  Bull. Chem. Soc. Jpn., 61, 835—839 (1988)

Effects of Methyl Substituent on Solvent Extraction of Copper(II) with *o*-, *m*-, and *p*-Methylbenzoic Acids

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(Received August 27, 1987)

The extraction of copper(II) with *o*-, *m*-, and *p*-methylbenzoic acids in 1-octanol was carried out at 25 °C and aqueous ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). In contrast to the extraction with benzoic acid, in which only the monomeric copper(II) benzoate is extracted, the dimeric copper(II) species is also responsible for the extraction of copper(II) with *o*- and *m*-methylbenzoic acids in 1-octanol together with the monomeric one. On the other hand, *p*-methylbenzoic acid has a poorer extracting capability than *o*- and *m*-methylbenzoic acids and only the monomeric copper(II) species is responsible for the extraction.

Compared with aliphatic carboxylic acids, aromatic carboxylic acids have been scarcely employed as extracting agents owing to their poor extracting capability. In the previous investigations on the extraction of copper(II) with benzoic,[1] and decanoic[2,3] acids, it has been shown that there was a remarkable difference in the extraction equilibrium between aromatic and aliphatic carboxylic acids. For example, copper(II) benzoate cannot be extracted in benzene, but can be easily extracted in 1-octanol as a monomeric species CuA_2 (A: carboxylate anion).[1] In the copper(II) decanoate extraction systems, the dimeric species $Cu_2A_4(HA)_2$ can be extracted in nonsolvating solvents such as benzene, while not only the dimeric copper(II) decanoates but also the monomeric ones are responsible for the extraction in solvating solvents[3-5] such as 1-octanol. These results suggest that the formation of the dimeric copper(II) carboxylate is essential for the extraction of copper(II) carboxylates into nonsolvating solvents such as benzene, and in solvating solvents the solvation of the monomeric copper(II) species by some solvent molecules makes possible the extraction of copper(II) without any detectable formation of the dimeric copper(II) species.

The present paper deals with the extraction of copper(II) with *o*-, *m*-, and *p*-methylbenzoic acids in 1-octanol. It was found that with *p*-methylbenzoic acid, the copper(II) ion is extracted through a mechanism different from the extraction with *o*- and *m*-methylbenzoic acids, in which the monomeric and dimeric copper(II) species are responsible for the extraction.

Experimental

Reagents. *o*-, *m*-, and *p*-Methylbenzoic Acids: Commercial methylbenzoic acids (purity: over 99%) were dissolved in 1-octanol. **Copper(II) perchlorate, sodium perchlorate, and 1-octanol** were the same as employed previously.[3] All other reagents were reagent grade and used without further purification.

Procedure. Partition was performed at a total copper concentration of 5×10^{-3} mol dm^{-3} and methylbenzoic acids concentration of 0.3—1.6 mol dm^{-3} in a bath thermostated at 25.0±0.2 °C. Ionic strength of the aqueous phase was adjusted to 0.1 mol dm^{-3} with sodium perchlorate. Shaking for about 1 h was sufficient for complete equilibration. The concentrations of copper(II) and hydrogen ions in the aqueous phase were determined by the same manner as employed previously.[1] The dissociation constants of methylbenzoic acids were potentiometrically estimated. In the determination of the partition constants of *o*-, *m*-, and *p*-methylbenzoic acids between water and 1-octanol, the absorption maxima at 279, 281, and 241 nm of the respective acids were used for the determination of the concentration of the respective acids in the aqueous phase.

Apparatus. For mechanical shaking in a thermostat, centrifugation, pH measurements, and spectrophotometric determinations, the apparatus were the same as employed previously.[1]

Results and Discussion

Partition of Methylbenzoic Acids. In the extraction of metals with carboxylic acids, it is indispensable to have information about the partition of the carboxylic acids. The following equilibria on the carboxylic acid HA should be considered: (a) The dissociation of HA in the aqueous phase ($K_a=[H^+][A^-]/[HA]$), (b) the partition of HA into the organic phase ($K_{D,HA}=[HA]_o/[HA]$), and (c) the dimerization of HA in the organic phase ($K_{2,HA}=[(HA)_2]_o/[HA]_o^2$). The dissociation constant of *o*-, *m*-, and *p*-methylbenzoic acids were potentiometrically determined at the ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). The values obtained are summarized in Table 1. These values are in agreement with those already presented[6] with making activity coefficient corrections.

