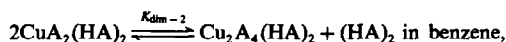**Pergamon**

EFFECT OF PHENYL SUBSTITUENT ON THE DIMERIZATION OF COPPER(II)-CARBOXYLATE IN SOLVENT EXTRACTION OF COPPER(II) WITH PHENYLACETIC ACID

HIROMICHI YAMADA,* YOSHIHIRO TAGUCHI and HIROKO WADA

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Summary—The effects of the phenyl substituent on the dimerization of copper(II) carboxylate in the solvent extraction of copper(II) with phenylacetic acid using benzene and 1-octanol as a solvent were investigated, at 25° and at the aqueous ionic strength of $0.1M$ (NaClO$_4$). The dimerization of copper(II) phenylacetate has been found to be written as:

$$2CuA_2 \xrightleftharpoons{K_{dim-1}} Cu_2A_4 \text{ in 1-octanol, and}$$

$$2CuA_2(HA)_2 \xrightleftharpoons{K_{dim-2}} Cu_2A_4(HA)_2 + (HA)_2 \text{ in benzene,}$$

with the dimerization constants, $\log K_{dim-1} = 2.24$ and $\log K_{dim-2} = 4.19$, respectively. It was proved that the phenyl group inhibits the formation of the dimeric copper(II) phenylacetate, and its effect is partially shielded by a methylene substituent.

Aromatic carboxylic acids are not so useful for the extraction of metal ions as aliphatic ones owing to their poor extracting capability. In the extraction of metal carboxylates the formation of the polymeric metal carboxylates and the adduct formation of the carboxylic acid molecules to the extracted carboxylates are necessary to enhance the extractability. In a series of investigations on the extraction of copper(II) with various carboxylic acids both the dimerization and the adduct formation of the copper(II) carboxylates have been found to be more difficult in the extraction with aromatic carboxylic acids than in that with aliphatic acids.[1–10] This can be anticipated to lead to a poor extractability for an aromatic carboxylic acid. In the subsequent investigation[11] on the extraction of copper(II) with 2,4-hexadienoic acid, which contains the conjugated double bonds, 2,4-hexadienoic acid was proved to be similar in the extraction behaviour for copper(II) to benzoic acid. According to these results, the presence of a conjugated system in

carboxylic acid can be regarded as giving some negative influence on the formation of the dimeric copper(II) carboxylate. Phenylacetic acid, in which the phenyl group is linked through the methylene group to the carboxylic group, has some aliphatic character and retains an inherent property of the phenyl substituent. In a series of investigations on the extraction of some metal ions with phenylacetic acid and its derivatives using chloroform as a solvent, the percent extraction of some metal ions under a few particular conditions and the selective extraction of copper(II) have been described by Adam and co-workers.[12–14] However, in their works they did not touch upon any extraction equilibrium at all.

In the present paper analysis of the extraction equilibrium on the extraction of copper(II) with phenylacetic acid using benzene and 1-octanol as a solvent was made in detail, and the results obtained from the present analysis were compared with those obtained for the other carboxylic acids as an extractant for copper(II). Phenylacetic acid has consequently been found to have the characteristics superior to the other carboxylic acids.

---

*Author for correspondence.

EXPERIMENTAL

Reagents

Commercial phenylacetic acid recrystallized from water was dissolved in purified benzene and 1-octanol, respectively. Benzene and 1-octanol were purified by the same method as employed previously.[11] Sodium perchlorate was also purified as described previously.[2] All other reagents were of reagent grade and used without further purification. Aqueous solutions were prepared with distilled, deionized water.

Procedures

Partition was carried out in a thermostatic bath kept at $25 \pm 0.2°$. A volume of 15 ml each of the aqueous and organic phases were contacted in a 50-ml centrifuge tube. The extraction of copper(II) was carried out under the following conditions: a total copper(II) concentration of $5 \times 10^{-3}M$ and the concentrations of phenylacetic acid are in the region of 0.3–2.0M for benzene, and 0.5–2.0M for 1-octanol, respectively. Shaking for about 1.5 hr was found to be sufficient for complete equilibration. The ionic strength of the aqueous phase was adjusted to 0.1M by sodium perchlorate. After the extraction equilibration, the concentrations of copper(II) and hydrogen ions in the aqueous phase were determined by the same method as described previously.[7] The dissociation constant of phenylacetic acid was potentiometrically determined to be $K_a = [H^+][A^-]/[HA] = 10^{-4.13}$ in the aqueous 0.1M perchlorate solution at 25°. In the estimation of the partition constant of phenylacetic acid between 0.1M perchloric acid and benzene, the concentration of phenylacetic acid in the aqueous phase was determined by the potentiometric titration. While, in partition between 0.1M perchloric acid and 1-octanol, it was determined by measuring the absorbance at 255 nm, the absorption maximum of the acid. The formation constants of copper(II) ion with phenylacetate ion were evaluated by emf measurements using a cupric ion selective electrode.

