Extraction of Monomeric Species together with Dimeric Copper(II) 2-Bromoaliphatic and Conjugated Carboxylates in Benzene

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The extraction equilibria of copper(II) with 2-bromoaliphatic carboxylic acids and with conjugated carboxylic acids in benzene were investigated using a curve-fitting method in order to grasp the bonding character of a functional carboxyl group. A monomeric species, $\text{CuL}_2(\text{HL})_a$, together with dimeric copper(II) carboxylate $\text{Cu}_2\text{L}_4(\text{HL})_2$ was extracted in the concentration region of copper(II) in the organic phase, $C_{\text{Cu,o}} > 3 \times 10^{-5} \text{ mol dm}^{-3}$. A new linear relationship between the extraction constant (K_{ex}) and the acid dissociation constant (K_a) was empirically obtained as $\log K_{\text{ex}(11)} = 1.74 \log K_a - 0.75$ (1) for $\text{CuL}_2\text{-HL}$ and $\log K_{\text{ex}(12)} = 1.37 \log K_a - 1.97$ (2) for $\text{CuL}_2(\text{HL})_2$, as well as $\log K_{\text{ex}(22)} = 1.71 \log K_a - 3.17$ (3) for the dimer. Thus, we can obtain an approximate value of the dimerization constant of copper(II) ($K_{\text{dim}(a,2)}$) in the organic phase from K_a by $\log K_{\text{dim}(a,2)} = \log K_{\text{ex}(22)} - 2 \log K_{\text{ex}(1a)}$ ($a=1$ or 2), except for cases of conjugated carboxylates, which deviate from Eq. (3), due to a lower $\log K_{\text{ex}(22)}$. The deviations would be correlated to the change in the dipole moment affected by electronic delocalization with resonance over the conjugated ligand in the bridging form. Therefore, the extraction of a monomer together with a dimer is easily found by using carboxylic acids of low $\text{p}K_a$ or of a conjugate.

Keywords Extraction, copper(II) carboxylate, monomer, 2-bromoaliphatic, conjugated carboxylic acid

The most remarkable feature of metal carboxylate extraction systems is that many metals are extracted with carboxylic acid (HL) as an oligomeric species constructed by carboxyl bridging between the two metal atoms and/or by hydroxo/oxo bridging among the metals.^{1,2} The well-known dimeric copper(II) species $\text{Cu}_2\text{L}_4(\text{HL})_2$ in a nonpolar solvent is a typical oligomer, where the four carboxyl groups bridge between the two copper(II) ions in a lantern-like structure. In copper(II) carboxylate systems, however, a monomeric species should essentially be extracted together with a dimeric one, for example, in a copper(II) decanoate system where a monomer $\text{CuL}_2(\text{HL})_2$ was analyzed together with the dimeric $\text{Cu}_2\text{L}_4(\text{HL})_2$ under the concentration of copper in the organic phase $C_{\text{Cu,o}} < 10^{-5} \text{ M}$ ($\text{M} \equiv \text{mol dm}^{-3}$).³ The appearance of a coextraction phenomenon possibly depends on the kind of carboxyl residue and $C_{\text{Cu,o}}$. In fact, coextraction at $C_{\text{Cu,o}} > 10^{-4} \text{ M}$ in a nonpolar solvent, such as benzene, has been reported in several acid systems, though no steric effect of the carboxyl residue on the dimeric extraction equilibrium appears to play an important role, as described previously.^{4,5} Furthermore, a single monomeric species⁶ without a dimer has also been reported for the copper(II) extraction system by 2-bromododecanoic acid in hexane, while a single dimeric species⁷ was analyzed for a system of 2-bromopentanoic acid in benzene.

