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Effect of the Chain Length of Carboxylic Acids and Alcohols on the Extraction of Copper(II) with the Acids Using Alcohols as Solvents

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The solvent extraction of copper(II) with aliphatic carboxylic acids ($CH_3(CH_2)_nCOOH$: n = 2—7) in alcohols ($CH_3(CH_2)_nOH$: n = 4—7) was carried out at 25 °C and an aqueous ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). Each extraction equilibrium for these systems was determined in detail by a slope analysis and a curve-fitting method. In all of the extraction systems, except for butanoic acid ones, copper(II) carboxylates were found to be extracted as monomeric and dimeric species: CuA_2, Cu_2A_4, and $Cu_2A_4(HA)_2$. The dimerization and the adduct formation constants of copper(II) carboxylates in the organic phase were estimated. The dimerization and the adduct formation constants in the organic phase were found to be dependent on the chain length of the acids and alcohols, although the extraction constant of CuA_2 were found to be independent of their chain length.

The solvent extraction of copper(II) with many kinds of carboxylic acids has been carried out, and various types of information on dimerization and adduct formation of copper(II) carboxylates were obtained.[1—4] These dimerization and adduct formation equilibria are found to be dependent on the solvents and extractants.

The solvent effects on the extraction of $Cu_2A_4(HA)_2$ with decanoic acid in several inert solvents,[1] and on the dimerization of copper(II) decanoates in alcohol[2] and ketone[3] solvents, have been explained in terms of the regular solution theory. The number of solvent molecules liberated in the dimerization of the monomeric copper(II) decanoate, CuA_2, in the organic phase was proven to be less in ketones than in alcohols, which have a stronger solvation ability caused by hydrogen bonding. In the systems of 1-ocntanol/benzene and 2-octanone/benzene mixed solvents, the monomeric benzoic acid was more strongly solvated by 1-octanol than 2-octanone molecules in the organic phase.[4]

Taking into account the preservation of the natural environment and the toxicity to human beings, halogenated solvents such as chloroform and aromatic solvents such as benzene and its derivatives should be controlled regarding their use as much as possible. Solvating solvents, such as alcohols, should be noted as a substitute for these harmful solvents. A number of usual investigations on the solvent effects on the extraction of metal ions, have been undertaken under conditions which neglect the solute–solvent interaction, although it is one of the important factors for extraction using a solvating solvent.

In the present work, in order to investigate the solute–solvent interaction in detail, the extraction of copper(II) with aliphatic carboxylic acids into alcohols was carried out. In preliminary experiments, it was found that the extraction equilibrium on systems using 1-butanol as a solvent could not be precisely determined owing to the large mutual solubility between water and 1-butanol, and 1-nonanol was not suitable for a solvent in the present extraction systems owing to its high viscosity. On account of the poor extractability for copper(II), we did not use 1-propanoic acid as an extractant. In the extraction of copper(II) with carboxylic acids, in which more than 14 carbon atoms were involved, the third phase, in which copper(II) carboxylates seem to be concentrated, was observed between the organic and aqueous phases.

By considering these results in the preliminary experiments, the present investigation made on carboxylic acids ranging in carbon number from 4 to 9 as extractants and alcohols from 5 to 8 as solvents. The effects of the chain length of carboxylic acid and alcohol on the extraction constants of the copper(II) species, the dimerization constants of monomeric copper(II) carboxylate and the adduct formation constants to the dimeric copper(II) species were investigated from the standpoint of the solute–solvent interaction.

Experimental

Reagents. Reagent grade alcohol solvents (1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol) were washed successively with a dilute sodium hydroxide solution, a dilute perchloric acid solution, and distilled deionized water. Copper(II) perchlorate, carboxylic acids (butanoic, pentanoic, hexanoic, heptanoic, octanoic, and nonanoic acids) and the other reagents were of reagent grade and were used without further purification. Aqueous solutions were prepared with distilled deionized water.

Procedure. The extraction of copper(II) by carboxylic acids using alcohols was carried out in a thermostatic bath at 25±0.2 °C. The ionic strength of the aqueous phase was adjusted to 0.1 mol dm^{-3} using sodium perchlorate. The total concentration of copper(II) was 5×10^{-3} mol dm^{-3}, and that of carboxylic acids was in the region of 0.5—2.0 mol dm^{-3}. The total concentration of copper(II) in the aqueous phase was determined by EDTA titration using TAR as an indicator, and that in the organic phase by mass balance. In extraction systems using butanoic and pentanoic acids, the concentration of copper(II) ion $[Cu^{2+}]$ in the aqueous phase was calculated according to the following equation: $[Cu^{2+}] = C_{Cu,w}/\alpha_{Cu(A)}$ where $\alpha_{Cu(A)} = 1+K_1[A^-]$. The concentration of carboxylate anion $[A^-]$ was calculated under the respective extraction conditions by $[A^-] = C_{HA}/(1+[H^+]/K_a)$. In the extraction systems other than these acids, $[Cu^{2+}]$ was found to be approximated by the total copper(II) concentration in the aqueous phase. The concentrations of monomeric acid in the organic and aqueous phases and carboxylate anion in the aqueous one were calculated from the partition and dissociation constants of each acid and $[H^+]$. The other procedures for the extraction of copper(II) with carboxylic acids were the same as those used in previous work.[2] The formation constants of copper(II) with butanoate and pentanoate anions in the aqueous solution were potentiometrically determined by emf and pH measurements using a copper(II) ion-selective electrode and a glass electrode.

