No Evidence of the Monomer in the Extraction of Copper(II) with Carboxylic Acids Having Bulky Substituent at α -Position

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The extraction behavior of copper(II) with three carboxylic acids having a bulky substituent at the α -position was investigated in order to clarify the steric effect on the dimerization of copper(II) carboxylate extracted in benzene. Pivalate and 2-ethylbutyrate were found to be extracted only as a dimeric species $\text{Cu}_2\text{L}_4(\text{HL})_2$ through the slope analyses, taking into account the formation constant of (1:1) copper carboxylate complex in the aqueous phase. A new computing method based on fixing the species to the composition, $\text{Cu}_2\text{L}_4(\text{HL})_2$, was proposed to estimate both the dimerization constant of carboxylic acid ($K_{2,\text{HL}}$) and the extraction constant of the dimeric copper species ($K_{\text{ex}(22)}$) for the case of carboxylic acid of higher carbon number in nonpolar solvents, and the extracted diphenylacetate was also found to be only a dimer as is usual. Consequently, under our experimental conditions, there was no evidence for the coextraction of monomeric copper(II) species caused by the steric hindrance as reported in other papers. Moreover, a linear relationship between $\log K_{\text{ex}(22)}$ and $\log K_a$ was maintained by adding the three bulky substituent carboxylic acids.

Keywords Extraction, copper(II), carboxylic acid, bulky substituent, steric hindrance, monomer

The extraction behavior of metals with carboxylic acids depends first on the bonding character of the metal ions to the oxygen atoms of the functional carboxyl group.¹ On the other hand, the influence of the carboxylic acid residue on metal extraction behavior can be sited as a secondary factor in the sense that it affects the extraction equilibria of the copper(II) carboxylates. This comes about the central copper(II) ion can occasionally be extracted as a monomeric species along with the well-known dimeric species, $\text{Cu}_2\text{L}_4(\text{HL})_2$, with certain carboxylic acids in nonpolar solvents.² A monomeric copper(II) carboxylate such as $\text{CuL}_2(\text{HL})_2$ would be extracted in preference to the dimeric one. The copper(II) decanoate system³ has been analyzed in the low concentration region present in the organic phase ($C_{\text{Cu},o} < 10^{-5}$ M). The coextraction of a monomer accompanied by a dimer in the region of $C_{\text{Cu},o}$ above 10^{-4} M was first reported by using pivalic acid in toluene.⁴ Similar behaviors were found in the systems of cyclohexanecarboxylic acid⁵, pivalic acid⁶, phenylacetic acid⁷, benzoic acid⁸ and recently in that of 1-naphthalenecarboxylic acid⁹ in benzene. Furthermore, a single monomeric species also has been reported for the system of 2-bromododecanoic acid¹⁰ in hexane. As for the system of 1-adamantanecarboxylic acid in benzene, however, we could not obtain any evidence for the coextraction of the monomeric copper species in the region of $C_{\text{Cu},o}$ above 30 μM as has already been described in a previous report.¹¹ The above result requires further experiment, in particular on the steric hindrance that is caused by some substituents contained in the carboxylic

acid.

In this paper, we describe the extraction behavior of copper(II) with three carboxylic acids (pivalic, 2-ethylbutyric and diphenylacetic acids) possessing bulky substituents at the α -position, in order to clarify the steric effect on the dimerization of copper(II) carboxylate extracted in benzene. We have also proposed a new method for the estimation of the two unknown constants in a nonpolar solvent system, *i.e.*, dimerization constant of carboxylic acid ($K_{2,\text{HL}}$) and extraction constant of dimeric copper(II) species ($K_{\text{ex}(22)}$), since we often face the need to use such constants when an acid of higher carbon number has to be examined.

Experimental

Reagents

Commercially obtained carboxylic acids (purities: over 99%, Tokyo Chemical Industry Co. Ltd.); pivalic, 2-ethylbutyric and diphenylacetic acids were dissolved in benzene saturated with deionized and distilled water. Copper(II) nitrate (purity 99.9%, Wako Pure Chem. Co. Ltd.) was employed to study the copper(II) extraction equilibria at a constant ionic strength ($I=0.1$ M, $(\text{Na},\text{H})\text{NO}_3$) as in our previous work.¹ However, perchloric acid and sodium perchlorate (Wako Pure Chem. Co. Ltd.) were also used for the fundamental studies of equilibria on both the dissociation and the partition of carboxylic acids or of the photometric determination of the aqueous formation constant of copper(II) car-

boxylate complex under the constant ionic strength ($I=0.1$ M, $(\text{Na,H})\text{ClO}_4$). For the latter, copper(II) perchlorate was prepared by the reaction of metallic copper (E. Merck, purity 99.99%) with 60% perchloric acid. All other chemicals were of analytical reagent grade.