In order to analyze the chemical character of the

functional carboxyl group, the extractions of copper(II) with 2-bromoaliphatic (octanoic, hexadecanoic) acids and with conjugated carboxylic (2-phenylbenzoic, 1-naphthoic) acids in benzene were investigated. In the present paper, we report that: (1) the appearance of coextraction phenomena of a monomer and a dimer at $C_{\text{Cu,o}}$ above 10^{-5} M depends on the electronic states of the functional carboxyl group coordinated to copper(II); (2) the specificity of conjugated carboxylic acid as an extractant appears when the carboxyl group is bridging between the two copper(II) ions; and (3) the dimerization constant of copper(II) for the monomer $\rightleftharpoons$ dimer equilibrium reaction in the organic phase can be estimated from the $\text{p}K_a$ value of the carboxylic acid, except for conjugated acids.

Experimental

Each commercially obtained carboxylic acid ((purities: over 98%); 2-bromohexadecanoic acid (Aldrich Chemical Company, Inc.), 2-bromooctanoic, 2-phenylbenzoic or 1-naphthoic acid (Tokyo Chemical Industry Co. Ltd.)) was dissolved in benzene saturated with deionized and distilled water. Copper(II) nitrate (purity: 99.9%, Wako Pure Chem. Co. Ltd.) was used for studying the copper(II) extraction equilibria at constant ionic strength ($I=0.1 \text{ M}$, $(\text{Na,H})\text{NO}_3$). All other chemicals were of analytical reagent grade. To avoid any

damage by light, low-actinic glassware was used in the 2-bromoaliphatic acid system. Shaking for 1 h (by a shaker for 30 min at room temperature ($25 \pm 1^\circ\text{C}$) and then in an incubator for 30 min) was carried out in our ordinary experiments, and was sufficient for complete equilibration at $25 \pm 0.2^\circ\text{C}$. The equilibrated pH in the aqueous phase was measured by a glass electrode (pH meter, Hitachi Horiba, Model F7-ss) within several ranges: 2.2 – 3.8, 2.5 – 3.7, 2.6 – 4.1 and 4.1 – 4.9 for 2-bromooctanoic, 2-bromohexadecanoic, 2-phenylbenzoic and 1-naphthoic acid systems, respectively. The concentrations of copper in both phases were determined complexometrically using EDTA (10 mM or 1 mM) with 4-(2-thiazolylazo)resorcinol (TAR) as an indicator. The other apparatus and procedures were the same as that employed previously.^{4,5}

Results and Discussion

Analysis of extraction equilibria of copper(II) carboxylates

The extraction equilibrium responsible for the formation of a single extracted species, $\text{Cu}_j\text{L}_{2j}(\text{HL})_m$, can be recognized by a simple slope-analysis method, as previously described.^{4,5} When a monomeric species, $\text{CuL}_2(\text{HL})_a$, is extracted together with a dimeric one $\text{Cu}_2\text{L}_4(\text{HL})_b$, however, the extraction equilibrium and the extraction constant ($K_{\text{ex}(jm)}$) should be written as follows:

$$K_{\text{ex}(1a)} = [\text{CuL}_2(\text{HL})_a]_o [\text{H}^+]^2 [\text{Cu}^{2+}]^{-1} [(\text{HL})_2]_o^{-0.5(2+a)}, \quad (1)$$

$$K_{\text{ex}(2b)} = [\text{Cu}_2\text{L}_4(\text{HL})_b]_o [\text{H}^+]^4 [\text{Cu}^{2+}]^{-2} [(\text{HL})_2]_o^{-0.5(4+b)}, \quad (2)$$

where $(\text{HL})_2$ represents the carboxylic acid dimer and subscript o refers to the organic phase. When the total concentration of copper(II) in the organic phase can be written as

$$C_{\text{Cu},o} = [\text{CuL}_2(\text{HL})_a]_o + 2[\text{Cu}_2\text{L}_4(\text{HL})_b]_o \quad (3)$$

we obtain the following equation:

$$\begin{aligned} \log C_{\text{Cu},o} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2}) = & \log K_{\text{ex}(1a)} \\ & + 0.5(2+a)\log[(\text{HL})_2]_o + \log\{1 + 2K_{\text{ex}(2b)}K_{\text{ex}(1a)}^{-1} \\ & \times [\text{Cu}^{2+}][\text{H}^+]^{-2}[(\text{HL})_2]_o^{0.5(2+b-a)}\}. \end{aligned} \quad (4)$$

