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Solvent Effects on Dimerization of Copper(II) Decanoate in Ketone Solvents

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The extraction of copper(II) with decanoic acid in some ketone solvents was carried out at 25 °C and at 0.1 mol/dm^3 ($NaClO_4$) aqueous ionic strength. Organic solvents used are 2-pentanone, 3-pentanone, 2-hexanone, 4-methyl-2-pentanone, 5-methyl-2-hexanone, and 2-octanone. For all solvents, the extracted species are CuA_2, CuA_2HA, Cu_2A_4, and $Cu_2A_4(HA)_2$ (HA: decanoic acid). The dimerization and adduct formation of copper(II) decanoates in each organic phase can be formulated as:

$$CuA_2 + HA \xrightleftharpoons{K_{ad,monomer}} CuA_2HA,$$

$$Cu_2A_4 + 2HA \xrightleftharpoons{\beta_{ad,dimer}} Cu_2A_4(HA)_2,$$

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

$$2CuA_2HA \xrightleftharpoons{K_{dim-2}} Cu_2A_4(HA)_2.$$

The solvent effects on the dimerization of copper(II) decanoate can be interpreted in terms of the regular solution theory. It was proved that the number of solvent molecules liberated in the formation of the dimeric copper(II) decanoate in ketones was less than that in alcohols.

In a series of investigations[1–7] on the extraction of copper(II) with aliphatic carboxylic acids in various inert solvents, the extracted species has been established to be the dimeric copper(II) carboxylates. On the other hand, by using 1-octanol as solvating solvent, the monomeric copper(II) decanoates were extracted together with the dimeric ones.[8] In the previous work,[9] it has been shown that the monomeric (CuA_2) and dimeric copper(II) decanoates (Cu_2A_4, and $Cu_2A_4(HA)_2$) are responsible for the extraction with decanoic acid in some alcohol solvents and the solvent effects on the dimerization of copper(II) decanoate in the alcohol phase can be interpreted by means of the regular solution theory.

The present paper describes the results of the extraction of copper(II) with decanoic acid in some ketone solvents. Through the comparison of the present results with those obtained for alcohol solvents, it was found that the dimerization constants of copper(II) decanoates in ketones was much larger than those in alcohols and the number of solvent molecules set free in the dimerization of copper(II) decanoate in ketones was less than that in alcohols.

Experimental

Reagents. *Solvents*: 2-Pentanone, 3-pentanone, 2-hexanone, 4-methyl-2-pentanone, 5-methyl-2-hexanone, and 2-octanone of reagent grade were purified by distillation and saturated with distilled water at 25 °C.

Reagent grade 8-quinolinol was used for the spectrophotometric determination of lower concentration of copper in the organic phase.

Copper(II) perchlorate was prepared in the same manner as presented previously.[8]

Sodium perchlorate and decanoic acid were purified by the method described previously.[8]

All other reagents were reagent grade and used without further purification.

Procedure. Experiments were carried out in the same manner as was stated in the previous work.[8]

Apparatus. For mechanical shaking in a thermostat, Taiyo Incubator M-100^N (Taiyokagaku-Kogyo Co., Tokyo) was used. A Orion Research Microprocessor Ionalyzer 901 (Orion Research Inc., USA) and Horiba pH Analyzer F-80 (Horiba Seisakusho Ltd., Kyoto) were used for the determination of hydrogen ion concentration in the aqueous phase. Spectrophotometric determination was carried out on a Shimadzu double-beam type UV-210A Spectrophotometer (Shimadzu Seisakusho Ltd., Kyoto).