Apparatus and procedure

The extractions of copper(II) carboxylates were carried out by mixing the same volume (10 ml) of aqueous and organic solutions under the following conditions: an initial copper concentration of 5 mM in aqueous phase and a total concentration in the region of 0.15–0.6 M of pivalic acid and 2-ethylbutyric acid, in benzene, and an initial copper(II) concentration of 2 mM and a total concentration in the region of 0.08–0.18 M of diphenylacetic acid in benzene. 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. Apparatus and the other procedures were the same as employed previously.¹¹

Results and Discussion

Several equilibrium constants

For the analyses of the extraction equilibria of metal carboxylates, we must obtain information on the partition of carboxylic acid itself, especially, of the lower fatty acids, since such information could not be found in the literature. For the pivalic acid or the 2-ethylbutyric acid systems, information is also needed about the formation constant of copper(II) complex in the aqueous phase, and also the dissociation constant of the carboxylic acid will be needed to be determined. These values relate to the side reaction coefficients in the aqueous phase and are used to analyze the extraction equilibria more precisely.

1. Dissociation constants

We determined the dissociation constants $K_a(=[\text{H}^+](\text{L}^-)/[\text{HL}])$ of pivalic acid and of 2-ethylbutyric acid in the aqueous phase potentiometrically at 25°C to be $10^{-4.86}$ and $10^{-4.54}$, respectively, after the correction of the activity coefficient of H^+ ion (γ_{H^+}) at $I=0.1$. The value of K_a for the diphenylacetic acid was photometrically determined using the equation:

$$C_{\text{HL}}^0/(A-A_{\text{HL}}^0)=1/(\varepsilon_{\text{L}^-}-\varepsilon_{\text{HL}})+[\text{H}^+]/\{(\varepsilon_{\text{L}^-}-\varepsilon_{\text{HL}})K_a\}, \quad (1)$$

where A_{HL}^0 and A denote the absorbances for the solution of undissociated carboxylic acid (HL) and for the equilibrated solution (HL and L^-) at the $[\text{H}^+]$ under the initial concentration C_{HL}^0 , while ε_{HL} and ε_{L^-} denote the molar absorption coefficients for carboxylic acid and for carboxylate ion, respectively. The solutions mentioned above were easily prepared by adding a trace amount (within a small droplet) of the concentrated solution of

HClO_4 or of NaOH to a 30–50 ml volume of the initial aqueous solution. A combination glass electrode was then inserted for pH measurement to maintain the final concentration of carboxylic acid as close to the initial concentration of C_{HL}^0 , i.e., within our experimental error. The mean value for K_a was $10^{-3.64}$ for the diphenylacetic acid under the conditions: C_{HL}^0 ; 0.1 mM, range of wavelength; 220–228 nm and pH range; 1.49–4.25. In the same manner, we also obtained $K_a=10^{-3.92}$ for 1-adamantanecarboxylic acid, with which we had previously dealt¹¹, under the conditions: C_{HL}^0 , 0.4 mM; wavelength, 200–210 nm and pH, 3.0–5.5.

2. Partitions of pivalic and 2-ethylbutyric acid

The partition ratio D of a carboxylic acid between the organic and the aqueous phase can be represented as:

$$D=C_{\text{HL,o}}/C_{\text{HL,w}} \\ = (K_{\text{D,HL}}+2K_{2,\text{HL}}K_{\text{D,HL}}^2[\text{HL}])(1+K_a/[\text{H}^+])^{-1}, \quad (2)$$

where $K_{\text{D,HL}}$ and $K_{2,\text{HL}}$ denote the partition constant between the organic and the aqueous phases and the dimerization constant in the organic phase, respectively. Since the aqueous dissociation of carboxylic acid can be ignored under such conditions $\text{pH} < (\text{p}K_a-2)$, the factor $(1+K_a/[\text{H}^+])^{-1}$ can be taken as unity. Then we can obtain the values of $K_{\text{D,HL}}$ and $K_{2,\text{HL}}$ from the intercept ($K_{\text{D,HL}}$) and the slope ($2K_{2,\text{HL}}K_{\text{D,HL}}^2$) of the straight line from the plot of D against $[\text{HL}]$. The partition was carried out between benzene and 1 mM perchloric acid containing 99 mM sodium perchlorate. The concentrations of carboxylic acid in both phases after equilibration were determined titrimetrically with the standard sodium hydroxide as described in the literature.¹² From Fig. 1, the values of $\log K_{\text{D,HL}}$ and $\log K_{2,\text{HL}}$ were calculated to be -0.03 , 2.32 for (a) pivalic acid and to be 0.04 , 2.83 for (b) 2-ethylbutyric acid, respectively. The values of the former were comparable to the known values⁶ of 0.02 , 2.16 .