Then, plots of $\log C_{\text{Cu},o} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2})$ vs. $\log([\text{Cu}^{2+}] \times [\text{H}^+]^{-2})$ at constant $[(\text{HL})_2]_o$ can be fitted on a normalized curve, written as follows:

$$y = \Delta y + \log(1 + 10^{x-\Delta x}), \quad (5)$$

where $(\Delta x, \Delta y)$, expressed by

$$\Delta x = -\log(2K_{\text{ex}(2b)}K_{\text{ex}(1a)}^{-1}) - 0.5(2+b-a)\log[(\text{HL})_2]_o, \quad (6)$$

$$\Delta y = \log K_{\text{ex}(1a)} + 0.5(2+a)\log[(\text{HL})_2]_o, \quad (7)$$

represent the node coordinates of the two asymptotes of the normalized curve. Each of the asymptotes (one with slope 0, another with slope 1), which is expressed by

$$\begin{aligned} \log C_{\text{Cu},o} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2}) = \\ \log\{K_{\text{ex}(1a)}[(\text{HL})_2]_o^{0.5(2+a)}\} \end{aligned} \quad (8)$$

or

$$\begin{aligned} \log C_{\text{Cu},o} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2}) = \\ \log([\text{Cu}^{2+}][\text{H}^+]^{-2}) + \log 2\{K_{\text{ex}(2b)}[(\text{HL})_2]_o^{0.5(4+b)}\}, \end{aligned} \quad (9)$$

shows the linear portion with which the plots have to fit if either $\text{CuL}_2(\text{HL})_a$ or $\text{Cu}_2\text{L}_4(\text{HL})_b$ is singly extracted.

The numbers a and b of acid molecules involved in the coextracted species can be determined by Eq. (7) and

$$\Delta y - \Delta x = \log(2K_{\text{ex}(2b)}) + 0.5(4+b)\log[(\text{HL})_2]_o \quad (10)$$

as a function of $[(\text{HL})_2]_o$. When each of the monomeric and dimeric compositions is consistent, all data plots of $\log C_{\text{Cu},o} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2}) - 0.5(2+a)\log[(\text{HL})_2]_o$ vs. $\log([\text{Cu}^{2+}][\text{H}^+]^{-2}) + 0.5(2+b-a)\log[(\text{HL})_2]_o$ should fit to a single normalized curve,

$$Y = \Delta Y + \log(1 + 10^{X-\Delta X}). \quad (11)$$

Here, the coordinates $(\Delta X, \Delta Y)$ of the node of two asymptotes represent the set value $\{-\log(2K_{\text{ex}(2b)}K_{\text{ex}(1a)}^{-1}), \log K_{\text{ex}(1a)}\}$. We can obtain the optimum values of ΔX and ΔY (or Δx and Δy in Eq.(5)) by means of a non-linear least-squares method (Marquardt method) at the minimum sum of squares ($\sum f_i^2$), defined by

$$\sum_i f_i(X_i)^2 = \sum_i [Y_i - \{\Delta Y + \log(1 + 10^{X_i - \Delta X})\}]^2, \quad (12)$$

where X_i and Y_i denote the experimental data for the plots.

The dimerization constant of copper(II) ($K_{\text{dim}(a,b)}$) in the organic phase for equilibrium is

and can be correlated to the extraction constants as

$$K_{\text{dim}(a,b)} = K_{\text{ex}(2b)} / K_{\text{ex}(1a)}^2. \quad (13)$$

The concentration of copper(II) in the aqueous phase ($C_{\text{Cu},w}$) can be written as

$$[\text{Cu}^{2+}] = C_{\text{Cu},w} / \alpha_{\text{Cu}}, \quad (14)$$

where α_{Cu} shows the side-reaction coefficient of copper(II) in the aqueous phase. It is generally accepted

that α_{Cu} is unity (e.g., $[\text{Cu}^{2+}] = C_{\text{Cu,w}}$) when extractants having a higher distribution ratio ($D_{\text{HL}} (= C_{\text{HL,o}}/C_{\text{HL}})$) are used. When D_{HL} is not very high⁵, however, it is necessary to take into account at least the following side-reaction coefficient:

