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Solvent Effects on the Extraction of Gallium(III) with Decanoic Acid

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Extraction of gallium(III) with decanoic acid (HA) in several solvents was carried out at 25 °C and at an aqueous ionic strength of 0.1 mol/dm^3($NaClO_4$). Organic solvents used are toluene, chlorobenzene, 1,2-dichloroethane, and 1-octanol. Extracted species differs from solvent to solvent: $Ga_6A_{18}(H_2O)_w$ for toluene, Ga_3A_9 for chlorobenzene, GaA_3 and Ga_3A_9 for 1,2-dichloroethane and $GaA_2(OH)$, $Ga_2A_4(OH)_2$ and Ga_2A_6 for 1-octanol. The less polar the solvent, the more extensive is the polymerization of the extracted species.

Polymeric metal carboxylates are known to be extracted into the organic phase with carboxylic acids. In particular, aluminium(III),[1] gallium(III),[2] indium(III),[3] and scandium(III)[4] are characterized to be extracted into benzene as hexameric species.

In the previous paper,[5] it has been shown that copper(II) is extracted with decanoic acid in various inert solvents as dimeric copper(II) decanoate, $Cu_2A_4(HA)_2$, and that the solvent effect on the extraction constants was interpreted in terms of the regular solution theory.

The present paper describes the results on the extraction of gallium(III) with decanoic acid in several organic solvents. The more polar the solvent, the less polymerized are the extracted decanoates.

Experimental

Reagents. *Gallium(III) Perchlorate Solution*: Metallic gallium (99.99%) was dissolved in a small excess of concentrated perchloric acid. The solution was diluted as required and standardized compleximetrically with the Cu–EDTA–TAR system as an indicator.[6] 8-Quinolinol was used for the determination of lower concentration of gallium in the organic phase.

Sodium Perchlorate: The reagent grade sodium perchlorate was recrystallized from distilled water after removal of the impurities (heavy metal ions) as hydroxides at pH$\simeq$8.

Decanoic Acid: Chemically pure grade decanoic acid was purified by distillation.

Solvents: Toluene and chlorobenzene of reagent grade were washed successively with concentrated sulfuric acid, with dilute sodium hydroxide solution and then with distilled water. Reagent grade 1,2-dichloroethane was washed with dilute potassium hydroxide solution and then with distilled water. Reagent grade 1-octanol was washed successively with dilute potassium hydroxide solution, with dilute perchloric acid solution and with distilled water.

All other reagents were reagent grade and used as purchased.

Procedure. Partition was carried out in a thermostat at 25±0.2 °C using a 50 cm^3 centrifuge tube in which 15 cm^3 each of the aqueous and organic phases were contacted. Shaking for overnight was found sufficient for complete equilibration in each solvent system used. Ionic strength in the aqueous phase was adjusted to 0.1 mol/dm^3 with sodium perchlorate. Total concentration of gallium was 5×10^{-3} mol/dm^3. Hydrogen ion concentration in the aqueous phase was measured without any phase separation with 1.00×10^{-2} mol/dm^3 perchloric acid solution (ionic strength 0.1 mol/dm^3) as a standard. Then the measured pH values were corrected for the apparent liquid junction potential.[3]

Apparatus. For mechanical shaking in a thermostat, TAIYO incubator, M-1 (Taiyokagaku-Kogyo Co., Tokyo) was used. The pH measurements were carried out with a Beckman research pH Meter Model 101900 (Beckman Instruments, Inc., Fullerton, California, U.S.A.) and Orion research microprocessor Ionalyzer 901 (Orion Research Inc., U.S.A.). The temperature of a sample solution was kept constant in a Coolnics Circulator Model CTE-1B (Komatsu Solidate Co., Komatsu, Japan). Colorimetric determination of gallium in the organic phase was carried out on a Shimadzu double-beam type UV-210A spectrophotometer (Shimadzu Seisakusho Ltd., Kyoto, Japan).

