\mathrm{o} + 4\mathrm{H}^+.$$

Brzozka and Rozycki found the monomer $\mathrm{CuA_2(HA)_4}$ and dimer $\mathrm{Cu_2A_4(HA)_4}$ in the extraction of copper(II) with cyclohexanecarboxylic acid in benzene.[4] Judging from the coordination number of copper(II), both extracted species seem unlikely. Because they estimated the composition of the extracted species under the region where both copper(II) species with different degree of polymerization coexist, erroneous results seem to be drawn. In addition, Rozycki reported that only the monomeric species $\mathrm{CuA_2(HA)_2}$ was responsible for the extraction of copper(II) with cyclopentylacetic acid in benzene.[5] According to his data, the slope of the plot of $\log C_{\mathrm{Cu,o}}$ against ($\log C_{\mathrm{Cu,w}} + 2\mathrm{pH}$) at constant $[(\mathrm{HA})_2]_\mathrm{o}$ (Fig. 1 in Ref. 5) is greater than unity. This suggests that the dimeric copper(II) species is expected to be involved in the extraction. Owing to take no account of a dimeric copper(II) species for analysis of extraction equilibrium, they failed to notice not only dimeric species but also another monomeric species $\mathrm{CuA_2}$.

Recently, the dimeric copper(II) carboxylate $\mathrm{Cu_2A_4(HA)_2}$ has been reported to be extracted with 2-bromopentanoic acid in benzene.[11] On the other hand, Bold and Balusescu proposed the monomeric copper(II) carboxylate, $\mathrm{CuA_2(HA)_2}$ in the extraction of copper(II) with 2-bromooctadecanoic acid in benzene.[12] Their results appear doubtful. Because recalculation[11] of their data led us to the dimeric species, $\mathrm{Cu_2A_4(HA)_2}$. Therefore, it seems likely that bromine at 2-position in the respective carboxylic acid does not inhibit the formation of a dimeric copper(II) carboxylate.

In contrast with these instances, the extraction of monomeric copper(II) species in the present extraction system indicate that the dimerization of copper(II) carboxylate is hindered by the cyclohexane moiety at 2-position in cyclohexanecarboxylic acid.

Effect of Cyclohexane Ring on Dimerization of Carboxylic Acid and Copper(II) Carboxylate in Benzene. The dissociation constant of cyclohexanecar-

Table 1. Comparison of Cyclohexanecarboxylic with Other Carboxylic Acids

Acid Constant	Cyclohexanecarboxylic	Heptanoic	Lipoic	Decanoic
pK_a	4.89[a]	4.89[b]	4.85[c]	4.92[d]
log $K_{D,HA}$	0.90	0.78[e]	1.17[f]	2.80[d]
log $K_{2,HA}$	1.54	2.61[g]	2.51[f]	2.41[d]
log $K_{ex(22)}$	−11.73	−11.58[h]	−11.00[f]	−11.36[i]
log $\beta_{Cu_2A_4(HA)_2}$[j]	12.45	15.81	15.93[f]	15.55[f]
	(12.72)	(16.04)	(16.28)	(16.39)

a) Ref. 13. b) Ref. 14. c) Ref. 17. d) Ref. 18. e) Ref. 15. f) Ref. 9. g) Ref. 16. h) Ref. 1. i) Ref. 2. j) Calculated by Eq. 10 in Ref. 9. The values in the parentheses are evaluated by taking into account the electro-striction of ligands in the complex (Eq. 11 in Ref. 9).

boxylic acid in the aqueous solution is reported to be pK_a=4.89[13] at 25 °C. This value is agreement with that of heptanoic acid[14] with the same carbon number as cyclohexanecarboxylic acid. This implies that the cyclohexane ring has no inductive effect on the carboxylate group. The partition constant of heptanoic acid between benzene and water, and its dimerization constant in benzene can be established from the constants of its homologs as follows: log $K_{D,HA}=0.78$[15] and log $K_{2,HA}=2.61$,[16] respectively. Judging from no inductive effect of the cyclohexane moiety, the similar constants for cyclohexanecarboxylic acid as those of heptanoic acid can be expected to be obtained. As expected, the value of the partition constant of cyclohexanecarboxylic acid was found to be close to that of heptanoic acid (see: Table 1). On the other hand, it was proved that the value of its dimerization constant in benzene is smaller by about one order of magnitude than that of heptanoic acid. This fact suggests that the cyclohexane ring would interfere in the dimerization of cyclohexanecarboxylic acid in benzene.

As stated previously,[9] the extraction constant of dimeric copper(II) species, $Cu_2A_4(HA)_2$ can be written as follows:

$$K_{ex(22)}=K_{D,Cu_2A_4(HA)_2}K_{D,HA}^{-6}K_{2,HA}^{-3}\beta_{Cu_2A_4(HA)_2}K_a^4 \quad (12)$$

where $K_{D,Cu_2A_4(HA)_2}$ and $\beta_{Cu_2A_4(HA)_2}$ denote the partition constant of $Cu_2A_4(HA)_2$ between benzene and water, and the overall formation constant of this complex in the aqueous phase, respectively. Then, the overall formation constant can be approximated by Eq. 12. The value is summarized in Table 1 together with other constants. As shown in Table 1, each of these acids has a similar dissociation constant. On the other hand, the overall formation constant of a dimeric copper(II) species, $Cu_2A_4(HA)_2$ for cyclohexanecarboxylic acid are decreased about three orders of magnitude under that for other three acids. It has been shown that the formation of copper(II) cyclohexanecarboxylate is inhibited by cyclohexane ring in the same manner as the dimerization of cyclohexanecarboxylic acid.

It is well-known that the copper(II) carboxylates have dimeric structure not only in the crystalline state but also in various organic solvents. Then, in the extraction of copper(II) carboxylates, only the dimeric copper(II) carboxylate, $Cu_2A_4(HA)_2$ has been widely proved to be responsible for the extraction by numerous investigators.[19] A few studies on the extraction of the monomeric copper(II) carboxylate have been merely published in the extraction systems presented below. In the extraction of copper(II) with decanoic acid in some alcohols[6,7] and ketones,[8] monomeric and dimeric copper(II) species are in equilibrium in these solvents, because of the extensive solvation by these solvents. In addition, the dimerization of copper(II) benzoate does not occur to any appreciable extent in the extraction of copper(II) with benzoic acid.[10] It is reasonable to imagine that the conjugated system in benzoic acid inhibits the dimerization of copper(II) benzoate.

On the other hand, the extraction of the monomeric copper(II) cyclohexanecarboxylates in the present extraction system can be due to the steric hindrance of the cyclohexane moiety on the dimerization of copper(II) carboxylate. The present result is contrast to the facts that "bromine" at 2-position in pentanoic[11] and octadecanoic[12] acids does not inhibit the dimerization of the respective copper(II) carboxylates.

The polymeric metal carboxylates are often involved in the extraction of metal carboxylates.[19] And the polymerization of metal carboxylate can be regarded as a kind of synergistic effect, and would contribute to a good extractability. According to the result obtained from this work, it can be anticipated that the introduction of the more bulky moiety at 2-position in carboxylic acid will also interfere with the polymerization of other metal carboxylates, and will lead to a lowering of the extractability, particularly in the extraction of metal carboxylates into nonsolvating solvents, for which the formation of polymerized species is essential. Therefore, it can be expected that the more crowded substituent at 2-position in carboxylic acid will result in a more favorable selectivity for the extraction of metal carboxylate.

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