Apparatus

For mechanical shaking in a thermostat, Cool Bath Shaker ML-10 (TAITEC Co., Koshigaya) was used. A Table Top Centrifuge Model 5100 (Kubota Seisakusho Ltd., Tokyo) was used for centrifugation. A DKK ION Meter, Model 10L-50 (DKK Co., Tokyo) was used for the determination of hydrogen ion concentration in

the aqueous phase. For emf measurement response to cupric ion activity, a DKK cupric ion selective electrode, Model 7140 and a DKK reference electrode, Model 4083, were used with a DKK ION Meter, Model 10L-50. Spectrophotometric determination was carried out on a UVIDEC-430A Double Beam Spectrophotometer (JASCO, Tokyo).

RESULTS AND DISCUSSION

Partition of phenylacetic acid

In general, taking into account the dimerization of a monomeric carboxylic acid in the organic phase and the dissociation of the acid in the aqueous phase, the distribution ratio of the acid can be represented as follows:

$$D = \frac{C_{HA,o}}{C_{HA,w}} = \frac{K_{D,HA} + 2K_{2,HA}K_{D,HA}^2[HA]}{1 + \dfrac{K_a}{[H^+]}}, \quad (1)$$

where K_a, $K_{D,HA}$, $K_{2,HA}$, and [HA] denote the dissociation constant in the aqueous phase, the partition constant between the organic and aqueous phases, the dimerization constant in the organic phase of the carboxylic acid, and the concentration of the monomeric acid in the aqueous phase, respectively. In the same manner as described previously,[15] the partition and dimerization constants of phenylacetic acid were evaluated. The results are summarized in Table 1 together with those for the other carboxylic acids. In 1-octanol it has been found that the dimerization of phenylacetic acid does not occur to any appreciable extent.

As shown in Table 1, the partition constant of phenylacetic acid between 1-octanol and water was found to be moderately smaller than that of toluic acids which are isomeric with phenyl-

Table 1. Dissociation, partition and dimerization constants of carboxylic acids

Acids	pK_a	Solvents	$\log K_{D,HA}$	$\log K_{2,HA}$
Phenylacetic	4.13	Benzene	0.19	1.68
		1-Octanol	1.42	
1-Decanoic	4.92	Benzene[16]	2.80	2.42
		1-Octanol[2]	>3	
1-Octanoic	4.89	Benzene[17]	1.67	2.51
1-Hexanoic	4.84	Benzene[18]	0.31	2.45
		1-Octanol[11]	1.90	
Cyclohexane-carboxylic[6]	4.89	Benzene	0.90	1.54
Pivalic[15]	4.83	Benzene	0.02	2.16
		1-Octanol	1.42	
Benzoic[7]	4.04	1-Octanol	1.88	
o-Toluic[8]	3.73	1-Octanol	2.21	
m-Toluic[8]	4.09	1-Octanol	2.41	
p-Toluic[8]	4.21	1-Octanol	2.33	

acetic acid. In addition, both the partition constant between benzene and water, and the dimerization constant of phenylacetic acid in benzene were proved to be smaller than those of 1-octanoic acid which is an aliphatic carboxylic acid with the same number of carbon atoms as phenylyacetic acid.