Apparatus. A Cool Bath Shaker ML-10 (Taitec Co., Koshigaya) was used for mechanical shaking. For centrifugation a Table Top Centrifuge Model 5100 (Kubota Seisakusho Ltd., Tokyo) was used. A DKK Ion Meter, Model IOL-50 (DKK Co., Tokyo) was used for determining the hydrogen ion concentration in the aqueous phase without phase separation. For an emf measurements of copper(II) ion activity, the same DKK Ion Meter mention above was used with a DKK copper(II) ion-selective electrode (Model 7140) and a DKK reference electrode (Model 4083).

Results and Discussion

Extraction Equilibrium of Copper(II) with Carboxylic Acids into Alcohol Solvents. The extraction equilibrium of copper(II) with carboxylic acids into alcohol solvents can be expressed as follows:

$$jCu^{2+} + (2j+a)(HA)_o \overset{K_{ex(ja)}}{\rightleftharpoons} (Cu_jA_{2j}(HA)_a)_o + 2jH^+,$$

$$K_{ex(ja)} = \frac{[Cu_jA_{2j}(HA)_a]_o[H^+]^{2j}}{[Cu^{2+}]^j[HA]_o^{(2j+a)}}, \tag{1}$$

where subscript "o" denotes an organic solvent and $K_{ex(ja)}$ represents the extraction constant of $Cu_jA_{2j}(HA)_a$.

The total concentration of copper(II) in the organic phase can be expressed as

$$\begin{aligned} C_{Cu,o} &= \sum_j \sum_a j[Cu_jA_{2j}(HA)_a]_o \\ &= \sum_j \sum_a jK_{ex(ja)}[Cu^{2+}]^j[HA]_o^{(2j+a)}[H^+]^{-2j}. \end{aligned} \tag{2}$$

If a copper(II) species other than the hydrated copper(II) ion in the aqueous phase can be neglected, the concentration of the hydrated copper(II) ion can be regarded as the total copper(II) concentration in the aqueous phase. If not so, the total concentration of copper(II) in the aqueous phase can be expressed as

$$\begin{aligned} C_{Cu,w} &= [Cu^{2+}] + [CuA^+] + [CuA_2] \\ &= [Cu^{2+}](1+K_1[A^-]+K_1K_2[A^-]^2) \\ &= [Cu^{2+}]\alpha_{Cu(A)}, \end{aligned} \tag{3}$$

where K_1, K_2, and $\alpha_{Cu(A)}$ denote the stepwise formation constants of CuA^+ and CuA_2 and the reaction coefficient of copper(II) ion with carboxylate anion, respectively. The stepwise formation constants of copper(II) carboxylates were determined in a similar manner to that previously described:[5] $\log K_1 = 1.74$ for butanoic and 1.85 for pentanoic acids, respectively, and the presence of CuA_2 was found to be neglected in the aqueous phase. For the extraction systems of other carboxylic acids used as extractants, it was found that the copper(II) species other than Cu^{2+} could be neglected in the aqueous phase.

According to the previous results obtained in the extraction of copper(II) with decanoic acid using some alcohol solvents,[2] it is suggested that the monomeric and dimeric copper(II) carboxylates are responsible for the extraction of copper(II) in the present extraction systems. Then, the following expression can be derived from Eq. 2:

$$\begin{aligned} &\log C_{Cu,o} - (\log[Cu^{2+}] - 2\log[H^+]) \\ &\quad = (2+a)\log[HA]_o + \log K_{ex(1a)} \\ &\quad + \log\left(1 + \frac{2K_{ex(2b)}}{K_{ex(1a)}}[HA]_o^{(2+b-a)}[Cu^{2+}][H^+]^{-2}\right). \end{aligned} \tag{4}$$