Results and Discussion

When a j-merized gallium(III) decanoate of the composition $Ga_jA_aH_h(3j=a-h)$ is responsible for the extraction of gallium ion with decanoic acid, the extraction equilibria for toluene, chlorobenzene and 1,2-dichloroethane are written as:

$$j\mathrm{Ga}^{3+}+\frac{a}{2}(\mathrm{HA})_{2,\mathrm{o}}\overset{K_{\mathrm{ex}(jah)}}{\rightleftharpoons}(\mathrm{Ga}_j\mathrm{A}_a\mathrm{H}_h)_\mathrm{o}+3j\mathrm{H}^+$$

$$\text{with}\quad K_{\mathrm{ex}(jah)}=\frac{[\mathrm{Ga}_j\mathrm{A}_a\mathrm{H}_h]_\mathrm{o}[\mathrm{H}^+]^{3j}}{[\mathrm{Ga}^{3+}]^j[(\mathrm{HA})_2]_\mathrm{o}{}^{a/2}},\tag{1}$$

where the subscript o refers to the organic phase and $(HA)_{2,o}$ denotes the dimeric decanoic acid in the organic phase.

On the other hand, the dimerization of decanoic acid does not occur to any appreciable extent in 1-octanol. The extraction equilibrium for 1-octanol is then expressed as follows:

$$j\mathrm{Ga}^{3+}+a(\mathrm{HA})_\mathrm{o}\overset{K_{\mathrm{ex}(jah)}}{\rightleftharpoons}(\mathrm{Ga}_j\mathrm{A}_a\mathrm{H}_h)_\mathrm{o}+3j\mathrm{H}^+$$

with the extraction constant:

$$K_{\mathrm{ex}(jah)}=\frac{[\mathrm{Ga}_j\mathrm{A}_a\mathrm{H}_h]_\mathrm{o}[\mathrm{H}^+]^{3j}}{[\mathrm{Ga}^{3+}]^j[\mathrm{HA}]_\mathrm{o}{}^a}.\tag{2}$$

Total concentration of gallium in the organic phase, $C_{Ga,o}$ is given by the following equations corresponding to Eqs. 1 and 2, respectively:

$$\begin{aligned}C_{\mathrm{Ga,o}}&=\sum_j\sum_a j[\mathrm{Ga}_j\mathrm{A}_a\mathrm{H}_h]_\mathrm{o}\\&=\sum_j\sum_a jK_{\mathrm{ex}(jah)}([\mathrm{Ga}^{3+}][\mathrm{H}^+]^{-3})^j[(\mathrm{HA})_2]_\mathrm{o}{}^{a/2}\end{aligned}\tag{3}$$

and

$$C_{\mathrm{Ga,o}}=\sum_j\sum_a jK_{\mathrm{ex}(jah)}([\mathrm{Ga}^{3+}][\mathrm{H}^+]^{-3})^j[\mathrm{HA}]_\mathrm{o}{}^a.\tag{4}$$

Under the present experimental conditions, the hydrolysis and complexation of gallium ion not being appreciable in the aqueous phase, the total concentration of gallium in the aqueous phase, $C_{Ga,w}$ may be regarded as $[Ga^{3+}]$.

Suppose that only $Ga_jA_aH_h$ is responsible for the

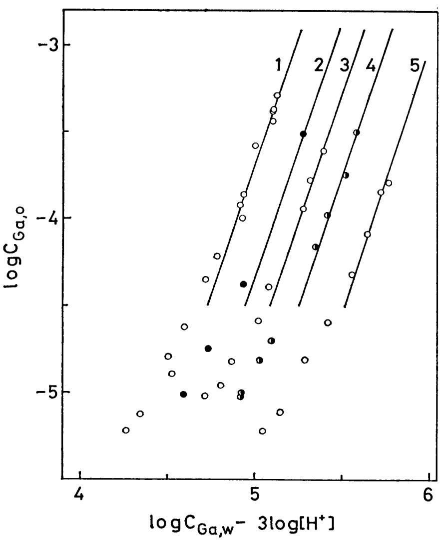

Fig. 1. Determination of the degree of polymerization of Ga(III) decanoate in 1,2-dichloroethane.
Solid lines are the straight lines with a slope of 3.0. C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.25, No. 4: 1.0, No. 5: 0.7 mol/dm^3.