Results and Discussion

Distribution of Decanoic Acid. Distribution ratio of decanoic acid between water and the organic solvent is written as follows:

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

where K_a, $K_{dim,HA}$, and $K_{D,HA}$ denote the dissociation constant in the aqueous phase, the dimerization constant in the organic phase, and the partition constant of decanoic acid, respectively. At lower pH where the dissociation of decanoic acid in the aqueous phase is negligible, Eq. 1 is rewritten as:

$$\log D = \log K_{D,HA} + \log(1+2K_{dim,HA}K_{D,HA}[HA]). \quad (2)$$

Distribution ratio of decanoic acid between water and 4-methyl-2-pentanone was illustrated in Fig. 1 as a function of the concentration of decanoic acid in the aqueous phase. In Fig. 1, the concentration of hydrogen ion in the aqueous phase is 10^{-3} mol/dm^3 and the ionic strength in the aqueous phase is 0.1 mol/

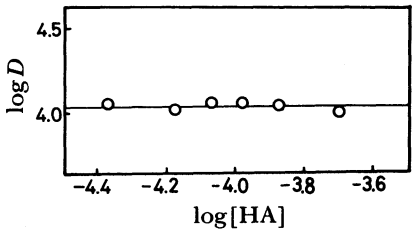

Fig. 1. Distribution of decanoic acid between water and 4-methyl-2-pentanone.
The ionic strength and $[H^+]$ in the aqueous phase are 0.1 mol/dm³ and 10^{-3} mol/dm³, respectively.

dm³ ($NaClO_4$). Under the present experimental conditions the distribution ratio of decanoic acid can be approximated by Eq. 2. As demonstrated in Fig. 1, the distribution ratio of decanoic acid seems to be constant, independent of the concentration of decanoic acid in the aqueous phase. This suggests that the dimerization of decanoic acid in the organic phase (4-methyl-2-pentanone) does not occur to any appreciable extent. Then, the distribution ratio of decanoic acid is equal to the partition constant: $D=K_{D,HA}$. From Fig. 1, the value of log $K_{D,HA}$ obtained was to be 4.04. G. K. Schweitzer and D. K. Morris[10] have reported that the partition constant of octanoic acid between water and 4-methyl-2-pentanone is about 10^3. In addition, it is evident that the increment of the partition constant of carboxylic acid for each methylene group is nearly constant irrespective of solvent, that is, $\Delta \log K_{D,HA}/\text{-}CH_2\text{-}=$ 0.56—0.60.[11] Then, from these results, the partition constant of decanoic acid between water and 4-methyl-2-pentanone can be expected to be $10^{4.12-4.20}$. This is in fairly good agreement with the present value.

Consequently, under the present experimental conditions, the concentration of the monomeric decanoic acid in the 4-methyl-2-pentanone phase can be adequately approximated by the total concentration of decanoic acid: $[HA]_o=C_{HA}$. For the other ketones used the similar relations are expected to hold.

Distribution of Sodium Perchlorate. In the present work, the ionic strength in the aqueous phase was kept constant by sodium perchlorate. Then, the distribution ratio of sodium perchlorate between water and some ketones were determined under the following experimental conditions: $C_{NaClO_4}=0.1$ mol/dm³ and $-\log[H^+]=3.5$. The results are summarized in Table 1. The distribution ratio of sodium perchlorate between water and 4-methyl-2-pentanone is reported[12] to be $10^{-2.60}$. The value for 4-methyl-2-pentanone in Table 1 is in fair agreement with this. As shown in Table 1, the distribution ratio of sodium perchlorate for any ketone is extremely small. Thus, the effect of perchlorate ion on the present extraction systems was proved to be negligible.

TABLE 1. DISTRIBUTION RATIO OF SODIUM PERCHLORATE BETWEEN WATER AND SOME KETONES

Solvent	log*D*[a]
2-Pentanone	−2.24
3-Pentanone	−2.50
2-Hexanone	−2.70
4-Methyl-2-pentanone	−2.82
5-Methyl-2-hexanone	−3.06
2-Octanone	−3.27

a) $C_{NaClO_4}=0.1$ mol/dm³ and $-\log[H^+]=3.5$.

