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Comparison of 2,4-Hexadienoic with 1-Hexanoic Acids as Extractant for Copper(II)

Hiromichi Yamada,* Chizuko Kato,†
and the late 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
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2,4-Hexadienoic and 1-hexanoic acids have been evaluated as extractant for copper(II). The extraction was carried out using benzene and 1-octanol as solvent at 25 °C and aqueous ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). The stoichiometry of the extracted species and their extraction constants were determined by graphical method. The extraction of copper(II) with 2,4-hexadienoic acid has been found to proceed through a mechanism different from that with 1-hexanoic acid. 2,4-Hexadienoic acid has been proved to be similar in the extraction behavior for copper(II) to benzoic acid. While, 1-hexanoic acid as extractant for copper(II) has been demonstrated to resemble decanoic acid.

A variety of carboxylic acids have been extensively investigated as extractant for a number of metal ions.[1] In these extraction systems, it is characterized by the extraction of the polymeric metal carboxylates. In particular, it is well known that the dimeric copper(II) carboxylate, $Cu_2A_4(HA)_2$ (HA: fatty acid) can be responsible for the extraction with various saturated fatty acids in nonsolvating solvents. In a series of researches on the extraction of various kinds of copper(II) carboxylates, aromatic carboxylic acids have been revealed to be markedly distinct in the extraction behavior from aliphatic ones.[2-4] It has been proved that copper(II) is scarcely extracted with benzoic acid in benzene, owing to the failure to form the dimeric copper(II) species which is essential for the extraction of copper(II) carboxylates into nonsolvating solvents, and that using 1-octanol as solvent the solvation of the monomeric copper(II) benzoate by some 1-octanol molecules makes possible to extract copper(II) without the formation of the dimeric copper(II) species to any appreciable extent.

Subsequently, it has been presented that the formation of the dimeric copper(II) species has been observed in the following mono-substituted benzoic acid systems: *o*- and *m*-toluic acids, and *m*-chlorobenzoic acid in 1-octanol, whereas it cannot be perceived to any appreciable extent in the extraction by *p*-toluic, *o*-, and *p*-chlorobenzoic acids, and the three kinds of methoxybenzoic acids in 1-octanol.[5-7] These results are summarized in Table 1 together with the other ones. According to these distinctions in the extraction behavior between aliphatic and aromatic carboxylic acids, it can be anticipated that the presence of a conjugated system makes it difficult to form the dimeric copper(II) carboxylates in the extraction process.

The present paper reports on the extraction of copper(II) with 2,4-hexadienoic and 1-hexanoic acids in 1-octanol. In analogy with aromatic carboxylic acids, the presence of a conjugated system in 2,4-hexadienoic acid has been found to give some influence on the formation of the dimeric copper(II) carboxylate.

Table 1. Dissociation and Partition Constants of Various Carboxylic Acids, and Extraction Constants of Their Copper(II) Compounds (at 25 °C and Aqueous Ionic Strength of 0.1 mol dm^{-3}; Solvent: 1-Octanol)

Acids	pK_a	log $K_{D,HA}$	log $K_{ex(10)}$	log $K_{ex(20)}$	log $K_{ex(22)}$
1-Hexanoic	4.92	1.90	−8.19	−13.65	−14.19
2,4-Hexadienoic	4.47	1.64	−7.96		
1-Decanoic[a]	4.92	>3	−8.41	−13.36	−13.77
Benzoic[b]	4.04	1.88	−7.70		
o-Toluic[c]	3.73	2.21	−7.84	−12.84	
m-Toluic[c]	4.09	2.41	−7.84	−13.15	
p-Toluic[c]	4.21	2.33	−7.84		
o-Chlorobenzoic[d]	2.74	2.07	−6.75		
m-Chlorobenzoic[d]	3.66	2.65	−7.03	−12.20	−12.04
p-Chlorobenzoic[d]	3.95	2.67	−7.15		
o-Methoxybenzoic[e]	3.90	1.21	−7.32		
m-Methoxybenzoic[e]	3.90	2.05	−7.75		
p-Methoxybenzoic[e]	4.34	1.97	Copper was scarcely extracted.		

a) Ref. 4: In this system CuA_2HA was also extracted (log $K_{ex(11)}$=−8.65). b) Ref. 2. c) Ref. 5. d) Ref. 6. e) Ref. 7.