extraction. Equations 5 and 6 can then be derived from Eqs. 3 and 4, respectively:

$$C_{Ga,o} = jK_{ex(jah)}(C_{Ga,w}[H^+]^{-3})^j[(HA)_2]_o{}^{a/2} \quad (5)$$

and

$$C_{Ga,o} = jK_{ex(jah)}(C_{Ga,w}[H^+]^{-3})^j[HA]_o{}^a \quad (6)$$

which are rewritten as a logarithmic form:

$$\log C_{Ga,o} = j(\log C_{Ga,w} - 3\log[H^+]) + \frac{a}{2}\log[(HA)_2]_o + \log j + \log K_{ex(jah)} \quad (7)$$

and

$$\log C_{Ga,o} = j(\log C_{Ga,w} - 3\log[H^+]) + a\log[HA]_o + \log j + \log K_{ex(jah)}. \quad (8)$$

These expressions provide a basis for the determination of the degree of polymerization of Ga(III) decanoates and the number of decanoic acid molecules involved in the extracted species. The degree of polymerization of the extracted species can be determined from the slope of the plot of $\log C_{Ga,o}$ against ($\log C_{Ga,w}-3\log[H^+]$) at constant $[(HA)_2]_o$ (or $[HA]_o$ in the case of 1-octanol). The plot for toluene fitting well the straight line with a slope of six, the hexameric Ga(III) decanoate is extracted into toluene. And in the lower concentration of gallium in the organic phase the plot deviates slightly upward from the straight line with a slope of 6.0. This suggests that there would be at least another extracted species less polymerized than the main hexameric species. The plot for chlorobenzene fitting well the straight line with a slope of 3.0, the trimeric Ga(III) decanoate is responsible for the extraction. In the case of 1,2-dichloroethane, as evident from Fig. 1, the degree of polymerization of extracted species depends on the concentration of gallium in the organic phase. The plot deviates upward from the straight line with a slope of three with decreasing concentration of gallium in the 1,2-dichloroethane phase. Therefore, another extracted species less polymerized than 3.0 is responsible for the extraction together with the main trimeric species. If the other extracted species is $Ga_{j'}A_{a'}H_{h'}$, the concentration of gallium in the organic phase is written as follows:

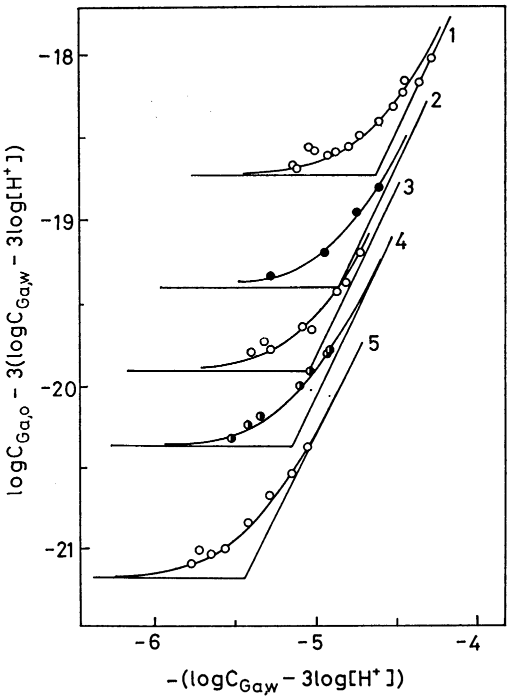

Fig. 2. Determination of the degree of polymerization of Ga(III) decanoate in 1,2-dichloroethane by the curve fitting method.
Solid curves are the normalized curves, $\log(1+X^2)$ *vs.* $\log X$. Solid lines are the asymptotes of the normalized curves. Numbers are the same as in Fig. 1.

$$C_{Ga,o} = 3[Ga_3A_aH_h]_o + j'[Ga_{j'}A_{a'}H_{h'}]_o, \quad (9)$$

where $j'<3$. And we have the following expression from Eq. 9:

$$\frac{C_{Ga,o}}{(C_{Ga,w}[H^+]^{-3})^3} = 3K_{ex(3ah)}[(HA)_2]_o{}^{a/2} \times \left\{1+\frac{j'K_{ex(j'a'h')}}{3K_{ex(3ah)}}[(HA)_2]_o{}^{(a'-a)/2} \times (C_{Ga,w}[H^+]^{-3})^{(j'-3)}\right\}, \quad (10)$$

where $K_{ex(3ah)}$ and $K_{ex(j'a'h')}$ represent the extraction constants of the trimer, $Ga_3A_aH_h$ and j'-mer, $Ga_{j'}A_{a'}H_{h'}$, respectively. According to Eq. 10, comparing the plot of $\{\log C_{Ga,o}-3(\log C_{Ga,w}-3\log[H^+])\}$ against $-(\log C_{Ga,w}-3\log[H^+])$ at constant $[(HA)_2]_o$ with the normalized curves, $\log(1+X^n)$ *vs.* $\log X$, we find the degree of polymerization of the other extracted species, $Ga_{j'}A_{a'}H_{h'}$. The results are shown in Fig. 2. The plot fits well the normalized curve with $n=2$, that is, $-(j'-3)=2$ or $j'=1$.