Complex formation of copper(II) ion with phenyl-acetate ion in the aqueous phase

Taking into account the formation of CuA^+ and CuA_2 complexes (A: phenylacetate anion), the reaction coefficient of copper(II) ion with phenylacetate anion can be expressed as follows:

$$\alpha_{Cu(A)} = 1 + K_1[A^-] + K_1 K_2 [A^-]^2, \qquad (2)$$

where K_1 and K_2 denote the stepwise formation constants: $K_1 = [CuA^+]/[Cu^{2+}][A^-]$ and $K_2 = [CuA_2]/[CuA^+][A^-]$, respectively. From equation (2) the following expression can be derived:

$$\log \frac{(\alpha_{Cu(A)} - 1)}{[A^-]} = \log K_1 + \log(1 + K_2[A^-]). \quad (3)$$

If $\log\{(\alpha_{Cu(A)} - 1)/[A^-]\} - \log K_1 = Y$ and $K_2[A^-] = X$ (that is, $\log K_2 + \log[A^-] = \log X$), equation (3) is equal to $Y = \log(1 + X)$. Then, according to equation (3), by fitting the plots of $\log\{(\alpha_{Cu(A)} - 1)/[A^-]\}$ against $\log[A^-]$ with the normalized curve, $\log(1 + X)$ vs. $\log X$, the values of K_1 and K_2 can be obtained from the respective deviations of the ordinate and abscissa between the plots and the normalized curve. $\alpha_{Cu(A)}$ was evaluated from the relation, $\alpha_{Cu(A)} = C_{Cu}/[Cu^{2+}]$, where $[Cu^{2+}]$ was determined from emf measurements using a cupric ion selective electrode, and $[A^-]$ was calculated under the respective conditions by the following expression:

$$[A^-] = \frac{C_{HA}}{1 + \dfrac{[H^+]}{K_a}}, \qquad (4)$$

where C_{HA} refers to the total concentration of phenylacetic acid, and phenylacetic acid is in large excess compared to copper under the present experimental conditions. The plots are shown in Fig. 1, and the values were obtained as follows: $\log K_1 = 1.54$ and $\log K_2 = 1.10$, respectively.

Extraction of copper(II) with phenylacetic acid

According to the similar plots previously described,[11] the monomeric and dimeric copper(II) phenylacetates have been suggested to be
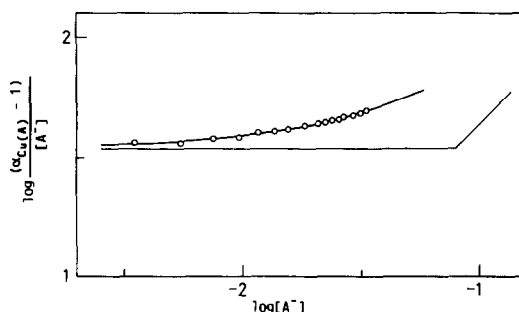

Fig. 1. Estimation of the formation constants of copper(II) phenylacetates in the aqueous phase. Solid curve denotes the normalized curve, $\log(1 + X)$ vs. $\log X$. The straight lines with slopes of 0 and 1 are the asymptotes of the normalized curve.

extracted by phenylacetic acid both in benzene and 1-octanol. Then, in the same manner as the previous work,[15] the following relations can be expected to hold for the total concentration of copper(II) in the organic phase: for the extraction using benzene,

$$\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2\log[H^+]$$

$$= \log\left\{ 1 + \frac{2K_{ex(2b)}}{K_{ex(1a)}} [(HA)_2]_o^{(2+b-a)/2} \right.$$

$$\left. \times (C_{Cu,w} \, \alpha_{Cu(A)}^{-1} [H^+]^{-2}) \right\}$$

$$+ \log K_{ex(1a)} + \frac{(2+a)}{2} \log[(HA)_2]_o, \qquad (5)$$

and for that using 1-octanol,

$$\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2\log[H^+]$$

$$= \log\left\{ 1 + \frac{2K_{ex(2b')}}{K_{ex(1a')}} [HA]_o^{(2+b'-a')} \right.$$

$$\left. \times (C_{Cu,w} \, \alpha_{Cu(A)}^{-1} [H^+]^{-2}) \right\}$$

$$+ \log K_{ex(1a')} + (2+a')\log[HA]_o, \qquad (6)$$

respectively, where $\alpha_{Cu(A)}$ refers to the reaction coefficient which can be calculated by equation (2), and K_{ex} denotes the extraction constants for each extracted species:

$$K_{ex(jn)} = \frac{[Cu_j A_{2j}(HA)_n]_o [H^+]^{2j}}{[Cu^{2+}]^j [(HA)_2]_o^{(2j+n)/2}} \qquad (7)$$

for the system using benzene as a solvent, and

$$K_{ex(in')} = \frac{[Cu_i A_{2i}(HA)_{n'}]_o [H^+]^{2i}}{[Cu^{2+}]^i [HA]_o^{(2i+n')}} \qquad (8)$$

for that using 1-octanol as a solvent, respectively.[15] The symbols n and n' represent as a and a' for the monomeric species and as b and b' for the dimeric ones, respectively.