Experimental

Reagents. Hexanoic acid purified by distillation and commercial 2,4-hexadienoic acid (purity: over 99%) were dissolved in purified 1-octanol and benzene, respectively. Benzene was washed successively with concentrated sulfuric acid, with dilute sodium hydroxide solution, and then with distilled water. 1-Octanol and sodium perchlorate were purified by the same methods as employed previously.[4] All other reagents were of reagent grade and used without further purification.

Procedure. The extraction of copper(II) was performed under the following conditions: a total copper(II) concentration is 5×10^{-3} mol dm^{-3}, and the concentrations of extractants are in the region of 0.5 to 2.0 mol dm^{-3} for 1-hexanoic acid, and 0.05 to 0.5 mol dm^{-3} for 2,4-hexadienoic acid, respectively. Partition was carried out in a bath thermostated at 25.0±0.2 °C. The concentrations of copper(II) and hydrogen ions in the aqueous phase were determined by the same methods as employed previously.[2] Ionic strength of the aqueous phase was adjusted to 0.1 mol dm^{-3} by sodium perchlorate. Shaking for about 1 h was found to be sufficient for complete equilibration. The dissociation constant of 2,4-hexadienoic acid in the aqueous phase was potentiometrically determined. In the estimation of the partition constant of 2,4-hexadienoic acid between 0.1 mol dm^{-3} perchloric acid and 1-octanol, the concentration of the acid in the aqueous phase was determined by measuring the absorbance at 263 nm, the absorption maximum of the acid.

Apparatus. Each apparatus for mechanical shaking in a thermostat, centrifugation, pH measurements, and spectrophotometric determination were the same as employed previously.[2]

Results and Discussion

Partition of 2,4-Hexadienoic Acid. In the extraction of metal ions with carboxylic acids, the extraction equilibrium is influenced by the partition behavior of the acid which is correlated with its dissociation in the aqueous phase, its partition between the organic and aqueous phases, and its dimerization in the organic phase.

The dissociation constant of 2,4-hexadienoic acid was determined by potentiometric method in 0.1 mol dm^{-3} sodium perchlorate medium. Further, the partition of 2,4-hexadienoic acid was carried out between 1-octanol and 0.1 mol dm^{-3} perchloric acid solution. The results obtained are listed in Table 1 together with the reference values on 1-hexanoic acid. The dimerization of both acids in 1-octanol phase was found not to occur to any appreciable extent. Then, as shown in the previous paper,[6] the concentration of the monomeric acid in the organic phase can be calculated by the following expression:

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

where $[\mathrm{HA}]_\mathrm{o}$, C_HA, $K_\mathrm{D,HA}$, and K_a represent the monomeric acid concentration in the organic phase, the total concentration of the acid, the partition constant between the organic and aqueous phases, and the dissociation constant in the aqueous phase of the acid, respectively. According to Eq. 1, the monomeric concentration of 1-hexanoic acid in 1-octanol phase has been found to be kept practically constant, though it was slightly low than its total concentration, under the present extraction conditions: C_HA=2.0 mol dm^{-3} ($-\log[\mathrm{H}^+]$=3.0—3.5), 1.5 (3.3—3.9), 1.0 (3.5—4.0), 0.7 (3.6—4.1), and 0.5 (3.8—4.3), respectively. On the other hand, the concentration of the monomer for 2,4-hexadienoic acid in 1-octanol has proved to vary slightly with the hydrogen ion concentration in the aqueous phase under the present conditions: C_HA=0.5 mol dm^{-3} ($-\log[\mathrm{H}^+]$=3.7—4.0), 0.3 (4.0—4.3), 0.2 (4.1—4.5), 0.1 (4.5—4.8), and 0.05 (4.8—5.2), respectively, but the variation in the concentration of the monomeric 2,4-hexadienoic acid in 1-octanol was within the limit allowed for the analysis of the extraction equilibrium by the present graphical method.