The partition of the respective methylbenzoic acids was carried out between 1-octanol and 0.1 mol dm^{-3} perchloric acid, in which the dissociation of the methylbenzoic acids can be neglected. The distribution ratio of methylbenzoic acids was observed to be constant, irrespective of the concentration of the acids. Then it was recognized that the dimerization of the respective acids in 1-octanol does not occur to any appreciable extent and that the distribution ratio of each acid is equal to its partition constant $K_{D,HA}$. The respective partition constants are shown in Table 1.

The partition constant obtained increases in the following order: *m*-methylbenzoic>*p*-methylbenzoic> *o*-methylbenzoic>benzoic acids. Replacement of a hydrogen atom on the aromatic ring in benzoic acid with methyl moiety results in an increase in the partition constant of the acids, as expected. From the information about three kinds of methylbenzoic acids, the concentration of monomeric methylbenzoic acids in 1-octanol can be regarded as the total concentration of the respective acids under the present experimental conditions, that is, $[HA]_o=C_{HA}$.

Extraction of Copper(II) with Methylbenzoic Acids. If a *j*-merized copper(II) methylbenzoate, $Cu_jA_{2j}(HA)_a$ is extracted, the extraction equilibrium can be represented as:

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

with the extraction constant:

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

where the subscript o refers to the organic phase.

Total concentration of copper(II) in the organic phase, $C_{Cu,o}$ is written as follows:

$$C_{Cu,o} = \sum_j \sum_a jK_{ex(ja)}[Cu^{2+}]^j[HA]_o^{(2j+a)}[H^+]^{-2j}. \quad (2)$$

Suppose that only $Cu_jA_{2j}(HA)_a$ is responsible for the extraction, the following expression can be obtained:

$$\log C_{Cu,o} = j(\log[Cu^{2+}] - 2\log[H^+]) + (2j + a)\log[HA]_o + \log j + \log K_{ex(ja)}. \quad (3)$$

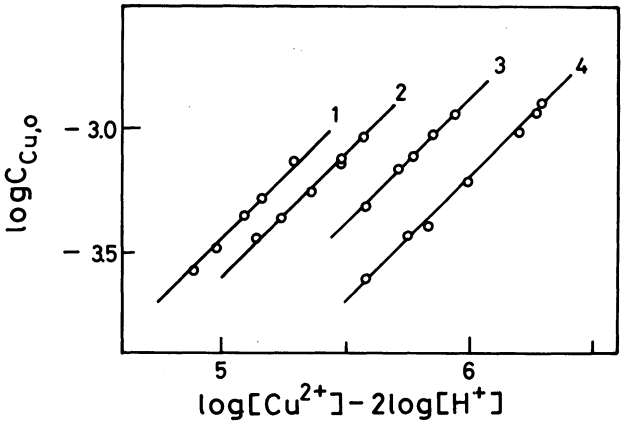

Fig. 2. Determination of the degree of polymerization of the copper(II) *p*-methylbenzoate.
Solid lines are the straight lines with a slope of 1.0.
C_{HA}; 1: 0.5, 2: 0.4, 3:0.3, 4: 0.2 mol dm^{-3}.