$$\alpha_{\text{Cu}} = 1 + k_{\text{CuL}}[\text{L}^-], \quad (15)$$

where k_{CuL} is the stability constant of a 1:1 copper(II) carboxylate complex in the aqueous phase. The values of both $[(\text{HL})_2]_0$ and $[\text{L}^-]$ can be calculated under the total acid concentration ($C_{\text{HL,T}}$) in a large excess of copper from the following equation:

$$2K_{\text{D,HL}}^2 K_{2,\text{HL}} [\text{HL}]^2 + (K_{\text{D,HL}} + 1 + K_{\text{a}}/[\text{H}^+]) [\text{HL}] - C_{\text{HL,T}} = 0, \quad (16)$$

where $K_{\text{D,HL}} (= [\text{HL}]_0/[\text{HL}])$, $K_{2,\text{HL}} (= [(\text{HL})_2]_0/[\text{HL}]_0^2)$ and $K_{\text{a}} (= ([\text{H}^+][\text{L}^-])/[\text{HL}])$ denote the partition constant between the organic and the aqueous phases, the dimerization constant in the organic phase and the dissociation constant of carboxylic acid, respectively.

Extraction of copper(II) with 2-bromoaliphatic carboxylic acids

The extractions of copper(II) with 2-bromooctanoic acid and with 2-bromohexadecanoic acid were started at an initial copper concentration of 5 mM.

For the copper(II) 2-bromooctanoate system, it is better to take into account several constants, such as $K_{\text{D,HL}}$, $K_{2,\text{HL}}$, K_{a} and k_{CuL} , because D_{HL} is not very high compared with that of 2-bromohexadecanoic acid. Here, we have adopted estimated values, $\log K_{\text{D,HL}} = 2.20$, $\log K_{2,\text{HL}} = 1.80$, $\text{p}K_{\text{a}} = 2.80$ and $k_{\text{CuL}} = 31.6$, by reference to the literature.^{7,8} Plots of $\log C_{\text{Cu,o}}$ vs. $\log([\text{Cu}^{2+}][\text{H}^+]^{-2})$ for $C_{\text{HL,T}} = 2.0, 1.2, 0.60, 0.30$ and 0.15 M of 2-bromooctanoic acid are given with open symbols in Fig. 1.

Fig. 1 Determinations of the degree of oligomerization for copper(II) 2-bromooctanoate (open symbols) and 2-bromohexadecanoate (closed symbols) in benzene. The solid and dotted curves were drawn on the basis of the result obtained from the present work.

The variation of the plots is depicted by a curve with a slope of 1–2 for each $C_{\text{HL,T}}$, which suggests that both the monomeric and dimeric species should exist. As for the copper(II) 2-bromohexadecanoate system, it is feasible to analyze the extraction equilibrium under the assumption $\alpha_{\text{Cu}} = 1$. Plots of $\log C_{\text{Cu,o}}$ vs. $\log([\text{Cu}^{2+}][\text{H}^+]^{-2})$ are also given with closed symbols in Fig. 1 for $C_{\text{HL,T}} = 0.60, 0.30$ and 0.15 M of 2-bromohexadecanoic acid. The plots varied in analogy with the copper(II) 2-bromooctanoate system. The stability of α -brominated reagents was confirmed by the fact that each curvature was essentially maintained by shortening the shaking time from 1 h to 20 min. Therefore, the plots in Fig. 1 suggest that a monomeric species was extracted together with dimeric copper(II) 2-bromoaliphatic carboxylates. The co-existing monomeric and dimeric species in each system were confirmed by the good fit of plots of $\log C_{\text{Cu,o}} - \log([\text{Cu}^{2+}][\text{H}^+]^{-2})$ vs. $\log[(\text{HL})_2]_0$ with the normalized curves drawn using Eq.(5), which yielded the respective coordinates ($\Delta x, \Delta y$).

