

Utility of 1-Octanol/Octane Mixed Solvents for the Solvent Extraction of Aluminum(III), Gallium(III), and Indium(III) with 8-Quinolinol

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Using 1-octanol/octane mixed solvents, the extraction of aluminum(III), gallium(III) and indium(III) with 8-quinolinol was carried out at 25°C. The formation constants of the respective metal(III) 8-quinolinolates in the aqueous phase and their partition constants between the mixed solvents and water were determined based on an analysis of the extraction equilibria. The relationship between the partition constants of 8-quinolinol and its complexes was analyzed by the regular solution theory. The molar volumes of aluminum(III), gallium(III) and indium(III) 8-quinolinolates, calculated from the present results, suggest that the electrostriction effect functions in complex forming. It has been found that octane/1-octanol mixed solvents were available not only for the extraction of metal ions, but also for determining the formation constants of these metal 8-quinolinolates in the aqueous phase and their partition constants.

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8-Quinolinol is one of the most famous reagents for the extraction of metal ions, and has been extensively investigated as a useful extraction reagent for various metal cations. In these extraction systems, a chlorinated hydrocarbon, such as chloroform and carbon tetrachloride, and an aromatic solvent, such as benzene and toluene, have been used with very high frequencies. From the point of view of preserving the natural environment, these chlorinated solvents should be controlled regarding their use as much as possible. In addition, aromatic solvents, such as benzene and toluene, are pointed out to possess carcinogenic activity. Taking into account these situations, a less toxic solvent than these conventional solvents, which were pointed out to be harmful, is expected to be developed for keeping to use 8-quinolinol as an extracting reagent.

Neat 1-octanol and octane were scarcely used for solvent extraction, because the latter has a poor solubility of a reagent, and the former possesses a poor phase-separating ability. However, neat octane has a good phase-separating ability and neat 1-octanol possesses good extractability. Thus, a mixture of these solvents can be expected to be available for extraction as a good solvent by compensating for each disadvantage.

In our previous investigations, the 1-octanol(or 1-nonanol)/octane mixed solvent was found to be useful for analyses of ion-pair extraction systems¹⁻⁴ and for analyzing the partition equilibrium of 8-quinolinol⁵ as a lower toxic solvent.

The present paper describes analyses of the extraction equilibria of aluminum(III), gallium(III) and indium(III) ions with 8-quinolinol using 1-octanol and 1-octanol/octane mixed solvents, as well as the relationship between the partition constants of 8-quinolinol (HO_x) and these metal 8-quinolinolates ($\text{M}(\text{O}_x)_3$) based on the present results by regular solution theory.

Experimental

Reagents

Octane, 1-octanol and 8-quinolinol were used as same reagents as those in previous work.⁵ An 1-octanol/octane mixed solvent was prepared by the same method as that in a previous study.⁵ An aluminum(III) perchlorate solution was prepared by dissolving commercial $\text{Al}(\text{ClO}_4)_3$ (98%, Aldrich Chemical Company, Inc.) in a 0.1 mol dm^{-3} perchloric acid solution. Gallium(III) and indium(III) perchlorate solutions were prepared by dissolving metallic gallium and indium (99.9999%, Nacalai Tesque Inc., Kyoto, and 99.99%, Wako Pure Chemical Industries, Ltd., Osaka) in a small excess of perchloric acid. In order to adjust the ionic strength in the aqueous phase, a proper quantity of sodium perchlorate was added in these metal perchlorate solutions, respectively. All other reagents were of reagent grade and were used without further purification. Aqueous solutions were prepared with distilled-deionized water.

Apparatus

For mechanical shaking, a Cool Bath Shaker ML-10 (TAITEC Co., Koshigaya) was used. A Table Top Centrifuge Model 5100 (Kubota Seisakusho Ltd., Tokyo) was used for centrifugation. A DKK Ion Meter (Model IOL-50 (DKK Co., Tokyo)) was used for determining the hydrogen-ion concentration in the aqueous phase after complete equilibration. A spectrophotometric determination of aluminum was performed using a Ubest-55 UV/Vis spectrophotometer (JASCO, Tokyo). A SAS-727 Atomic Absorption Spectrophotometer (Seiko Instruments Inc., Tokyo) was used for determining the gallium and indium concentrations.