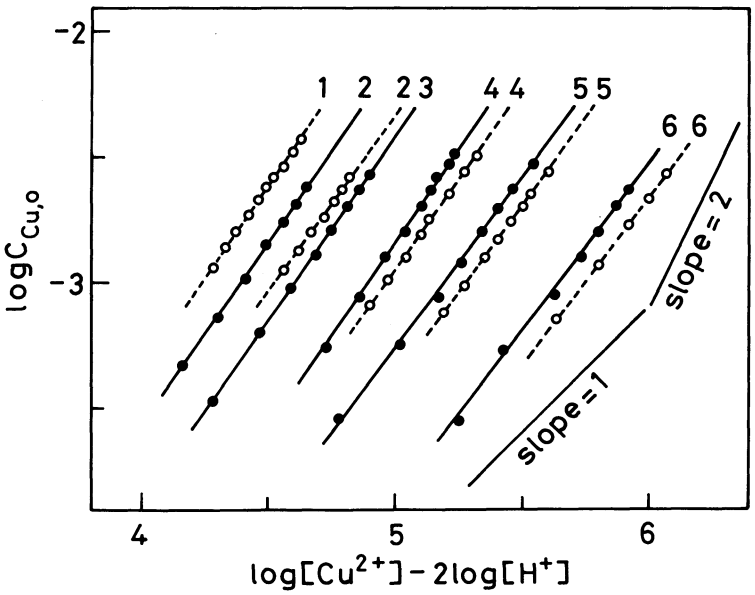

Fig. 1. Determination of the degree of polymerization of the extracted species.
Closed and open symbols refer to *o*- and *m*-methylbenzoic acids, respectively.
C_{HA}; 1: 1.6, 2: 1.2, 3: 1.0, 4: 0.7, 5: 0.5, 6: 0.3 mol dm^{-3}.

Table 1. Various Constants (at 25 °C and Aqueous Ionic Strength of 0.1 mol dm^{-3})

Acid	pK_a	log $K_{D,HA}$	log $K_{ex(10)}$	log $K_{ex(20)}$	log K_{2,CuA_2}
o-Methylbenzoic	3.73	2.21	−7.84	−12.84	2.84
m-Methylbenzoic	4.09	2.41	−7.84	−13.15	2.53
p-Methylbenzoic	4.21	2.33	−7.84		
Benzoic[a)]	4.04	1.88	−7.70		

Solvent: 1-Octanol. a) Ref. 1.

According to Eq. 3, the degree of polymerization of the extracted species can be found from the slope of the plot of $\log C_{Cu,o}$ against $(\log[Cu^{2+}]-2\log[H^+])$ at constant $[HA]_o$.

The results are shown in Figs. 1 and 2. As shown in Fig. 1, the slope of the plots lies from 1.3 to 1.5 and tends to be steeper with increasing copper concentration in the organic phase. Therefore, it is expected that the monomeric and dimeric copper(II) methylbenzoates are responsible for the extraction with *o*- and *m*-methylbenzoic acids. On the other hand, the plots in Fig. 2 fall on a straight lines with a slope of 1.0. This suggests that only the monomeric copper(II) species is responsible for the extraction with *p*-methylbenzoic acid.

In the extraction of copper(II) with *o*- and *m*-methylbenzoic acids, the following relation can be derived from Eq. 2:

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

where $K_{ex(1a)}$ and $K_{ex(2b)}$ represent the extraction constants of the monomer $CuA_2(HA)_a$ and the dimer $Cu_2A_4(HA)_b$, respectively. According to Eq. 4, by comparing the plot of $(\log C_{Cu,o}-\log[Cu^{2+}]+2\log[H^+])$ against $(\log[Cu^{2+}]-2\log[H^+])$ at constant $[HA]_o$ with the normalized curve, $\log(1+X)$ vs. $\log X$, the degree of polymerization of the extracted species can be identified. As shown in Fig. 3, the plots fit well with the normalized curve. It was proved that the monomeric and dimeric copper(II) species are responsible for the extraction with *o*- and *m*-methylbenzoic acids in 1-octanol.