Figure 3 depicts the results for 1-octanol. As shown in Fig. 3, the slope of the plot according to Eq. 8 is close to two at higher concentration of gallium in the organic phase. The plot, however, deviates grad-

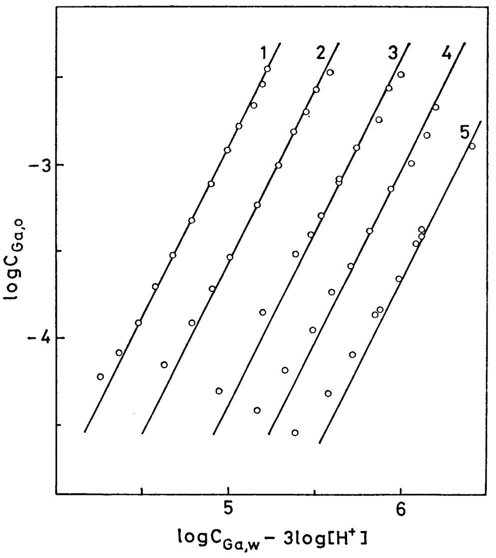

Fig. 3. Determination of the degree of polymerization of Ga(III) decanoate in 1-octanol.
Solid lines are the straight lines with a slope of 2.0. C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.0, No. 4: 0.7, No. 5: 0.5 mol/dm^3.

ually upward from the straight line with a slope of two with decreasing gallium concentration in the organic phase. Therefore, the monomer and dimer may be involved in the extraction for 1-octanol. Now suppose a monomer GaA_aH_h and a dimer $Ga_2A_{a'}H_{h'}$ are responsible for the extraction, the following expression can be derived from Eq. 4:

$$\log C_{Ga,o} - (\log C_{Ga,w} - 3\log[H^+]) = \log K_{ex(1ah)} + a\log[HA]_o$$
$$\log\left\{1 + \frac{2K_{ex(2a'h')}}{K_{ex(1ah)}}[HA]_o^{(a'-a)}C_{Ga,w}[H^+]\right\}, \quad (11)$$

where $K_{ex(1ah)}$ and $K_{ex(2a'h')}$ represent the extraction constants of the monomer GaA_aH_h and the dimer $Ga_2A_{a'}H_{h'}$, respectively. According to Eq. 11, fitting the plot of $\{\log C_{Ga,o} - (\log C_{Ga,w} - 3\log[H^+])\}$ against $(\log C_{Ga,w} - 3\log[H^+])$ at constant $[HA]_o$ with the normalized curve, $\log(1+X)$ *vs.* $\log X$, we can confirm the degree of polymerization of the extracted species. The results are depicted in Fig. 4. The obtained curves fitting well the normalized curve, $\log(1+X)$ *vs.* $\log X$, the monomeric and dimeric gallium decanoates are involved in the extraction in 1-octanol.

Thus, the degree of polymerization of the extracted species is determined as follows: Hexamer for toluene, trimer for chlorobenzene, monomer and trimer for 1,2-dichloroethane and monomer and dimer for 1-octanol.

Subsequently, the number of decanoic acid molecules involved in the extracted species was determined. In the region where the j-mer prevails, the following equation is derived from Eq. 3:

$$\frac{1}{j}\log C_{Ga,o} - (\log C_{Ga,w} - 3\log[H^+])$$
$$= \frac{1}{j}\log\sum_a (K_{ex(jah)}[(HA)_2]_o^{a/2}) + \frac{1}{j}\log j. \quad (12)$$