The number of acid molecules involved in the monomeric and dimeric copper(II) species can be determined from the slopes on plots of Δy (on the left-hand side of Eq.(7)) and $\Delta y - \Delta x$ (on the left-hand side of Eq.(10)) versus $\log[(\text{HL})_2]_0$, respectively. The values of $[(\text{HL})_2]_0$ in the 2-bromooctanoic acid system were calculated using Eq.(16) as $[(\text{HL})_2]_0 = 0.5(C_{\text{HL,T}} - [\text{HL}]_0 - [\text{L}^-])$, while that in the 2-bromohexadecanoic acid system were calculated by using $K_{2,\text{HL}} = 1.9$ of the acid in the benzene phase^{7,8}, assuming $[(\text{HL})_2]_0 \approx 0.5(C_{\text{HL,T}} - [\text{HL}]_0)$. As shown in Fig. 2, the plots fall on each of the two straight lines (correlation coefficient, $r \geq 0.998$ by using the least-squares method) with slopes of 1.5 for the monomeric species and of 3.0 for the dimeric species in both 2-bromoaliphatic car-

Fig. 2 Determination of the number of 2-bromoaliphatic acid molecules involved in the monomeric and dimeric copper(II) species. The open and closed symbols refer to 2-bromooctanoic and 2-bromohexadecanoic acid systems, respectively.

Fig. 3 Confirmation of the compositions of monomeric and dimeric copper(II) 2-bromoaliphatic carboxylates and determination of the respective extraction constants. See the symbols in Fig. 1. The lines with slopes of 0 and 1 are the asymptotes of the respective normalized curves.

boxylate systems. Then, the values of a and b for both systems were determined to be 1 and 2, which mean that the monomeric and dimeric species can be represented as $CuL_2 \cdot HL$ and $Cu_2L_4(HL)_2$, respectively.

When the two compositions of the extracted species are reasonable, the plots of $\log C_{Cu,o} - \log([Cu^{2+}][H^+]^{-2}) - 1.5 \log[(HL)_2]_o$ vs. $\log([Cu^{2+}][H^+]^{-2}) + 1.5 \log[(HL)_2]_o$ should fit with a single normalized curve represented by Eq.(11) for the 2-bromoaliphatic acid systems. As shown in Fig. 3, all of the data in Fig. 1 fit well with the respective normalized curves with $\sum_{i=1}^n f_i^2 = 0.018$ ($n=56$) for the 2-bromooctanoic acid system and with $\sum_{i=1}^n f_i^2 = 0.023$ ($n=30$) for the 2-bromohexadecanoic acid system. From the coordinates $(\Delta X, \Delta Y)$ of the node of two asymptotes, the extraction constants were determined to be $\log K_{ex(11)} = -5.76$, $\log K_{ex(22)} = -7.97$ for the 2-bromooctanoic acid system and $\log K_{ex(11)} = -5.49$, $\log K_{ex(22)} = -7.97$ for the 2-bromohexadecanoic acid system, respectively. The values of $K_{ex(11)}$ differed slightly, while those of $K_{ex(22)}$ were equal to each other.

Extraction of copper(II) with conjugated carboxylic acids

The extractions of copper(II) with 2-phenylbenzoic acid and with 1-naphthoic acid were started at a total copper concentration of 5 mM and of 0.5 mM, respectively, and were analyzed under the assumption $\alpha_{Cu}=1$ for both systems.

The extraction of copper(II) with 2-phenylbenzoic acid was examined under the $C_{HL,T}=1.0, 0.60, 0.30$ and 0.15 M, while that with 1-naphthoic acid under the lower $C_{HL,T}$: $0.10, 0.070, 0.055$ and 0.040 M because of the much lower solubility of the reagent in benzene. The plots of $\log C_{Cu,o}$ vs. $\log([Cu^{2+}][H^+]^{-2})$ are shown in Fig. 4 with open symbols for the 2-phenylbenzoic acid system and with closed symbols for the 1-naphthoic acid system. The variation in the plots for the 2-phenylbenzoic acid system is depicted by a slightly curved line with $1 \ll \text{slope} \leq 2$ for every $C_{HL,T}$. This result suggests that a small amount of the monomeric

Fig. 4 Determination of the degree of oligomerization for copper(II) 2-phenylbenzoate (open symbols) and 1-naphthoate (closed symbols) in benzene.

