Formation of Zinc(II) Complexes with Several Carboxylic Acids and Their Extraction with Carbon Tetrachloride

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The distribution of zinc(II) was determined between 0.1 M constant-ionic-strength media containing sodium perchlorate and/or carboxylate ions, A^-, and carbon tetrachloride containing a neutral ligand, quinonline, Q, or the dimer of the same carboxylic acid, $(HA)_2$. The distribution ratio was measured as a function of the concentration of carboxylate ions in the aqueous phase or of that of one of the above neutral ligands, in the organic phase. The extraction constant of the ZnA_2 species in the caproic acid system was found to be $K_{exA}=[ZnA_2]_{org}/[Zn^{2+}][A^-]^2=10^{-0.15}$, while that in the valeric or butyric acid system was too small to be determined. The distribution ratio of zinc(II) increased with an increase in the concentration of the ligand in the organic phase. These increases were explained by the formation of adducts in the organic phase; in the caproate system, the species found were ZnA_2Q and ZnA_2Q_2, ($\beta_{1(org)}=[ZnA_2Q]_{org}/[ZnA_2]_{org}[Q]_{org}=10^{1.92}$, $\beta_{2(org)}=[ZnA_2Q_2]_{org}/[ZnA_2]_{org}[Q]_{org}^2=10^{2.84}$) or $ZnA_2(HA)_4$ ($\beta_{2(org)}=[ZnA_2(HA)_4]_{org}/[ZnA_2]_{org}[(HA)_2]_{org}^2=10^{2.92}$). No polynuclear species was found in these organic phases when the initial zinc(II) concentration in the aqueous phase was less than 10^{-3} M.

Carboxylic acids, especially acetic acid, are widely employed as buffering agents in weakly acidic solutions because they buffer aqueous solutions at around pH 5 and they usually form only weak complexes with various metal ions.

For solvent extraction work, they are also useful buffering reagents. However, the equilibria of carboxylic acid in liquid-liquid distribution systems are rather complicated; in such systems, not only the dissociation of protons in the aqueous phase, but also the two-phase distribution of the acid and its dimerization in the organic phase, should be taken into account. The distribution and dimerization of several carboxylic acids have been studied in systems of carbon tetrachloride by the present authors[1] and in systems of benzene and various other solvents by Kojima, Yoshida, and Tanaka.[2]

The solvent extraction equilibria of metal ions with carboxylic acids are more complicated; the extracted metal species very often contain an undissociated form of the acid as well as the carboxylate anions, and in many cases, various types of polymerized metal species are also found in the organic phase, as has been reported by many authors.

The present study has been carried out in order to determine the distribution equilibria of zinc(II) in the carbon tetrachloride-aqueous system containing carboxylic acids; zinc(II) was extracted with these acids into carbon tetrachloride containing various amounts of quinoline. The results were statistically analyzed, and the equilibrium constants were evaluated. The results were considered on the basis of the present authors' previous work on the distribution equilibria of several carboxylic acids between carbon tetrachloride and the aqueous phase.[1] The extractability of this metal ion in these systems under vairous conditions was also considered.

Experimental

Reagents. The zinc-65 tracer was used throughout this study; it was obtained from the New England Nuclear Co. as a hydrochloric acid solution. In some experiments, a zinc(II) carrier which has been prepared by dissolving a reagent-grade zinc powder in perchloric acid was added. The stock solution of the tracer or of the carrier always contained 0.01 M perchloric acid. Analytical-grade butyric, valeric, and caproic acids were obtained from the Tokyo Kasei Co., the Kanto Chemical Co., or the Merck Co. (Germany). They were of a reagent grade and were distilled before use. The quinoline was obtained from the Merck Co. Carbon tetrachloride was washed three times with same volume of water before use. The other reagents were the same as those reported in previous paper.[1,3,4]