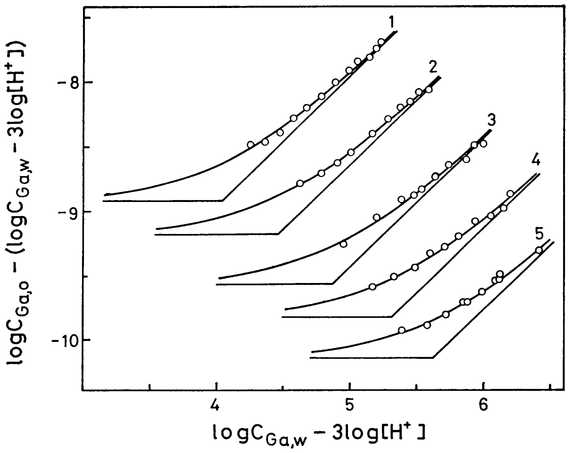

Fig. 4. Determination of the degree of polymerization of Ga(III) decanoate in 1-octanol by the curve fitting method.
Solid curves are the normalized curves, $\log(1+X)$ *vs.* $\log X$. Solid lines are the asymptotes of the normalized curves. Numbers are the same as in Fig. 3.

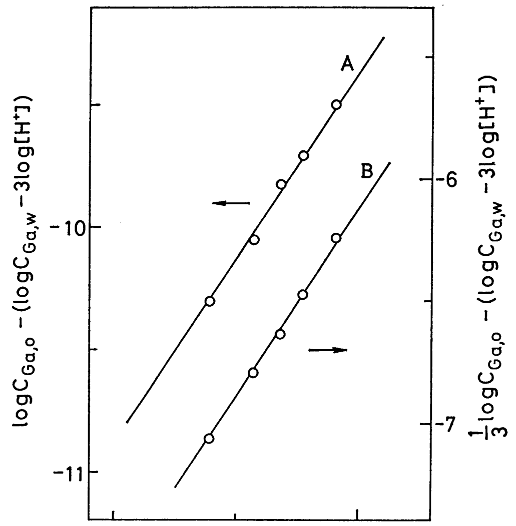

Fig. 5. Determination of the number of decanoic acid involved in Ga(III) decanoates in 1,2-dichloroethane. Solid lines are the straight lines with a slope of 1.5. A: Monomeric Ga(III) decanoate. B: Trimeric Ga(III) decanoate.

This is corresponding to toluene, chlorobenzene and 1,2-dichloroethane. On the basis of Eq. 12, the total number of decanoic acid molecules involved in the j-mer can be determined from the slope of the plot of $\{(1/j)\log C_{Ga,o} - (\log C_{Ga,w} - 3\log[H^+])\}$ against $\log[(HA)_2]_o$. Both plots for toluene and chlorobenzene fit the straight line with a slope of 1.5, that is, $a=18$ and $a=9$, respectively. In addition, by the coulometric titration using the Karl-Fischer reagent, it was proved that more than one water molecule per atom of gallium was involved in the hexameric Ga(III) decanoate in the toluene phase. Consequently, we conclude that the extracted species involved in the

TABLE 1. EXTRACTED SPECIES AND EXTRACTION CONSTANTS

Solvent	ε[a)]	δ[b)]	Extracted species	Extraction constants $\log K_{ex(jah)}$
Benzene[2)]	2.3	9.15	$Ga_6A_{12}(OH)_6$	-35.8 ± 0.1
			$Ga_6A_{18}(H_2O)_6$	-34.3 ± 0.1
			$Ga_jA_aH_h:(j<6)$	
Toluene	2.4	8.9	$Ga_6A_{18}(H_2O)_w:(w>6)$	-33.21 ± 0.05
			$Ga_jA_aH_h:(j<6)$	
Chlorobenzene	5.5	9.5	Ga_3A_9	-19.14 ± 0.03
1,2-Dichloroethane	10.4	9.9	GaA_3	-9.42 ± 0.03
			Ga_3A_9	$-18.9\ \pm0.1$
1-Octanol	10.3	10.3	$GaA_2(OH)$	-9.54 ± 0.02
			$Ga_2A_4(OH)_2$	-14.92 ± 0.02
			Ga_2A_6	-15.26 ± 0.02

a) Dielectric constant. b) Solubility parameter.

toluene phase are $Ga_6A_{18}(H_2O)_w(w>6)$ and $Ga_jA_aH_h$ $(j<6)$. While, only Ga_3A_9 is extracted into the chlorobenzene phase. Figure 5 shows the number of decanoic acid involved in the monomeric and trimeric Ga(III) decanoates which are extracted into the 1,2-dichloroethane solution. The straight lines with a slope of 1.5 are obtained in both the monomer and trimer, that is, $a/2=1.5$ and $a/6=1.5$, respectively. Thus, the monomer GaA_3 and trimer Ga_3A_9 are responsible for the extraction with decanoic acid in 1,2-dichloroethane.

