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

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The extraction of copper(II) with decanoic acid in some alcohol solvents was carried out at 25 °C and at 0.1 mol/dm^3 ($NaClO_4$) aqueous ionic strength. Alcohols used are cyclohexanol, 1-pentanol, 1-hexanol, and 1-heptanol. In these solvents, monomeric and dimeric copper(II) decanoates are responsible for the extraction. Species involved in each organic phase are CuA_2, 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 are written as:

$$2CuA_2 \overset{K_{dim-1}}{\rightleftharpoons} Cu_2A_4$$

$$Cu_2A_4 + 2HA \overset{\beta_{ad,dim}}{\rightleftharpoons} Cu_2A_4(HA)_2$$

The following dimerization and adduct formation constants were obtained: $\log K_{dim-1}=2.23$ and $\log \beta_{ad,dim}=0.26$ for cyclohexanol, 2.26 and -0.03 for 1-pentanol, 2.77 and -0.04 for 1-hexanol, and 3.04 and -0.24 for 1-heptanol, respectively.

It is well-known that the dimeric copper(II) carboxylate involving free carboxylic acids, $Cu_2A_4(HA)_2$ is responsible for the extraction of copper(II) with aliphatic carboxylic acids in various inert solvents.[1-6] In the previous paper,[7] it has been shown that copper(II) is extracted with decanoic acid in several inert solvents as dimeric copper(II) decanoate, $Cu_2A_4(HA)_2$, and that the solvent effect on the extraction constants is interpreted in terms of the regular solution theory. In the subsequent paper,[8] the extracted species of copper(II) with decanoic acid in 1-octanol have been established to be not only the dimeric copper(II) decanoates(Cu_2A_4 and $Cu_2A_4(HA)_2$) but also the monomeric ones(CuA_2 and CuA_2HA). Also, the adduct formation and dimerization of copper(II) decanoates in 1-octanol have been mentioned.

The following solvent series, in which the formation of dimeric copper(II) carboxylates becomes more prominent, is reported: water, pyridine<methanol<ethanol, acetone, chloroform, benzene<carbon tetrachloride, dioxane<diethyl ether, and it is remarked that this solvent series can be discussed in terms of the dielectric constant of the solvents and the coordination power of the solvents to the metal or complex ion.[9]

The present paper describes the results of the extraction of copper(II) decanoates in several alcohol solvents. The solvent effect on the dimerization constant of copper(II) decanoate is interpreted in terms of the regular solution theory.

Experimental

Reagents. *Solvents*: 1-Pentanol, 1-hexanol, and 1-heptanol of reagent grade were washed successively first with dilute sodium hydroxide solution, secondly with dilute perchloric acid solution and thirdly with distilled water. Furthermore, they were purified by distillation and saturated with distilled water at 25 °C. Cyclohexanol of reagent grade was purified by distillation and saturated with distilled water at 25 °C.

Copper(II) perchlorate, sodium perchlorate, and decanoic acid were the same as presented 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 report.[8]

Apparatus. The apparatus were similar to those previously used,[8] except for the use of Orion research microprocessor Ionalyzer 901(Orion Research Inc., U.S.A.) for the determination of hydrogen ion concentration in the aqueous phase.

Results and Discussion

Extraction Equilibrium. As previously described, if a j-merized copper(II) decanoate, $Cu_jA_{2j}(HA)_a$ is extracted into the organic phase, the extraction equilibrium can be expressed as follows:

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

with the extraction constant:

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

where the subscript o refers to the organic phase.

Total concentration of copper in the organic phase, $C_{Cu,o}$ is represented as:

$$C_{Cu,o} = \sum_j\sum_a j[Cu_jA_{2j}(HA)_a]_o$$

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

It is expected from the results of the extraction of copper(II) with decanoic acid in 1-octanol that the monomer $CuA_2(HA)_a$ and the dimer $Cu_2A_4(HA)_p$ are both responsible for the present extraction systems. Then, the following equation can be derived from Eq. 2:

$$\log C_{Cu,o} - (\log C_{Cu,w} - 2\log [H^+]) = \log K_{ex(1a)} + (2+a)\log[HA]_o + \log\left(1+\frac{2K_{ex(2p)}}{K_{ex(1a)}}[HA]_o^{(2+p-a)}C_{Cu,w}[H^+]^{-2}\right), \tag{3}$$

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. Then, by comparing the plot of the values of the left-hand side of Eq. 3 against ($\log C_{Cu,w}$—$2\log [H^+]$) at constant $[HA]_o$ with the normalized curve, $\log(1+X)$ *vs.* $\log X$, we can check the degree of polymerization of the extracted species. The result obtained for 1-hexanol is shown in Fig. 1. As expected, it was proved that the monomeric and dimeric copper(II) decanoates were responsible for the extraction in which 1-hexanol was used as a diluent. For the other alcohols used the same results were obtained.