Table 1 Solubility parameter and molar volume of solvents and the partition constants of 8-quinolinol

Solvent	$\delta_o(\delta_{\text{mix}})^{21}/$ $J^{1/2} \text{ cm}^{-3/2}$	$\delta_o'/$ $J^{1/2} \text{ cm}^{-3/2}$	$V_o/$ $\text{cm}^3 \text{ mol}^{-1}$	$\log K_{D,\text{HOx}}^5$
1-Octanol	21.1	12.8	158.4	1.94
4 M 1-octanol/octane mixed solvent	19.0 ^a	11.8	160.2	1.81
2 M 1-octanol/octane mixed solvent	17.2 ^a	10.7	161.7	1.64
Octane	15.4	9.4	163.2	1.33
Benzene	18.7	12.3	89.4	2.22
Chloroform	18.7	12.5	80.8	2.59
Water ^b	35.8 ²²		18.1	

a. The values were calculated by Eq. (18).

b. Perchloric acid solution adjusted ionic strength to be 0.1 mol dm⁻³ by perchlorate anion.

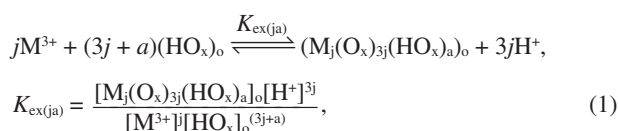
Procedure

The extraction of each metal(III) ion was carried out in a cool bath shaker described above, kept at 25.0°C. The ionic strength in the aqueous phase was adjusted to 0.1 mol dm⁻³ with sodium perchlorate. The extraction of each metal(III) was performed under the following conditions: the organic and aqueous phases were of equal volumes (15 ml each), the total metal concentration was 5 × 10⁻⁴ mol dm⁻³ and the total 8-quinolinol concentration was 2 × 10⁻² mol dm⁻³. The shaking time was 3 h for aluminum and 2 h for gallium and indium, which were sufficient for complete equilibration. After centrifuging for 5 min at 3000 rpm, the pH of the aqueous phase was measured without any phase separation, and the hydrogen-ion concentration was determined by correcting the apparent liquid junction potential. The concentration of aluminum in the aqueous phase was determined spectrophotometrically after extracting aluminum at pH 5 with 8-quinolinol in benzene. The concentrations of gallium and indium in each aqueous phase were determined by atomic absorption spectrometry. The concentrations of each metal in the respective organic phases were determined by subtracting those in the aqueous phase from the total one.

Results and Discussion

Analyses of extraction equilibria of aluminum(III), gallium(III) and indium(III) with 8-quinolinol using neat octane and 1-octanol, and their mixtures as a solvent

In the extraction of divalent transition metal ions with 8-quinolinol, the dimeric metal 8-quinolinolates were reported to be extracted.⁶⁻¹¹ Taking into account these results, the polymeric species can be expected to be extracted. Thus, the following extraction equilibrium can be responsible for the present extraction systems:



where $K_{\text{ex(ja)}}$ denotes the extraction constant of $\text{M}_j(\text{Ox})_{3j}(\text{HOx})_a$ and subscript o refers to the organic phase.

If metal species other than M^{3+} can be neglected in the aqueous phase, and only $\text{M}_j(\text{Ox})_{3j}(\text{HOx})_a$ is extracted, the total metal

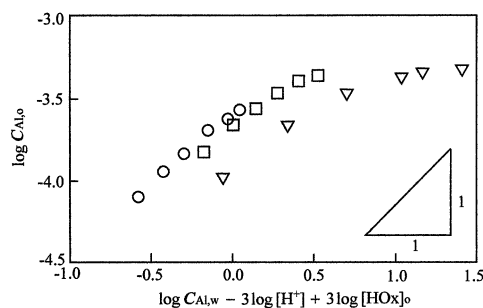


Fig. 1 Determination of the degree of polymerization of the extracted species for aluminum(III). Symbols: ○, 1-octanol; □, 4 mol dm⁻³ 1-octanol/octane mixed solvent; ▽, 2 mol dm⁻³ 1-octanol/octane mixed solvent.

concentration in the organic phase can be expressed as

$$C_{M,o} = jK_{\text{ex(ja)}}(C_{M,w}[\text{H}^+]^{-3})^j[\text{HOx}]_o^{(3j+a)}. \quad (2)$$

