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Selective separation of samarium(III) by synergistic extraction with β-diketone and methylphenylphenanthroline carboxamide

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ABSTRACT

Synergistic extraction of trivalent lanthanides (Lns(III)) with pivaloyltrifluoroacetone (HA) and *N*-methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) was evaluated across the Ln series. The distribution ratio (*D*) of Sm(III) under an identical condition was the largest among all Lns(III). The separation factor (SF) between Sm(III) and Nd(III) (SF = $D_{\mathrm{Sm}}/D_{\mathrm{Nd}}$) was 2.0 and SF between Sm(III) and Eu(III), ($D_{\mathrm{Sm}}/D_{\mathrm{Eu}}$) was 1.4. Upon analyzing the extraction data in detail on the basis of mass balance, it was found that the dominant extracted species of light Lns(III) was a stable ternary complex consisting of Ln(III), HA, and MePhPTA (B), namely, $\mathrm{LnA_3B}$, while the dominant extracted species of heavy Lns(III) was the ion pair, $[\mathrm{LnA_2B}]^+\mathrm{ClO_4}^-$.

The complex for Pr(III) was very stable (the stability constant, $\bar{\beta}$, denoted as $[\mathrm{LnA_3B}]_\mathrm{o}[\mathrm{LnA_3}]_\mathrm{o}{}^{-1}[\mathrm{B}]_\mathrm{o}{}^{-1}$, was $10^{8.3}$). It suggests that $\mathrm{LnA_3}$ can form two 5-membered rings with MePhPTA, and the size of Pr(III) matches to the distance between the donor atoms in MePhPTA. Although the stability constant decreased with increasing Ln atomic number, the synergistic extraction constant ($K_{\mathrm{ex31}} = [\mathrm{LnA_3B}]_\mathrm{o}[\mathrm{H^+}]^3[\mathrm{Ln^{3+}}]^{-1}[\mathrm{HA}]_\mathrm{o}{}^{-3}[\mathrm{B}]_\mathrm{o}{}^{-1}$) was the largest for Sm(III). Since the constant, K_{ex31}, is given by $K_{\mathrm{ex31}} = K_{\mathrm{ex30}} \times \bar{\beta}$ where $K_{\mathrm{ex30}} = [\mathrm{LnA_3}]_\mathrm{o}[\mathrm{H^+}]^3[\mathrm{Ln^{3+}}]^{-1}[\mathrm{HA}]_\mathrm{o}{}^{-3}$, the largest K_{ex31} of Sm(III) is attributable to the difference of the degree of the variation of K_{ex30} between the light and the heavy Lns(III); the increment of extraction constant of $\mathrm{LnA_3}$ ($\log K_{\mathrm{ex30}}$) for light Lns is larger than the decrement of the stability constant of $\mathrm{LnA_3B}$ ($\log \bar{\beta}$), while the increment of $\log K_{\mathrm{ex30}}$ of post-Sm lessens than the decrement of $\log \bar{\beta}$. From these results, it is concluded that selective separation of a particular Ln(III) among all Lns(III) is possible using synergistic extraction with a suitable combination of a multidentate β-diketone and a Lewis base.

1. Introduction

In these days, rare earths or lanthanides are extensively used in functional materials. Each trivalent lanthanide (Ln(III)) has unique functions; for example, europium(III) and terbium(III) show specific fluorescence, and neodymium, samarium and dysprosium are important materials in permanent magnets. Hence the development of a selective separation method of a necessary Ln(III) should be desirable. However, in general, since the properties of Lns(III) are very similar, the mutual separation is very difficult. Further, since in the detailed observation, the properties change gradually across the Ln series, e.g., the ionic size and the coordination number decrease while the surface charge density increases, a selective separation of a particular Ln(III) among the Ln series seems to be impossible, except for the first and the last Ln(III), i.e., La(III) [1,2] and Lu(III) [3], or Eu(III) which can be separated from other Lns(III) by reducing to Eu(II) [4]. It was also reported that Y(III) was separated from heavy Lns(III) using different stability constants of aminopolycarboxylic acids [5,6].