Fig. 5 Determination of the number of acid molecules involved in the monomeric and dimeric copper(II) 2-phenylbenzoates.

species co-exists with dimeric copper(II) 2-phenylbenzoate in the organic phase. On the other hand, the plots for the 1-naphthoic acid system obviously reveal the extraction of a monomer together with dimeric copper(II) 1-naphthoate, as shown by the closed symbols in Fig. 4. The degree of oligomerization was confirmed by the fact that plots of $\log C_{Cu,o} - \log([Cu^{2+}][H^+]^{-2})$ vs. $\log([Cu^{2+}][H^+]^{-2})$ fit well with the normalized curve at each $C_{HL,T}$ for the two systems. As for the 2-phenylbenzoic acid system, the number of acid molecules involved in each of the species was determined from the slope of plots of Δy or $\Delta y - \Delta x$ versus $\log[(HL)_2]_o$ based on the assumption $[(HL)_2]_o = C_{HL,T}/2$. As shown in Fig. 5, the plots fall on each of the straight lines with a slope of 2.0 ($r=0.999$) for the monomer or of 3.0 ($r=1.000$) for the dimer. The latter value supports the assumption that $[(HL)_2]_o = C_{HL,T}/2$ is reasonable

Table 1 Several equilibrium constants at 25°C ($I=0.1$ M)

Acid	pK _a	log K _{ex(11)}	log K _{ex(12)}	log K _{ex(22)}	log K _{dim(1,2)}	log K _{dim(2,2)}
1. 1-Adamantanecarboxylic ⁴	4.92			-11.45		
2. Decanoic ³	4.92		-8.91	-11.45		6.37
3. Pivalic ⁵	4.86			-11.70		
4. 2-Ethylbutyric ⁵	4.54			-10.99		
5. Phenylacetic ¹⁰	4.13	-8.07	-7.30	-10.41	5.73	4.19
6. Diphenylacetic ⁵	3.64			-9.25		
7. 2-Bromohexadecanoic	2.80 ^a	-5.49		-7.97	3.01	
8. 2-Bromooctanoic	2.80 ^a	-5.76		-7.97	3.55	
9. 2-Bromopentanoic ⁷	2.79			-7.87		
10. Benzoic ¹¹	4.04 ^b		-7.42	-11.40		3.44
10'. Benzoic ¹²	4.04	-7.63		-11.38	3.88	
11. 1-Naphthoic	3.52		-6.96	-10.83		3.09
11'. 1-Naphthoic ⁹	3.52		-6.90	-10.77		3.03
12. 2-Phenylbenzoic	3.35 ^c		-7.13	-9.92		4.34

a. Estimated by Refs. 7 and 8. b. Ref.12. c. Calculated from the data in Ref. 13.

Fig. 6 Confirmation of the compositions of monomeric and dimeric copper(II) 2-phenylbenzoates and 1-naphthoates, and determination of the respective extraction constants. See the symbols in Fig. 4.

for this system. Then, the compositions of the monomeric and dimeric species can be represented as $\text{CuL}_2(\text{HL})_2$ and $\text{Cu}_2\text{L}_4(\text{HL})_2$, respectively. In the 1-naphthoic acid system, however, plots of $\Delta y - \Delta x$ vs. $\log(\text{C}_{\text{HL,T}}/2)$ yielded a slope $0.5(4+b)$ of ca. 3.6, which gave an unreasonable composition $\text{Cu}_2\text{L}_4(\text{HL})_3$ for the dimeric species. It is obviously caused by the assumption $[(\text{HL})_2]_o \doteq \text{C}_{\text{HL,T}}/2$ which may not be valid under the much lower $\text{C}_{\text{HL,T}}$. We then adopted a computational method based on the fixed dimeric composition of $\text{Cu}_2\text{L}_4(\text{HL})_2$ to obtain the tentative values of $K'_{\text{ex(22)}}$ and K'_{HL} , as described previously.⁵ Supposing that the concentration of free acid ($2[(\text{HL})_2]_o + [\text{HL}]_o$) nearly equals $\text{C}_{\text{HL,T}}$ under our experimental conditions, the values of $\log K'_{\text{ex(22)}}$ and $\log K'_{\text{HL}}$ were calculated to be -10.84 and 2.58, respectively. From a slope analysis for plots of Δy against the calculated $\log[(\text{HL})_2]_o$, the composition and extraction constant for the monomeric species were derived as $\text{CuL}_2(\text{HL})_2$ and $\log K'_{\text{ex(12)}} = -6.99$,