Procedures. All of the experiments were carried out in a thermostated room at 25°±0.3 °C. Five ml of carbon tetrachloride containing a carboxylic acid and, in some cases, quinoline, and 5 ml of an aqueous solution containing sodium hydroxide and sodium perchlorate (the total salt concentration was 1.0×10^{-1} M) and 10^{-3}—10^{-6} M zinc(II) (except when stated otherwise) were placed in stoppered glass tubes (volume, 20 ml); the two phases were agitated by hand or by means of a shaker until the distribution equilibrium was reached, after which the two phases were centrifuged. The distribution ratio of zinc(II) was determined from the γ-radioactivity of each phase. The details of the procedures were the same as those described in previous papers.[3,4] The distribution ratio is always defined as;

$$D=\frac{[\mathrm{Zn(II)}]_{\mathrm{org.total}}}{[\mathrm{Zn(II)}]_{\mathrm{total}}}=\frac{\gamma\text{-count-rate in 1 ml of the org. phase}}{\gamma\text{-count-rate in 1 ml of the aq. phase}}$$

Statistical

The complex formation equilibrium of zinc(II) in the aqueous phase with the anion of a carboxylic acid, HA, can be written as follows;

$$Zn^{2+}+nA^- \rightleftarrows ZnA_n^{2-n} \quad (1)$$

$$\beta_n=\frac{[ZnA_n^{2-n}]}{[Zn^{2+}][A^-]^n} \quad (2)$$

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[1] T. Sekine, M. Isayama, S. Yamaguchi, and H. Moriya, This Bulletin, **40**, 27 (1967).

[2] I. Kojima, M. Yoshida, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 987 (1970).

[3] H. Moriya and T. Sekine, This Bulletin, **44**, 3347 (1971).

[4] H. Moriya and T. Sekine, *ibid.*, **45**, 1626 (1972).

and the total concentration of zinc(II) in such an aqueous phase can be represented by;

$$[\mathrm{Zn^{2+}}]_{\mathrm{total}} = [\mathrm{Zn^{2+}}](1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots) \tag{3}$$

The extraction of zinc(II) as the uncharged complex with this anion into a nonpolar solvent can be represented as follows;

$$\mathrm{Zn^{2+}} + 2\mathrm{A^-} \rightleftarrows \mathrm{ZnA_2(org)} \tag{4}$$

$$K_{\mathrm{exA}} = \frac{[\mathrm{ZnA_2}]_{\mathrm{org}}}{[\mathrm{Zn^{2+}}][\mathrm{A^-}]^2} \tag{5}$$

When the extracted species, $\mathrm{ZnA_2}$, can add n molecules of a neutral ligand, L, such as quinoline or dimerized acid molecule, in the organic phase, the equilibrium can be written as follows;

$$\mathrm{ZnA_2(org)} + n\mathrm{L(org)} \rightleftarrows \mathrm{ZnA_2L}_n\mathrm{(org)} \tag{6}$$

$$\beta_{n\mathrm{(org)}} = \frac{[\mathrm{ZnA_2L}_n]_{\mathrm{org}}}{[\mathrm{ZnA_2}]_{\mathrm{org}}[\mathrm{L}]_{\mathrm{org}}^{\,n}} \tag{7}$$

The distribution ratio of zinc(II) in the presence of quinoline can be written as follows when the adduct formation with the dimer of the carboxylic acid is assumed to be negligible, and, furthermore, when only the first and the second quinoline adducts are formed in the organic phase, while only the first complex with the acid is formed in the aqueous phase;

$$D = \frac{[\mathrm{ZnA_2}]_{\mathrm{org}} + [\mathrm{ZnA_2Q}]_{\mathrm{org}} + [\mathrm{ZnA_2Q_2}]_{\mathrm{org}}}{[\mathrm{Zn^{2+}}] + [\mathrm{ZnA^+}]} \tag{8}$$

By introducing Eqs. (5) and (7) and the stability constant in Eq. (2), Eq. (8) can be rewritten as follows:

$$D = \frac{K_{\mathrm{exA}}[\mathrm{A^-}]^2(1 + \beta_{1\mathrm{(org)}}[\mathrm{Q}]_{\mathrm{org}} + \beta_{2\mathrm{(org)}}[\mathrm{Q}]_{\mathrm{org}}^2)}{1 + \beta_1[\mathrm{A^-}]} \tag{9}$$