Extraction of Copper(II) with Decanoic Acid. The extraction equilibrium in the present systems was elucidated according to the previously described manner.[9]

As previously reported, if a *j*-merized copper(II) decanoate, $Cu_jA_{2j}(HA)_a$ is responsible for the extraction, the extraction equilibrium can be expressed as follows:

$$j\mathrm{Cu}^{2+} + (2j+\mathrm{a})(\mathrm{HA})_o \rightleftharpoons (\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a)_o + 2j\mathrm{H}^+,$$

with the extraction constant:

$$K_{ex(ja)} = \frac{[\mathrm{Cu}_j\mathrm{A}_{2j}(\mathrm{HA})_a]_o[\mathrm{H}^+]^{2j}}{[\mathrm{Cu}^{2+}]^j[\mathrm{HA}]_o^{(2j+a)}}, \tag{3}$$

where the subscript o refers to the organic phase.

From the results obtained for alcohols,[9] it is expected that the monomeric and dimeric copper(II) decanoates are responsible for the extraction of copper(II) with decanoic acid in ketones. Then, the following equation can be expected to hold for the present extraction systems:

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

where the subscript w refers to the aqueous phase, and $K_{ex(1a)}$ and $K_{ex(2p)}$ represent the extraction constants of the monomer $CuA_2(HA)_a$ and the dimer $Cu_2A_4(HA)_p$, respectively. By comparing the plot of the values of the left-hand side of Eq. 4 against ($\log C_{Cu,w}-2\log[H^+]$) at constant $[HA]_o$ with the normalized curve, $\log(1+X)$ *vs.* $\log X$, it is confirmed that the monomeric and dimeric copper(II) decanoates are responsible for the extraction. The results obtained for 2-hexanone are shown in Fig. 2. As expected, it was proved that the monomer $CuA_2(HA)_a$ and the dimer $Cu_2A_4(HA)_p$ were extracted into the 2-hexanone phase. The same results were obtained for the other ketones.

In the region where the monomer prevails, it was found by the same approach as in the previous work[9] that the two monomeric copper(II) decanoates were responsible for the extraction and they were CuA_2 and $CuA_2(HA)_a (a \geqq 1)$. Then, we have the following expression in the similar manner described in the previous report:[9]

$$\log C_{\mathrm{Cu,o}} - (\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H}^+]) - 2\log[\mathrm{HA}]_o = \log K_{ex(10)} + \log\left(1 + \frac{K_{ex(1a)}}{K_{ex(10)}}[\mathrm{HA}]_o^{a}\right), \tag{5}$$

where $K_{ex(10)}$ and $K_{ex(1a)}$ represent the extraction constants of the monomeric species, CuA_2 and $CuA_2(HA)_a$, respectively. By comparing the plot of the values of

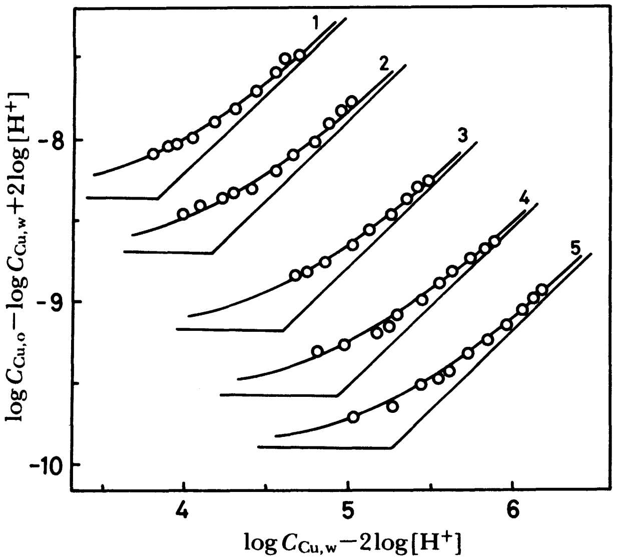

Fig. 2. The identification of the degree of polymerization of Cu(II) decanoates.
C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.0, No. 4: 0.7, No. 5: 0.5 mol/dm^3. Solvent: 2-hexanone.
Solid curves are the normalized curves, log(1+X) *vs.* log$X$. Solid lines are the asymptotes of the normalized curves.

the left-hand side of Eq. 5 against log[HA]$_o$ with the following normslized curves: log(1+X^n) *vs.* log$X$, we can find the number of decanoic acid molecules involved in another monomeric copper(II) decanoate. The results are shown in Figs. 3a and 3b. As can be seen in Figs. 3a and 3b, for all the solvents the plots fit well the normalized curve with n=1, that is, a=n=1. Thus, CuA_2 and CuA_2HA are found to be responsible for the extraction. From Figs. 3a and 3b, we can also obtain the respective extraction constants $K_{ex(10)}$ and $K_{ex(11)}$ by fitting the normalized curve to the observed values. The results obtained for each solvent are listed in Table 2 together with the other constants.