respectively.

The validity of the compositions was confirmed by the fact that plots of $\log C_{\text{Cu,o}} - \log([Cu^{2+}][H^+]^{-2}) - 2\log[(\text{HL})_2]_o$ vs. $\log([Cu^{2+}][H^+]^{-2}) + \log[(\text{HL})_2]_o$ fit well with the respective single normalized curves, as shown in Fig. 6 with $\sum_{i=1}^n f_i^2 = 0.029$ ($n=54$) for 2-phenylbenzoic acid system (open symbols) and with $\sum_{i=1}^n f_i^2 = 0.025$ ($n=38$) for 1-naphthoic acid system (closed symbols), respectively. From the coordinates ($\Delta X, \Delta Y$), the extraction constants of the monomeric and dimeric species were finally determined to be $\log K_{\text{ex(12)}} = -7.13$, $\log K_{\text{ex(22)}} = -9.92$ for the 2-phenylbenzoic acid system and $\log K_{\text{ex(12)}} = -6.96$, $\log K_{\text{ex(22)}} = -10.83$ for the 1-naphthoic acid system, respectively. The compositions of copper(II) 1-naphthoates agreed with those of the recent literature, where values of $\log K_{\text{ex(12)}} = -6.90$ and $\log K_{\text{ex(22)}} = -10.77$ were reported.⁹

Correlations among $\log K_{\text{ex(jm)}}$, $\log K_a$ and $\log K_{\text{dim(a,b)}}$

The extraction constants ($K_{\text{ex(jm)}}$) for the monomeric and dimeric copper(II) species obtained in this work and the dimerization constant of copper(II) ($K_{\text{dim(a,b)}}$), calculated by Eq.(13), are summarized in Table 1 together with other constants reported in the literature.^{3,7,9,10-13} The system number (from 10 to 12 in italics) corresponds to a conjugated acid system. In the copper(II) 2-bromoaliphatic carboxylate system, we found the monomeric and dimeric copper(II) species (neither single monomeric nor single dimeric one) at $C_{\text{Cu,o}} \geq 10^{-4}$ M, as described above. The existence of the monomeric copper(II) species in this system would not be due to a steric effect of the bromine at the α -position, because no evidence of a monomer was found at $C_{\text{Cu,o}}$ above 10^{-4} M in such a system as 1-adamantanecarboxylic, pivalic, 2-ethylbutyric or diphenylacetic acid in benzene.^{4,5} The extraction of a monomer together with the dimeric copper(II) species was also found in conjugated acid systems.

The result obtained in this work is very significant for

Fig. 7 Relationship between the extraction constant of copper(II) carboxylate and the dissociation constant of the corresponding acid. See the numbers in Table 1. Open symbols are our works. Straight lines A, B and C were tried to apply to the plots for $\text{Cu}_2\text{L}_4(\text{HL})_2$ (except for No. 9, 10 - 12), $\text{CuL}_2\cdot\text{HL}$ and $\text{CuL}_2(\text{HL})_2$ (except for No. 12), respectively.

clarifying the chemical character of the functional carboxyl group and for estimating the extraction of monomeric species in acid systems. Fujii *et al.* have proposed⁷ an equation, $\log K_{\text{ex}(22)} = 1.7 \log K_a - 3.2$, for the aliphatic carboxylic acid system. In fact, the equation fitted well with plots of $\log K_{\text{ex}(22)}$ vs. $\log K_a$ for nonconjugating acid systems, as described previously.⁵ When we use $\log K_a$ and $\log K_{\text{ex}(22)}$ of the series numbered from 1 to 8 in Table 1, we merely find a slightly renewed equation,

$$\log K_{\text{ex}(22)} = 1.71 \log K_a - 3.17, \quad (17)$$

with $r=0.996$, which is drawn as a solid line (A) in Fig. 7.

