March, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 789—794 (1986) 789

Solvent Effects on Extraction of Aluminum(III), Gallium(III), and Indium(III) with Decanoic Acid

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(Received September 11, 1985)

Extraction of aluminum(III) and indium(III) with decanoic acid in 1-octanol was carried out at 25 °C and at an aqueous ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). Monomeric and tetrameric aluminum(III) decanoates and monomeric indium(III) decanoate are responsible for the extraction. From a comparison of the present results with those obtained from the previous works,[1-4] the polymerization of the extracted species was found to be more extensive in benzene than in 1-octanol, and the metal decanoates were highly polymerized in the following order in both solvents: Al>Ga>In.

In the extraction of metal ions with carboxylic acids, polymerized metal carboxylates are sometimes found as an extracted species. In particular, trivalent aluminum, gallium, and indium are characterized to form up to hexameric decanoate in non-coordinating solvents such as benzene.[1-3] In the previous work which has described the results on the extraction of gallium(III) with decanoic acid in some inert solvents, it was noted that the more polar the solvent, the less polymerized were the extracted decanoates.[4] Subsequently, also in the extraction of copper(II) decanoate, the extracted species has been established to be only the dimeric copper(II) decanoate for the various inert solvents[5] but to be the monomeric and dimeric copper(II) decanoates for some alcohols[6,7] and ketones.[8]

The present paper deals with the extraction of aluminum(III) and indium(III) with decanoic acid in 1-octanol, and by comparison of the present results with those obtained from the previous papers,[1-4] it was found that the degree of polymerization of the metal decanoates decreased in the following order in both benzene and 1-octanol: Al>Ga>In, and the metal decanoates were more extensively polymerized in benzene than in 1-octanol.

Experimental

Reagents. Aluminum(III) perchlorate: Commercial aluminum(III) perchlorate nine hydrates (99.9%) was recrystallized from distilled water.

Indium(III) perchlorate was prepared in the same manner as presented previously.[3]

Sodium perchlorate, decanoic acid, and 1-octanol were purified by the method described previously.[6]

Reagent grade Xylenol Orange was used for the compleximetric titration of aluminum and indium as an indicator and for the spectrophotometric determination of lower concentration of aluminum.

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

Procedure. Partition was carried out in the same manner as was stated in the previous report.[4] Shaking for 17 h was found to be sufficient for complete equilibration in each extraction system. Total concentrations of metals and decanoic acid were 5×10^{-3} and 0.5—2.0 mol dm^{-3}, respectively. Ionic strength in the aqueous phase was adjusted to 0.1 mol dm^{-3} with sodium perchlorate. Hydrogen ion concentration in the aqueous phase was determined by the same method as presented previously.[4]

Apparatus. The apparatus were similar to those previously used.[4]

Results and Discussion

Extraction Equilibrium. When a j-merized metal decanoate of the composition $M_jA_aH_h(3j=a-h)$ is responsible for the extraction of a trivalent metal ion with decanoic acid, the extraction equilibrium is written as:

$$jM^{3+} + a(HA)_o \xrightleftharpoons{K_{ex(jah)}} (M_jA_aH_h)_o + 3jH^+$$

with $(HA)_o$ denoting the monomeric decanoic acid in the organic phase, and the extraction constant defined as

$$K_{ex(jah)} = \frac{[M_jA_aH_h]_o[H^+]^{3j}}{[M^{3+}]^j[HA]_o^a}, \tag{1}$$

where the subscript o refers to the organic phase and as described previously, the dimerization of decanoic acid does not occur to any appreciable extent in 1-octanol.[6] The total concentration of a metal in the organic phase, $C_{M,o}$ is represented by the following expression:

$$\begin{aligned} C_{M,o} &= \sum_j\sum_a j[M_jA_aH_h]_o \\ &= \sum_j\sum_a jK_{ex(jah)}([M^{3+}][H^+]^{-3})^j[HA]_o^a. \end{aligned} \tag{2}$$