From Eq. (2) the following expression can be derived:

$$\log C_{M,o} - a \log [\text{HOx}]_o = j(\log C_{M,w} - 3 \log [\text{H}^+] + 3 \log [\text{HOx}]_o) + \log j + \log K_{\text{ex(ja)}}. \quad (3)$$

Since $[\text{HOx}]_o$ varies with the extraction conditions in the present extraction systems, it was calculated by the following equation:

$$[\text{HOx}]_o = \frac{C_{\text{HOx}}}{1 + \frac{1}{K_{D,\text{HOx}}} \left(1 + \frac{[\text{H}^+]}{K_{a1}}\right)}, \quad (4)$$

where $K_{D,\text{HOx}}$ and K_{a1} denote the partition and first dissociation constants of 8-quinolinol, and C_{HOx} is the total concentration of 8-quinolinol. In a calculation of $[\text{HOx}]_o$, values that were determined in our previous investigation⁵ were used. The first dissociation constant, $\text{p}K_{a1} = 5.08$, and $K_{D,\text{HOx}}$ for each solvent system are summarized in Table 1.

In systems using neat 1-octanol as a solvent, taking into account the extraction of the 8-quinolinolium ion, H_2Ox^+ , with the perchlorate anion, $[\text{HOx}]_o$ was calculated by the following expression:

$$[\text{HOx}]_o = \frac{C_{\text{HOx}}}{1 + \frac{1}{K_{D,\text{HOx}}} \left[1 + \frac{[\text{H}^+]}{K_{a1}} \{1 + K_f[\text{ClO}_4^-](1 + K_{D,(\text{H}_2\text{Ox}^+\text{ClO}_4^-)})\right]}}, \quad (5)$$

where $K_{D,(\text{H}_2\text{Ox}^+\text{ClO}_4^-)}$ and K_f denote the partition and formation constants of an ion-pair, $(\text{H}_2\text{Ox}^+\text{ClO}_4^-)$. The values of $\log K_f$ and $\log K_{D,(\text{H}_2\text{Ox}^+\text{ClO}_4^-)}$ were found to be 0.27 and -0.12, respectively.⁵

Taking into account the coordination number and charge of the present metal ions, the value of a can be expected to be 0. Based on Eq. (3) ($a = 0$), plots of $\log C_{M,o}$ against $(\log C_{M,w} - 3 \log [\text{H}^+] + 3 \log [\text{HOx}]_o)$ should be straight lines with a slope of j . Plots for aluminum(III) are shown in Fig. 1. Irrespective of the solvent, the plots display curvature and deviate downward from a straight line with a slope of 1 with increasing the concentration of aluminum in the organic phase. Therefore, it is suggested that the extracted species is a monomer, and that the species of aluminum other than Al^{3+} in the aqueous phase can be responsible for the extraction equilibrium. In the cases of gallium and indium, similar results were obtained.

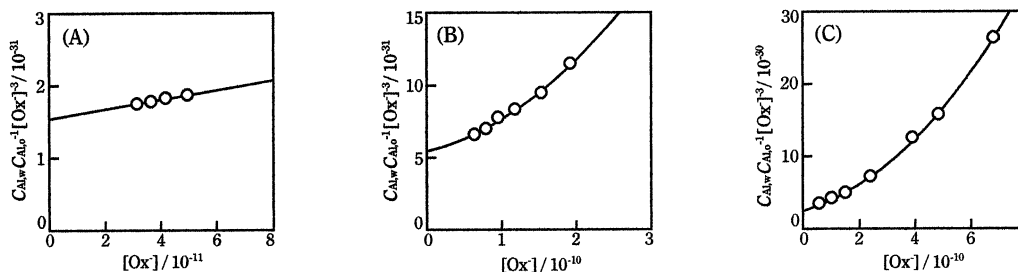
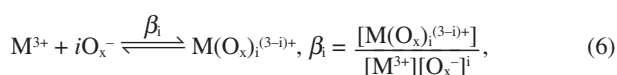


Fig. 2 Estimation of the extraction constant (K_{ex}') and the formation constants of aluminum(III) 8-quinolinolate using neat 1-octanol (A), 4 mol dm⁻³ 1-octanol/octane (B) and 2 mol dm⁻³ 1-octanol/octane (C) mixed solvents as a solvent. The solid line (A) is a straight line that was drawn by the least-squares method. The solid curves are quadratic (B) and cubic (C) curves that were drawn by the least-squares method.