On the other hand, it is worth correlating $\log K_{\text{ex}(1a)}$ (as well as the $\log K_{\text{ex}(22)}$) to $\log K_a$. We obtain two empirical equations,

$$\log K_{\text{ex}(11)} = 1.74 \log K_a - 0.75 \quad (18)$$

and

$$\log K_{\text{ex}(12)} = 1.37 \log K_a - 1.97, \quad (19)$$

for $\text{CuL}_2\cdot\text{HL}$ and $\text{CuL}_2(\text{HL})_2$ (except for No. 12 in Table 1) with $r=0.992$ and 0.963 , which are drawn as solid lines (B) and (C) in Fig. 7, respectively. The deviation of the plot for monomeric 2-phenylbenzoate (numbered as 12) may suggest a steric hindrance by the *ortho*-phenyl group of benzoic acid. In the other systems, Eqs.(18) and (19) could be used to estimate $K_{\text{ex}(11)}$ and $K_{\text{ex}(12)}$ by using K_a in both the conjugated and nonconjugated acid systems in benzene.

Fig. 8 Schematic drawing of the structures envisaged for copper(II) carboxylates extracted in this work. The symbol A refers to an alkyl or aryl group.

The monomers $\text{CuL}_2(\text{HL})_2$ and $\text{CuL}_2\cdot\text{HL}$ may be stipulated as (1-1) and (1-2) in Fig. 8, where dimeric carboxylate coordinates to copper(II) as a bidentate ligand³ LHL^- , though the water molecule in (1-2) is not distinguishable from the dissolved water in the benzene phase, because of the much lower concentration of the monomeric species. The validity of Eqs. (18) and (19) for both systems of conjugated and nonconjugated acids may then be explained based on the idea that the bidentate ligand does not resonate. On the other hand, the dimer $\text{Cu}_2\text{L}_4(\text{HL})_2$ for nonconjugated acid systems, such as the decanoic acid system³, may be envisaged as (2-1) in Fig. 8, where the four carboxyl groups bridge between the two copper(II) ions. The plots for the conjugated acid systems (No. 10 - 12), however, deviate to a great extent from line (A) in Fig. 7. For the systems, therefore, it may be feasible to envisage another dimeric structure, (2-2) in Fig. 8. In any case, the deviations would be correlated to the change of the dipole moment affected by electronic delocalization with resonance over the conjugated ligand in the bridging form.

Based on the empirical Eqs.(17) - (19), Eq.(13) for the $\text{CuL}_2\cdot\text{HL}$ and $\text{CuL}_2(\text{HL})_2$ could be rewritten as

$$\log K_{\text{dim}(1,2)} = \log K_{\text{ex}(22)} - 2 \log K_{\text{ex}(11)} = 1.77 \text{p}K_a - 1.67 \quad (20)$$

and

$$\log K_{\text{dim}(2,2)} = \log K_{\text{ex}(22)} - 2 \log K_{\text{ex}(12)} = 1.03 \text{p}K_a - 0.77, \quad (21)$$

respectively. It is natural that the coextraction phenomena of a monomer together with a dimer is easily found in such a system of $K_{\text{dim}(a,b)}$ much lower than 2.34×10^6 of the copper(II) decanoate system.³ The Eqs.(20) and (21) suggest that the coextraction phenomena would be caused by acid systems of lower $\text{p}K_a$ or of lower $\log$

$K_{\text{ex}(22)}$; the former has been verified by the 2-bromo-aliphatic acid systems while the latter was verified by the conjugated acid systems as a result of this work. Furthermore, Eqs. (17) – (21) will be useful to search for a suitable extraction system of copper(II) carboxylate in a nonpolar solvent.

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