When only $M_jA_aH_h$ is responsible for the extraction, the following equation is obtained under the conditions where any side reaction of a metal ion is not appreciable in the aqueous phase:

$$\begin{aligned} \log C_{M,o} &= j(\log C_{M,w} - 3\log[H^+]) + a\log[HA]_o \\ &\quad + \log j + \log K_{ex(jah)}. \end{aligned} \tag{3}$$

According to Eq. 3, the degree of polymerization of the extracted species can be determined from the slope of the plot of log $C_{M,o}$ against (log $C_{M,w}$−3 log[H^+]) at constant $[HA]_o$. The results for aluminum(III) and indium(III) are shown in Figs. 1 and 2, respectively. From Fig. 1, it is expected that the monomeric and tetrameric aluminum(III) decanoates are preferentially extracted in 1-octanol. Then the following expression can be derived from Eq. 2:

$$\log C_{Al,o} - (\log C_{Al,w} - 3\log[H^+]) - a\log[HA]_o - \log K_{ex(1ah)} = \log\left\{1 + \frac{4K_{ex(4a'h')}}{K_{ex(1ah)}}[HA]_o^{(a'-a)}(C_{Al,w}[H^+]^{-3})^3\right\}, \quad (4)$$

where $K_{ex(1ah)}$ and $K_{ex(4a'h')}$ denote the extraction constants of the monomeric and tetrameric aluminum(III) decanoates, respectively. It is expected that the plot of {log $C_{Al,o}$−(log $C_{Al,w}$−3 log[H^+])} against (log$C_{Al,w}$−3 log[H^+]) at constant $[HA]_o$ fits with the normalized curve, log(1+X^3) vs. log X. The results are depicted in Fig. 3. As shown in Fig. 3, it is confirmed that the monomeric and tetrameric species are responsible for the extraction. The plots deviate upward from the normalized curve at the middle region. This suggests that a small amount of the dimeric and/or trimeric species exists together with the main monomeric and tetrameric species.

As evident from Fig. 2, on the other hand, the monomeric indium(III) species is predominantly extracted. With decreasing concentration of decanoic acid in the organic phase and with increasing indium concentration in the organic phase, that is, with decreasing hydrogen ion concentration in the aqueous phase, the plots get to deviate from the straight line with a slope of 1.0. It seems most likely that these "deviations" are resulted from the hydrolysis of

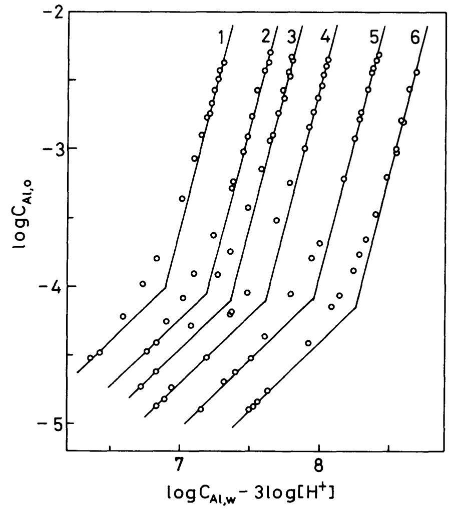

Fig. 1. Determination of the degree of polymerization of aluminum(III) decanoates.
C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.25, No. 4: 1.0, No. 5: 0.7, No. 6: 0.5 mol dm^{-3}. Solid lines are the straight lines with slopes of 1.0 and 4.0, respectively.