Extraction of Copper(II) with 2,4-Hexadienoic and 1-Hexanoic Acids. In the extraction system using 1-octanol as solvent, the extraction equilibrium can be represented as follows:

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

with the extraction constant:

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

where $j\geqq1$, $a\geqq0$, both j and a are integers, and the subscript o refers to the organic phase. The total concentrations of copper(II) in the organic and aqueous phases can be expressed as:

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

and $C_\mathrm{Cu,w}=[\mathrm{Cu}^{2+}]\alpha_\mathrm{Cu}$, respectively, where α_Cu denotes the side-reaction coefficient of copper(II) in the aqueous phase, and has been found to be unity under the present extraction conditions.

Determination of the Degree of Polymerization of the Extracted Species. Acoding to the same manner as employed previously, the degree of polymerization of the extracted species can be determined from the slope of the plots of $\log C_\mathrm{Cu,o}$ against ($\log[\mathrm{Cu}^{2+}]-2\log[\mathrm{H}^+]$), holding $[\mathrm{HA}]_\mathrm{o}$ constant (Cf. Eq. 4 in Ref. 6). The results are shown in Figs. 1 and 2 for 1-hexanoic and 2,4-hexadienoic acids, respectively. In Fig. 1 for 1-hexanoic acid, the slope lies between unity and two in every case. This suggests that the monomer and dimer can be presented as extracted species under these conditions. As described in the previous paper,[6] by fitting the plots of ($\log C_\mathrm{Cu,o}-\log[\mathrm{Cu}^{2+}]+2\log[\mathrm{H}^+]$)

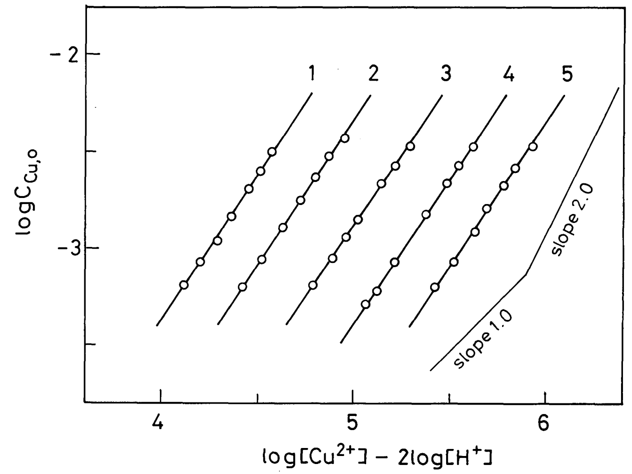

Fig. 1. Determination of the degree of polymerization of copper(II) 1-hexanoates in 1-octanol system. No. 1: C_{HA}=2.0, No. 2: 1.5, No. 3: 1.0, No. 4: 0.7, and No. 5: 0.5 mol dm^{-3}, respectively.

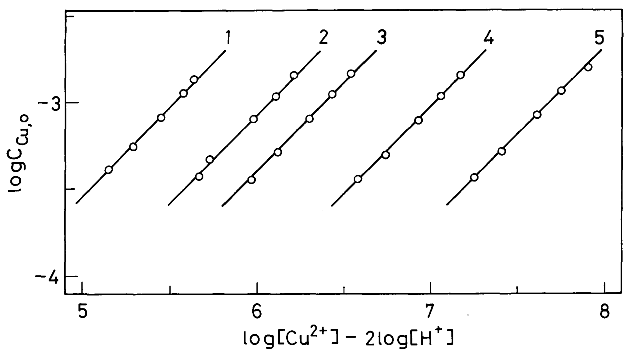

Fig. 2. Determination of the degree of polymerization of copper(II) 2,4-hexadienoate in 1-octanol system. No. 1: C_{HA}=0.5, No. 2: 0.3, No. 3: 0.2, No. 4: 0.1, and No. 5: 0.05 mol dm^{-3}, respectively. Solid lines are the straight ones with slope of 1.0.