In the present study, it was attempted to separate a particular Ln(III) by using extraction with β-diketone (HA) and Lewis base (B). When Ln(III) is extracted with HA and B, it is well-known that the extraction of Ln(III) is remarkably improved due to the extraction of the ternary complex. The advantage in using the synergistic extraction to selective separation is that the different properties of two extractants (HA and B) can be utilized to extract Ln(III). Even if the difference is small for each Ln(III), the total difference should be larger. The extraction of the ternary complex can be separated into two steps. The first step is the extraction of β-diketonato chelate as $\mathrm{LnA_3}$, and the second step is the formation of the complex between $\mathrm{LnA_3}$ and B in the organic phase. Actually when the synergistic extraction data of Lns(III) with pivaloyltrifluoroacetone

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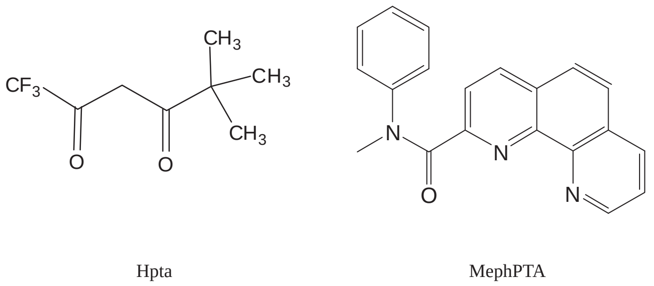

Fig. 1. Structure of pivaloyltrifluoroacetone and MePhPTA.

(Hpta) as β-diketone (HA) and 2,2′-bipyridyl (B) were carefully analyzed, it was found that the dominant extracted species was LnA_3B, and that the stability constant increased with increasing Ln atomic number, reached a maximum at Dy(III) or Ho(III), and decreased thereafter [7]. However, the synergistic extraction constant simply increased along with increasing Ln atomic number. With these findings borne in mind, we postulated that if a much stronger Lewis base is used, with which a Ln(III) can form a much more stable complex, the extraction constant should give a maximum for the Ln(III). *N*-Methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA), which is capable of forming three 5-membered rings, should be promising Lewis base for achieving good extraction of Lns(III) and selective separation of a particular Ln(III).

In the present work, the synergistic extraction of Lns(III) with Hpta and MePhPTA was evaluated across the Ln series.

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Pivaloyltrifluoroacetone (Hpta) was purchased from Dojin Laboratories. The Lewis base, MePhPTA, was prepared as follows; 1,10-phenanthroline-2-carboxylic acid (0.2 g, 0.89 mmol) was refluxed in thionyl chloride (3.18 g, 26.7 mmol) for 8 h, and then residual thionyl chloride was removed by rotary evaporation. Without isolation and purification, the resulting 1,10-phenanthroline-2-carbonyl chloride was used in the subsequent step. The crude product was dissolved in DMF (1.5 mL) at room temperature, and *N*-methylaniline (0.95 g, 8.9 mmol) was added. The mixture was stirred for 18 h at room temperature. The reaction mixture was concentrated by rotary evaporation and poured into chloroform (30 mL). The chloroform solution was washed with an aqueous solution of 1 M ($1\,M = 1\,mol\,dm^{-3}$) NaOH (3× 30 mL) and water (3× 30 mL), and the product was purified by column chromatography (silica gel, ethyl acetate/$CHCl_3$ = 1:1). ^1H NMR ($CDCl_3$) data of MePhPTA are as follows: δ 9.2 (br, 1H), 8.2 (br d, 1H), 8.1 (br d, 1H), 7.8 (br d, 1H), 7.7–7.5 (br m, 3H), 7.2 (br, 2H), 7.1 (br, 2H), 7.0 (br, 1H), 3.7 (s, 3H) [8]. The chemical structure of MePhPTA (B) is depicted in Fig. 1 together with Hpta. Lanthanide(III) oxides (purity > 99.9%) were purchased from the following companies: Shin-Etsu Chemical Co. (La and Gd), Nacalai Tesque Inc. (Nd), and Mitsuwa Chemicals (other Lns). Aqueous solutions of Ln(III) were prepared by dissolving the respective oxide with perchloric acid, of which concentration was stoichiometrically equivalent to the amount of substance of Ln(III), and was used after filteration. Chloroform was washed with deionized water three times just before use. Other reagents were used without purification.