As described in previous work,[2] by fitting the plots of left-hand side of Eq. 4 against $(\log[Cu^{2+}]-2\log[H^+])$ at constant $[HA]_o$ with a normalized curve, $\log(1+X)$ vs. $\log X$, it could be confirmed that both the monomeric and dimeric species are extracted. The results are shown in Fig. 1. For the nonanoic acid/1-heptanol system, the plots fit well with the normalized curve at the total concentration of nonanoic acid ranging from 0.5 to 2.0 mol dm^{-3}. Therefore, the monomeric and dimeric copper(II) species have been found to be responsible for the extraction. The same results as those for the nonanoic/1-heptanol system were obtained for the other extraction systems, except for butanoic/1-pentanol and butanoic/1-hexanol systems. In the butanoic/1-hexanol system,

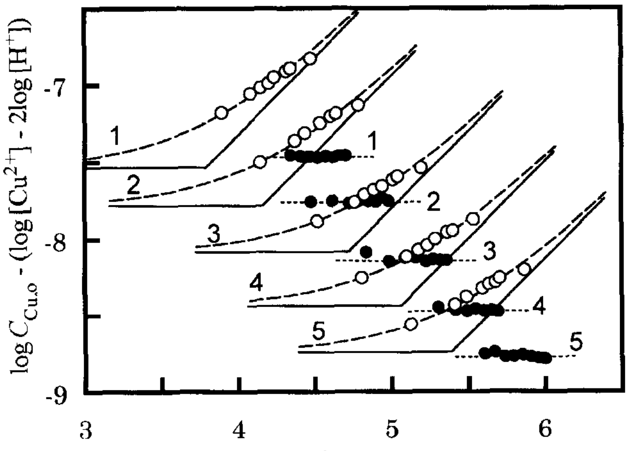

Fig. 1. Determination of the degree of polymerization of copper(II) carboxylates. C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.0, No. 4: 0.7, No. 5: 0.5 mol dm^{-3}. Open and closed symbols refer to nonanoic acid/1-heptanol and butanoic acid/1-pentanol systems, respectively. The dashed curve denotes the normalized curve, $\log(1+X)$ vs. $\log X$. The solid and dotted lines are the asymptotes of the normalized curve and horizontal line, respectively.

the plots were parallel to the horizontal axis as well as the butanoic/1-pentanol system shown in Fig. 1, so that only the monomeric copper(II) species were found to be extracted.

In the region where the monomeric copper(II) species prevails, the following expression can be derived from Eq. 2:

$$\log C_{\mathrm{Cu,o}} - \left(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]\right) = \log \sum_a \left(K_{\mathrm{ex}(1a)}[\mathrm{HA}]_{\mathrm{o}}^{(2+a)}\right). \tag{5}$$

From the slope of the plots of $\log C_{\mathrm{Cu,o}} - (\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+])$ against $\log[\mathrm{HA}]_{\mathrm{o}}$ on the basis of Eq. 5, the number of carboxylic acid molecules involved in the monomeric species can be estimated. For the octanoic/1-hexanol system, as shown in Fig. 2, the plots fall on a straight line with a slope of 2.0 over the concentration range studied; that is, the monomeric species was found to be $\mathrm{CuA_2}$. The extraction constant of $\mathrm{CuA_2}$ was estimated from the intercept of the straight line. The results are listed in Table 1 together with other results. In the butanoic/1-pentanol system, as indicated in Fig. 2, the plots gradually deviate upward from a straight line with a slope of 2.0, with increasing the concentration of butanoic acid in 1-pentanol. Then, it is suggested that another monomeric species, $\mathrm{CuA_2(HA)}_a$ ($a > 0$), other than $\mathrm{CuA_2}$ is extracted, and the following expression can be obtained:

$$\log C_{\mathrm{Cu,o}} - \left(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]\right) - 2\log[\mathrm{HA}]_{\mathrm{o}} = \log K_{\mathrm{ex}(10)} + \log\left(1 + \frac{K_{\mathrm{ex}(1a)}}{K_{\mathrm{ex}(10)}}[\mathrm{HA}]_{\mathrm{o}}^{a}\right). \tag{6}$$

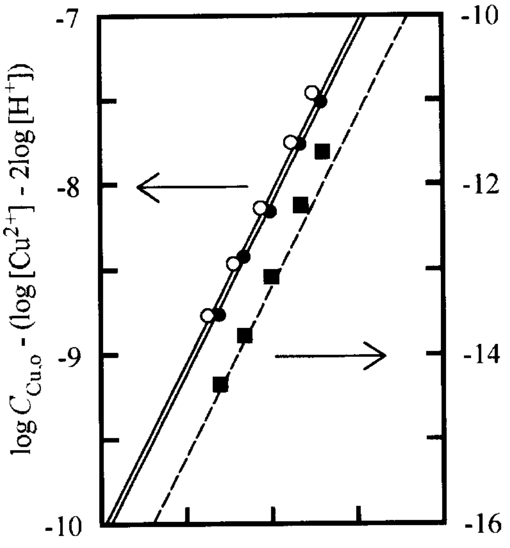

Fig. 2. Determination of the number of carboxylic acid molecules involved in the extracted species. Symbols: ○ refers to the monomeric copper(II) butanoate in 1-pentanol, and ● and ■ refer to monomeric and dimeric species for octanoic/1-hexanol system, respectively. The solid and dashed lines are straight ones with slopes of 2.0 and 4.0, respectively.