The distribution ratio of zinc(II) in the absence of quinoline can be rewritten as follows if the formation of only the first and second adducts in the organic phase, and that of only the first complex in the aqueous phase, are assumed:

$$D = \frac{[\mathrm{ZnA_2}]_{\mathrm{org}} + [\mathrm{ZnA_2(HA)_2}]_{\mathrm{org}} + [\mathrm{ZnA_2(HA)_4}]_{\mathrm{org}}}{[\mathrm{Zn^{2+}}] + [\mathrm{ZnA^+}]} \tag{10}$$

By introducing Eqs. (5) and (7), and the stability constant for the complexes in the aqueous phase, Eq. (10) can be rewritten as follows:

$$D = \frac{K_{\mathrm{exA}}[\mathrm{A^-}]^2(1 + \beta_{1\mathrm{(org)}}[\mathrm{(HA)_2}]_{\mathrm{org}} + \beta_{2\mathrm{(org)}}[\mathrm{(HA)_2}]_{\mathrm{org}}^2)}{1 + \beta_1[\mathrm{A^-}]} \tag{11}$$

Since only the initial concentrations of the carboxylic acid and the hydroxide ion, and the equilibrium concentration of the hydrogen ion are usually obtained, the following treatments are necessary in order to calculate the other concentrations at equilibrium.

When the volumes of the two phases are the same, the following relation can be given for the total concentration of the carboxylic acid in the initial organic phase:

$$C_{\mathrm{HA(org)}} = [\mathrm{A^-}] + [\mathrm{HA}] + [\mathrm{HA}]_{\mathrm{org}} + 2[\mathrm{(HA)_2}]_{\mathrm{org}} \tag{12}$$

The total concentration of the carboxylic acid in the aqueous phase can be written as follows:

$$[\mathrm{HA}]_{\mathrm{total}} = [\mathrm{A^-}] + [\mathrm{HA}] \tag{13}$$

By introducing the dissociation constant, $K_{\mathrm{a}} = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}]$, Eq. (13) can be written as:

$$[\mathrm{HA}]_{\mathrm{total}} = [\mathrm{A^-}](1 + [\mathrm{H^+}]/K_{\mathrm{a}}) \tag{14}$$

When the sodium hydroxide concentration in the initial aqueous phase is denoted by C_{OH}, the $C_{\mathrm{OH}} + [\mathrm{H^+}] = [\mathrm{A^-}] + [\mathrm{OH^-}]$ relation is obtained; when the pH is not too high and not too low (for example, $10^{-10}\,\mathrm{M} < [\mathrm{H^+}] < 10^{-4}\,\mathrm{M}$), this can be written as $C_{\mathrm{OH}} = [\mathrm{A^-}]$. The $[\mathrm{HA}]_{\mathrm{total}}$ value can be estimated from Eq. (14) by using this relation, the value of $[\mathrm{H^+}]$ experimentally obtained, and the value of the dissociation constant.

The following relation is obtained from Eqs. (12) and (13):

$$\begin{aligned}[\mathrm{HA}]_{\mathrm{org.total}} &= C_{\mathrm{HA(org)}} - [\mathrm{HA}]_{\mathrm{total}} \\ &= 2[\mathrm{(HA)_2}]_{\mathrm{org}} + [\mathrm{HA}]_{\mathrm{org}}\end{aligned} \tag{15}$$

By introducing the dimerization constant, $K_{\mathrm{dim(org)}} = [\mathrm{(HA)_2}]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{org}}^2$, Eq. (15) can be rewritten as:

$$[\mathrm{HA}]_{\mathrm{org.total}} = 2[\mathrm{(HA)_2}]_{\mathrm{org}} + \sqrt{[\mathrm{(HA)_2}]_{\mathrm{org}}/K_{\mathrm{dim(org)}}} \tag{16}$$