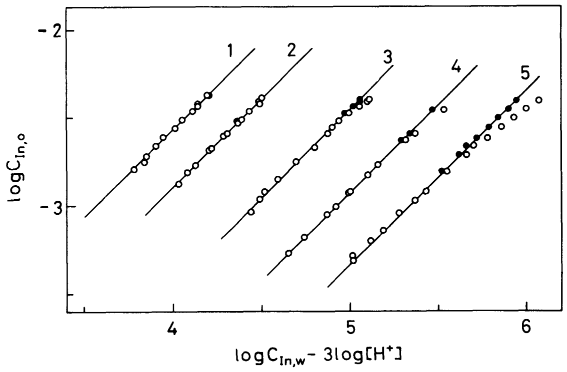

Fig. 2. Determination of the degree of polymerization of indium(III) decanoate.
C_{HA}; No. 1: 2.0, No. 2: 1.5, No. 3: 1.0, No. 4: 0.7, No. 5: 0.5 mol dm^{-3}. Solid lines are the straight lines with a slope of 1.0. Solid points are the corrected ones by considering the hydrolysis of indium(III) ion in the aqueous phase: log $C_{In,o}$, vs. log $C_{In,w}$ − 3 log [H^+] − log $\alpha_{In(OH)}$.

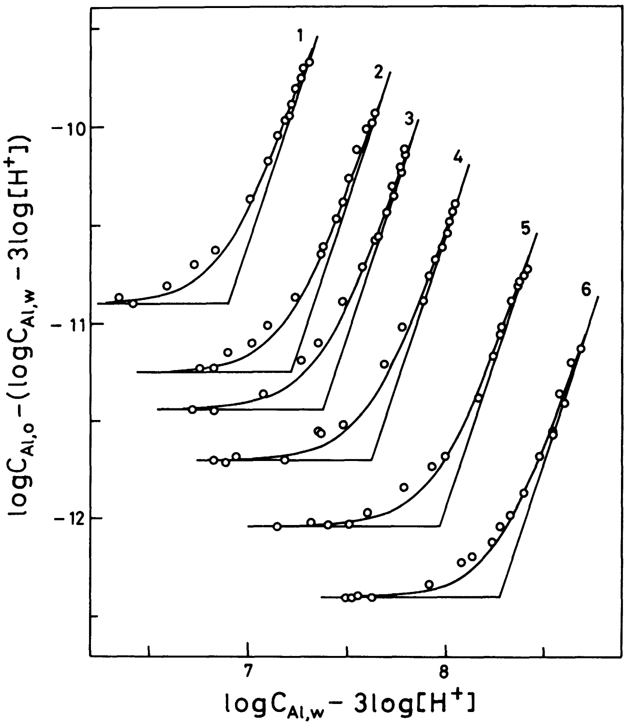

Fig. 3. The identification of the degree of polymerization of aluminum(III) decanoates.
Solid curves are the normalized curves, log(1+X^3) vs. log X. Solid lines are the asymptotes of the normalized curves. Numbers are the same as in Fig. 1.

indium(III) ion in the aqueous phase. Under the present experimental conditions, we can expect the following hydrolysis reactions of indium(III) ion in the aqueous phase:

$$\mathrm{In^{3+} + H_2O \rightleftharpoons In(OH)^{2+} + H_3O^+}$$
$$\mathrm{In(OH)^{2+} + H_2O \rightleftharpoons In(OH)_2^{+} + H_3O^+}$$

with the hydrolysis constants,

$$K_1 = \frac{[\mathrm{In(OH)^{2+}}][\mathrm{H_3O^+}]}{[\mathrm{In^{3+}}]}$$

and

$$K_2 = \frac{[\mathrm{In(OH)_2^{+}}][\mathrm{H_3O^+}]}{[\mathrm{In(OH)^{2+}}]},$$

respectively. Taking into account these reactions, the following expression instead of Eq. 3 can be derived from Eq. 2:

$$\log C_{\mathrm{In,o}} = \log C_{\mathrm{In,w}} - 3\log[\mathrm{H^+}] - \log \alpha_{\mathrm{In(OH^-)}} + a\log[\mathrm{HA}]_\mathrm{o} + \log K_{\mathrm{ex}(1ah)}, \qquad (5)$$

where $\alpha_{\mathrm{In(OH^-)}}$ denotes the side reaction coefficient of indium(III) ion in the aqueous phase:

$$\alpha_{\mathrm{In(OH^-)}} = 1 + \frac{K_1}{[\mathrm{H_3O^+}]} + \frac{K_1 \cdot K_2}{[\mathrm{H_3O^+}]^2}. \qquad (6)$$