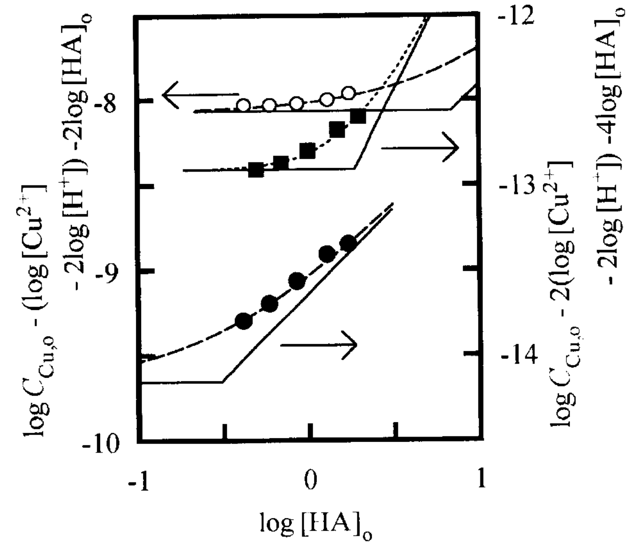

Fig. 3. Determination of the number of carboxylic acid molecules involved in the copper(II) carboxylates. Symbols, ○, ●, and ■ refer to monomeric species in the butanoic/1-pentanol system, dimeric species in the butanoic/1-heptanol system, and dimeric species for the heptanoic/1-octanol system. The dashed and dotted curves denote the normalized curve, $\log(1+X^n)$ vs. $\log X$ with $n = 1$ and 2, respectively. The solid lines are the asymptotes of the respective normalized curves.

As shown in Fig. 3, plots of $\log C_{\mathrm{Cu,o}} - (\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]) - 2\log[\mathrm{HA}]_{\mathrm{o}}$ against $\log[\mathrm{HA}]_{\mathrm{o}}$ fit well with a normalized curve, $\log(1+X)$ vs. $\log X$. From this results, it was found that both $\mathrm{CuA_2}$ and $\mathrm{CuA_2HA}$ were extracted into the organic phase, and the respective extraction constants were estimated from the respective deviations of the ordinate and abscissa between the plots and the normalized curve.

On the other hand, in the region where the dimeric species is predominantly extracted, the total concentration of copper(II) in the organic phase was derived from Eq. 2 as follows:

$$\log C_{\mathrm{Cu,o}} - 2\left(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]\right) = \log 2 \sum_b \left(K_{\mathrm{ex}(2b)}[\mathrm{HA}]_{\mathrm{o}}^{(4+b)}\right). \tag{7}$$

As shown in Fig. 2, the plots of the values on the left-hand side of the above equation against $\log[\mathrm{HA}]_{\mathrm{o}}$ are close to a straight line with a slope of 4.0 in the lower concentration range of octanoic acid, and gradually shift upward with an increase in $[\mathrm{HA}]_{\mathrm{o}}$. It is expected that $\mathrm{Cu_2A_4}$ and $\mathrm{Cu_2A_4(HA)}_b$ ($b > 0$) are extracted, and the following equation can be obtained:

$$\log C_{\mathrm{Cu,o}} - 2\left(\log[\mathrm{Cu}^{2+}] - 2\log[\mathrm{H}^+]\right) - 4\log[\mathrm{HA}]_{\mathrm{o}} = \log K_{\mathrm{ex}(20)} + \log 2 + \log\left(1 + \frac{K_{\mathrm{ex}(2b)}}{K_{\mathrm{ex}(20)}}[\mathrm{HA}]_{\mathrm{o}}^{b}\right). \tag{8}$$

Plots of the left-hand side of Eq. 8 against $\log[\mathrm{HA}]_{\mathrm{o}}$ in the butanoic/1-heptanol and heptanoic/1-octanol systems are shown in Fig. 3. As can be seen from Fig. 3, the plots fit well with a normalized curve with $n = 1$ for the former and $n = 2$