However, when $[\mathrm{HA}]_{\mathrm{org}} \ll [\mathrm{(HA)_2}]_{\mathrm{org}}$ as under the conditions employed in this study (this will be discussed later), the following relation is obtained from Eq. (15):

$$[\mathrm{(HA)_2}]_{\mathrm{org}} = \frac{1}{2}[\mathrm{HA}]_{\mathrm{org.total}} \tag{17}$$

The experimental data of D at a given value of $[\mathrm{A^-}]$, determined as a function of $[\mathrm{Q}]_{\mathrm{org}}$ or as a function of $[\mathrm{(HA)_2}]_{\mathrm{org}}$, can be transformed to the following equation:

$$\log y = \log c_0(1 + c_1x + c_2x^2) \tag{18}$$

The c_0, c_1, and c_2 constants can be obtained from the plot of the experimental data by a curve-fitting method, as has already been demonstrated.[3,4] The equilibrium constants in Eqs. (5) and (7) can be obtained from these values of c_0, c_1, and c_2.

Results

The experimental results were reproducible, and the recovery of zinc(II) from the two phases was quantitative within the limit of experimental accuracy.

It was found in another work of the present authors[5] that only the first zinc(II) complex is formed with the carboxylic acid in a 0.1 M sodium perchlorate constant ionic medium at 25 °C; the values for $\beta_1 = [\mathrm{ZnA^+}]/[\mathrm{Zn^{2+}}][\mathrm{A^-}]$ are $10^{1.10}$(butyrate), $10^{1.10}$(valerate) and $10^{1.10}$(caproate). These values were used for the analysis of the experimental data of the present work.

The following equation can be written on the basis of the electrical neutrality:

$$[\mathrm{Na^+}] + [\mathrm{H^+}] + 2[\mathrm{Zn^{2+}}] + [\mathrm{ZnA^+}] = [\mathrm{OH^-}] + [\mathrm{ClO_4^-}]$$

Since the concentration of zinc(II) was very low (less than 10^{-5} M), the hydrogen-ion concentrations was in the range of $10^{-5}\,\mathrm{M} > [\mathrm{H^+}] > 10^{-9}\,\mathrm{M}$ (and thus $[\mathrm{H^+}] \ll 0.1\,\mathrm{M}$ and $[\mathrm{OH^-}] \ll 0.1\,\mathrm{M}$), and the initial aqueous phase was a mixture of 0.1 M sodium

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[5] H. Moriya and T. Sekine, to be published.

perchlorate and 0.1 M sodium hydroxide at various mixing ratios, the following relation can be introduced:

$$0.1 \simeq C_{\mathrm{OH}} + [\mathrm{ClO_4^-}] = [\mathrm{A^-}] + [\mathrm{CO_4^-}]$$

The term of the concentration of the undissociated acid in the aqueous phase, [HA], can be regarded as negligible in the statistical analysis of the results of experiments with quinoline because the K_a values for these acids are about 10^{-5}(in 0.1 M sodium perchlorate at 25 °C, they are 1.51×10^{-5}(butyric acid), 1.41×10^{-5} (valeric acid) and 1.45×10^{-5}(caproic acid)),[2] it can be assumed that $[\mathrm{A^-}]\gg[\mathrm{HA}]$ when $-\log\ [\mathrm{H^+}]$ is higher than 7 (in Figs. 1 and 2). For the experiments in the absence of quinoline, the $[\mathrm{H^+}]$ values ranges from $10^{-5.5}$ to $10^{-6.5}$; thus, the [HA] term can not be neglected. This value was calculated from $[\mathrm{H^+}]$, which was determined by potentiometry, $[\mathrm{A^-}]$ (which is equal to C_{OH}), and K_a.