In the region where the monomer prevails, Eq. 2 is simplified to:

$$\log C_{\mathrm{Cu,o}} - (\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H}^+]) = \log \sum_{a} (K_{\mathrm{ex}(1a)}[\mathrm{HA}]_{\mathrm{o}}^{(2+a)}). \qquad (4)$$

According to Eq. 4, we can find the number of decanoic acid molecules involved in the monomer from the slope of the plots of $\{\log C_{\mathrm{Cu,o}} - (\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H}^+])\}$ against $\log[\mathrm{HA}]_{\mathrm{o}}$. The result for 1-hexanol is illustrated in Fig. 2. As evident from Fig. 2, the plot fits well a straight line with a slope of two, that is, $2+a=2$ or $a=0$. The same results were obtained for the other solvents. Consequently, the composition of the monomeric copper(II) decanoate is $\mathrm{CuA_2}$ irrespective of the solvent. The monomeric species $\mathrm{CuA_2HA}$ for 1-octanol[8] is not extracted to any appreciable extent in these extraction systems. The extraction constant $K_{\mathrm{ex}(10)}$ of the monomer can be determined from Eq. 4($a=0$). The values obtained for the respective solvent are summarized in Table 1 together with the other constants. The previous results for 1-octanol are also included in Table 1 for comparison.

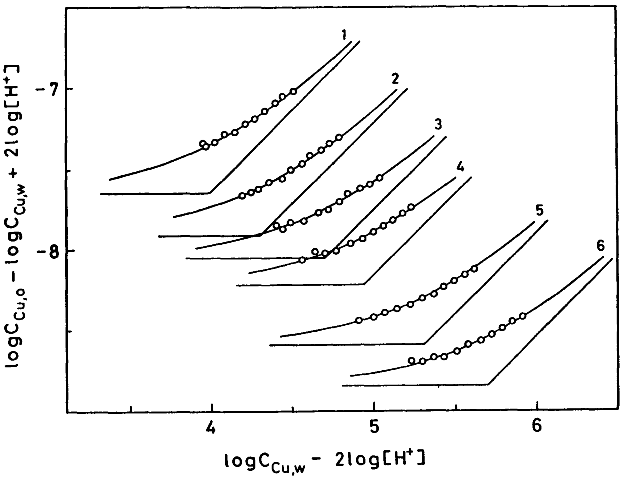

Fig. 1. The identification of the degree of polymerization of Cu(II) decanoates.

Solid curves are the normalized curves, $\log(1+X)$ *vs.* $\log X$. Solid lines are the asymptotes of the normalized curves. C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.25, No. 4: 1.0, No. 5: 0.7, No. 6: 0.5 mol/dm^3. Solvent: 1-hexanol.

On the other hand, in the region where the predominant extracted species are the dimer, that is, the plots shown in Fig. 1 fit with the straight line asymptotes with a slope of unity, the following expression is derived from Eq. 2:

$$\log C_{\mathrm{Cu,o}} - 2(\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H}^+]) = \log 2\sum_{p}(K_{\mathrm{ex}(2p)}[\mathrm{HA}]_{\mathrm{o}}^{(4+p)}). \qquad (5)$$

According to Eq. 5, the slope of the plot of the left-hand side of Eq. 5 against $\log[\mathrm{HA}]_{\mathrm{o}}$ gives the number of decanoic acid molecules involved in the dimeric species. The results for 1-hexanol are shown in Fig. 3. As evident from Fig. 3, at least two dimeric copper(II) decanoates with the different number of decanoic acid molecules are responsible for the extraction. At lower concentration of decanoic acid in the organic phase, the plot is close to a straight line with a slope of 4.0. Therefore, one of the dimers is certainly $\mathrm{Cu_2A_4}$($p=0$ in Eq. 5). In addition, the slope of the plot described above gets steeper with the concentration of decanoic acid in the organic phase. It is suggested that another dimer $\mathrm{Cu_2A_4(HA)}_p$($p\geqq 1$) is responsible for the extraction at higher $[\mathrm{HA}]_{\mathrm{o}}$. Then, in the region where the dimer predominates, the fol-