Then in Fig. 2, the deviations of the observed points from the straight line with a slope of 1.0 refer to $\log \alpha_{\mathrm{In(OH^-)}}$. According to Eq. 6, a plot of $(\alpha_{\mathrm{In(OH^-)}}-1)[\mathrm{H^+}]$ against $1/[\mathrm{H^+}]$ for the markedly deviated points at C_HA=0.5 mol dm^{-3} (No. 5) in Fig. 2 is shown in Fig. 4. The plot is found to be linear and the following hydrolysis constants were calculated from the intercept and slope of the straight line by the least-squares method: $\log K_1 = -4.1$ and $\log K_2 = -2.7$. Various hydrolysis constants for indium(III) ion have been presented: $\log K_1 = -4.41$ and $\log K_2 = -4.16$ at 25 °C and at ionic strength of 3 mol dm^{-3} ($\mathrm{NaClO_4}$),[9] $\log K_1 = -3.48$, $\log K_2 = -4.19$, and $\log K_3 = -5.08$ at 25 °C and at ionic strength of 0.1 mol dm^{-3} ($\mathrm{NaClO_4}$),[10] and $\log K_1 = -4.22$ and $\log K_2 = -2.92$ at 25 °C and at ionic strength of 3 mol dm^{-3} ($\mathrm{LiClO_4}$).[11] As shown in Fig. 2, the solid points, which are corrected by considering the hydrolysis of indium(III) ion in the aqueous phase, fit well the straight line with a slope of 1.0 also at C_HA=1.0 and 0.7 mol dm^{-3}.

Subsequently, the number of decanoic acid molecules involved in the extracted species was determined in the following manner. In the region where the j-meric species prevails, the following expression is derived from Eq. 2:

$$\frac{1}{j}\log C_{\mathrm{M,o}} - (\log C_{\mathrm{M,w}} - 3\log[\mathrm{H^+}]) = \frac{1}{j}\log \sum_a (K_{\mathrm{ex}(jah)}[\mathrm{HA}]_\mathrm{o}^{\,a}) + \frac{1}{j}\log j. \qquad (7)$$

According to Eq. 7, the total number of decanoic acid molecules involved in the j-mer can be determined from the slope of the plot of $\{\frac{1}{j}\log C_{\mathrm{M,o}} - (\log C_{\mathrm{M,w}} - 3\log[\mathrm{H^+}])\}$ against $\log[\mathrm{HA}]_\mathrm{o}$. The results for both aluminum and indium are shown in Figs. 5 and 6, respectively. In the region where the monomeric aluminum decanoate prevails, the plot falls on the straight line with a slope of 3.0 at higher concentration of decanoic acid in the organic phase but deviates upward from the straight line at lower concentration of decanoic acid in the organic phase.

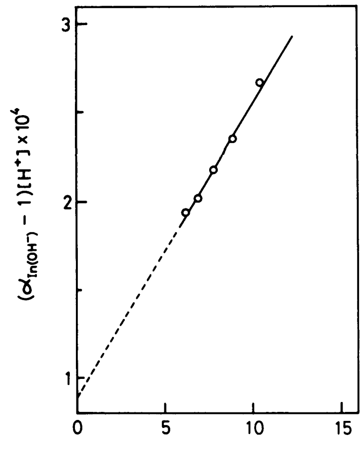

Fig. 4. Determination of the hydrolysis constants of indium(III) ion in the aqueous phase.
The intercept and slope of the straight line were calculated by the least-squares method.