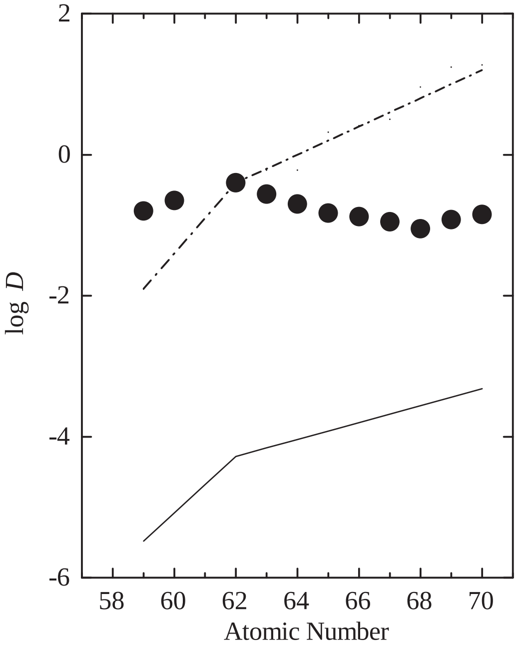

Fig. 2. Variation of log *D* across the lanthanide series under identical experimental conditions. Aqueous phase: 0.10 M $NaClO_4$, pC_H 3.5, organic phase: ● $CHCl_3$ containing 0.04 M Hpta and 2×10^{-4} M MePhPTA, –·– $CHCl_3$ containing 0.04 M Hpta and 2×10^{-4} M phen, — $CHCl_3$ containing 0.04 M Hpta.

2.2. Procedure

Most experiments were performed in a thermostatted room at 298 ± 1 K. The total ionic concentration was adjusted to 0.1 M with sodium perchlorate. The procedure used was similar to that described elsewhere [7,9]. Eight milliliters of aqueous solution containing Ln(III) (1×10^{-4} M) was vigorously shaken with an identical volume of chloroform solution containing Hpta and/or MePhPTA for 15 min and then, the two phases were centrifuged. The aqueous phase in which lanthanide(III) remained was diluted with 0.1 M perchloric acid by a factor of 10 to exclude the effect of the Na ion, and Ln(III) transferred into chloroform phase was back-extracted into 0.1 M $HClO_4$. The concentration was then measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Horiba Ultima 2000). The distribution ratio was denoted as the total concentration ratio of Ln(III) between both phases. The hydrogen ion concentration ($pC_H = -\log[H^+]$) at equilibrium was measured potentiometrically using a solution containing 1.00×10^{-2} M perchloric acid at 0.1 M (H, Na)ClO_4 as the standard of $pC_H = 2.00$ (Corning, Mode1 445).

3. Results and discussion

3.1. Variation pattern of extraction of Lns(III) with Hpta and MePhPTA across the Ln series

First the trend of the difference of the extraction across the Ln series under a same experimental condition was compared. Fig. 2 shows the variation of the distribution ratio (*D*) of Ln(III) across the Ln series (●) when each Ln(III) was extracted at pC_H 3.5 with 0.04 M Hpta and 2×10^{-4} M MePhPTA into $CHCl_3$. The variation of log *D* under the identical experimental condition except for the absence of MePhPTA is also shown by solid line. The distribution ratio was calculated using the extraction constant of LnA_3, K_{ex30} [7]. As seen in Fig. 2, in the extraction with Hpta and MePhPTA, a greater synergistic effect was clearly observed for the lighter Lns(III) than for the heavier ones. The value of log *D* for Sm(III) was the largest among