3. Formation of copper(II) carboxylate in aqueous solution

Considering that the $[\text{HL}]$ calculated by Eq. (2) is relatively low for the system of pivalic acid and 2-ethylbutyric acid systems and that the stability constants k_{CuL} for the (1:1) copper(II) carboxylates¹³ are around 10^2 (that belong to a so-called weak complex), it is feasible for us under our experimental conditions to take into account of only the (1:1) copper(II) carboxylate formation equilibrium:

which relates to the side reaction coefficient in the aqueous phase. The formation constant K_1 for copper(II) pivalate or 2-ethylbutyrate in aqueous solution was determined by means of spectrophotometry. When the molar concentration of CuL^+ after equilibration at the $[\text{H}^+]$ is represented by X under the condition

Fig. 1 Determinations of the distribution constant between benzene and aqueous phases and of the dimerization constant in the organic phase for (a) pivalic acid and (b) 2-ethylbutyric acid.

where the molar concentration (C^0) of copper(II) is equal to that of carboxylic acid, the formation constant K_1 can be written as Eq. (4):

$$K_1 = X[H^+]/(C^0 - X)^2. \quad (4)$$

The absorbance of the solution is represented as:

$$A = X\varepsilon_{CuL} + (C^0 - X)\varepsilon_{HL} + (C^0 - X)\varepsilon_{Cu} \\ = X(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu}) + A_{HL}^0 + A_{Cu}^0, \quad (5)$$

where ε_{Cu} and ε_{CuL} denote the molar absorption coefficients for hydrated Cu^{2+} ion and for (1:1) copper(II) carboxylate complex, respectively, and A_{Cu}^0 is the absorbance for aqueous copper(II) solution at the initial concentration C^0 . Therefore, we can derive the final Eq. (6) by combining Eq. (4) with $X = (A - A_{HL}^0 - A_{Cu}^0)/(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu})$ from Eq. (5):

$$C^0/(A - A_{HL}^0 - A_{Cu}^0) = 1/(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu}) \\ + [1/\{(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu})K_1\}]^{1/2} \{ [H^+]/(A - A_{HL}^0 - A_{Cu}^0) \}^{1/2}. \quad (6)$$

The linear plots of $C^0/(A - A_{HL}^0 - A_{Cu}^0)$ vs. $\{[H^+]/(A - A_{HL}^0 - A_{Cu}^0)\}^{1/2}$ obtained at several values of pH and wavelength for an initial concentration of $C^0 = 9.83 \times 10^{-3}$ M are shown in Fig. 2(a) for copper(II) pivalate and Fig. 2(b) for copper(II) 2-ethylbutyrate. Since the value of K_1 is obtained from the intercept, $1/(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu})$ and the slope $\{1/(\varepsilon_{CuL} - \varepsilon_{HL} - \varepsilon_{Cu})K_1\}^{1/2}$, the stability constant, $k_{CuL} (= [CuL^+][Cu^{2+}]^{-1}[L^-]^{-1})$ can be calculated as:

$$k_{CuL} = K_1/K_a \quad (7)$$

The mean value of $\log k_{CuL}$ was calculated to be 2.10 for copper(II) pivalate and 1.92 for copper(II) 2-ethylbutyrate.

Extraction of copper(II) carboxylates

When the extracted species is generally expressed as

Fig. 2 Determination of the formation constant for (1:1) copper(II) carboxylate complex in the aqueous solution at the initial concentrations $C^0 = C_{HL}^0 = C_{Cu}^0 = 9.83 \times 10^{-3}$ M. Ligand: (a) pivalic acid, (b) 2-ethylbutyric acid.

Fig. 3 Determination of the degree of oligomerization for (a) copper(II) pivalate or (b) copper(II) 2-ethylbutyrate in benzene. Open symbols show the experimental data. Solid lines are calculated from the results obtained in this work. Closed marks are calculated as $\alpha_{Cu}=1$.