Table 1. Extraction Constants of Copper(II) Carboxylates

Acids	pK_a	CuA_2	CuA_2HA	$CuA_2(HA)_2$	Cu_2A_4	Cu_2A_4HA	$Cu_2A_4(HA)_2$
		log $K_{ex(10)}$	log $K_{ex(11)}$	log $K_{ex(12)}$	log $K_{ex(20)}$	log $K_{ex(21)}$	log $K_{ex(22)}$
Solvent: 1-Pentanol							
Butanoic	4.63[a]	−8.08	−8.92	—	—	—	—
Pentanoic	4.64[a]	−8.04	—	—	−13.80	—	−14.46
Hexanoic	4.84[b]	−8.06	—	—	−14.17	—	−14.38
Heptanoic	4.89[a]	−8.03	—	—	−13.91	—	−14.17
Octanoic	4.89[a]	−8.08	—	—	−13.80	—	−14.01
Nonanoic	4.89[b]	−8.06	—	—	−13.72	—	−13.90
Decanoic[c]	4.92[d]	−8.13	—	—	−14.00	—	−14.03
Solvent: 1-Hexanol							
Butanoic		−8.12	−8.79	—	—	—	—
Pentanoic		−8.12	—	—	−13.61	—	−14.28
Hexanoic		−8.13	—	—	−13.77	—	−14.23
Heptanoic		−8.13	—	—	−13.62	—	−14.03
Octanoic		−8.14	—	—	−13.51	—	−13.96
Nonanoic		−8.12	—	—	−13.50	—	−13.79
Decanoic[c]		−8.25	—	—	−13.73	—	−13.77
Solvent: 1-Heptanol							
Butanoic		−8.10	—	—	−14.47	−13.95	—
Pentanoic		−8.14	—	—	−13.39	—	−14.14
Hexanoic		−8.14	—	—	−13.54	—	−14.04
Heptanoic		−8.06	—	—	−13.45	—	−13.93
Octanoic		−8.14	—	—	−13.30	—	−13.84
Nonanoic		−8.13	—	—	−13.28	—	−13.64
Decanoic[c]		−8.26	—	—	−13.48	—	−13.72
Solvent: 1-Octanol							
Butanoic		−8.33	−8.77	—	−13.60	—	—
Pentanoic		−8.08	—	—	−13.19	—	−14.02
Hexanoic[e]		−8.19	—	—	−13.65	—	−14.19
Heptanoic		−8.08	—	—	−13.21	—	−13.77
Octanoic		−8.15	—	—	−13.25	—	−13.51
Nonanoic		−8.17	−8.82	—	−13.21	—	−13.69
Decanoic[f]		−8.41	−8.65	—	−13.36	—	−13.77

a) Ref. 6. b) Ref. 7. c) Ref. 2. d) Ref. 8. e) Ref. 9. f) Ref. 10.

for the latter systems, respectively. From these results, it was found that Cu_2A_4 and Cu_2A_4HA in the former, and Cu_2A_4 and $Cu_2A_4(HA)_2$ in the latter were extracted as the dimeric species. In a similar manner to the monomer, the respective extraction constants were estimated. The results are listed in Table 1.

Extraction Curves for the Present Systems. The dependence of the extraction curves on the chain length of alcohol for octanoic acid systems and that of carboxylic acid for 1-octanol systems is shown in Fig. 4. In each system, the observed plots fit well with the respective calculated curves on the basis of the present results, so that the validity of the results is supported.

As shown in Fig. 4(a), the longer chain length of alcohol, the higher gets slightly the extractability of copper(II). And as indicated in Fig. 4(b), the longer chain length of carboxylic acid, the higher is the extractability of the copper(II), except for decanoic acid. The extremely low extractability of copper(II) for the butanoic acid system can be due to the presence of the CuA^+ species other than Cu^{2+} in the aqueous phase.

Effect of the Chain Length on the Extraction, Dimerization, and Adduct Formation Constants. The extraction equilibrium in the present system consists of some equilibria, as shown in Fig. 5. The extraction constant of CuA_2, $K_{ex(10)}$, is expressed using the four kinds of equilibrium constants as follows:

$$K_{ex(10)} = K_{D,HA}^{-2} \cdot K_a^{2} \cdot \beta_2 \cdot K_{D,CuA_2}, \tag{9}$$

where $K_{D,HA}$, K_{D,CuA_2}, and β_2 denote the partition constants of HA and CuA_2 and the overall formation constant of CuA_2 in the aqueous phase, respectively. The extracted species, CuA_2, Cu_2A_4, and $Cu_2A_4(HA)_2$ were observed for the present systems other than the butanoic acid ones. The effect of the chain length in the acids on the respective extraction constants ($K_{ex(10)}$, $K_{ex(20)}$, and $K_{ex(22)}$) are shown in Fig. 6.