Side-reaction of metal ions in the aqueous phase

The species of each metal other than the respective hydrate metal ions in the aqueous phase can be expected to be hydrolysis products and metal 8-quinolinolates. Taking into account the hydrolysis of metal cations in the aqueous phase, the deviation of the plots in Fig. 1 was still not elucidated. Metal(III) 8-quinolinolate species can be expected as species other than M^{3+} . Then, the reaction of metal ions (M^{3+}) with 8-quinolinolate anion (Ox^-) should be considered:



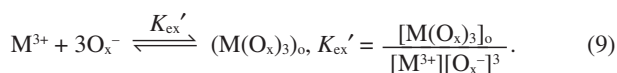
where β_i denotes the overall formation constant of metal(III) 8-quinolinolate.

The total concentration of metal(III) in the aqueous phase can be expressed as:

$$\begin{aligned} C_{M,w} &= [M^{3+}] + [M(Ox)_2^{+}] + [M(Ox)_3] \\ &= [M^{3+}](1 + \beta_1 [Ox^-] + \beta_2 [Ox^-]^2 + \beta_3 [Ox^-]^3) \\ &= [M^{3+}] \alpha_{M(Ox)}, \end{aligned} \quad (7)$$

$$\alpha_{M(Ox)} = 1 + \beta_1 [Ox^-] + \beta_2 [Ox^-]^2 + \beta_3 [Ox^-]^3, \quad (8)$$

where $\alpha_{M(Ox)}$ refers to the side-reaction coefficient, which is expressed by Eq. (8). As shown in Fig. 1, the extracted species can be expected to be $M(Ox)_3$. A new extraction constant (K_{ex}') of $M(Ox)_3$ can be defined as



This extraction constant can be related to the extraction constant ($K_{ex(10)}$), which is expressed by Eq. (1) as

$$K_{ex}' = K_{ex(10)} K_{D,HOx}^3 K_{a2}^{-3}, \quad (10)$$

where K_{a2} denotes the second dissociation constant of 8-quinolinol, and was determined as $pK_{a2} = 9.47$ in our previous work.⁵ From Eq. (7) the following equation can be derived:

$$[M^{3+}] = C_{M,w} / (1 + \beta_1 [Ox^-] + \beta_2 [Ox^-]^2 + \beta_3 [Ox^-]^3). \quad (11)$$

The following relation can be expressed from Eqs. (9) and (11):

$$\frac{C_{M,w}}{C_{M,o}} [Ox^-]^3 = \frac{1}{K_{ex}'} + \frac{\beta_1}{K_{ex}'} [Ox^-] + \frac{\beta_2}{K_{ex}'} [Ox^-]^2 + \frac{\beta_3}{K_{ex}'} [Ox^-]^3, \quad (12)$$

where the concentration of the 8-quinolinolate anion, $[Ox^-]$ was calculated by substituting the experimental values of $[HOx]_o$ and $[H^+]$ in:

$$[Ox^-] = \frac{K_{a2}[HOx]_o}{K_{D,HOx}[H^+]}. \quad (13)$$

Equation (12) is equal to $y = d + cx + bx^2 + ax^3$. Then, based on the above expression, fitting plots of the values of the left-hand side of Eq. (12) against $[Ox^-]$ to the equation $y = d + cx + bx^2 + ax^3$ with proper values of a , b , c , and d , by the least-squares method, the values of K_{ex}' , β_1 , β_2 , and β_3 can be calculated from the values of d , c , b and a , respectively. The results for the extraction of aluminum(III) using neat 1-octanol, 4 mol dm⁻³ 1-octanol/octane, and 2 mol dm⁻³ 1-octanol/octane mixed solvents as a solvent are shown in Figs. 2(A), (B) and (C), respectively. As can be seen from Fig. 2(A), the plots fit well with the straight line. This suggests that the species of $Al(Ox)_2^+$ and $Al(Ox)_3$ can be neglected in the case of using 1-octanol as a solvent. The values of K_{ex}' and β_1 were calculated from the intercept and slope of the straight line. The values are summarized together with the other constants in Table 2. Since in Fig. 2(B) the plot fits well with the quadratic curve, the species of $Al(Ox)_3$ has been found to be negligibly small in the extraction systems using a 4 mol dm⁻³ 1-octanol/octane mixed solvent. The extraction constant, K_{ex}' , and the overall formation constants, β_1 and β_2 , were determined by the least-squares method. As shown in Fig. 2(C), in the extraction of aluminum(III) using a 2 mol dm⁻³ 1-octanol/octane mixed solvent, the plots fit well with a cubic curve. Then, all of the 8-quinolinolates were found to be not neglected for the Al^{3+} species. The respective constants were estimated by the method described above. In the extraction systems for gallium(III) and indium(III), similar results as those in the extraction of aluminum(III), shown in Fig. 2, were obtained. In the extraction of indium(III) using 1-octanol, however, the plot on the basis of Eq. (12) fit well with the quadratic curve in contrast with the aluminum(III) and gallium(III) systems, in which the plots fit with the respective straight lines. The values of the respective constants for gallium(III) and indium(III) obtained by the least-squares method are summarized together with those for aluminum(III) in Table 2.