As shown in Fig. 2 on the basis of equations (5) and (6), the plots of $(\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2 \log[H^+])$ against $(\log C_{Cu,w} - \log \alpha_{Cu(A)} - 2 \log[H^+])$ at constant $[(HA)_2]_o$ for benzene and $[HA]_o$ for 1-octanol fit well in the normalized curve, $\log(1 + X)$ *vs.* $\log X$. Therefore, the data is consistent with the monomeric and dimeric copper(II) phenylacetates being responsible for the extraction of copper(II) with phenylacetic acid using both benzene and 1-octanol as a solvent.

As noted in detail previously,[2] the following relations hold in the region where the monomeric copper(II) species prevails:

$$\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2 \log[H^+]$$

$$= \log \sum_a K_{ex(1a)} [(HA)_2]_o^{(2+a)/2}, \quad (9)$$

for the system using benzene, and

$$\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2 \log[H^+]$$

$$= \log \sum_{a'} K_{ex(1a')} [HA]_o^{(2+a')}, \quad (10)$$

for that using 1-octanol as a solvent, respectively.

On the other hand, the following relations were obtained for the dimeric extracted species: in the system using benzene,

$$\log C_{Cu,o} - 2(\log C_{Cu,w} - \log \alpha_{Cu(A)} - 2 \log[H^+])$$

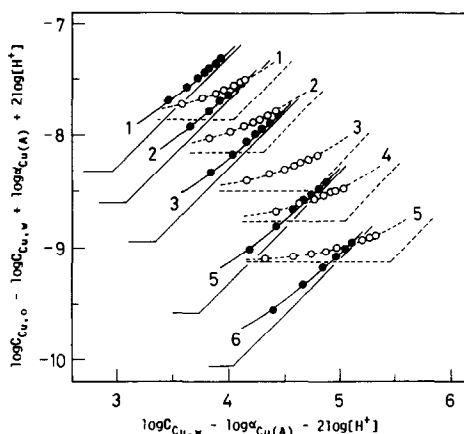$$= \log 2 \sum_b K_{ex(2b)} [(HA)_2]_o^{(4+b)/2}, \quad (11)$$

Fig. 2. Confirmation of the degree of polymerization of the extrated species. Solid and dotted curves are the normalized curves, $\log(1 + X)$ *vs.* $\log X$, and solid and dotted lines are the asymptotes of the respective normalized curves. Open and closed symbols refer to 1-octanol and benzene, respectively. C_{HA}; (1) 2.0, (2) 1.5, (3) 1.0, (4) 0.75, (5) 0.5, and (6) 0.3M.

and in that using 1-octanol as a solvent,

$$\log C_{Cu,o} - 2(\log C_{Cu,w} - \log \alpha_{Cu(A)} - 2 \log[H^+])$$

$$= \log 2 \sum_{b'} K_{ex(2b')} [HA]_o^{(4+b')}. \quad (12)$$

In the system using benzene as a solvent, the number of phenylacetic acid molecules involved in the monomeric and dimeric copper(II) species can be determined from the slope of the plots of the left-hand side of the expressions (9) and (11) against $\log[(HA)_2]_o$, respectively. While, using 1-octanol as a solvent, those can be estimated from the slope of the plots, the left-hand side of the expressions (10) and (12) *vs.* $\log[HA]_o$, respectively. The individual results for the systems using benzene and 1-octanol are shown in Figs 3 and 4, respectively. As shown in Fig. 3, in the system using benzene as a solvent, the plots for the determination of the number of phenylacetic acid molecules involved in the monomeric copper(II) species deviate slightly upward from the straight line with a slope of 2.0 with decreasing $[(HA)_2]_o$. This suggests that the main monomeric copper(II) phenylacetate is $CuA_2(HA)_2$ and another one $CuA_2(HA)_a(a < 2)$ is also extracted into benzene phase. Then, in the region where the monomeric species prevails in the system using benzene as a solvent, the following relation can be obtained:

$$\log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2 \log[H^+]$$

$$- 2 \log[(HA)_2]_o = \log K_{ex(12)}$$

$$+ \log \left\{ 1 + \frac{K_{ex(1a)}}{K_{ex(12)}} ([(HA)_2]_o^{-1})^{(2-a)/2} \right\}. \quad (13)$$