against ($\log[\mathrm{Cu}^{2+}]-2\log[\mathrm{H}^+]$) at constant $[\mathrm{HA}]_{\mathrm{o}}$ with the normalized curve, $\log(1+X)$ vs. $\log X$, it can be confirmed that both the monomeric and dimeric copper(II) hexanoates are extracted in 1-octanol (cf. Eq. 9 in Ref. 6). As shown in Fig. 3, the plots fit well in the normalized curve at any C_{HA} condition. Therefore, both the monomer and dimer have been found to be extracted in 1-hexanoic acid/1-octanol system.

Determination of the Number of the Acid Molecules Involved in the Extracted Species. In the region where the monomeric copper(II) species prevails, the following relation can be derived in a similar manner as reported previously,[5]

$$\log C_{\mathrm{Cu,o}} - \log[\mathrm{Cu}^{2+}] + 2\log[\mathrm{H}^+] = \log\sum_a (K_{\mathrm{ex}(1a)}[\mathrm{HA}]_{\mathrm{o}}^{(2+a)}). \tag{4}$$

By plotting the values of the left-hand side of Eq. 4 against $\log[\mathrm{HA}]_{\mathrm{o}}$, the number of the respective acid molecules involved in each monomeric copper(II) species can be estimated. The results are shown in Figs. 4 and 5 for 1-hexanoic and 2,4-hexadienoic acids, respectively. Both of the figures indicate that the monomer species is $\mathrm{CuA_2}$. From the respective intercept of the plots in Figs. 4 and 5, the corresponding extraction constants were found to be $10^{-8.19}$ for 1-hexanoate, and $10^{-7.96}$ for 2,4-hexadienoate, respectively.

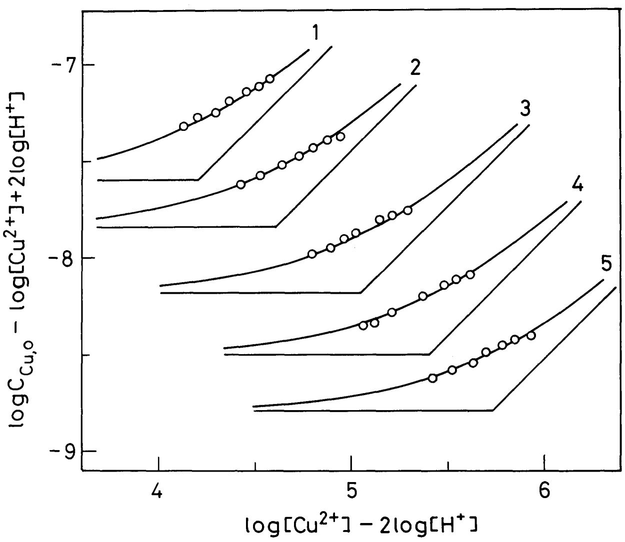

Fig. 3. Identification of the degree of polymerization of copper(II) 1-hexanoates in 1-octanol system. Curves are the normalized ones, $\log(1+X)$ vs. $\log X$. Solid lines are the straight ones with slope of 0 and 1.0, which are the asymptotes of the respective normalized curves. Numbers are the same as in Fig. 1.