And further, from the intercepts of the plots of the left hand side of Eq. 12 against $\log[(HA)_2]_o$, we can determine the extraction constants for each extracted species. The results obtained for each extracted species are summarized in Table 1.

On the other hand, for 1-octanol the following relation is set up in place of Eq. 12:

$$\frac{1}{j}\log C_{Ga,o} - (\log C_{Ga,w} - 3\log[H^+])$$
$$= \frac{1}{j}\log\sum_a (K_{ex(jah)}[HA]_o{}^a) + \frac{1}{j}\log j. \qquad (13)$$

The plot of the left hand side of Eq. 13 against $\log[HA]_o$ (Fig. 6) illustrates the number of decanoic acid molecules involved in the monomer and dimer which are extracted into 1-octanol. As evident from Fig. 6, the number of molecules of decanoic acid involved in the monomer is equal to 2 and then h is equal to -1. Therefore, from the electroneutrality of the extracted species, one hydroxide ion should be involved in the extracted monomer, since no perchlorate ion was found in the extracted species. The extraction constant $K_{ex(12-1)}$ for $GaA_2(OH)$ was determined from the intercept of the plot in Fig. 6. Decanoic acid molecules involved in the dimer depends on the concentration of decanoic acid in the organic phase. At lower concentration of decanoic acid in the organic phase, the plot falls on the straight line with a slope of 4.0, that is, $a=4$, and then $h=-2$. In analogy with the monomer described above, two hydroxide ions should be involved in the dimeric extracted species. But at higher concentration of $[HA]_o$, the slope tends to be steeper. This result suggests the presence of another dimeric species in which is involved more than four decanoic acid molecules. Now, suppose the two dimeric species $Ga_2A_4(OH)_2$ and $Ga_2A_aH_h(a>4)$ are both responsible for the extraction. In this case, the total concentration of gallium in the organic phase can be expressed as follows:

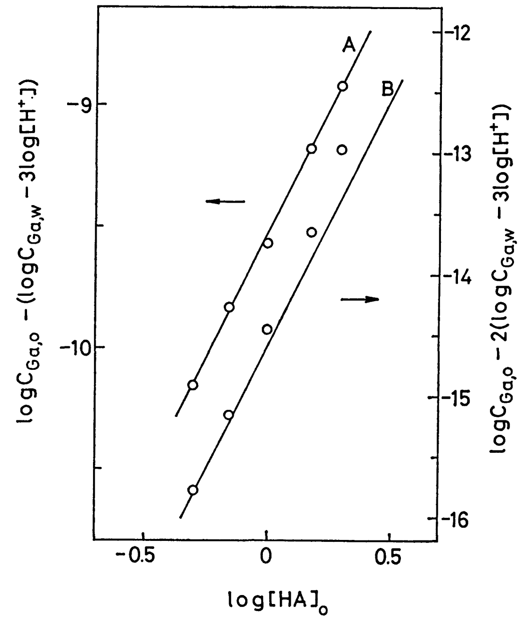

Fig. 6. Determination of the number of decanoic acid involved in Ga(III) decanoates in 1-octanol. Solid lines, A and B are the straight lines with a slope of 2.0 and 4.0, respectively. A: Monomeric Ga(III) decanoate. B: Dimeric Ga(III) decanoate.

$$C_{Ga,o} = 2[Ga_2A_4(OH)_2]_o + 2[Ga_2A_aH_h]_o. \qquad (14)$$

And with the aid of the extraction constants $K_{ex(24-2)}$ and $K_{ex(2ah)}$, Eq. 14 can be rewritten as:

$$\log C_{Ga,o} - 2(\log C_{Ga,w} - 3\log[H^+]) - 4\log[HA]_o$$
$$= \log\left\{1+\frac{K_{ex(2ah)}}{K_{ex(24-2)}}[HA]_o{}^{(a-4)}\right\}$$
$$+ \log 2 + \log K_{ex(24-2)}. \qquad (15)$$