Since it has been found that the monomeric species, $M(Ox)_3$, was extracted and metal 8-quinolinolates were not negligible in the aqueous phase in the present extraction systems, the following relationship can be set up:

$$\begin{aligned} \log C_{M,o} &= \log C_{M,w} - 3\log[H^+] + 3\log[HOx]_o \\ &\quad - \log \alpha_{M(Ox)} + \log K_{ex(10)}, \end{aligned} \quad (14)$$

Table 2 Extraction, overall formation, and partition constants of metal(III) 8-quinolinolates

Metal	Solvent	$\log K_{ex}'$	$\log K_{ex(10)}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log K_{D,M(Ox)_3}$
Al(III)	1-Octanol	30.77	-3.46	9.7			3.27
	4 M 1-octanol/octane mixed solvent	30.23	-3.52	9.8	19.1		2.82
	2 M 1-octanol/octane mixed solvent	29.59	-3.74	9.7	19.0	27.5	2.09
				Mean 9.7	19.0	27.5	
	Octane	28.53	-4.77				1.03 ^a
	Benzene	30.08	-4.99				2.58
Ga(III)	1-Octanol	40.27	6.04	14.2			4.17
	4 M 1-octanol/octane mixed solvent	39.64	5.80	13.8	25.4		3.54
	2 M 1-octanol/octane mixed solvent	39.27	5.94	(12.8) ^b	25.2	36.1	3.17
				Mean 14.0	25.3	36.1	
	Octane	38.15	5.75				2.05 ^a
	Benzene	39.68	4.61				3.58
In(III)	1-Octanol	36.37	2.14	11.7	23.1		2.67
	4 M 1-octanol/octane mixed solvent	35.97	2.13	11.8	23.2		2.27
	2 M 1-octanol/octane mixed solvent	35.35	2.02	(12.4) ^b	22.7	33.7	1.65
				Mean 11.7	23.0	33.7	
	Octane	34.43	1.13				0.73 ^a
	Benzene	35.70	0.63				2.00
	Chloroform	37.74	1.56				4.04

a. The partition constants of $M(O_x)_3$ for octane were estimated by extrapolating the respective straight lines to the solubility parameter of octane ($\delta_o' = 9.4 \text{ J}^{1/2} \text{ cm}^{-3/2}$). The extraction constants, $K_{ex(10)}$ and K_{ex}' were calculated by Eqs. (14) and (9). b. The values in parentheses were rejected in calculations of the mean values of β_1 and β_2 , since they vary considerably from the other ones.

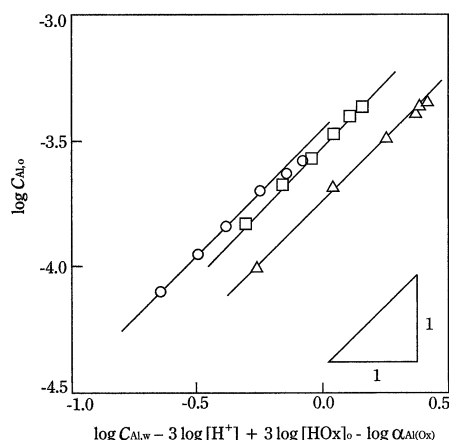


Fig. 3 Determination of the extraction constant ($K_{ex(10)}$) and a comparison of the observed values with the calculated straight lines based on the results obtained in the present study. The symbols are the same as in Fig. 1. The solid lines are straight lines with a slope of 1.

where $\alpha_{M(O_x)}$ can be calculated by substituting the values of β obtained from each analysis for the respective extraction systems into Eq. (8). According to Eq. (14), plots of $\log C_{M,o}$ against $(\log C_{M,w} - 3\log[H^+] + 3\log[HO_x]_o - \log \alpha_{M(O_x)})$ can be expected to be a straight line with a slope of 1. As can be seen from Fig. 3, the plots fit well with a straight line with a slope of 1 for any solvent used. From the intercept of each straight line the extraction constants, $K_{ex(10)}$, were obtained.