In the region where the monomer prevails, that is, the whole region in Fig. 2 and the region on the straight line asymptotes with a slope of zero in Fig. 3, the following expression can be derived from Eq. 2:

$$\log C_{Cu,o} - \log[Cu^{2+}] + 2\log[H^+] = \log\sum_a (K_{ex(1a)}[HA]_o^{(2+a)}). \quad (5)$$

According to Eq. 5, the number of methylbenzoic acid molecules involved in the monomeric copper(II) methylbenzoates can be determined from the slope of the plot of $(\log C_{Cu,o}-\log[Cu^{2+}]+2\log[H^+])$ against $\log[HA]_o$. The results are illustrated in Fig. 4 for *o*-, *m*-, and *p*-methylbenzoates. The plots fall on the same straight line with a slope of 2.0 in each acid: $2+a=2$, that is, $a=0$. Then, the composition of the monomer is CuA_2, irrespective of the position of the methyl substituent. The extraction constant of CuA_2 for each acid can be obtained from the intercept of the straight line with a slope of two. The values are listed in Table 1 together with other constants. Though

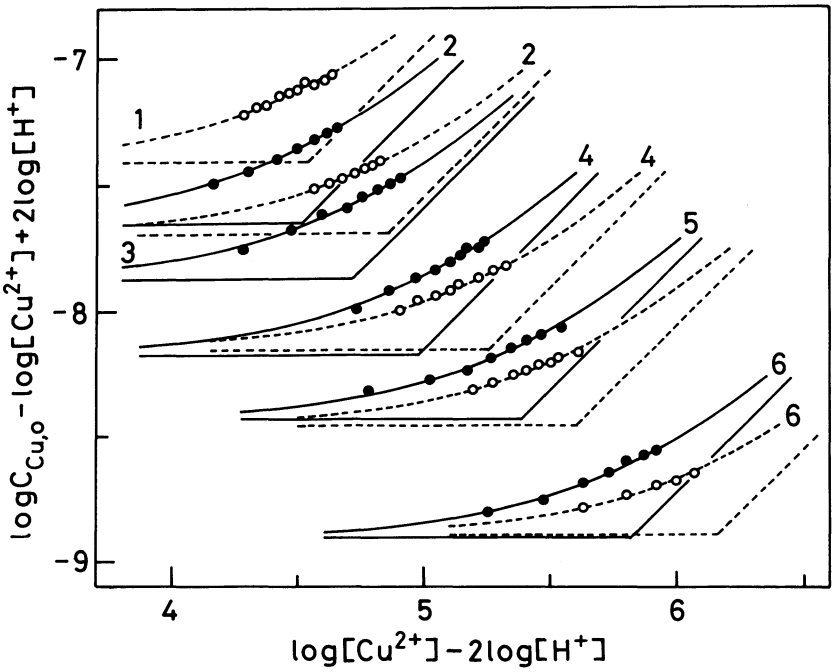

Fig. 3. The identification of the degree of polymerization of the copper(II) *o*- and *m*-methylbenzoates.
Symbols and numbers are the same as in Fig. 1. Curves are the normalized curve, $\log(1+X)$ vs. $\log X$. Straight lines are the asymptotes of the respective normalized curves.

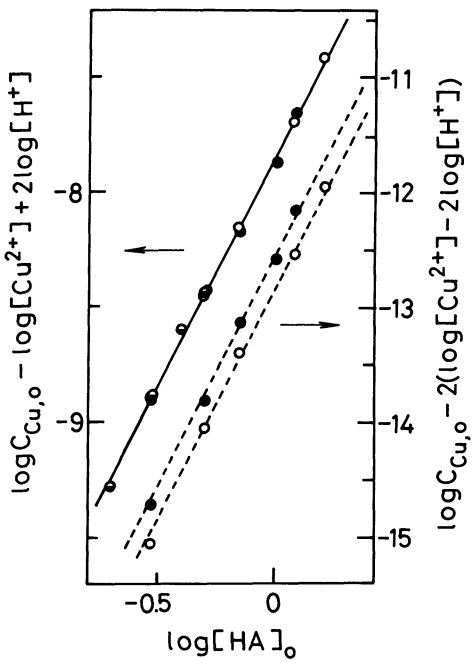

Fig. 4. Determination of the number of *o*-, *m*-, and *p*-methylbenzoic acid molecules involved in the monomeric and dimeric copper(II) species, respectively.
Solid and dotted lines are the straight lines with a slope of 2.0 and 4.0, respectively. Closed, open, and half-closed symbols refer to *o*-, *m*-, and *p*-methylbenzoic acids, respectively.

each of the three kinds of acids has a clear individuality, the same value for $K_{ex(10)}$ was obtained for each acid.