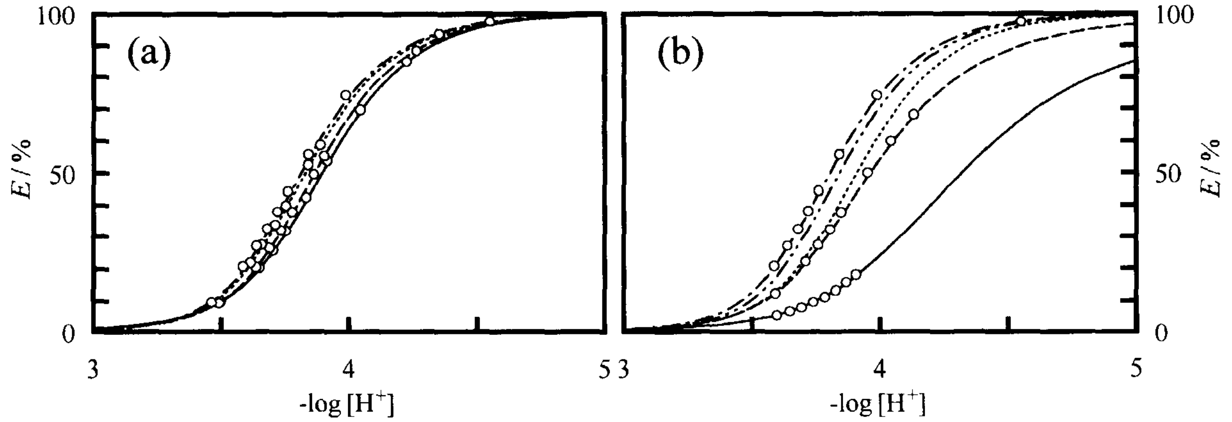

Fig. 4. The dependence of the chain length of alcohol (a) and carboxylic acid (b) for the extraction curves. Initial concentration of copper(II) and carboxylic acid are 5.0×10^{-3} and 1.0 mol dm^{-3}, respectively. Open symbols refer to the observed values. (a) The extractant is octanoic acid. The lines are as follows: —— = 1-pentanol, ---- = 1-hexanol, ···· = 1-heptanol, and –·–·= 1-octanol, respectively. (b) The solvent is 1-octanol. The lines are as follows: —— = butanoic, ---- = pentanoic, ···· = hexanoic, –·–·= octanoic, and –··–·· = decanoic acids, respectively. The curves without the observed values were drawn on the results obtained from the previous works.[9,10]

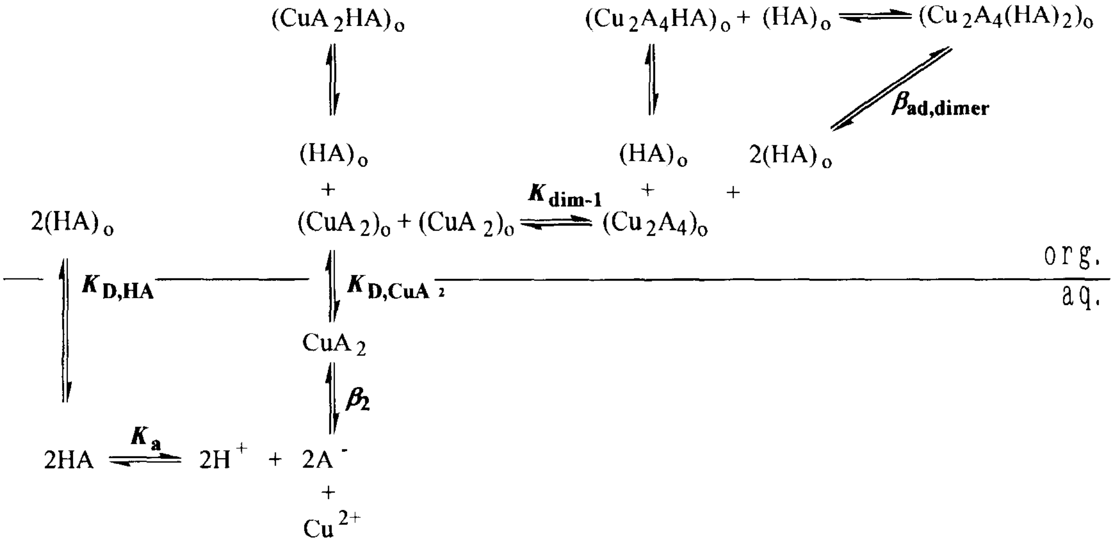

Fig. 5. The extraction scheme for the extraction of copper(II) with carboxylic acids in alcohols.