On the other hand, in the region where the predominant copper(II) species are the dimer, that is, the plots in Fig. 3 fall on the straight line asymptotes with slope of unity, the following expression can be obtained in a same manner as previously described.

$$\log C_{\mathrm{Cu,o}} - 2(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]) = \log 2 + \log\sum_b (K_{\mathrm{ex}(2b)}[\mathrm{HA}]_{\mathrm{o}}^{(4+b)}). \tag{5}$$

The number of 1-hexanoic acid molecules involved in the dimeric copper(II) hexanoate can be estimated from the slope of the plots of $\log C_{\mathrm{Cu,o}} - 2(\log[\mathrm{Cu}^{2+}]-2\log[\mathrm{H}^+])$ against $\log[\mathrm{HA}]_{\mathrm{o}}$. As can be seen from Fig. 4, the slope of the plots, which is close to four at lower $[\mathrm{HA}]_{\mathrm{o}}$, tends to be steeper with increasing $[\mathrm{HA}]_{\mathrm{o}}$. Then it has been found 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). Therefore, the following relation can be obtained:

$$\log C_{\mathrm{Cu,o}} - 2(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]) - 4\log[\mathrm{HA}]_{\mathrm{o}}$$
$$= \log\left(1 + \frac{K_{\mathrm{ex}(2b)}}{K_{\mathrm{ex}(20)}}[\mathrm{HA}]_{\mathrm{o}}^{b}\right) + \log 2 + \log K_{\mathrm{ex}(20)}\,. \tag{6}$$

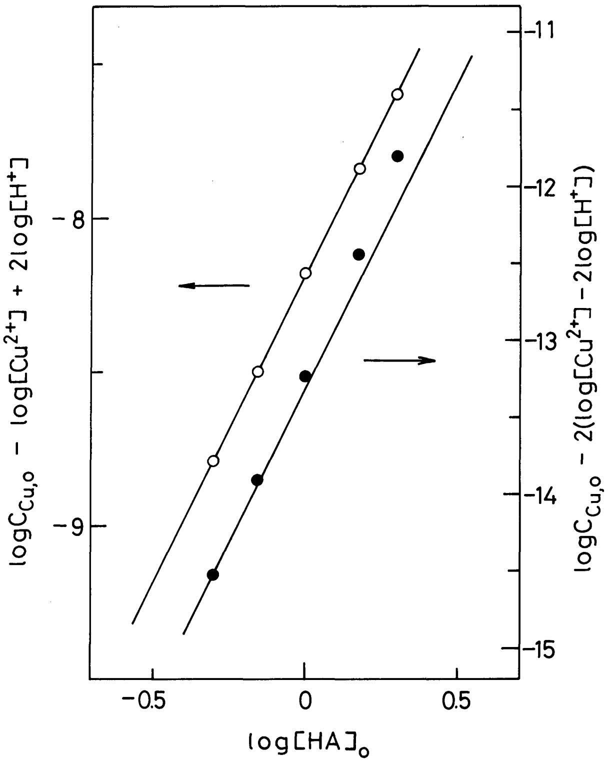

Fig. 4. Estimation of the number of 1-hexanoic acid molecules involved in the monomeric and dimeric copper(II) 1-hexanoates in 1-octanol system. Solid lines are the straight ones with slope of 2.0 and 4.0, respectively. Open and closed symbols refer to the monomeric and dimeric copper species.

In analogy with the manner presented previously, by fitting the plots of the values of left-hand side of Eq. 6 against $\log[\mathrm{HA}]_o$ to the following normalized curves with the optimum n: $\log(1+X^n)$ vs. $\log X$, we can determine the composition of the other dimer and the respective extraction constants of the two dimers. As represented in Fig. 6, the plots fit well with the normalized curve with n=2. This suggests that the other dimer is $\mathrm{Cu_2A_4(HA)_2}$. And both the extraction constants of $\mathrm{Cu_2A_4}$ and $\mathrm{Cu_2A_4(HA)_2}$ were estimated as follows: $\log K_{\mathrm{ex}(20)}=-13.65$, and $\log K_{\mathrm{ex}(22)}=-14.19$, respectively.