In the extraction systems of gallium(III) and indium(III) the plots of $\log C_{M,o}$ against $(\log C_{M,w} - 3\log[H^+] + 3\log[HO_x]_o - \log \alpha_{M(O_x)})$ based on Eq. (14) were confirmed to fit well with the respective straight lines with a slope of 1 as well as in the extraction of aluminum(III).

For a comparison, analyses of the extraction equilibria of

aluminum(III), gallium(III) and indium(III) using benzene and chloroform as a solvent were carried out on the basis of Eq. (14). These analyses were based on the assumption that the extracted species and the formation constant of the respective metal 8-quinolinolates in the aqueous phase are the same as in the extraction systems using 1-octanol and 1-octanol/octane mixed solvents as a solvent. The results for aluminum, gallium and indium(III) are drawn in Figs. 4(A), (B) and (C). The plots fit well with each straight line with a slope of 1 in the respective systems using benzene and chloroform, respectively. The extraction constant, $K_{ex(10)}$, were obtained from the intercepts of the straight lines. The extraction constants, $K_{ex(10)}$, for the respective systems were obtained from the intercepts of each straight line with a slope of 1. These constants are summarized together with another extraction constants, K_{ex}' , calculated by Eq. (10) in Table 2.

Determination of the partition constant of metal 8-quinolinolate, $M(O_x)_3$, between respective organic and aqueous phases

The extraction constant of $M(O_x)_3$ can be expressed by

$$K_{ex(10)} = K_{D,M(O_x)_3} K_{D,HO_x}^{-3} \beta_3 K_{a2}^3, \quad (15)$$

where $K_{D,M(O_x)_3}$ refers to the partition constant of $M(O_x)_3$. The values of $K_{ex(10)}$ and β_3 were obtained in the present study, and those of K_{D,HO_x} and K_{a2} were found in our previous work.⁵ Therefore, the values of $K_{D,M(O_x)_3}$ for the present extraction systems can be calculated by Eq. (15), and are summarized together with the other constants in Table 2.

Based on the additivity of the molar cohesive energy and the molar volume of the ligand in a complex, it has been known that the partition constant of a complex MR_n can be approximately correlated to that of the ligand HR as $K_{D,MRn} \approx K_{D,HR}^n$.¹² In our previous paper on the solvent effect on the extraction of copper(II)benzoates using 1-octanol(or 2-octanone)/benzene mixed solvents, on the other hand, the following relation

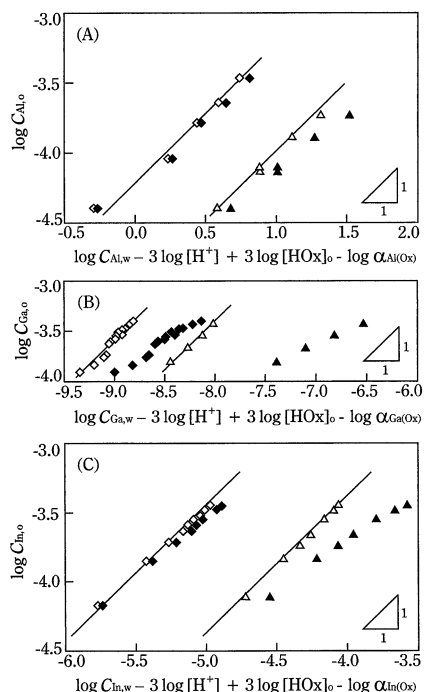


Fig. 4 Confirmation of the extraction equilibrium and determination of the extraction constant ($K_{ex(10)}$) for aluminum (A), gallium (B) and indium(III) (C) in the systems using benzene and chloroform, respectively. Symbols: Δ and \square refer to benzene and chloroform; \blacktriangle and \blacksquare denote plots neglecting the existence of the respective metal(III) 8-quinolinolates in the aqueous phase; that is, $\log C_{M,o}$ vs. $(\log C_{M,w} - 3\log[H^+] + 3\log[HOx]_o - \log \alpha_{M(Ox)})$. The solid lines are straight lines with a slope of 1.