Extraction in the Presence of Quinoline. The distribution ratio of zinc(II) in an aqueous phase at a given $[\mathrm{A^-}]$ is enhanced by the addition of quinoline to the organic phase. Since the distribution constant of quinoline is not small (77 between carbon tetrachloride and 3 M sodium perchlorate[6]), the $[\mathrm{Q}]_{\mathrm{org\cdot initial}}=[\mathrm{Q}]_{\mathrm{org}}$ relation can be assumed. Figure 1 shows the change in the distribution ratio with the change in the quinoline concentration when $[\mathrm{A^-}]$ is 1.0×10^{-1} M and when the total concentration of carboxylic acid in the organic phase at equilibrium is less than 10^{-2} M. Figure 2 shows the dependence of the distribution ratio on the concentration of the caproate anion in the aqueous phase when the organic phase contains less than 10^{-2} M of the carboxylic acid and a certain amount of quinoline (0.1 M, 0.25 M or 0.5 M). In this figure, the effect of the carboxylate complex in the aqueous phase has been corrected by plotting $\log\ D(1+\beta_1[\mathrm{A^-}])$ instead of $\log\ D$ (*cf.* Eq. 9). As may be seen from Fig. 2, the extraction is proportional to the square of $[\mathrm{A^-}]$; thus, it can be concluded that the metal species in these organic phases contains at least two carboxylate anions. Furthermore, as will be seen later, no adduct of zinc(II) caproate with the dimer of the acid is formed under these conditions, the distribution ratio can well be represented by Eqs. (8) and (9). Since the extraction with butyric and valeric acid is very poor in the absence of quinoline, the K_{exA} value in Eq. (5) for these extractions could not be determined and the distribution ratio could be given for these systems by the equation:

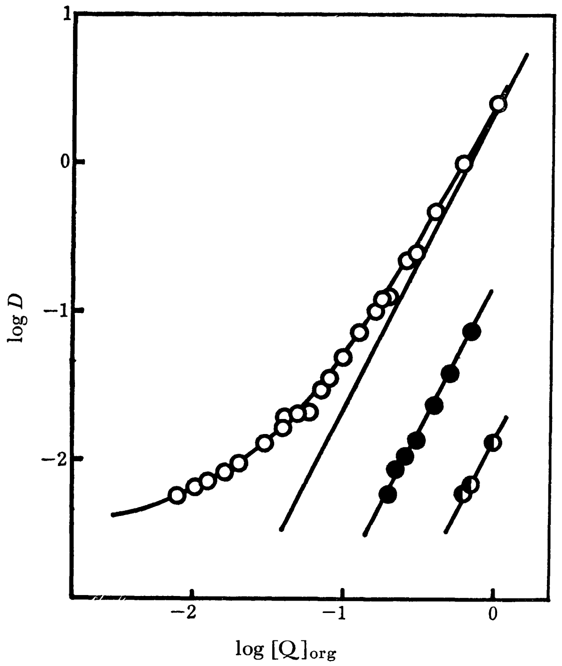

Fig. 1. Extraction as a function of quinoline concentration when the aqueous phase initially contains 1.0×10^{-1} M of caproate (○), valerate (●) and butyrate (◑) anion. The solid curve for caproate represents; $\log D=\log K_{\mathrm{exA}}[\mathrm{A^-}]^2(1+\beta_1[\mathrm{A^-}])^{-1}(1+\beta_{1(\mathrm{org})}[\mathrm{Q}]_{\mathrm{org}}+\beta_{2(\mathrm{org})}[\mathrm{Q}]_{\mathrm{org}}^2)$ and the straight lines for these three acids represent; $\log D=\log K_{\mathrm{exA}}[\mathrm{A^-}]^2(1+\beta_1[\mathrm{A^-}])^{-1}\beta_{2(\mathrm{org})}[\mathrm{Q}]_{\mathrm{org}}^2$.
These constants are listed in Table 1.