Consequently, in the present extraction systems, the extraction equilibria are summarized as follows:

2,4-Hexadienoic Acid/1-Octanol System:

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

1-Hexanoic Acid/1-Octanol System:

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

$$2\mathrm{Cu^{2+}} + 4(\mathrm{HA})_o \overset{K_{\mathrm{ex}(20)}}{\rightleftharpoons} (\mathrm{Cu_2A_4})_o + 4\mathrm{H^+}.$$

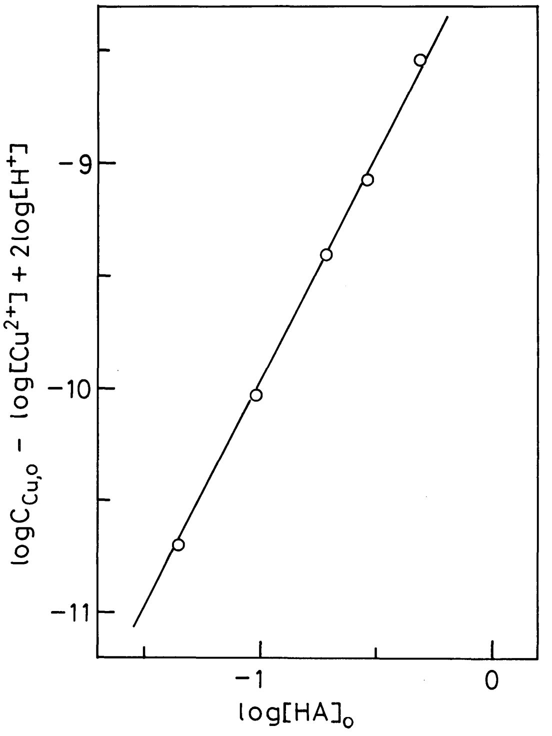

Fig. 5. Estimation of the number of 2,4-hexadienoic acid molecules involved in the monomeric copper(II) 2,4-hexadienoate in 1-octanol system. Solid line is the straight one with slope of 2.0.

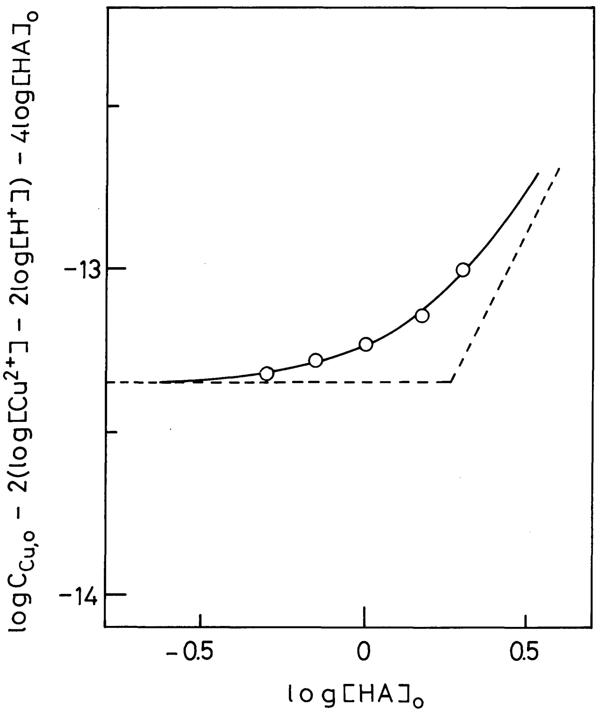

Fig. 6. Estimation of the number of 1-hexanoic acid molecules involved in the dimeric copper(II) 1-hexanoates in 1-octanol system by the curve-fitting method. Solid curve is the normalized one: $\log(1+X^2)$ vs. $\log X$. Dotted lines are the asymptotes with slope of 0 and 1.0 of the normalized curve.

$$2\mathrm{Cu}^{2+} + 6(\mathrm{HA})_\mathrm{o} \xrightleftharpoons{K_{\mathrm{ex}(22)}} (\mathrm{Cu}_2\mathrm{A}_4(\mathrm{HA})_2)_\mathrm{o} + 4\mathrm{H}^+.$$

2,4-Hexadienoic Acid/Benzene System: Copper was scarcely extracted as well as in the extraction with benzoic acid. The emulsion, even at the percent extraction of copper(II) as low as only a few percents, appeared under the present extraction conditions, and so the extraction equilibrium could not be clarified.

