Extractive Separation of Aluminum(III), Gallium(III) and Indium(III) Using Bis(1,1,3,3-tetramethylbutyl)phosphinic Acid and Its Sulfur Analogues

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The extraction behavior of Al(III), Ga(III) and In(III) was investigated using bis(1,1,3,3-tetramethylbutyl)phosphinic acid (MBP) and its sulfur analogues, bis(1,1,3,3-tetramethylbutyl)monothiophosphinic acid (MTP) and bis(1,1,3,3-tetramethylbutyl)dithiophosphinic acid (DTP) as extractants. A typical chelate extraction behavior was observed in these extraction systems in the pH range examined. The degree of extraction was in the order of In(III) > Ga(III) > Al(III). Moreover, the ability of extractants for mutual separation of these metals from one another decreased in the following order: DTP > MTP > MBP. The quantitative mutual separation of these metals can be achieved using DTP/hexane with single extraction. In the higher HCl concentration range, however, slight extraction of Ga(III) and In(III) was observed; this is due to the extraction of GaCl_4^- and InCl_4^- pairing with the protonated extractants.

Keywords Chelate extraction, aluminum, gallium, indium, bis(1,1,3,3-tetramethylbutyl)phosphinic acid, bis(1,1,3,3-tetramethylbutyl)monothiophosphinic acid, bis(1,1,3,3-tetramethylbutyl)dithiophosphinic acid

Gallium and indium have become very important in the advanced electronic industries in recent years, *e.g.*, they have been used as semiconductor materials such as GaAs and InP. Gallium and indium exhibit similar chemical behavior, and generally associate with aluminum ores in nature. Thus, the mutual separation of these metals certainly has both theoretical and practical significance. The separation methods of these metals including ion exchange and solvent extraction had been reviewed by Korkisch;¹ after that, Strelow separated gallium from other metals, and indium, gallium as well as aluminum from each other in hydrobromic acid–acetone and hydrochloric acid–acetone systems using a cation-exchange resin AG50W-X4;^{2–5} Brajter *et al.* modified Xylenol Orange on an anion-exchange resin Amberlyst A-26 to separate aluminum, gallium and indium from one another;⁶ Pesavento *et al.* modified T-azo-R[1-(tetrazolylazo)-2-hydroxynaphthalene-3,6-disulphonic acid on an anion-exchange resin, AG MP-1, to separate trace gallium from aluminum.⁷ Since the class of substances–liquid ion exchangers emerged, their advantages have stimulated separation chemists to investigate the mutual separation of metal ions which are chemically similar.⁸ Cerrai and Gherisni separated Al, Ga, In and Tl from one another with di-(2-ethylhexyl) orthophosphoric acid (HDEHP);^{9,10} 7-alkylated 8-hydroxyquino-

line¹¹ and alkylated cupferron^{12,13} were also used to separate Ga from Al through a chelate extraction mechanism. Liquid anionic exchangers such as trioctylamine (TOA), tri-*iso*-octylamine (TIOA) and Aliquat¹⁴, Amberlite LA-1¹⁵, Amberlite LA-2¹⁶, Aliquat 336S¹⁷ as well as octyl-aniline¹⁸ have also been employed in the mutual separation of these elements. An ion pair of the anionic complex of these elements with halo acids or organic acids and the anion liquid exchanger is extracted into an organic phase.

In the present work, the extraction behavior of Al(III), Ga(III) and In(III) has been investigated in HCl medium with extractants, bis(1,1,3,3-tetramethylbutyl)phosphinic acid (MBP) and its sulfur analogues, bis(1,1,3,3-tetramethylbutyl)monothiophosphinic acid (MTP) and bis(1,1,3,3-tetramethylbutyl)dithiophosphinic acid (DTP). These extractants were used for the first time for the extraction study of Al(III), Ga(III) and In(III). The effect of coordinating elements in these compounds on the extraction behavior of the metals was particularly of interest. The quantitative mutual separation of Al(III), Ga(III) and In(III) from one another could be achieved by using DTP.

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Fig. 1 Structure of the extractants.

Experimental

Materials and chemicals

Bis(1,1,3,3-tetramethylbutyl)phosphinic acid (MBP), bis(1,1,3,3-tetramethylbutyl)monothiophosphinic acid (MTP) and bis(1,1,3,3-tetramethylbutyl)dithiophosphinic acid (DTP) (Fig. 1) were obtained from Japan Chemical Industry, Ltd; the purities of MBP, MTP and DTP were 100%, 98.16% and 93.46%, respectively. Aluminum, gallium and indium stock standard solutions ($1000 \mu\text{g cm}^{-3}$) were from Wako Pure Chemical Industry, Ltd. All other chemicals used were of guaranteed grade, and deionized water was used throughout.