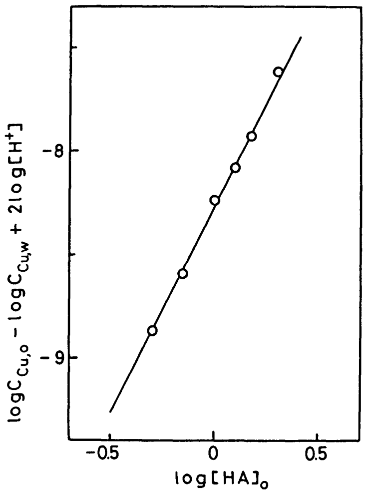

Fig. 2. Determination of the number of decanoic acid molecules involved in the monomeric Cu(II) decanoate.

Solid line is the straight line with a slope of 2.0. Solvent: 1-hexanol.

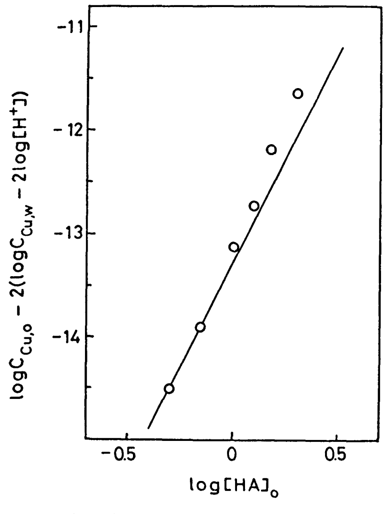

Fig. 3. Determination of the number of decanoic acid molecules involved in the dimeric Cu(II) decanoates.

Solid line is the straight line with a slope of 4.0. Solvent: 1-hexanol.

lowing expression can be written from Eq. 2:

$$C_{\mathrm{Cu,o}} = 2([\mathrm{Cu_2A_4}]_\mathrm{o} + [\mathrm{Cu_2A_4(HA)}_p]_\mathrm{o})$$
$$= 2K_{\mathrm{ex(20)}}[\mathrm{Cu^{2+}}]^2[\mathrm{HA}]_\mathrm{o}{}^4[\mathrm{H^+}]^{-4}$$
$$\times\left(1+\frac{K_{\mathrm{ex}(2p)}}{K_{\mathrm{ex(20)}}}[\mathrm{HA}]_\mathrm{o}{}^p\right), \tag{6}$$

which is rewritten as a logarithmic form:

$$\log C_{\mathrm{Cu,o}} - 2(\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H^+}]) - 4\log[\mathrm{HA}]_\mathrm{o}$$
$$= \log\left(1+\frac{K_{\mathrm{ex}(2p)}}{K_{\mathrm{ex(20)}}}[\mathrm{HA}]_\mathrm{o}{}^p\right) + \log K_{\mathrm{ex(20)}} + \log 2, \tag{7}$$

where $K_{\mathrm{ex(20)}}$ and $K_{\mathrm{ex}(2p)}$ represent the extraction constants of $\mathrm{Cu_2A_4}$ and $\mathrm{Cu_2A_4(HA)}_p$, respectively. Compared the plot of $\{\log C_{\mathrm{Cu,o}} - 2(\log C_{\mathrm{Cu,w}} - 2\log[\mathrm{H^+}]) - 4\log[\mathrm{HA}]_\mathrm{o}\}$ *vs.* $\log[\mathrm{HA}]_\mathrm{o}$ with the normalized curves, $\log(1+X^n)$ *vs.* $\log X$, we find the composition of another dimeric copper(II) decanoate. The result for 1-hexanol is shown in Fig. 4. Figure 4 shows that the plot fits well the normalized curve, $\log(1+X^2)$ *vs.* $\log X$, that is, $p=n=2$. Thus, we have $\mathrm{Cu_2A_4(HA)_2}$ together with $\mathrm{Cu_2A_4}$ in the organic phase. From Fig. 4 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. In a similar manner as above, it was found that the same dimeric copper(II) decanoates as just described were responsible for the other extraction systems in which 1-heptanol, 1-pentanol, and cyclohexanol were used as solvents.