1-Hexanoic Acid/Benzene System: The extraction equilibrium has been reported as given below.[8]

$$2\mathrm{Cu}^{2+} + 3(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(22)}} (\mathrm{Cu}_2\mathrm{A}_4(\mathrm{HA})_2)_\mathrm{o} + 4\mathrm{H}^+,$$

with

$$K_{\mathrm{ex}(22)} = \frac{[\mathrm{Cu}_2\mathrm{A}_4(\mathrm{HA})_2]_\mathrm{o}[\mathrm{H}^+]^4}{[\mathrm{Cu}^{2+}]^2[(\mathrm{HA})_2]_\mathrm{o}^3} = 10^{-11.48},$$

where $(\mathrm{HA})_{2,\mathrm{o}}$ denotes the dimeric species of 1-hexanoic acid in benzene, and its dimerization constant was reported as $\log K_{2,\mathrm{HA}}=2.45$.[9]

Comparison of 2,4-Hexadienoic with 1-Hexanoic Acids as Extracting Agent for Copper(II). In a series of investigations on the solvent extraction of copper(II) with various carboxylic acids by employing various solvents, it has been found that there is a remarkable difference in the extraction equilibrium between aliphatic and aromatic carboxylic acids,[2,5–7] and that the extraction behavior of copper(II) carboxylates is significantly dependent on whether a solvent used is solvating or nonsolvating.[3,10,11] Also in the present work, the pronounced differences in the extraction behavior between benzene and 1-octanol systems were observed for both 1-hexanoic and 2,4-hexadienoic acids. It seems reasonable to conclude that the monomeric copper(II) 2,4-hexadienoate(CuA_2) is solvated by some octanol molecules in the extraction system using 1-octanol as solvent. In general, the extracted metal compounds can be regarded as being hydrophobic as well as extracting reagent itself. In the present system using benzene the monomeric copper(II) 2,4-hexadienoate can be anticipated to become not only hydrophobic but also oleophobic owing to its hydration. Therefore, it has become soluble in neither organic nor aqueous phase, that is, an emulsion, which appears to be some hydrated copper(II) species, has developed near the interface between the organic and aqueous phases.

On the other hand, in the system of 1-octanol the formation of some solvated monomeric copper(II) species by octanol molecules can be allowed to increase the affinitiy for the organic phase, and leads to a good extractability.

The extraction behavior by 1-hexanoic acid for copper(II) is similar to that by its homolog, 1-decanoic acid for both systems in which either benzene or 1-octanol was used as solvent.

As can be seen in Table 1, the values of $\mathrm{p}K_\mathrm{a}$, $K_{\mathrm{D,HA}}$, and $K_{\mathrm{ex}(10)}$ between 1-hexanoic and 2,4-hexadienoic acids do not differ so much, but the pronounced difference in the formation of the dimeric copper(II) species between these acids is observed, that is, the dimeric copper(II) species was not detected to any appreciable extent in the latter extraction system. In containing the conjugated double bonds, 2,4-hexadienoic acid is markedly distinct from 1-hexanoic acid, although both acids contain six carbon atoms in each molecule, and belong to an aliphatic carboxylic acid group. 2,4-Hexadienoic acid as extracting reagent for copper(II) is similar to benzoic acid. Judging from these results and the fact that both benzoic and 2,4-hexadienoic acids contain the conjugated double bonds in each molecule, it seems reasonable to assume that the conjugated double bonds inhibit the formation of the dimeric copper(II) carboxylate in the extraction of copper(II) carboxylates. Although, the alkyl substituent in a saturated straight chain carboxylic acid such as 1-hexanoic acid is able to change the shape of the chain by rotating the carbon–carbon bond so as not to inhibit the formation of the dimeric copper(II) carboxylate, the rotation of the carbon–carbon bond in the alkadienyl group such as 2,4-hexadienyl one is prevented owing to the conjugated double bonds. Then, the 2,4-hexadienyl substituent may cause obstruction of the formation of the dimeric copper(II) carboxylate.

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