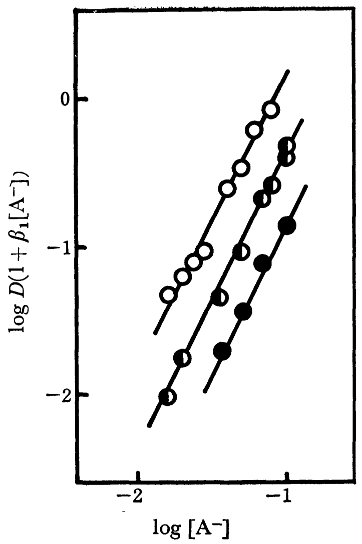

Fig. 2. Extraction as a function of the concentration of the caproate ion in the aqueous phase when the quinoline concentration in the organic phase is 0.5 M (○), 0.25 M (◐) and 0.1 M (●), the straight lines represent; $\log D(1+\beta_1[\mathrm{A^-}])=\log K_{\mathrm{exA}}[\mathrm{A^-}]^2(1+\beta_{1(\mathrm{org})}[\mathrm{Q}]_{\mathrm{org}}+\beta_{2(\mathrm{org})}[\mathrm{Q}]_{\mathrm{org}}^2)$. These constants are listed in Table 1.

$$D=\frac{K_{\mathrm{exA}}\beta_{2(\mathrm{org})}[\mathrm{A^-}]^2[\mathrm{Q}]_{\mathrm{org}}^2}{1+\beta_1[\mathrm{A^-}]} \tag{19}$$

On the other hand, the distribution ratio in the caproate system in the absence of quinoline was $10^{-2.50}$ when $[\mathrm{A^-}]$ is 0.1 M; it was enhanced by the increase in the quinoline concentration. Hence, the data can be concluded to be well represented by Eq. (9).

The constants for the butyrate and valerate systems were determined directly from the data in Fig. 1, but those for the caproate were determined by the curve-fitting. The constants are listed in Table 1.

Extraction in the Absence of Quinoline. The extraction of zinc(II) in the absence of quinoline was further studied by changing $[\mathrm{A^-}]$, $[\mathrm{HA}]_{\mathrm{org.total}}$, or the total zinc(II) concentration.

Since the distribution and dimerization constants are knwon for butyric acid,[1] but are not known for valeric and caproic acids in carbon tetrachloride sys-

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[6] P. Antikainen and D. Dyrssen, *Acta Chem. Scand.*, **14**, 86 (1960).

Table 1. EQUILIBRIUM CONSTANTS FOR ZINC(II) EXTRACTION WITH CARBOXYLIC ACIDS (HA) IN THE PRESENCE AND ABSENCE OF QUINOLINE AT 25 °C

Org. phase: CCl_4
Aq. phase: 0.1 M $Na(A^-, ClO_4)$
a) $K_{exA}=[ZnA_2]_{org}/[Zn^{2+}][A^-]^2=10^{-0.15}$ (for caproate ion)
$\beta_{n(org)}=[ZnA_2L_n]_{org}/[ZnA_2]_{org}[L]_{org}^n$

(a) In the presence of quinoline ($[HA]_{org.total}<10^{-2}$ M)

Acids	$\log K_{exA}\beta_{2(org)}$	$\log \beta_{1(org)}$	$\log \beta_{2(org)}$
caproic	2.69	1.92	2.84
valeric	1.53	—	—
butyric	0.47	—	—

(b) Adduct formation with dimer molecules of the acid in the absence of quinoline (10^{-2} M $<[(HA)_2]_{org}<9.0\times10^{-1}$ M)

Acids	$\log K_{exA}\beta_{2(org)}$	$\log \beta_{2(org)}$
caproic	2.77	2.92
valeric	1.20	—

a) The distribution ratio of zinc(II) between CCl_4 containing a very small amount of caproic acid and an aqueous phase containing 0.1 M caproate ion is $10^{-2.50}$.
b) The formation of the first adduct $ZnA_2(HA)_2$ is negligible.

tems, the concentrations of the monomer and of the dimer of these acids in the organic phase were treated as follows.

The dimerization constants for acetic, propionic, and butyric acids in carbon tetrachloride are 5.92×10^2, 9.40×10^2, and 2.91×10^3,[1] respectively. From these facts, it can reasonably be assumed that the dimerization constants for valeric and caproic acid are large; it should not be unreasonable to asume that the dimerization constants for these acids are higher than 3×10^3. From this assumption and Eq. (16), we find that even when $[HA]_{org.total}$ is only 5×10^{-2} M, less than 5% of the acid in the organic phase exists in the form of the monomer, and since the total concentration of the acid in the organic phase in the following experiments is always higher than 5×10^{-2} M, all the acid in the organic phase can be regarded as existing in the form of a dimer, —in other words, Eq. (17) can be used for these experimental results.