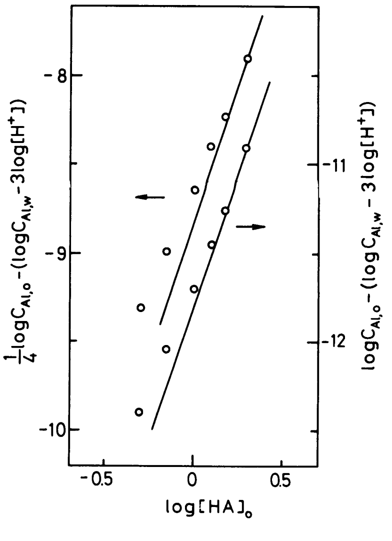

Fig. 5. Determination of the number of decanoic acid molecules involved in the monomeric and tetrameric aluminum(III) decanoates.
Solid lines are the straight lines with a slope of 3.0.

This result suggests that the two monomeric aluminum(III) decanoates are responsible for the extraction in the lower concentration of aluminum in 1-octanol: one of them is AlA_3 and the other $AlA_aH_h(a<3)$. Under these conditions the total concentration of aluminum in the organic phase can be written as:

$$\log C_{Al,o} - (\log C_{Al,w} - 3\log[H^+]) = 3\log[HA]_o + \log K_{ex(130)} + \log\left(1+\frac{K_{ex(1ah)}}{K_{ex(130)}}[HA]_o{}^{(a-3)}\right). \tag{8}$$

Comparing the plot of the left-hand side of Eq. 8 against $-\log[HA]_o$ with the normalized curves, $\log(1+X^n)$ vs. $\log X$, we can determine another monomeric species. The result is shown in Fig. 7. The plot fits well the normalized curve: $\log(1+X)$ vs. $\log X$, that is, $n=3-a=1$ or $a=2$. From the electroneutrality of the extracted species, it can be noted that another monomeric species involves one hydroxyl group. From Fig. 7, we can also obtain the respective extraction constants, $K_{ex(130)}$ and $K_{ex(12-1)}$ by the curve-fitting method. The results obtained are summarized in Table 1 together with the other constants.

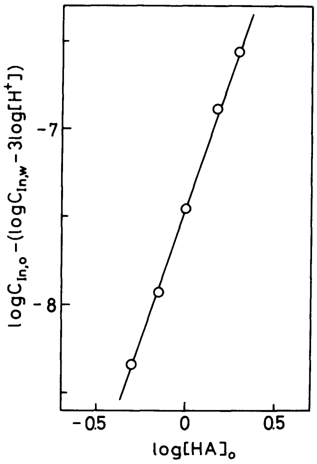

Fig. 6. Determination of the number of decanoic acid molecules involved in the monomeric indium(III) decanoate.
Solid line is the straight line with a slope of 3.0.

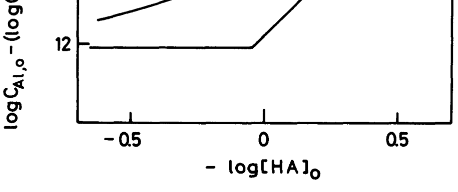

Fig. 7. Determination of the number of decanoic acid molecules involved in the monomeric aluminum(III) decanoates by the curve-fitting method.
Solid curve is the normalized curve, $\log(1+X)$ vs. $\log X$. Solid lines are the asymptotes of the normalized curve.

In the region where the tetrameric aluminum decanoate prevails, the slope of the plot of $\{\frac{1}{4}\log C_{Al,o}-(\log C_{Al,w}-3\log[H^+])\}$ against $\log[HA]_o$ on the basis of Eq. 7 ($j=4$) gets steeper with the concentration of decanoic acid in the organic phase, and approaches 3.0. This result indicates the following species: Al_4A_{12} and $Al_4A_aH_h(a<12)$ as the tetrameric extracted species. Then the following relation can be derived:

$$\log C_{Al,o} - 4(\log C_{Al,w} - 3\log[H^+]) - 12\log[HA]_o = \log\left(1+\frac{K_{ex(4ah)}}{K_{ex(4120)}}[HA]_o{}^{(a-12)}\right) + \log 4 + \log K_{ex(4120)}. \tag{9}$$