between the partition constants of CuA_2 and HA (benzoic acid) was found to hold:

$$K_{D,CuA_2} = CK_{D,HA}^2;$$

where C is an intrinsic constant corresponding to each analogous solvent, and is smaller than 1.¹³

The relationship between the partition constants of metal 8-quinolinolates and 8-quinolinol is displayed in Fig. 5. The plots of $\log K_{D,M(O_3)}$ against $\log K_{D,HO_3}$ were proved to be linear, except for those using benzene as a solvent. In the extraction systems using solvents other than benzene, the plots for aluminum(III), gallium(III) and indium(III) fit well with the respective straight lines with a slope of 2.8 and intercepts of -2.4 , -1.5 and -2.9 , respectively. The slope of each plot is smaller than 3, thus suggesting the electrostriction effect to function in complex forming. The deviation of the plot for benzene from the respective straight lines may be attributable to the difference in the solvating ability between benzene and the other solvents.

According to the regular solution theory, the partition constant of an extracted species, A, can be expressed as follows:¹⁴

$$\frac{\log K_{D,A}}{\delta_w - \delta_o} = \frac{V_A}{2.30RT} (\delta_w + \delta'_o - 2\delta_A) \quad (16)$$

with

$$\delta'_o = \delta_o + \frac{RT}{\delta_w - \delta_o} \left(\frac{1}{V_o} - \frac{1}{V_w} \right), \quad (17)$$

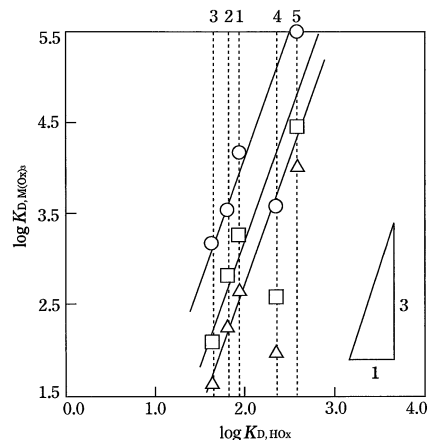


Fig. 5 Relationship between the partition constants of metal 8-quinolinolates for aluminum, gallium and indium(III) and 8-quinolinol. Symbols: \square , aluminum; \circ , gallium; and Δ , indium. The solid lines are straight lines with a slope of 2.8. Solvents: 1, 1-octanol; 2, 4 mol dm^{-3} 1-octanol/octane mixed solvent; 3, 2 mol dm^{-3} 1-octanol/octane mixed solvent; 4, benzene; 5, chloroform.

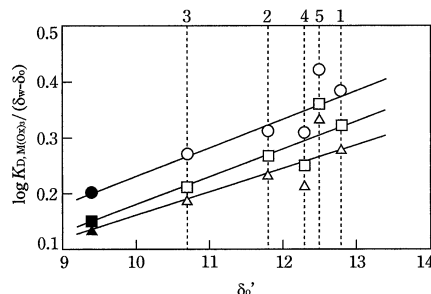


Fig. 6 Relationship of the partition constants of aluminum, gallium and indium(III) 8-quinolinolates along with the solubility parameter of the solvents. Symbols: \circ , aluminum; \square , gallium; Δ , indium. Solvents: 1, 1-octanol; 2, 4 mol dm^{-3} 1-octanol/octane mixed solvent; 3, 2 mol dm^{-3} 1-octanol/octane mixed solvent; 4, benzene; and 5, chloroform. The solid lines are straight lines drawn by the least-squares method for the points of neat 1-octanol and 1-octanol/octane mixed solvents. The solid symbols refer to the points for neat octane extrapolated from the respective straight lines to the solubility parameter of octane.