On the other hand, in the region where the predominant extracted species is the dimer, that is, the plots in Fig. 3 fit by extrapolation with the straight line asymptotes with a slope of unity, the following expression is derived from Eq. 2:

$$\log C_{Cu,o} - 2(\log[Cu^{2+}] - 2\log[H^+]) = \log 2\sum_b (K_{ex(2b)}[HA]_o^{(4+b)}). \quad (6)$$

According to Eq. 6, the number of the acid molecules involved in the dimeric copper(II) species was found to be four, as the plots of $\{\log C_{Cu,o} - 2(\log[Cu^{2+}] - 2\log[H^+])\}$ against $\log[HA]_o$ shown in Fig. 4 fell on the straight lines with a slope of 4.0 in both *o*- and *m*-methylbenzoates. The extraction constant of Cu_2A_4 can be determined from the intercept of the respective straight lines in Fig. 4. The values obtained are listed in Table 1 together with other constants.

Consequently, we conclude that the extraction equilibria for the present extraction systems are expressed as follows:

o- and *m*-methylbenzoic acids:

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

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

p-methylbenzoic acid:

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

Irrespective of the *o*- and *p*-orientations of the methyl group, the extraction equilibrium for copper(II) ortho-substituted benzoate coincides not with that for para-substituted one but for meta-substituted one.

In the extraction systems for *o*- and *m*-methylbenzoic acids the dimerization reaction of copper(II) species in the 1-octanol phase can be expressed as follows:

$$2(CuA_2)_o \overset{K_{2,CuA_2}}{\rightleftharpoons} (Cu_2A_4)_o,$$

where K_{2,CuA_2} refers to the dimerization constant of copper(II) *o*- and *m*-methylbenzoates, which can be calculated from the respective extraction constants. The values are summarized in Table 1. As the dimerization of copper(II) carboxylate in the organic phase in the extraction of copper(II) with a carboxylic acid results in an effect similar to the synergistic effect, substituting a hydrogen atom at the ortho- and meta-positions in benzoic acid by the methyl group can enhance the extractability of copper(II). It was found that the formation of the dimeric copper(II) species was not sterically hindered by the methyl group at the *o*-position.

The introduction of methyl substituent at the *p*-position in benzoic acid results in the decrease in the solubility of the acid in both water and 1-octanol. In this extraction system, the emulsion was observed in the region where the percent extraction of copper(II) exceeds 30%, and only the monomeric copper(II) species was responsible for the extraction under the conditions where the emulsion does not appear.

By preliminary experiments, it has been revealed that substituting a hydrogen atom at the *o*-, *m*-, and *p*-positions in benzoic acid by the methyl moiety has partially enabled the extraction of copper(II) using benzene as solvent, which was impossible in the unsubstituted benzoic acid–benzene extraction system. This is attributable to an increase in the affinity of copper(II) methylbenzoates for benzene by the introduction of the methyl substituent.

Judging from the present results, it seems reasonable to assume that the mesomeric effect of the methyl group on the conjugated system in benzoic acid has enabled the formation of the dimeric copper(II) species which was not perceived in the extraction of copper(II) with unsubstituted benzoic acid,[1] and some special function only for *p*-methylbenzoic acid will result in the fact that for *p*-methylbenzoic acid the dimerization of copper(II) species cannot be detected to any appreciable extent. This problem will be elucidated by the more detail investigations from different points of view.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 62540432 from the Ministry of Education, Science and Culture.

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