Figure 3 shows the change in the distribution ratio when the concentration of the anions, $[A^-]$, is kept at 9.6×10^{-2} M, but when the concentration of the dimer of the acid changes and when quinoline is absent. Figure 4 gives the dependence of the extraction on the concentration of the carboxylate anions in the aqueous phase. Since the total concentration, $[HA]_{org,total}$, is high (2M), it can be assumed as will be described later, that only the second adduct exists in the organic phase. In order to make a correction for the small change in the $[(HA)_2]_{org}$ and for the change in the complex formation in the aqueous phase, $\log D(1+\beta_1[A^-])[(HA)_2]_{org}^{-2}$ is plotted in this figure instead of $\log D$. As may be seen from Fig. 4, the extraction is proportional to the square of $[A^-]$; thus, it was concluded that the metal species in these organic phases also contains two carboxylate anions.

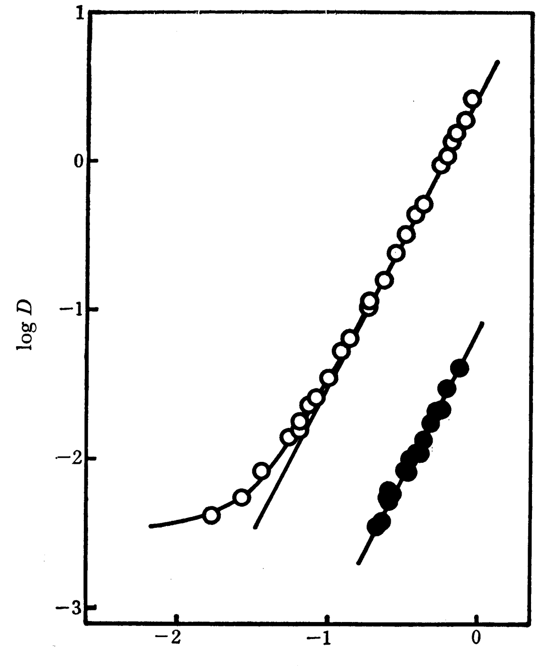

Fig. 3. Extraction in the absence of the quinoline as a function of the concentration of dimer of caproic acid (○) and valeric acid (●) in the organic phase when the concentration of $[A^-]$ is kept at 9.6×10^{-2} M. The solid curve for caproic acid represents; $\log D=\log K_{exA}[A^-]^2(1+\beta_1[A^-])^{-1}(1+\beta_{2(org)}[(HA)_2]_{org}^2)$ and the straight lines for the two acids; $\log D=\log K_{exA}[A^-]^2(1+\beta_1[A^-])^{-1}\beta_{2(org)}\cdot[(HA)_2]_{org}^2$.
These constants are listed in Table 1.

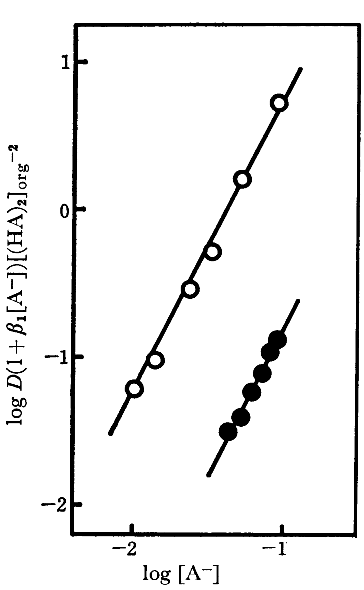

Fig. 4. Extraction in the absence of quinoline as a function of the concentration of caproate ion (○) and valerate ion (●) in the aqueous phase, the straight lines for the two acids; $\log D(1+\beta_1[A^-])[(HA)_2]_{org}^{-2}=\log K_{exA}[A^-]^2\beta_{2(org)}$. These constants are listed in Table 1.