As the plots of left-hand side of the above equation against $-\log[(HA)_2]_o$ fall on the normalized curve, $\log(1 + X^{1/2})$ *vs.* $\log X$ in Fig. 5, $(2 - a)/2 = 1/2$, that is, the other monomer was found to be CuA_2HA. According to this curve-fitting method, the respective extraction constants, $K_{ex(12)}$ and $K_{ex(11)}$ were estimated as follows: $\log K_{ex(12)} = -7.30$ and $\log K_{ex(11)} = -8.07$, respectively. The plots for the dimeric copper(II) species fit well in the straight line with a slope of 3.0. Then, the dimeric extracted species was found to be $Cu_2A_4(HA)_2$ in the extraction system using benzene as a solvent. And its extraction constant was evaluated to be $\log K_{ex(22)} = -10.41$ from the intercept of the straight line with a slope of 3.0 in Fig. 3.

On the other hand, in the system using 1-octanol as a solvent the plots for the monomeric extracted copper(II) species fall on the straight
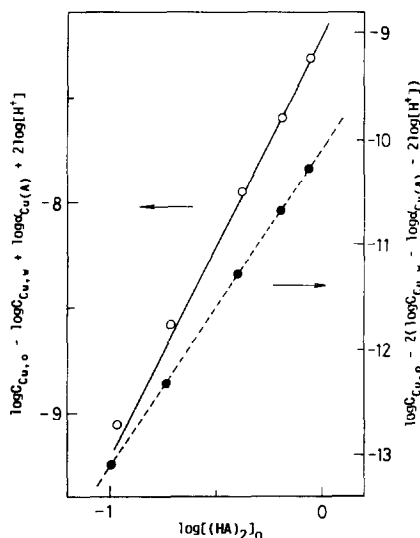
Fig. 3. Determination of the number of phenylacetic acid molecules involved in the monomeric and dimeric copper(II) phenylacetates in benzene. Solid and dotted lines are the straight ones with slopes of 2.0 and 3.0, respectively. Open and closed symbols refer to the monomeric and dimeric copper(II) species, respectively.

line with a slope of 2.0 as shown in Fig. 4. Only the CuA_2 species was found to be extracted as a monomeric extracted species. And its extraction constant was evaluated to be log $K_{ex(10)} = -7.46$ from the intercept of the straight line with a slope of 2.0. As can be seen from Fig. 4, the plots for the determination of the composition of the dimeric copper(II) species are gradually deviating upward from the straight line with
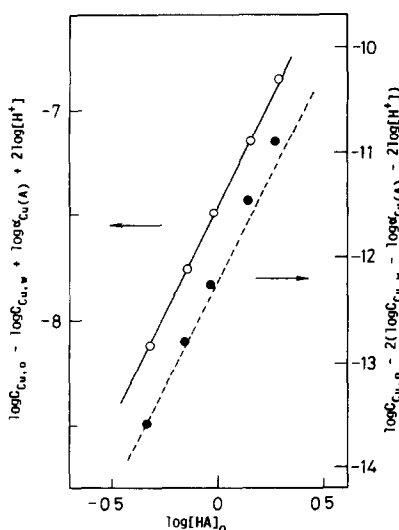

Fig. 4. Determination of the number of phenylacetic acid molecules involved in the monomeric and dimeric copper(II) species in 1-octanol. Solid and dotted lines are the straight ones with slopes of 2.0 and 4.0, respectively. Open and closed symbols are the same as in Fig. 3.
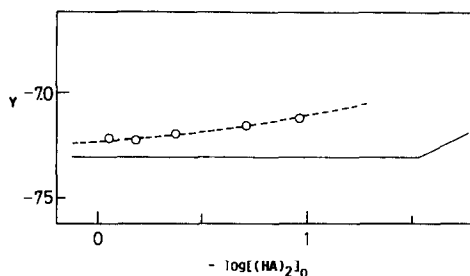

Fig. 5. Estimation of the composition and extraction constants of the monomeric copper(II) species in benzene. $Y = \log C_{Cu,o} - \log C_{Cu,w} + \log \alpha_{Cu(A)} + 2 \log[H^+] - 2 \log[(HA)_2]_o$. Dotted curve is the normalized curve, $\log(1 + X^{1/2})$ vs. $\log X$, and solid lines are the asymptotes with slopes of 0 and 0.5 of the normalized curve.