Apparatus

A Horiba pH meter F-16 was used for pH measurements; an Iwaki KM shaker was used for shaking the separatory funnels; a Shimadzu ICPS-1000 III ICP-atomic emission spectrometer was used to determine the contents of Al(III), Ga(III) and In(III) in the aqueous phase.

Procedure

Determination of distribution ratios and extractability of Al(III), Ga(III) and In(III) in the media of MBP-HCl, MTP-HCl and DTP-HCl. At a temperature of $298 \pm 1 \text{ K}$, an appropriate amount of Al(III), Ga(III) and In(III) as well as the buffer solution of sodium acetate-HCl or an appropriate concentration of HCl for controlling the acidity of the aqueous phase were added in a separatory funnel. Then the volume of the aqueous phase was made to 20 cm^3 with water which was deionized and mixed with calculated amounts of NaCl to maintain the ionic strength constant in the aqueous phase. The separatory funnel was shaken for 30 min after the addition of 20 ml of 0.05 mol dm^{-3} MBP or MTP or DTP/hexane, although the equilibrium was achieved within 10 min. The contents of Al(III), Ga(III) and In(III) in the aqueous phase were then determined by ICP-AES. The distribution ratio (D) and extractability ($\%E$) of Al(III), Ga(III) and In(III) can be calculated using

$$D = (w - w_{\text{aq}})V_{\text{aq}} / w_{\text{aq}}V_{\text{org}}$$

$$\%E = 100D / (D + V_{\text{aq}} / V_{\text{org}})$$

Fig. 2 Relationship between pH and $\%E$ using MBP, MTP and DTP as extractants. a, MBP; b, MTP; c, DTP. $\circ$, $\%E/\text{Al}$; $\bullet$, $\%E/\text{Ga}$; $\blacktriangle$, $\%E/\text{In}$. The concentrations of the metals: 5 ppm; the concentration of the extractants: 0.05 mol dm^{-3} .

in which w is the total amount of Al(III), Ga(III) and In(III) originally added to the aqueous phase, w_{aq} is the amount of Al(III), Ga(III) and In(III) left unextracted after equilibrium, and V_{aq} and V_{org} denote the volume of the aqueous phase and the organic phase, respectively.

Results and Discussion

The extraction species of Al(III), Ga(III) and In(III)

Figure 2 shows the dependence of the extractabilities of Al(III), Ga(III) and In(III) upon pH in MBP-HCl,

Table 1 K_{ex} and $\text{pH}_{1/2}$ values of Al(III), Ga(III) and In(III) in the systems of MBP-HCl, MTP-HCl and DMP-HCl

	K_{ex}^a			$\text{pH}_{1/2}$			$\Delta\text{pH}_{1/2}$		
	Al	Ga	In	Al	Ga	In	Al/Ga	Ga/In	Al/In
MBP	4.45×10^{-5}	3.69×10^{-2}	4.40×10^{-1}	2.75	1.80	1.42	0.95	0.38	1.33
MTP	2.35×10^{-11}	6.92×10^{-7}	1.42×10^{-3}	4.96	3.75	2.55	1.21	1.20	2.41
DTP	— ^b	3.69×10^{-2}	— ^c	— ^b	1.80	— ^c			

a. $\log K_{\text{ex}} = \log \alpha_{\text{M(OH)}} - 3 \log [\text{HR}]_{\text{org}} - 3 \text{pH}_{1/2}$, in which $\log \alpha_{\text{M(OH)}} = \log(1 + 10^{(\text{pH} + \log \beta_1)} + 10^{(2\text{pH} + \log \beta_2)})$, and the overall stability constants β_i are as follows: Al, $\log \beta_1 = -5.4$, $\log \beta_2 = -9.98$; Ga, $\log \beta_1 = -2.6$, $\log \beta_2 = -6.1$; In, $\log \beta_1 = -4.42$, $\log \beta_2 = -8.34$. $[\text{HR}]_{\text{org}} = 0.05 \text{ mol dm}^{-3}$. b. Al(III) was not extracted at all over the pH range tested [see Fig. 2(c)]. c. In(III) was quantitatively extracted over the pH range tested [see Fig. 2(c)].