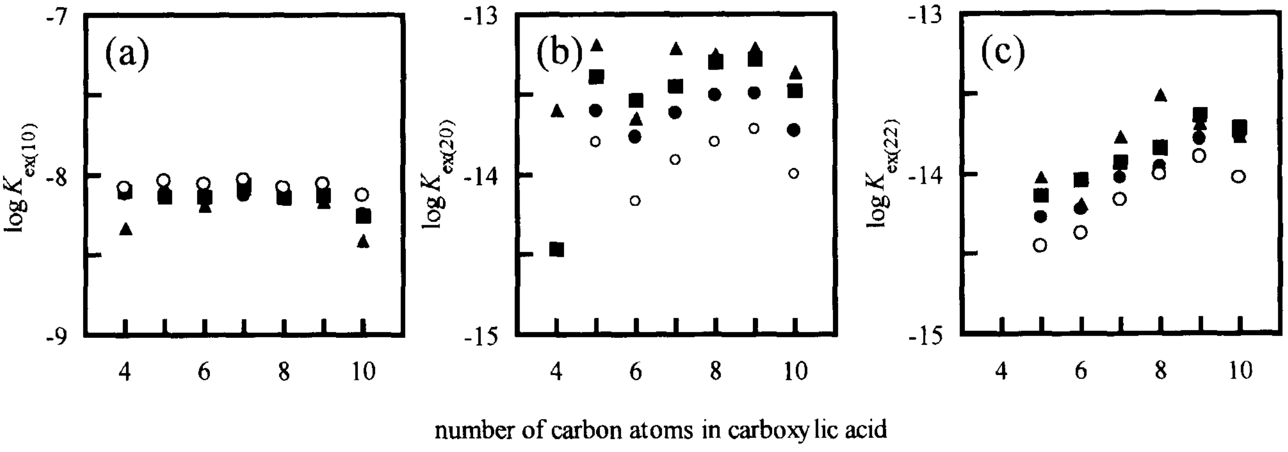

Fig. 6. Effect of the chain length of carboxylic acid on the extraction constants of CuA_2 (a), Cu_2A_4 (b), and $Cu_2A_4(HA)_2$ (c). Symbols, ○, ●, ■, and ▲ denote 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, respectively.

In the extraction of MR_n with HR, it is well known that the following relationship holds between $K_{D,HR}$ and K_{D,MR_n} : $K_{D,MR_n} = K_{D,HR}{}^n$. In addition, $K_a{}^n$ and β_n are known to compensate each other. Then, $K_{ex(10)}$ can be expected to be constant irrespective of the extracting agent. In Fig. 6(a), as expected, the extraction constant of CuA_2 was shown to be constant, although it is slightly dependent on the solvent.

The plots of $K_{ex(20)}$ and $K_{ex(22)}$, on the other hand, were demonstrated to vary widely concerning the dependence of the number of carbon atoms involved in the acids and alcohols, as shown in Figs. 6(b) and 6(c), respectively.

Similar to $K_{ex(10)}$ expressed by Eq. 9, $K_{ex(20)}$ and $K_{ex(22)}$ can be expressed by the following equations using each equilibrium constant shown in Fig. 5:

$$K_{ex(20)} = K_{dim-1}\cdot\left(K_{D,HA}{}^{-2}\cdot K_a{}^2\cdot\beta_2\cdot K_{D,CuA_2}\right)^2$$
$$= K_{dim-1}\cdot K_{ex(10)}^2, \qquad (10)$$

and

$$K_{ex(22)} = \beta_{ad,dimer}\cdot K_{dim-1}\left(K_{D,HA}{}^{-2}\cdot K_a{}^2\cdot\beta_2\cdot K_{D,CuA_2}\right)^2$$
$$= \beta_{ad,dimer}\cdot K_{dim-1}\cdot K_{ex(10)}^2, \qquad (11)$$

respectively, where K_{dim-1} $(=K_{ex(20)}\cdot K_{ex(10)}{}^{-2})$ and $\beta_{ad,dimer}$ $(=K_{ex(22)}\cdot K_{ex(20)}{}^{-1})$ denote the dimerization constant of copper(II) carboxylates, CuA_2 in organic phase and the adduct formation constant of free carboxylic acid to dimeric copper(II) carboxylate, Cu_2A_4 defined in Fig. 5, respectively. According to Eqs. 10 and 11, $K_{ex(20)}$ and $K_{ex(22)}$ are expressed by three kinds of equilibrium constants: $K_{ex(10)}$, K_{dim-1}, and $\beta_{ad,dimer}$.

The variation of $K_{ex(20)}$ and $K_{ex(22)}$ in Figs. 6(a) and 6(b) are attributable to that in the dimerization and adduct formation constants (K_{dim-1} and $\beta_{ad,dimer}$) in each organic phase on the basis of Eqs. 10 and 11. Then, the plots of these constants against the number of carbon atoms in the acids are shown in Figs. 7(a) and 7(b), respectively.

As shown in Fig. 7(a), the dimerization constant of monomeric copper(II) carboxylates in the alcohol solution increased with the number of carbon atoms involved in the alcohols for each acid. Also, the constant is minimum at hexanoic acid for each alcohol, although for the heptanol systems it is minimum at heptanoic acid. This tendency, which was observed between the dimerization constant of monomeric copper(II) carboxylate and the chain length of alkyl group in the carboxylic acid, can be speculated to be related to the solubility parameters of the copper(II) carboxylate and solvents and/or the structure of the alkyl group, which is expected to be dependent on its chain length. Unfortunately, we cannot clarify this interesting phenomenon from the present results.