Subsequently, the composition of the dimeric copper(II) decanoates was determined by the same manner as in the previous paper.[9] It was proved that the dimeric species in each ketone phase were Cu_2A_4 and $Cu_2A_4(HA)_p (p \geqq 1)$. Then, we can obtain the following expression:

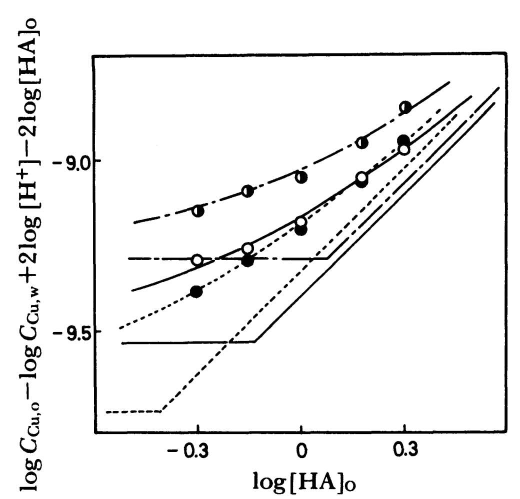

Fig. 3a. Determination of the number of decanoic acid molecules involved in the monomeric Cu(II) decanoates.
Curves are the normalized curves, log(1+X) *vs.* log$X$. Straight lines are the asymptotes of the normalized curves. Solvent; ◑: 3-pentanone, ○: 2-hexanone, ●: 2-octanone.

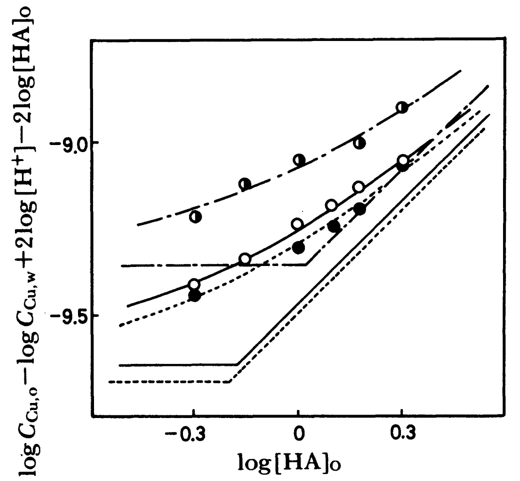

Fig. 3b. Determination of the number of decanoic molecules involved in the monomeric Cu(II) decanoates.
Curves and straight lines are the same as in Fig. 3a. Solvent; ◑: 2-pentanone, ○: 4-methyl-2-pentanone, ●: 5-methyl-2-hexanone.

Table 2. Extraction, dimerization, and adduct formation constants of copper(II) decanoates

	3-Pentanone	2-Pentanone	2-Hexanone	4-Methyl-2-pentanone	5-Methyl-2-hexanone	2-Octanone
$\delta^{a)}/J^{1/2}cm^{-3/2}$	18.5	18.4	17.7	17.6	17.7	17.8
$V^{b)}/cm^3$	106	108	124	126	141	158
log $K_{ex(10)}$	−9.29	−9.36	−9.54	−9.65	−9.70	−9.74
log $K_{ex(11)}$	−9.37	−9.39	−9.40	−9.47	−9.50	−9.33
log $K_{ex(20)}$	−14.70	−14.74	−14.35	−14.34	−14.18	−13.88
log $K_{ex(22)}$	−14.50	−14.74	−14.43	−14.58	−14.44	−14.22
log K_{dim-1}	3.88	3.98	4.73	4.96	5.22	5.60
log K_{dim-2}	4.24	4.04	4.37	4.36	4.56	4.44
log $K_{ad,monomer}$	−0.08	−0.03	0.14	0.18	0.20	0.41
log $\beta_{ad,dimer}$	0.20	0.00	−0.08	−0.24	−0.26	−0.34

a) : Solubility parameter. b) : Molar volume.