Then the values of $\{\log C_{Ga,o} - 2(\log C_{Ga,w} - 3\log[H^+]) - 4\log[HA]_o\}$ are plotted against $\log[HA]_o$. According to the curve-fitting method, in which the plot is compared with the normalized curves, $\log(1+X^n)$

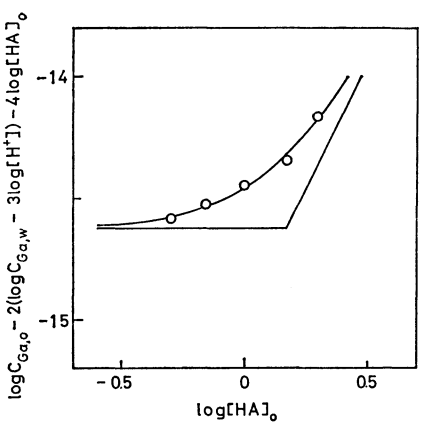

Fig. 7. Determination of the number of decanoic acid involved in dimeric Ga(III) decanoates in 1-octanol by the curve fitting method.
Solid curve is the normalized curve, $\log(1+X^2)$ *vs.* $\log X$. Solid lines are the asymptotes of the normalized curve.

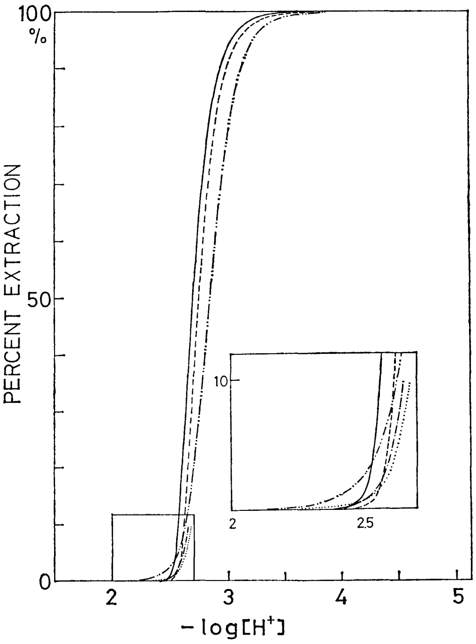

Fig. 8. The calculated extraction curves based on the results obtained in this study.
——: Toluene, ---: benzene, —··—: 1-octanol, ···: 1,2-dichloroethane, —·—: chlorobenzene. $C_{\mathrm{Ga,tot}}=5\times10^{-3}$ mol/dm³, $C_{\mathrm{HA}}=1.0$ mol/dm³.

vs. $\log X$, the number of decanoic acid molecules in another dimeric species can be determined together with the extraction constants of the two dimeric Ga(III) decanoates. The results are shown in Fig. 7. As shown in Fig. 7, the plot fits well with the normalized curve, $\log(1+X^2)$ *vs.* $\log X$, that is, $n=a-4=2$, or $a=6$. The extraction constants $K_{\mathrm{ex}(24-2)}$ and $K_{\mathrm{ex}(260)}$ determined by the curve-fitting method are given in Table 1. Consequently, $\mathrm{GaA_2(OH)}$, $\mathrm{Ga_2A_4(OH)_2}$, and $\mathrm{Ga_2A_6}$ are extracted in the 1-octanol phase.

Then, the extraction equilibria for different solvents are described as follows:

toluene:

$$6\mathrm{Ga}^{3+} + 9(\mathrm{HA})_{2,\mathrm{o}} + w\mathrm{H_2O} \xrightleftharpoons{K_{\mathrm{ex}(6180)}} (\mathrm{Ga_6A_{18}(H_2O)}_w)_\mathrm{o} + 18\mathrm{H}^+$$

chlorobenzene:

$$3\mathrm{Ga}^{3+} + \frac{9}{2}(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(390)}} (\mathrm{Ga_3A_9})_\mathrm{o} + 9\mathrm{H}^+$$

1,2-dichloroethane:

$$\mathrm{Ga}^{3+} + \frac{3}{2}(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(130)}} (\mathrm{GaA_3})_\mathrm{o} + 3\mathrm{H}^+$$

$$3\mathrm{Ga}^{3+} + \frac{9}{2}(\mathrm{HA})_{2,\mathrm{o}} \xrightleftharpoons{K_{\mathrm{ex}(390)}} (\mathrm{Ga_3A_9})_\mathrm{o} + 9\mathrm{H}^+$$