Contrary to the dimerization constant, the overall adduct formation constant on the dimeric copper(II) species, Cu_2A_4, by the two carboxylic acids was found to decrease with increasing the number of carbon atoms in the alcohols in Fig. 7(b). This adduct formation reaction seems to be a replacement the solvated alcohol molecules by the carboxylic acid molecules. The solvating ability of the alcohol solvent is suggested to increase with increasing the number of carbon atoms in the alcohol. As a rough estimate, increasing the number of carbon atoms in the carboxylic acid also tends to increase the adduct formation constant ($\beta_{ad,dimer}$); that is, the coordinating ability of the monomeric carboxylic acid molecule is suggested to increase with increasing the number of carbon atoms involved in carboxylic acid.

Consequently, the extraction of the monomeric copper(II) carboxylate, CuA_2, is virtually independent of the number of carbon atoms involved in the carboxylic acid and the alcohol solvent because the partition constant of CuA_2 is compensated for that of HA, but the dimerization of CuA_2 and the adduct formation on Cu_2A_4 by the acid molecules are dependent on the solute–solvent interaction. In previous work on the partition of benzoic acid in extraction systems using the 1-octanol/benzene mixed solvents with various mixed ratios, the main monomeric species of benzoic acid were found to be HA and HA·ROH in the organic phase.[4] In the latter species, one 1-octanol molecule is linked by a hydrogen bond to benzoic acid. The monomeric copper(II) carboxylate appeared to be $Cu(A\cdot ROH)_2$. Thus, the carboxylate anion is

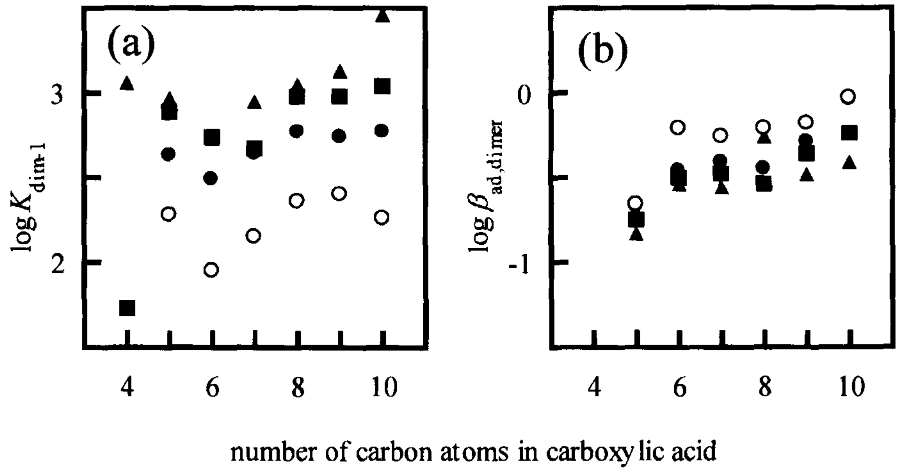

Fig. 7. Effect of the chain length of carboxylic acid on the dimerization (a) and adduct formation constants (b). Symbols are same as in Fig. 6.

expected to link to copper(II) ion through two kinds of oxygen atoms, which are assigned to the carboxyl group and 1-octanol. The monomeric copper(II) species can be stabilized by solvation. This suggests that the dimerization constant of monomeric copper(II) species decreases. That is to say, the interaction between carboxylic acid and alcohol molecules can be expected to influence the dimerization of copper(II) carboxylate and the adduct formation on the dimeric species, Cu_2A_4 by the acid molecules.

Broadly speaking from the present results, in the extraction of metal complex, the extraction can be regarded as not being essentially influenced by the solvent if any reaction on the metal complex, such as the adduct formation or the dimerization, does not occur in the organic phase. In other words, selection of the solvent is important for extraction in which the adduct formation and/or dimerization on the extracted species appear in the organic phase.

References

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

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

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

4 H. Yamada, K. Yajima, H. Wada, and G. Nakagawa, *Talanta*, **42**, 789 (1995).

5 H. Yamada, K. Yajima, and H. Wada, *Anal. Sci.*, **11**, 715 (1995).

6 E. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York (1977), Vol. 3.

7 I. Kojima, M. Yoshida, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 987 (1970).

8 Y. Fujii, Y. Kawachi, and M. Tanaka, *J. Chem. Soc., Faraday Trans. 1*, **77**, 63 (1981).

9 H. Yamada, C. Kato, and M. Mizuta, *Bull. Chem. Soc. Jpn.*, **65**, 186 (1992).

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