a slope of 4.0 with increasing the concentration of phenylacetic acid in 1-octanol phase. This suggests that the Cu_2A_4 and $Cu_2A_4(HA)_{b'}$ $(b' \geqslant 1)$ exist as a dimric copper(II) species. Then, in the region where the dimeric copper(II) species prevails in the system using 1-octanol as a solvent, the following relation for the total concentration of copper(II) in the organic phase can be held:

$$\log C_{Cu,o} - 2(\log C_{Cu,w} - \log \alpha_{Cu(A)} - 2 \log[H^+])$$

$$- 4 \log[HA]_o = \log 2 + \log K_{ex(20)}$$

$$+ \log\left(1 + \frac{K_{ex(2b')}}{K_{ex(20)}} [HA]_o^{b'}\right). \qquad (14)$$

According to the above equation, by fitting the plots of the left-hand side of the equation against $\log[HA]_o$ with the normalized curve, $\log(1 + X^n)$ vs. $\log X$ with the suitable n value, another dimeric copper(II) species and the respective extraction constants of Cu_2A_4 and $Cu_2A_4(HA)_{b'}$ can be determined. As shown in Fig. 6, the plots fall on the normalized curve with $n = 1$. Then, the other dimeric species is
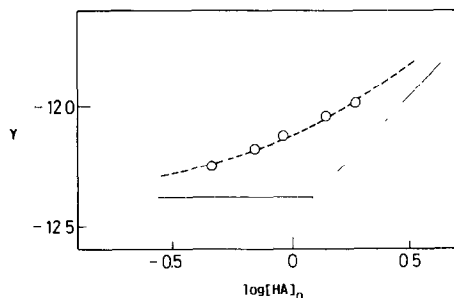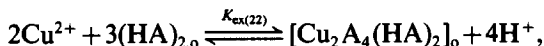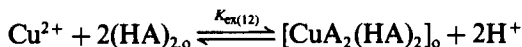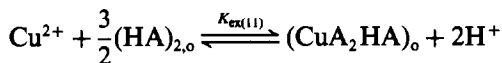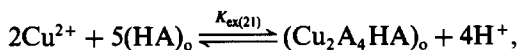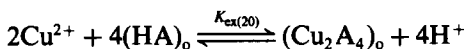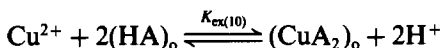

Fig. 6. Estimation of the dimeric copper(II) species and their extraction constants in 1-octanol. $Y = \log C_{Cu,o} - 2(\log C_{Cu,w} - \log \alpha_{Cu(A)} - 2 \log[H^+]) - 4 \log[HA]_o$. Dotted curve is the normalized curve with $n = 1$, $\log(1 + X^n)$ vs. $\log X$, and solid lines are the asymptotes of the normalized curve.

Cu_2A_4HA and the extraction constants of Cu_2A_4 and Cu_2A_4HA were found to be $\log K_{ex(20)} = -12.68$ and $\log K_{ex(21)} = -12.77$, respectively.

Consequently, the extraction equilibria for the present extraction systems can be written as: for the system using benzene as a solvent,
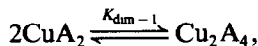
$$Cu^{2+} + \frac{3}{2}(HA)_{2,o} \xrightleftharpoons{K_{ex(11)}} (CuA_2HA)_o + 2H^+$$

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

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

and for the system using 1-octanol as a solvent,

$$Cu^{2+} + 2(HA)_o \xrightleftharpoons{K_{ex(10)}} (CuA_2)_o + 2H^+$$

$$2Cu^{2+} + 4(HA)_o \xrightleftharpoons{K_{ex(20)}} (Cu_2A_4)_o + 4H^+$$

$$2Cu^{2+} + 5(HA)_o \xrightleftharpoons{K_{ex(21)}} (Cu_2A_4HA)_o + 4H^+,$$

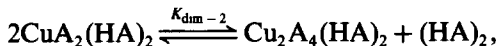respectively.

Then, the dimerization of copper(II) phenylacetates in the organic phase can be represented as follows:

in 1-octanol phase,

$$2CuA_2 \xrightleftharpoons{K_{dim-1}} Cu_2A_4,$$

and in benzene phase,

$$2CuA_2(HA)_2 \xrightleftharpoons{K_{dim-2}} Cu_2A_4(HA)_2 + (HA)_2,$$

with the individual dimerization constants calculated from the respective extraction constants: $\log K_{dim-2} = 4.19$ and $\log K_{dim-1} = 2.24$, respectively.