The values of $\{\log C_{Al,o}-4(\log C_{Al,w}-3\log[H^+])-12\log[HA]_o\}$ are plotted against $-\log[HA]_o$ as depicted in Fig. 8. According to the curve-fitting method, in which the plot is compared with the normalized curves, $\log(1+X^n)$ vs. $\log X$, the number of decanoic acid molecules involved in another tetrameric species can be determined together with the extraction constants of the two tetrameric Al(III) decanoates. In Fig. 8, the plot fits the normalized curve, $\log(1+X^4)$ vs. $\log X$, that is, $n=12-a=4$, or $a=8$ and then h is equal to -4. In analogy with the monomer stated above, four hydroxide ions should

Table 1. Extracted Species and Extraction Constants$^{a)}$ of Al(III)-, Ga(III)-, and In(III)-Decanoates

Metals	1-Octanol	Benzene
Al(III)	$AlA_3(-12.01)$	$Al_6A_{12}(OH)_6(-46.1)^{b)}$
	$AlA_2(OH)(-11.96)$	
	$Al_4A_{12}(-35.86)$	
	$Al_4A_8(OH)_4(-35.38)$	
Ga(III)	$GaA_2(OH)(-9.54)^{c)}$	$Ga_6A_{12}(OH)_6(-35.8)^{d)}$
	$Ga_2A_4(OH)_2(-14.92)$	$Ga_6A_{18}(H_2O)_6(-34.3)$
	$Ga_2A_6(-15.26)$	$Ga_jA_aH_h(j<6)$
In(III)	$InA_3(-7.45)$	$InA_3(HA)_3(-7.34)^{e)}$
		$In_3A_9(HA)_3(-18.6)$
		$In_6A_{12}(OH)_6(-36.1)$

a) The respective extraction constants($\log K_{ex(jah)}$) are listed in parentheses. b) Ref. 1. c) Ref. 4. d) Ref. 2. e) Ref. 3.

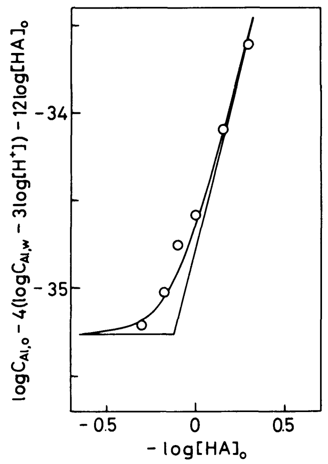

Fig. 8. Determination of the number of decanoic acid molecules involved in the tetrameric aluminum (III) decanoates by the curve-fitting method.
Solid curve is the normalized curve, $\log(1+X^4)$ vs. $\log X$. Solid lines are the asymptotes of the normalized curve.

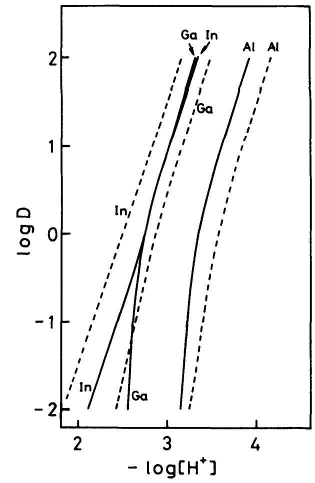

Fig. 9. Extraction curves calculated on the basis of the results obtained from the present and previous works.
$C_{M,tot}=5\times10^{-3}$ mol dm^{-3}. $C_{HA}=1.0$ mol dm^{-3}.
Solid and dotted curves correspond to benzene and 1-octanol, respectively.

be involved in another tetrameric aluminum(III) decanoate. The extraction constants $K_{ex(4120)}$ and $K_{ex(48-4)}$ determined by the curve-fitting method are given in Table 1. Consequently, AlA_3, $AlA_2(OH)$, Al_4A_{12}, and $Al_4A_8(OH)_4$ are responsible for the extraction with decanoic acid in 1-octanol.