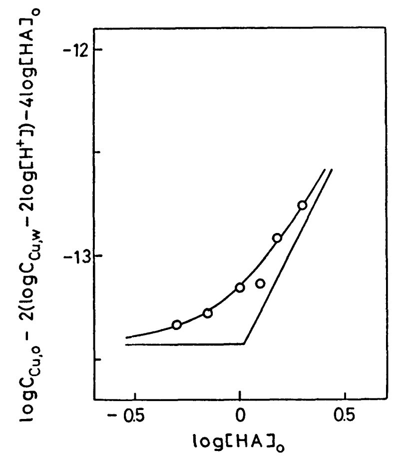

Fig. 4. Determination of the number of decanoic acid molecules involved in the dimeric Cu(II) decanoates by the curve fitting method.
Solid curve is the normalized curve, $\log(1+X^2)$ *vs.* $\log X$. Solid lines are the asymptotes of the normalized curve. Solvent: 1-hexanol.

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

$$\mathrm{Cu^{2+}} + 2(\mathrm{HA})_\mathrm{o} \xrightleftharpoons{K_{\mathrm{ex(10)}}} (\mathrm{CuA_2})_\mathrm{o} + 2\mathrm{H^+},$$
$$2\mathrm{Cu^{2+}} + 4(\mathrm{HA})_\mathrm{o} \xrightleftharpoons{K_{\mathrm{ex(20)}}} (\mathrm{Cu_2A_4})_\mathrm{o} + 4\mathrm{H^+},$$
$$2\mathrm{Cu^{2+}} + 6(\mathrm{HA})_\mathrm{o} \xrightleftharpoons{K_{\mathrm{ex(22)}}} (\mathrm{Cu_2A_4(HA)_2})_\mathrm{o} + 4\mathrm{H^+}.$$

The corresponding extraction constants are summarized in Table 1.

Then, the adduct formation and dimerization of copper(II) decanoates in these alcohol solutions can be described as follows:

$$\mathrm{Cu_2A_4} + 2\mathrm{HA} \xrightleftharpoons{\beta_{\mathrm{ad,dim}}} \mathrm{Cu_2A_4(HA)_2},$$
$$2\mathrm{CuA_2} \xrightleftharpoons{K_{\mathrm{dim\text{-}1}}} \mathrm{Cu_2A_4}.$$

The corresponding adduct formation and dimerization constants can be calculated from the respective extraction constants for each solvent. The results obtained are summarized in Table 1 together with the extraction constants.

Solvent Effects on the Dimerization of Copper(II) Decanoate in the Alcohol Solutions. According to the regular solution theory,[10] the activity of a solute A in a solvent S can be approximated in a dilute solution by the following equation:

$$\ln a_\mathrm{A} = \ln \phi_\mathrm{A} + \ln (V_\mathrm{S}/V_\mathrm{A}) + V_\mathrm{A}(\delta_\mathrm{S}-\delta_\mathrm{A})^2/RT, \tag{8}$$

where ϕ, V, and δ refer to the volume fraction, the molar volume and the solubility parameter, respectively. The molar concentration of a solute A is written as:

$$[\mathrm{A}] = 1000\phi_\mathrm{A}/V_\mathrm{A}. \tag{9}$$

From Eqs. 8 and 9, the following expression can be derived:

$$\log a_\mathrm{A} = \log[\mathrm{A}] + \log V_\mathrm{s} + 0.43V_\mathrm{A}(\delta_\mathrm{S}-\delta_\mathrm{A})^2/RT - 3. \tag{10}$$

The dimerization constant of copper(II) decanoate,

TABLE 1. EXTRACTION, DIMERIZATION, AND ADDUCT FORMATION CONSTANTS OF COPPER(II) DECANOATES

	Cyclohexanol	1-Pentanol	1-Hexanol	1-Heptanol	1-Octanol[8]
ε[a]	15.0	13.9	13.3	11.5	10.3
δ[b]$/\mathrm{J^{1/2}\,cm^{-3/2}}$	23.3	22.7	22.0	21.5	21.1
V[c]$/\mathrm{cm^3}$	103	108	125	142	158
$\log K_{\mathrm{ex(10)}}$	−8.34	−8.13	−8.25	−8.26	−8.41
$\log K_{\mathrm{ex(11)}}$					−8.65
$\log K_{\mathrm{ex(20)}}$	−14.45	−14.00	−13.73	−13.48	−13.36
$\log K_{\mathrm{ex(22)}}$	−14.19	−14.03	−13.77	−13.72	−13.77
$\log K_{\mathrm{dim\text{-}1}}$	2.23	2.26	2.77	3.04	3.46
$\log \beta_{\mathrm{ad,\,dim}}$	0.26	−0.03	−0.04	−0.24	−0.41

a) Dielectric constant. b) Solubility parameter. c) Molar volume.