$$\log C_{\mathrm{Cu,o}} - 2(\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H^+}]) - 4\log[\mathrm{HA}]_\mathrm{o}$$
$$= \log\left(1+\frac{K_{\mathrm{ex(2}p)}}{K_{\mathrm{ex(20)}}}[\mathrm{HA}]_\mathrm{o}{}^{p}\right) + \log K_{\mathrm{ex(20)}} + \log 2, \quad (6)$$

where $K_{\mathrm{ex(20)}}$ and $K_{\mathrm{ex(2p)}}$ refer to the extraction constants of Cu_2A_4 and $Cu_2A_4(HA)_p$, respectively. The values of the left-hand side of Eq. 6 were plotted against $\log[HA]_o$. As shown in Figs. 4a and 4b, for all the solvents the plots fit well the normalized curve, $\log(1+X^2)$ *vs.* $\log X$, that is, $p=n=2$. As expected, the dimeric species were Cu_2A_4 and $Cu_2A_4(HA)_2$ irrespective of the solvent. From Figs. 4a and 4b we can also obtain the respective extraction constants, $K_{\mathrm{ex(20)}}$ and $K_{\mathrm{ex(22)}}$ by fitting the normalized curve to the observed values. The results are summarized in Table 2 together with the other constants.

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

$$\mathrm{Cu^{2+}} + 2(\mathrm{HA})_\mathrm{o} \overset{K_{\mathrm{ex(10)}}}{\rightleftharpoons} (\mathrm{CuA_2})_\mathrm{o} + 2\mathrm{H^+},$$
$$\mathrm{Cu^{2+}} + 3(\mathrm{HA})_\mathrm{o} \overset{K_{\mathrm{ex(11)}}}{\rightleftharpoons} (\mathrm{CuA_2HA})_\mathrm{o} + 2\mathrm{H^+},$$
$$2\mathrm{Cu^{2+}} + 4(\mathrm{HA})_\mathrm{o} \overset{K_{\mathrm{ex(20)}}}{\rightleftharpoons} (\mathrm{Cu_2A_4})_\mathrm{o} + 4\mathrm{H^+},$$
$$2\mathrm{Cu^{2+}} + 6(\mathrm{HA})_\mathrm{o} \overset{K_{\mathrm{ex(22)}}}{\rightleftharpoons} (\mathrm{Cu_2A_4(HA_2)_o}) + 4\mathrm{H^+}.$$

Then, the adduct formation and dimerization of copper(II) decanoates in the present ketone solutions can be formulated as:

$$\mathrm{CuA_2} + \mathrm{HA} \overset{K_{\mathrm{ad,monomer}}}{\rightleftharpoons} \mathrm{CuA_2HA},$$
$$\mathrm{Cu_2A_4} + 2\mathrm{HA} \overset{\beta_{\mathrm{ad,dimer}}}{\rightleftharpoons} \mathrm{Cu_2A_4(HA)_2},$$
$$2\mathrm{CuA_2} \overset{K_{\mathrm{dim-1}}}{\rightleftharpoons} \mathrm{Cu_2A_4},$$
$$2\mathrm{CuA_2HA} \overset{K_{\mathrm{dim-2}}}{\rightleftharpoons} \mathrm{Cu_2A_4(HA)_2}.$$

We can readily calculate the corresponding adduct formation and dimerization constants from the respective extraction constants for each solvent. The values obtained are listed in Table 2 together with the extraction constants. In addition, the dimerization constants of copper(II) decanoate in alcohols[9] are shown in Table 3 for comparison.