where δ'_o is calculated by Eq. (17) and δ_w , δ_o , δ_A , V_w , V_o and V_A denote the solubility parameters and the molar volumes for water (aqueous phase), organic solvents and the extracted species, respectively. The solubility parameter of the mixed solvents is given by the following equation:¹⁵

$$\delta_{mix} = \frac{\phi_1 \delta_1 + \phi_2 \delta_2}{\phi_1 + \phi_2}, \quad (18)$$

where ϕ denotes the volume fraction and subscripts 1 and 2 refer to 1-octanol and octane, respectively. A similar method as the solubility parameter was applied for estimating the molar volume of the mixed solvents. The values of the solubility parameters and the molar volumes for each solvent are summarized in Table 1. As can be seen from Fig. 6, plots of the left-hand side of Eq. (16) against δ'_o for each metal 8-quinolinolate were found to be linear for neat 1-octanol and 1-octanol/octane mixed solvents in the extraction of any metal 8-quinolinolate. The plots for chloroform and benzene, on the other hand,

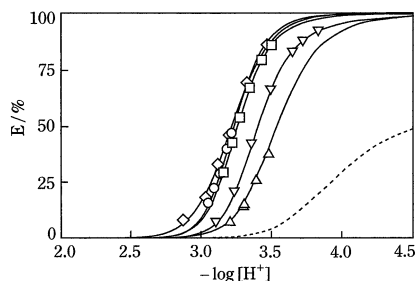


Fig. 7 Extraction curves of aluminum(III) calculated by employing the results obtained from the present work. Symbols: \circ , 1-octanol; \square , 4 mol dm⁻³ 1-octanol/octane mixed solvent; ∇ , 2 mol dm⁻³ 1-octanol/octane mixed solvent; \triangle , benzene; \diamond , chloroform. The solid curves are the respective calculated extraction curves, and the dotted curve refers to the calculated curve for the octane system that was estimated from the results by extrapolation.

deviate significantly up and down from each straight line, respectively. It is suggested that there is a remarkable difference in the interaction between a solute and a solvent between these solvents and the other three kinds of solvents. The regular solution theory is useful for the analogous solvents, even if the solvents possess a solvating ability.¹⁶⁻¹⁹ The molar volume of each extracted species was obtained from the slope of each straight line as follows: $V_{\text{Al}(\text{O}_x)_3} = 287 \text{ cm}^3$, $V_{\text{Ga}(\text{O}_x)_3} = 295 \text{ cm}^3$, and $V_{\text{In}(\text{O}_x)_3} = 243 \text{ cm}^3$, respectively. The order of these molar volumes agrees with that of the corresponding partition constants of each metal 8-quinolinolate, irrespective of the solvent used. Their molar volumes were found to be considerably smaller than the expected volume from that of the 8-quinolinol molecule ($V_{\text{HO}_8} = 124 \text{ cm}^3$).²⁰ Then, in addition to the electrostriction effect to function in complex forming, some interaction between the extracted species and the solvent suggests an affect in the present mixed solvent systems.

Extraction curves calculated by employing the results obtained from the present work

The extraction curves for aluminum(III), calculated by employing the results obtained from the present work, are depicted in Fig. 7. As can be seen from Fig. 7, the observed plots fit well with the respective extraction curves. This has substantiated the validity of the present results. For a comparison, the calculated curve for the system using octane as a solvent, which was estimated from the results obtained by extrapolation of the linear plots based on regular solution theory, was drawn. It was shown that octane is a poor solvent for the present extraction systems. This can be attributed to the small partition constants of $\text{M}(\text{O}_x)_3$ for the present metal. The extraction curves for gallium(III) and indium(III) have been found to show a similar tendency as those for aluminum(III) in Fig. 7.

As shown in Fig. 7, a difference in the extractability of aluminum(III) among chloroform, 1-octanol and 4 mol dm⁻³ 1-octanol/octane mixed solvent is scarcely discernible. However, for the extraction of gallium(III) and indium(III) chloroform is superior to the other solvents; 1-octanol and 4 mol dm⁻³ 1-octanol/octane mixed solvent are found to be superior to

benzene.

In the conventional extraction systems both the partition and formation constants of the extracted species are scarcely known. In the present systems this makes it possible to prepare a solvent that possesses an appropriate extractability by controlling the mixing ratio of 1-octanol and octane. Using a 2 mol dm⁻³ 1-octanol/octane mixed solvent, the formation constant of $\text{M}(\text{O}_x)_3$ was consequently determined for each metal.

The present results suggest that it has become possible to prepare an appropriate solvent by mixing two kinds of solvents; also, 1-octanol and 1-octanol/octane mixed solvents are useful for the extraction of aluminum(III), gallium(III) and indium(III) with 8-quinolinol being used as a less toxic solvent than chloroform or benzene.

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