As may be seen from Fig. 3, the distribution ratio in the higher-acid-concentration region is proportional to the square of $[(HA)_2]_{org}$. This fact indicates that the zinc(II) species in the organic phase of this region is $ZnA_2(HA)_4$. Furthermore, since the increase in the distribution ratio is very abrupt, we assumed that the first adduct was not formed. This was confirmed by the fact that the extraction curve can be well fitted with the standard-curve $Y=\log(1+v^2)$; $X=\log v$. The equilibrium constants obtained by the curve-fitting are also given in Table 1.

Since extractions of polynuclear species have very often been observed in systems containing carboxylic acid, the effect of the total metal concentration of zinc(II) on the distribution ratio was determined. It was found that when the acid is caproic, when $[HA]_{org,total}$ is 0.9 M, and when $[A^-]$ is 0.1 M, the distribution ratio of zinc(II) is constant in the range of $[Zn^{2+}]_{initial}$, 10^{-3}—10^{-6} M. Thus there was no extraction of polynuclear species within this range of metal concentrations.

Discussion

The chemical equilibria of metal extraction with carboxylic acids are generally very complicated because the distribution equilibria of the carboxylic acid are complicated as a result of dimerization in the organic phase and the extraction of polynuclear species combining various numbers of the dimer of the acid molecules. However, as has been described above, the chemical equilibria in the systems studied in this paper could be treated much more easily than those systems previously reported.

This is because of the following reasons: (i) The extraction of the ZnA_2 species could be determined separately. This was possible because the extraction could be carried out when $[A^-]$ was relatively high and $[HA]_{org,total}$ was small; in order to achieve this condition, the pH of the solution must be high (for example, when $[A^-]$ is 0.1 M and when $[HA]_{org,total}$ is less than 10^{-2} M, $[H^+]$ should be $10^{-6.5}$ M). Many other metal ions undergo hydrolysis at such high pH values, and thus the equilibria become very complicated. However, the hydrolysis of zinc(II) at this pH is fortunately negligible provided the metal concentration is very low.[7] (ii) It was possible to assume that all the acid in the organic phase can be regarded as existing as the dimers, judging from the results of Ref. 1. The dimerization constant in carbon tetrachloride is much larger than that, for example, in benzene; thus, the above assumptions are possible in the former solvent under the conditions employed. (iii) The fact that $C_{OH}\simeq[A^-]$ could be reasonably assumed under the conditions employed also simplified the analysis.

There have been several reports on the extraction of zinc(II) with carboxylic acids.[8-11] Among these, Schweizer and Clifford have made a systematic analysis of their extraction date and have concluded that the distribution ratio of zinc(II) increased (i) upon an increase in the molecular weight of the acid, (ii) upon an increase in the concentration of the acid, (iii) upon an increase in the concentration of 1-aminobutane added to the system, and (iv) upon a decrease in the hydrogen-ion concentration, but that the distribution ratio is independent of the metal concentration. These observations agree qualitatively with the present results. However, their interpretation of the results is different from that by the present authors, although the solvent of the present study is different from that employed in the previous work.[11] It seems difficult to explain why the conclusion in that work[11] is different from that of the present work. However, some oversimplified assumptions, such as that there is no formation of the zinc(II) carboxylate complex in the aqueous phase, might be one of the reasons.

Among the systems studied in the comprehensive series of papers on metal extraction with carboxylic acid carried out by Tanaka and his co-workers,[12-18] only lead(II)[18] was found to be extractable as a monomeric species over a wide range of metal concentrations. The extraction of zinc(II) is similar to that of lead(II) although only the $MA_2(HA)_4$ species was found to be extracted in addition to the MA_2 species. The extraction of the MA_2 species has not been found for the metal ions studied by the above workers.

As long as we are concerned only with the data obtained by distribution experiments, no information about the structure of the extracted metal species can be obtained. Thus, we do not know the nature of the bonds between the ZnA_2 species and the quinoline or the carboxylic acid in the organic phase. It is very remarkable that the stability constants for the second adduct, $\beta_{2(org)}$, with quinoline and carboxylic acid dimer are similar to each other.

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