Solvent Effects on the Dimerization of Copper(II) Decanoate in the Ketone Solutions. According to the regular solution theory,[13,14] the dimerization constant of copper(II) decanoate, $K_{\mathrm{dim-1}}$ is given as follows by the same approach as in the previous work:[9]

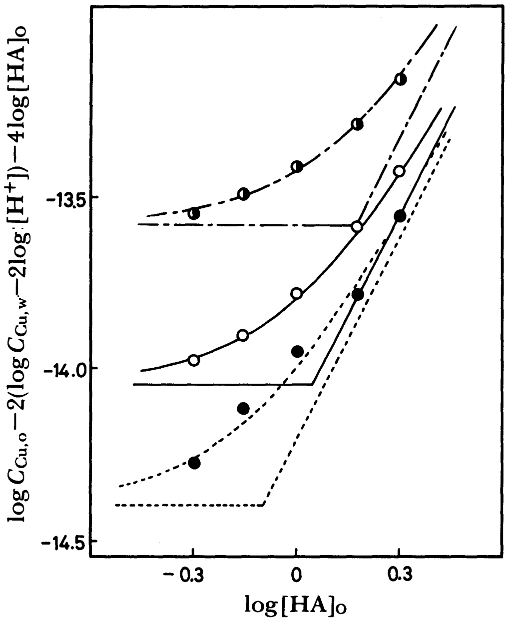

Fig. 4a. Determination of the number of decanoic acid molecules involved in the dimeric Cu(II) decanoates.
Curves and straight lines are the normalized curves, $\log(1+X^2)$ *vs.* $\log X$ and their asymptotes, respectively. Solvent; ◑: 2-octanone, ○: 2-hexanone, ●: 3-pentanone.

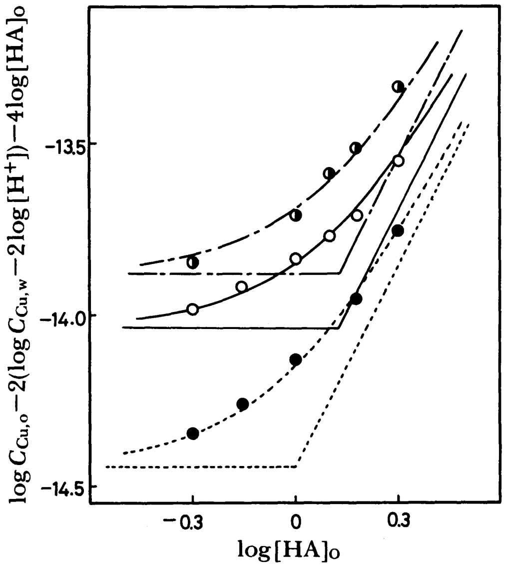

Fig. 4b. Determination of the number of decanoic acid molecules involved in the dimeric Cu(II) decanoates.
Curves and straight lines are the same as in Fig. 4a. Solvent; ◑: 5-methyl-2-hexanone, ○: 4-methyl-2-pentanone, ●: 2-pentanone.

TABLE 3. DIMERIZATION CONSTANTS OF COPPER(II) DECANOATE IN ALCOHOLS[9]

	Cyclohexanol	1-Pentanol	1-Hexanol	1-Heptanol	1-Octanol[8]
$\delta^{a)}/\mathrm{J^{1/2}cm^{-3/2}}$	23.3	22.7	22.0	21.5	21.1
$V^{b)}/\mathrm{cm^3}$	103	108	125	142	158
$\log K_{\mathrm{dim-1}}$	2.23	2.26	2.77	3.04	3.46

a) : Solubility parameter. b) : Molar volume.

$$\log K_{\mathrm{dim-1}} - \log V_s = 0.43 n V_s(\delta_s - \delta')^2/RT + \log K_{\mathrm{dim-1}}{}^\circ - 3, \qquad (7)$$