$Cu_jL_{2j}(HL)_m$, the extraction equilibrium and the extraction constant can be written as follows:

where $(HL)_2$ represents the carboxylic acid dimer in a nonpolar solvent and the subscript o refers to the organic phase. Then, the total concentration of copper(II) in the organic phase can be expressed as follows:

$$C_{Cu,o} = \sum_j \sum_m j [Cu_jL_{2j}(HL)_m]_o \\ = \sum_j \sum_m (jK_{ex(jm)} [(HL)_2]_o^{0.5(2j+m)} [Cu^{2+}]^j [H^+]^{-2j}) \quad (9)$$

When only one species of $Cu_jL_{2j}(HL)_m$ exists in the organic phase, the following equation is obtained:

$$\log C_{Cu,o} = j(\log[Cu^{2+}] - 2\log[H^+]) \\ + 0.5(2j+m)\log[(HL)_2]_o + \log(jK_{ex(jm)}) \quad (10)$$

The concentration of copper(II) in the aqueous phase, $C_{Cu,w}$ can be used for $[Cu^{2+}]$ in Eq. (10), when we ignore the concentration of the carboxylic acid distributed into the aqueous phase as in the case of diphenylacetic acid.

In the case of pivalic acid or 2-ethylbutyric acid, however, it is necessary to take into account at least the following side reaction coefficient:

$$\alpha_{Cu} = 1 + k_{CuL}[L^-] \quad (11)$$

which is based on the formation of 1:1 copper(II) carboxylate complex in the aqueous phase because of their lower $K_{D,HL}$ values. Therefore, Eq. (10) must be rewritten by replacing $[Cu^{2+}]$ by $C_{Cu,w}/\alpha_{Cu}$ to yield the following equation:

$$\log C_{Cu,o} = j\{\log(C_{Cu,w}/\alpha_{Cu}) - 2\log[H^+]\} \\ + 0.5(2j+m)\log[(HL)_2]_o + \log(jK_{ex(jm)}) \quad (12)$$

The values of both $[(HL)_2]_o$ and $[L^-]$ for the above two acids can be calculated from the next Eq. (13) under the total acid concentration $C_{HL,T}$ in a large excess of copper:

$$2K_{D,HL}^2 K_{2,HL} [HL]^2 + (K_{D,HL} + 1 + \\ K_a/[H^+])[HL] - C_{HL,T} = 0 \quad (13)$$

1. Extractions of copper(II) pivalate and 2-ethylbutyrate

The extraction of copper(II) with pivalic acid or with 2-ethylbutyric acid was started at an initial copper concentration (5 mM). The plots of $\log C_{Cu,o}$ vs. $\log(C_{Cu,w}/\alpha_{Cu}) - 2\log[H^+]$ for $C_{HL,T}=0.60, 0.30$ and 0.15 M of pivalic acid and of 2-ethylbutyric acid are shown in Figs. 3(a) and 3(b), respectively. Linear relationships with a slope (j) of 2.0 are observed for each $C_{HL,T}$, and the result shows that the extracted species may be only a dimer for both pivalic and 2-ethylbutyric acid systems. It should be noted in the figure that an unreasonable nonlinear relation is produced (closed symbols are plotted if $\alpha_{Cu}=1$ in Figs. 3(a) and 3(b)) unless one takes into account of the formation of copper carboxylate in aqueous phase.

The plots of $\log C_{Cu,o} - 2\{\log(C_{Cu,w}/\alpha_{Cu}) - 2\log[H^+]\}$ vs. $\log[(HL)_2]_o$ gave a linear relation with a slope of 3.0 that means the integer $m=2$ for (a) pivalic acid or (b) 2-

Fig. 4 Determination of the number of (a) pivalic acid molecules and of (b) 2-ethylbutyric acid molecules involved in their dimeric copper(II) species. The slope is 3.0 for the solid line.

ethylbutyric acid, as shown in Fig. 4. Therefore, the likely composition must be $\text{Cu}_2\text{L}_4(\text{HL})_2$ for both extracted species.