1-octanol:

$$\mathrm{Ga}^{3+} + 2(\mathrm{HA})_\mathrm{o} + \mathrm{H_2O} \xrightleftharpoons{K_{\mathrm{ex}(12-1)}} (\mathrm{GaA_2(OH)})_\mathrm{o} + 3\mathrm{H}^+$$

$$2\mathrm{Ga}^{3+} + 4(\mathrm{HA})_\mathrm{o} + 2\mathrm{H_2O} \xrightleftharpoons{K_{\mathrm{ex}(24-2)}} (\mathrm{Ga_2A_4(OH)_2})_\mathrm{o} + 6\mathrm{H}^+$$

$$2\mathrm{Ga}^{3+} + 6(\mathrm{HA})_\mathrm{o} \xrightleftharpoons{K_{\mathrm{ex}(260)}} (\mathrm{Ga_2A_6})_\mathrm{o} + 6\mathrm{H}^+.$$

In the 1,2-dichloroethane and 1-octanol phases, the trimerization and dimerization of Ga(III) decanoates are written as follows, respectively:

1,2-dichloroethane phase:

$$3\mathrm{GaA_3} \xrightleftharpoons{K_{\mathrm{trim}}} \mathrm{Ga_3A_9}$$

1-octanol phase:

$$2\mathrm{GA_2(OH)} \xrightleftharpoons{K_{\mathrm{dim}-1}} \mathrm{Ga_2A_4(OH)_2}.$$

$$2\mathrm{GaA_2(OH)} + 2\mathrm{HA} \xrightleftharpoons{K_{\mathrm{dim}-2}} \mathrm{Ga_2A_6} + 2\mathrm{H_2O}$$

with the following trimerization and dimerization constants calculated from the respective extraction constants: $\log K_{\mathrm{trim}}=9.4\pm0.2$, $\log K_{\mathrm{dim}-1}=4.16\pm0.06$ and $\log K_{\mathrm{dim}-2}=3.82\pm0.06$ (where the deviation of each polymerization constant originates in the uncertainties in the respective extraction constants).

Figure 8 shows the calculated extraction curves based on the results obtained in this investigation. The extracted species and the extraction constants are summarized in Table 1 together with the dielectric constants and the solubility parameters of solvents. The uncertainties in the respective extraction constants represent the probable deviations of the experimental data from the best fit curve or straight line. The previous results for benzene are also included in Fig. 8 and Table 1 for comparison.

The extraction of Ga(III) differs from that of copper(II): We observe the same extracted species with the similar extraction constant for the extraction of copper(II) decanoate in different inert solvents(hexane, cyclohexane, carbon tetrachloride, toluene, benzene, chlorobenzene and 1,2-dichloroethane).[5] The main extracted species are the hexameric Ga(III) decanoate for benzene and toluene, the trimer for chlorobenzene and the monomer and trimer for 1,2-dichloroethane, respectively. The less polar the solvent, the more extensive is the polymerization of the extracted species. In chlorobenzene and 1,2-dichloroethane the emulsion was observed in the region where the percent extraction of gallium exceeds 10%. This low extractability of gallium in these nonsolvating polar solvents results from the formation of some hydrated less polymerized species.

As was expected from the similarity of the physical properties of the two solvents, the same hexameric species with the similar extraction constant is extracted for both benzene and toluene, and the same trimer with the similar extraction constant is found for both chlorobenzene and 1,2-dichloroethane.

On the other hand, it was found that the quite different species from those in nonsolvating solvents were extracted into 1-octanol. As we have already reported, also in the extraction of copper(II) there was a remarkable difference in the extracted species between 1-octanol⁷⁾ and nonsolvating solvents.⁵⁾ Though the less polymerized species are responsible for the extraction of gallium(III) with decanoic acid in 1-octanol, no emulsion appeared, which was the feature different from chlorobenzene and 1,2-dichloroethane. Then, the formation of some solvated, less polymerized species would contribute to a good extractability. Therefore, it can be assumed that Ga(III) decanoate in 1-octanol is polymerized through a mechanism different from that in nonsolvating solvents such as benzene and toluene *etc.*

Consequently, the results obtained in this paper suggest that the solvent used plays an important part in the extraction of metals with carboxylic acids.

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