In the case of indium(III), on the other hand, the plot of $\{\log C_{In,o}-(\log C_{In,w}-3\log[H^+])\}$ against $\log[HA]_o$ falls on the straight line with a slope of 3.0. Then only InA_3 is extracted with decanoic acid in 1-octanol. The extraction constant $K_{ex(130)}$ can be obtained from the intercept of the straight line in Fig. 6. The result is given in Table 1.

Consequently, the extraction equilibria for aluminum(III) and indium(III) are represented as follows:

Aluminum(III):

$$Al^{3+} + 3(HA)_o \xrightleftharpoons{K_{ex(130)}} (AlA_3)_o + 3H^+$$

$$Al^{3+} + 2(HA)_o + H_2O \xrightleftharpoons{K_{ex(12-1)}} (AlA_2(OH))_o + 3H^+$$

$$4Al^{3+} + 12(HA)_o \xrightleftharpoons{K_{ex(4120)}} (Al_4A_{12})_o + 12H^+$$

$$4Al^{3+} + 8(HA)_o + 4H_2O \xrightleftharpoons{K_{ex(48-4)}} (Al_4A_8(OH)_4)_o + 12H^+$$

Indium(III):

$$In^{3+} + 3(HA)_o \xrightleftharpoons{K_{ex(130)}} (InA_3)_o + 3H^+.$$

Solvent Effects. The previous results[1-4] are also listed in Table 1 for comparison. Table 1 suggests that the degree of polymerization of the extracted species for aluminum(III), gallium(III), and indium(III) is more extensive in benzene than in 1-octanol and increases in the following order in both solvents: Al>Ga>In. In 1-octanol the addition of a decanoic acid molecule to each metal decanoate did not occur to any appreciable extent. It is convenient to imagine that some octanol molecules are solvated to the extracted species. As shown in Table 1, the dimeric and tetrameric extracted species in benzene were not observed, while in 1-octanol the trimeric and hexameric ones were not detected. Then it can be expected that the polymerization of metal decanoates in benzene and 1-octanol proceeds through the different mechanism. Further, the difference in the composition of the monomeric indium(III) decanoates in benzene($InA_3(HA)_3$) and 1-octanol(InA_3) can be explained by a notion that in benzene decanoic acid behaves primarily as a dimer and, then a dimeric decanoate(HA_2^-) coordinates to indium ion as a bidentate ligand, whereas in 1-octanol decanoic acid exists only in a monomer form and, then a monomeric decanoate solvated by some octanol molecules binds to indium ion. As we have already reported, also in the extraction of copper(II) there was a remarkable difference in the extracted species between solvating[7,8] and nonsolvating[5] solvents.

The extraction curves calculated from the results given in Table 1 are illustrated in Fig. 9. As shown in Fig. 9, aluminum(III) and gallium(III) ions are extracted with decanoic acid in 1-octanol at the higher pH region than in benzene, while indium(III) decanoate is extracted in 1-octanol at the lower pH region than in benzene. Then it is expected that indium(III) is selectively extracted from a mixture of these three metal ions with decanoic acid by using 1-octanol as a diluent. Usually but not always, much attention must be paid to the coextraction caused by the formation of mixed metal carboxylates in the extraction of polymerized metal carboxylates. Fortunately under the present experimental conditions, only the monomeric indium(III) decanoate is extracted with decanoic acid in 1-octanol. Therefore, there is scarcely a fear that aluminum(III) and gallium(III) are coextracted with indium(III) as a mixed metal decanoate.

Consequently, the selection of a solvent used in the extraction of metal carboxylates is one of the important considerations, and may occasionally results in the improvement of the selectivity.

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