If the $\text{Cu}_2\text{L}_4(\text{HL})_2$ composition is the only extracted species, then all of the data in Figs. 3(a) or 3(b) should fit to the equation:

$$\begin{aligned} \log C_{\text{Cu},o} - 3\log[(\text{HL})_2]_o \\ = 2\{\log(C_{\text{Cu},w}/\alpha_{\text{Cu}}) - 2\log[\text{H}^+]\} + \log(2K_{\text{ex}(22)}). \end{aligned} \quad (14)$$

The plots of $\log C_{\text{Cu},o} - 3\log[(\text{HL})_2]_o$ vs. $2\{\log(C_{\text{Cu},w}/\alpha_{\text{Cu}}) - 2\log[\text{H}^+]\}$ are shown in Fig. 5 for every combination of $C_{\text{HL},T}$ of (a) pivalic acid and of (b) 2-ethylbutyric acid. The two plots both fit well with their respective straight lines with a slope of 1.0 (correlation coefficient, $r=1.000$ by using the least squares method). This result shows that the extracted species is $\text{Cu}_2\text{L}_4(\text{HL})_2$ and also that there is no evidence for the monomeric species with our experimental conditions. The intercept at $2\{\log(C_{\text{Cu},w}/\alpha_{\text{Cu}}) - 2\log[\text{H}^+]\}=0$ in Fig. 5 yields the value of $\log(2K_{\text{ex}(22)})$. Thus, we obtained $\log K_{\text{ex}(22)} = -11.70$ for dimeric copper(II) pivalate and -10.99 for dimeric copper(II) 2-ethylbutyrate. The former is slightly higher than that reported as -11.81 .⁶

2. Extraction of copper(II) diphenylacetate

The extractions of copper(II) with diphenylacetic acid were carried out under the following experimental conditions: a 2 mM aqueous solution of the initial copper and a total acid concentration, $C_{\text{HL},T}$; 0.18, 0.12 and 0.08 M, because of the lower solubility of the acid in benzene. Considering the lower solubility of diphenylacetic acid in water (*ca.* 0.1 mM), the assumption $\alpha_{\text{Cu}}=1$ will be acceptable in our experimental conditions.

Fig. 5 Confirmations of the composition $\text{Cu}_2\text{L}_4(\text{HL})_2$ and the extraction constant for (a) pivalate and for (b) 2-ethylbutyrate. See the captions in Fig. 3.

Fig. 6 Determination of the degree of oligomerization for copper(II) diphenylacetate in benzene. Solid lines are calculated from the results obtained in this work.

The plots of $\log C_{\text{Cu},o}$ vs. $\log C_{\text{Cu},w} - 2\log[\text{H}^+]$ are shown in Fig. 6. A linear relation with a slope of 2.0 is observed for each $C_{\text{HL},T}$ measurement. The results show that the extracted species could only be a dimer in the concentration range $-4.2 < \log C_{\text{Cu},o} < -2.7$. The linear plots of $\log C_{\text{Cu},o} - 2\{\log C_{\text{Cu},w} - 2\log[\text{H}^+]\}$ vs. $\log(C_{\text{HL},T}/2)$, however, yield a slope of *ca.* 3.5 which produced an impossible composition of $\text{Cu}_2\text{L}_4(\text{HL})_3$, which seems to be caused by the assumption, $[(\text{HL})_2]_o = C_{\text{HL},T}/2$ adopted due to lack of a value for $K_{2,\text{HL}}$, in spite of the low $C_{\text{HL},T}$.

According to the literature², we can suppose that the

Table 1 Several equilibrium constants

	Acid	pK _a	log K _{D,HL}	log K _{2,HL}	log K _{ex(22)}
1.	Pivalic	4.86	-0.03	2.32	-11.70
2.	2-Ethylbutyric	4.54	0.08	2.75	-10.99
3.	Diphenylacetic	3.64	—	1.67	-9.25
4.	1-Adamantanecarboxylic	4.92	—	—	-11.45 ¹¹
5.	Decanoic ³	4.92	2.41	2.80	-11.45
6.	Phenylacetic ⁷	4.13	0.19	1.68	-10.41
7.	2-Bromopentanoic ¹⁴	2.79	0.41	1.75	-7.87

dimeric copper(II) carboxylate extracted into nonpolar solvents ought to be Cu₂L₄(HL)₂. Therefore, both constants K_{ex(22)} and K_{2,HL} must be calculated by using a fixed composition and all the extraction data in Fig. 6 through out the following procedure.