where V_s and δ_s represent the molar volume and the solubility parameter of the solvent, δ' refers to the solubility parameter of copper(II) decanoate, $K_{\mathrm{dim-1}}{}^\circ$ denotes the dimerization constant of copper(II) decanoate in an ideal solution, and n denotes the number of solvent molecules set free in the dimerization of copper(II) decanoate, that is, $nV_s = 2V_{\mathrm{CuA_2}} - V_{\mathrm{Cu_2A_4}}$, where $V_{\mathrm{CuA_2}}$ and $V_{\mathrm{Cu_2A_4}}$ represent the molar volume of the monomeric and dimeric copper(II) decanoates, respectively. The optimum δ' value based on the assumption, that the monomeric and dimeric copper(II) decanoates have the same solubility parameter, was found to be 24.1 ($\mathrm{J^{1/2}cm^{-3/2}}$) from the previous work.[9] According to Eq. 7, the plot of ($\log K_{\mathrm{dim-1}} - \log V_s$) against $0.43\, V_s(\delta_s - \delta')^2/RT$ should result in a straight line with a slope of n. The straight line shown in Fig. 5 leads to the validity of Eq. 7. The previous results for alcohol solvents are also implied in Fig. 5 for comparison. The values of n and $\log K_{\mathrm{dim-1}}{}^\circ$ were calculated to be 2.8 and 3.19, respectively, by the least squares method. The value of n for alcohols was revealed to be 4.5 in the previous paper.[9] Thus, it was proved that the number of solvent molecules liberated in the formation of the dimeric copper(II) decanoate in ketones was less than that in alcohols. This suggests that the solvation of copper(II) decanoates in these two kinds of solvents differs from each other. Taking into account the hydrogen bonding abilities of the two types of solvents, it can be expected that in alcohols the copper(II) decanoates are much more solvated than in ketones. Further, judging from the difference in the n value between alcohols and ketones, the monomeric copper(II) species in alcohols seems to be more extensively solvated compared to the dimeric species. This is consistent with the view that the lower dimerization constant of copper(II) decanoate in alcohols is attributable to the more favorable solvation of the monomeric copper(II) decanoate by alcohol molecules.

On the other hand, as seen in Fig. 5, the intercept of the respective straight lines for alcohols and ketones agreed closely with one another. Then, the dimerization constant of copper(II) decanoate in an ideal solution, which was estimated by the extrapolation of the respective linear plots for alcohols and ketones, were found to be practically equal: $\log K_{\mathrm{dim-1}}{}^\circ = 3.14$ and 3.19, respectively.

Thus, the dimerization of copper(II) decanoate in the organic solvent seems to be strongly influenced by the solvation. The difference between the solvation of copper(II) decanoates in alcohols and ketones can be primarily attributable to the hydrogen bonding abilities of these two types of solvents.

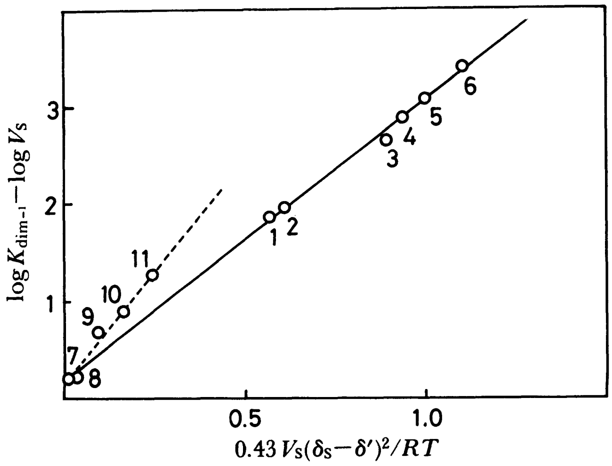

Fig. 5. Correlation of the dimerization constant of Cu(II) decanoate with the solubility parameter of solvents. Solid and dotted lines are the straight lines with a slope of 2.8 and 4.5, and with a intercept of 0.19 and 0.14, respectively. $\delta' = 24.1$ ($\mathrm{J^{1/2}cm^{-3/2}}$). Ketones; No. 1: 3-pentanone, No. 2: 2-pentanone, No. 3: 2-hexanone, No. 4: 4-methyl-2-pentanone, No. 5: 5-methyl-2-hexanone, No. 6: 2-octanone, Alcohols; No. 7: cyclohexanol, No. 8: 1-pentanol, No. 9: 1-hexanol, No. 10: 1-heptanol, No. 11: 1-octanol.

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