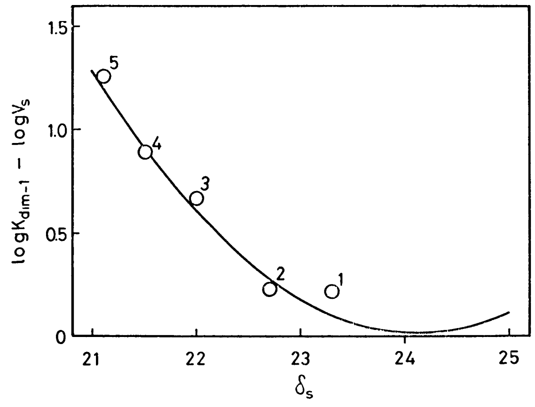

Fig. 5. Estimation of the solubility parameter of Cu(II) decanoate.
Solid line is the calculated curve of the second order with respect to δ_s on the basis of Eq. 12. No. 1: Cyclohexanol, No. 2: 1-pentanol, No. 3: 1-hexanol, No. 4: 1-heptanol, No. 5: 1-octanol.

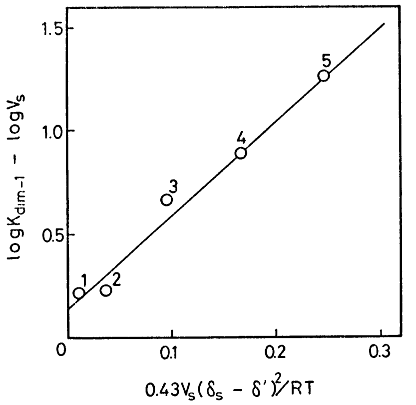

Fig. 6. Correlation of the dimerization constant of Cu(II) decanoate with the solubility parameter of solvents.
Solid line is the straight line with a slope of 4.5. $\delta'=24.1$ ($J^{1/2}/\mathrm{cm}^{3/2}$). Numbers are the same as in Fig. 5.

K_{dim-1} is given as follows:

$$\log K_{dim-1} = \log K_{dim-1}{}^{\circ} + \log\frac{(f_{CuA_2})^2}{f_{Cu_2A_4}}, \qquad (11)$$

where $K_{dim-1}{}^{\circ}$ denotes the dimerization constant of copper(II) decanoate in an ideal solution and f's are the activity coefficients of the monomeric and dimeric copper(II) decanoates. If the monomeric and dimeric copper(II) decanoates have the same solubility parameter, we can obtain the following expression from Eq. 10:

$$\log K_{dim-1} - \log V_s = 0.43nV_s(\delta_s-\delta')^2/RT + \log K_{dim-1}{}^{\circ} - 3, \qquad (12)$$

where n denotes the number of solvent molecules set free in the dimerization of copper(II) decanoate, that is, $nV_s=2V_{CuA_2}-V_{Cu_2A_4}$, and $\delta'=\delta_{CuA_2}=\delta_{Cu_2A_4}$. Although the value of V_s in Eq. 12 varies from solvent to solvent, that of ($\log K_{dim-1}-\log V_s$) can be approximately related to the second order with respect to δ_s. Then it is expected that the value of ($\log K_{dim-1}-\log V_s$) is minimized at $\delta_s=\delta'$. This relationship between ($\log K_{dim-1}-\log V_s$) and δ_s is illustrated in Fig. 5. In Fig. 5, the plot was extrapolated as smooth as possible to find the value of δ', and resulted in $\delta'=24.1$ ($J^{1/2}/\mathrm{cm}^{3/2}$). Further, according to Eq. 12, the plot of ($\log K_{dim-1}-\log V_s$) *vs.* $0.43V_s(\delta_s-\delta')^2/RT$ should yield a straight line with a slope of n. As expected, the validity of Eq. 12 is demonstrated in Fig. 6. The values of n and $\log K_{dim-1}{}^{\circ}$ were calculated to be 4.5 and 3.14, respectively, by the least squares method. Therefore, it is suggested that 4 to 5 molecules of solvent are liberated in the dimerization of copper(II) decanoate.

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