MTP-HCl and DTP-HCl systems. The half extraction pH values, $\text{pH}_{1/2}$, and the extraction constants, K_{ex} , are also summarized in Table 1. The substitution of oxygen with sulfur in the group of OH or P=O in MBP has a significant influence on the extraction behavior of these metals, especially, in the case of DTP. In the pH range, a typical chelating extraction behavior of Al(III), Ga(III) and In(III) was observed, and the extraction process may be assumed through the following reaction,

where HR and M denote an extractant and metal, respectively. The subscript org denotes an organic phase. Thus, when the temperature and ionic strength in the aqueous phase were kept constant, the extraction constant, K_{ex} , can be expressed as

$$K_{\text{ex}} = [\text{MR}_{n\text{org}}][\text{H}^+]^n / [\text{M}^{3+}][\text{HR}]_{\text{org}}^n \quad (2)$$

On the other hand, the hydrolysis of these metals must also be taken into account. If the polynuclear complexation can be neglected here, the hydrolysis of M^{3+} results in

where $i=1, 2, \dots$. The overall stability constant β_i can be represented as

$$\beta_i = [\text{M(OH)}_i^{(3-i)+}][\text{H}^+]^i / [\text{M}^{3+}] \quad (3)$$

Thus, the side reaction coefficient, $\alpha_{\text{M(OH)}}$, can be expressed as

$$\alpha_{\text{M(OH)}} = [\text{M}'] / [\text{M}^{3+}] = ([\text{M}^{3+}] + [\text{M(OH)}_2^{2+}] + [\text{M(OH)}_2^{+}] + \dots) / [\text{M}^{3+}] \quad (4)$$

where $[\text{M}']$ is the total concentration of the metal in the aqueous phase. The Eqs. (3) and (4) give

$$\alpha_{\text{M(OH)}} = 1 + 10^{(\text{pH} + \log \beta_1)} + 10^{(2\text{pH} + \log \beta_2)} + \dots \quad (5)$$

According to the definition of the distribution ratio, D , this can be represented as

$$D = [\text{MR}_n]_{\text{org}} / [\text{M}'] \quad (6)$$

Combining Eqs. (2), (4) and (6), we find

$$D\alpha = K_{\text{ex}}[\text{HR}]_{\text{org}}^n / [\text{H}^+]^n,$$

thus,

$$\log D\alpha = \log K_{\text{ex}} + n \log [\text{HR}]_{\text{org}} + n \text{pH}. \quad (7)$$

The slope analysis based on Eq. (7) was done to estimate the extractable species, that is, the distribution ratios of Al(III), Ga(III) and In(III) were plotted against pH (or $[\text{HR}]_{\text{org}}$ at the fixed $[\text{HR}]_{\text{org}}$) (or pH), where the α values were calculated based on the stability constant data taken from the literature.¹⁹ The typical results are shown in Fig. 3. As shown in the figures, the so-called log-log plots showed the slope of 3 except for the cases of Al(III) and In(III) with DTP, where Al(III) was not extracted at all and In(III) was extracted quantitatively in the pH range examined. Thus, the extractable species can be considered to be MR_3 in these systems. The extraction constants of these metals in the systems of MBP-HCl, MTP-HCl and DTP-HCl were calculated and are listed in Table 1.

In the range of higher HCl concentration, on the other hand, Ga(III) and In(III) can be extracted slightly, as shown in Fig. 2. The distribution ratios of Ga(III) and In(III) increased along with the increase in HCl concentration. Similar phenomena had also been reported by Cerrai and Gherisni with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) as a extractant, where the ion pair formation of the protonated extractant and the halo anionic complex ions, GaCl_4^- or InCl_4^- , were recognized. Accordingly, one may also postulate that GaCl_4^- or InCl_4^- forms an ion associate with the protonated extractant and then can be extracted into the organic phase in these systems.

Mutual separation of Al(III), Ga(III) and In(III)

When the quantitative separation of two metals from

Fig. 3 ($\log D + \log \alpha$) vs. pH using MBP, MTP and DTP as extractants. The same data as Fig. 2 was used for obtaining $\log D$. a, MBP; b, MTP; c, DTP. $\circ$, $\log D\alpha/\text{Al}$; $\bullet$, $\log D\alpha/\text{Ga}$; $\blacktriangle$, $\log D\alpha/\text{In}$.

each other is defined as 99% or more extraction for one metal as against 1% or less extraction for the other metal, the difference of the $\log D$ values for the two metals has to be greater than 4 to achieve the quantitative separation with single extraction. Thus, the $\Delta\text{pH}_{1/2}$ of two metals in the present extraction systems must be more than $4/3$, i.e., 1.33, according to Eq. (7), when the contribution of the α value is ignored. As can easily be seen from Fig. 2 and Table 1, the ability of these three extractants for the mutual separation of Al(III), Ga(III) and In(III) from one another is in the order of $\text{DTP} > \text{MTP} > \text{MBP}$. Although the quantitative mutual separation of Al(III) and In(III) from each other with single extraction is possible even in the case of MBP, that of Al(III) and Ga(III) or Ga(III) and In(III) from each other can not be achieved with MBP or MTP. On the other hand, the

quantitative mutual separation of Al(III), Ga(III) and In(III) from one another can easily be achieved by using DMP with single extraction.

In conclusion, the ability of the extractant for the mutual separation of Al(III), Ga(III) and In(III) from one another was enhanced by employing a sulfur-containing ligand such as DTP.

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