If the composition, Cu₂L₄(HL)₂ is reasonable as the only extracted species, Eq. (14) must be valid when [(HL)₂]_o is known under the assumption, α_{Cu}=1. Since the aqueous [HL] is negligible under our experimental conditions, the concentration of free carboxylic acid in the organic phase can be written as:

$$\begin{aligned} C_{\text{HL},o}^f &= C_{\text{HL},T} - 6[\text{Cu}_2\text{L}_4(\text{HL})_2]_o \\ &= C_{\text{HL},T} - 3C_{\text{Cu},o} = 2[(\text{HL})_2]_o + [\text{HL}]_o, \end{aligned} \quad (15)$$

where [HL]_o can be obtained by using K_{2,HL}=[(HL)₂]_o/[HL]_o² from the following equation:

$$2K_{2,\text{HL}}[\text{HL}]_o^2 + [\text{HL}]_o - C_{\text{HL},o}^f = 0. \quad (16)$$

Then, [(HL)₂]_o in Eq. (14) under α_{Cu}=1 can be written as follows:

$$\begin{aligned} [(\text{HL})_2]_o &= (C_{\text{HL},o}^f - [\text{HL}]_o)/2 \\ &= 0.5[C_{\text{HL},o}^f + \{1 - (1 + 8K_{2,\text{HL}}C_{\text{HL},o}^f)^{1/2}\}/(4K_{2,\text{HL}})]. \end{aligned} \quad (17)$$

When variables Y_i, X_i and parameters p₁, p₂ are defined as

$$Y_i = \log C_{\text{Cu},o} - 2(\log C_{\text{Cu},w} - 2\log[\text{H}^+]), \quad X_i = C_{\text{HL},o}^f \quad (18)$$

$$p_1 = K_{2,\text{HL}}, \quad p_2 = \log(2K_{\text{ex(22)}}), \quad (19)$$

a residual function f_i for the difference of both sides of Eq. (14) is written as the following equation:

$$f_i = Y_i - 3\log\left[0.5\left\{X_i + \frac{1 - (1 + 8p_1X_i)^{1/2}}{4p_1}\right\}\right] - p_2. \quad (20)$$

Then, we can obtain the optimum values of p₁ and p₂ in Eq. (19) at the minimum sum of squares, Σ_if_i², by means of a nonlinear least squares method (Marquardt

method). The values of K_{2,HL} for diphenylacetic acid and of log(2K_{ex(22)}) for dimeric copper(II) diphenylacetate were calculated to be 47.3 and -8.95, which give log K_{2,HL}=1.67 and log K_{ex(22)}=-9.25, respectively. By using the value of K_{2,HL}=47.3, the plots of log C_{Cu,o}-3log[(HL)₂]_o vs. 2{log C_{Cu,w}-2log[H⁺]} produced a linear relationship with a slope of 1.0 (r=0.998).

Correlation between log K_{ex(22)} and log K_a

Consequently, the extraction equilibria and the extraction constants for the three copper(II) carboxylates which are studied in this work are represented in the same equation as:

in the concentration range, C_{Cu,o}>3 μM. The values are summarized in Table 1 together with other constants reported in the literature.^{3,7,11,14} The values of log K_{ex(22)} decrease in the following order:

2-bromopentanoic>diphenylacetic>phenylacetic>2-ethylbutyric>decanoic=1-adamantanecarboxylic>pivalic acid.

The dissociation constants of the acids decrease in the same order. The plots of log K_{ex(22)} vs. log K_a are shown in Fig. 7 with a solid line that shows the equation:

$$\log K_{\text{ex(22)}} = 1.7 \log K_a - 3.2, \quad (22)$$

which has already been proposed by Fujii *et al.*¹⁴ They have obtained the equation by connecting the values (log K_a, log K_{ex(22)}) for aliphatic carboxylic acid and for 2-bromopentanoic acid. The plots of our experimental data (No. 1-4, open circles) also fit well with the straight line shown in Fig. 7 including other data (open squares). According to the results obtained in this work, we conclude that the introduction of the more bulky substituent at the α-position in carboxylic acid does not interfere with the dimerization of copper(II) carboxylates significantly.

Thus, we can suppose that (1) the effect of the steric hindrance caused by substituents at the α-position in the acids on the dimerization of copper(II) carboxylate is not so significant, that (2) the extraction constant for most of

Fig. 7 Relation between the extraction constant of dimeric copper(II) carboxylate and the aqueous dissociation constant of the corresponding acid. The numbers in the figure are the same as those in Table 1. Solid line represents the equation: $\log K_{\text{ex}(22)} = 1.7 \log K_a - 3.2$.¹⁴

the dimeric copper(II) complexes in benzene can be predicted by Eq. (22) except for carboxylates such as benzoate⁸ and 1-naphthalenecarboxylate⁹, and that (3) the phenomenon of the coextraction of a monomeric copper(II) carboxylate accompanied with a dimeric copper(II) carboxylate comes about from a factor different from that of (1). Therefore, we will continue to investigate on this area in the near future.

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