According to the results obtained from the present work, the distribution diagrams of copper(II) phenylacetates in the respective organic phases were depicted in Fig. 7. As can be seen from Fig. 7, the main extracted species are CuA_2 in the lower concentration of copper(II) in the 1-octanol phase, and $Cu_2A_4(HA)_2$ for the extraction using benzene as a solvent. This implies that under the present extraction conditions in the system using 1-octanol as a solvent the dimerization of copper(II) phenylacetate and the adduct formation by phenylacetic acid molecules were strongly inhibited by the solvation with some 1-octanol molecules. In the extraction using benzene as a solvent in contrast to the
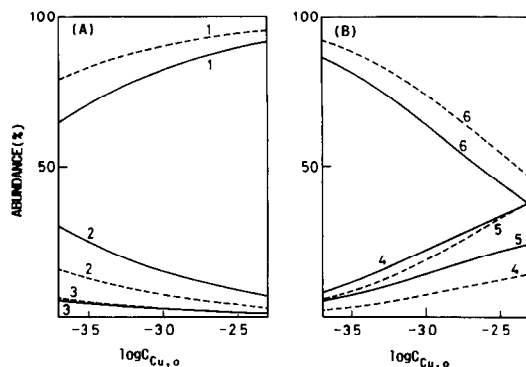

Fig. 7. Distribution diagrams of copper(II) phenylacetates in benzene(A), and 1-octanol(B), respectively. Solid and dotted curves refer to $C_{HA} = 2.0$ and $0.5M$, respectively. Numbers denote the following copper(II) phenylacetates: (1) $Cu_2A_4(HA)_2$, (2) $CuA_2(HA)_2$, (3)CuA_2HA, (4) Cu_2A_4HA, (5) Cu_2A_4, and (6) CuA_2, respectively.

case of 1-octanol, some water molecules can be expected to attach to the unsaturated sites of the coordination in the copper(II) phenylacetates, as the copper(II) species cannot be solvated by any benzene molecule. Then, by replacing the coordinated water molecules with some phenylacetic acid molecules, $Cu_2A_4(HA)_2$ and $CuA_2(HA)_2$ are anticipated to become stable in benzene, and to enhance the extractability of this extraction system for copper(II).

CONCLUSIONS

For comparison, the extraction and dimerization constants of copper(II) carboxylates for the other carboxylic acids were summarized together with the present values in Tables 2 and 3, respectively.

Compared with the extraction system with benzoic acid, in which the dimerization of copper(II) benzoate did not occur in the 1-octanol phase to any appreciable extent, the dimerization of copper(II) species occurred, though slightly, in the 1-octanol phase in the present extraction system. As shown in Table 3, the dimerization constant of copper(II) phenylacetate in the 1-octanol phase is smaller than that of the other carboxylates other than the benzoate and *p*-toluate whose dimerization does not occur to any appreciable extent in 1-octanol. In benzene the dimerization constant of copper(II) phenylacetate is shown to be appreciably large, but to be considerably smaller than that of copper(II) decanoate. This suggests that the effect of the phenyl substituent is shielded by a methylene group, but the interference of the dimerization of copper(II) carboxylate from the

Table 2. Extraction constants of copper(II) carboxylates

Acids	Solvents	$\log K_{ex(10)}$	$\log K_{ex(11)}$	$\log K_{ex(12)}$	$\log K_{ex(20)}$	$\log K_{ex(21)}$	$\log K_{ex(22)}$
Phenylacetic	Benzene		−8.07	−7.30			−10.41
	1-Octanol	−7.46			−12.68	−12.77	
1-Decanoic	Benzene[19]			−8.91			−11.45
	1-Octanol[2]	−8.41	−8.65		−13.36		−13.77
1-Hexanoic	Benzene[20]						−11.48
	1-Octanol[11]	−8.19			−13.65		−14.19
Cyclohexane-carboxylic[6]	Benzene	−8.34		−7.33	−12.47		−11.73
Pivalic[15]	Benzene	−8.39	−7.93				−11.81
	1-Octanol	−8.57	−9.35		−14.13	−14.65	
Benzoic[7]	1-Octanol	−7.70					
o-Toluic[8]	1-Octanol	−7.84			−12.84		
m-Toluic[8]	1-Octanol	−7.84			−13.15		
p-Toluic[8]	1-Octanol	−7.84					

The extraction constants are defined separately as equations (7) and (8), respectively in the text for the systems using benzene and 1-octanol as a solvent.

phenyl group is still not completely eliminated. As shown in Table 3, in the extraction of copper(II) with o- and m-toluic acids which are isomeric with phenylacetic acid, the dimerization constant of the respective copper(II) toluate is slightly larger than that in the present system in 1-octanol. This implies that the introduction of the methyl substituent into o- or m-positions in benzoic acid is more effective for the dimerization of copper(II) carboxylate than that of the methylene group between the phenyl and carboxylic groups. In addition the partition constant of phenylacetic acid between 1-octanol and $0.1M$ perchloric acid is fairly small compared to the three toluic acids as can be seen in Table 1.

Contrary to the dimerization constant of copper(II) carboxylate and the partition constant of carboxylic acid, it is noteworthy that the extraction constant of $Cu_2A_4(HA)_2$ in the present system using benzene is appreciably larger than that in the other extraction systems shown in Table 2. Not only $K_{ex(22)}$ but also the other five

Table 3. Dimerization constants of copper(II) carboxylates

Acids	Solvents	$\log K_{dim-1}$	$\log K_{dim-2}$
Phenylacetic	Benzene		4.19
	1-Octanol	2.24	
1-Decanoic	Benzene[19]		6.37
	1-Octanol[2]	3.46	
1-Hexanoic[11]	1-Octanol	2.73	
Cyclohexane-carboxylic[6]	Benzene	4.21	2.93
Pivalic[15]	1-Octanol	3.01	
Benzoic[7]	1-Octanol	ND	
o-Toluic[8]	1-Octanol	2.84	
m-Toluic[8]	1-Octanol	2.53	
p-Toluic[8]	1-Octanol	ND	

ND: The dimerization of copper(II) carboxylates does not occur to any appreciable extent.
K_{dim-1} and K_{dim-2} are denoted in the text.

extraction constants of copper(II) phenylacetates in Table 2 slightly larger than the constants in the other systems. These results suggest that the phenylacetic acid is superior to the other carboxylic acids summarized in Table 2 as the extractant for copper(II).

REFERENCES

1. H. Yamada and M. Tanaka, J. Inorg. Nucl. Chem., 1976, 38, 1501.
2. H. Yamada, S. Suzuki and M. Tanaka, ibid., 1981, 43, 1873.
3. H. Yamada, R. Kitazaki and I. Kakimi, Bull. Chem. Soc. Jpn., 1983, 56, 3302.
4. H. Yamada, K. Takahashi, Y. Fujii and M. Mizuta, ibid., 1984, 57, 2847.
5. H. Yamada, T. Okuda, Y. Fujii, M. Mizuta and M. Tanaka, ibid., 1986, 59, 3855.
6. H. Yamada, M. Ito and M. Mizuta, ibid., 1987, 60, 3557.
7. H. Yamada, K. Adachi, Y. Fujii and M. Mizuta, Solvent Extr. Ion Exch., 1986, 4, 1109.
8. H. Yamada, S. Horikawa, Y. Fujii and M. Mizuta, Bull. Chem. Soc. Jpn., 1988, 61, 835.
9. Idem, ibid., 1990, 63, 3542.
10. H. Yamada and M. Mizuta, Process Metallurgy 7A (Solvent Extraction, 1990), 1992, 153.
11. H. Yamada, C. Kato and M. Mizuta, Bull. Chem. Soc. Jpn., 1992, 65, 186.
12. J. Adam and R. Pribil, Talanta, 1972, 19, 1105.
13. J. Adam, R. Pribil and V. Vesely, ibid., 1972, 19, 825.
14. J. Adam and R. Pribil, ibid., 1974, 21, 113.
15. H. Yamada and C. Kato, ibid., 1993, 40, 1049.
16. M. Tanaka, N. Nakasuka and S. Sasane, J. Inorg. Nucl. Chem., 1969, 31, 2591.
17. G. K. Schweitzer and D. K. Morris, Anal. Chim. Acta, 1969, 45, 65.
18. I. Kojima, M. Yoshida and M. Tanaka, J. Inorg. Nucl. Chem., 1970, 32, 987.
19. Y. Fujii, N. Nakasuka, M. Tanaka, H. Yamada and M. Mizuta, Inorg. Chem., 1989, 28, 3600.
20. I. Kojima, M. Uchida and M. Tanaka, J. Inorg. Nucl. Chem., 1970, 32, 1333.