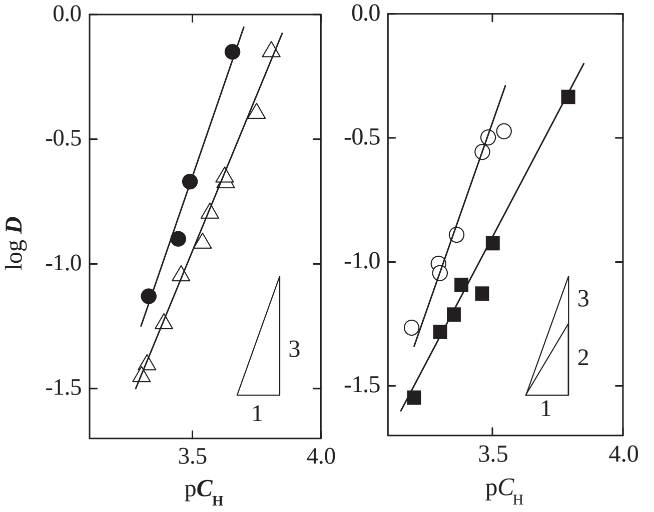

Fig. 3. Distribution ratio of Ln(III) as a function of pC_H in the extraction with 0.04 M Hpta and 2×10^{-4} M MePhPTA. ● (Nd), △ (Ho), ○ (Sm), ■ (Tm).

all Lns(III) studied. The separation factor (SF) denoted as the ratio of the distribution ratio between two Lns(III) under a constant experimental condition was 2 between Sm(III) and Nd(III) (SF = D_{Sm}/D_{Nd}) and the SF between Eu(III) and Sm(III), (D_{Eu}/D_{Sm}) was 0.7. These results suggest that the combination of Hpta and MePhPTA as synergistic extractants is promising to extract Sm(III) selectively from all Lns(III). To know the reason why the extraction of Sm(III) is better than other Lns(III), the synergistic extraction of Lns(III) was studied in more detail.

Fig. 3 shows the typical examples of the relation between the distribution ratio of Lns(III) and pC_H at equilibrium when Ln(III) was extracted with 0.04 M Hpta and 2×10^{-4} M MePhPTA. Similar experiments were performed for other Lns(III). It was found that the plot gave a straight line with slope of +3 for the extraction of lighter Lns(III) (Pr to Dy), whereas the slope of the plot for Tm(III) and Yb(III) was +2. The slope was a value between +2 and +3 for Ho(III) and Er(III), although these plots also seemed to be linear. These observations suggest that the number of proton involved the extraction of Ln(III) changes from +3 to +2 with increasing Ln atomic number. Fig. 4 shows log D as a function of log $[HA]_o$, for the case where Ln(III) was extracted at pC_H 3.5 with Hpta (HA) and 2×10^{-4} M MePhPTA. Similar to the relation between log D and pC_H, the slope changed from +3 to +2 with increasing Ln atomic number. It was concluded that the number of Hpta involved in the synergistic extraction was similar to the number of protons across the Ln series. Fig. 5 shows the distribution ratio of Sm(III) and Tm(III) (log D) as a function of the MePhPTA (B) concentration at equilibrium, when these Lns(III) were extracted from 0.1 M $NaClO_4$ at pC_H 3.5 into $CHCl_3$ containing 0.04 M Hpta and different concentrations of MePhPTA. Both plots are linear, having slope of unity. For other Lns(III), the slope of the plot was also +1. This observation suggests that all extracted species are accompanied by one molecule of MePhPTA.

From these results it was found that the LnA_3B type complex should be the dominant extracted species for light Lns(III), whereas for heavy Lns(III), the dominant extracted species is postulated to be $[LnA_2B]^+X^-$ type complex, that is, the latter should be extracted as a cationic ion-pair accompanied by ClO_4^- ion as a counter anion. Accordingly, the distribution ratio can be generally represented as follows:

$$D = \frac{[LnA_3]_o + [LnA_3B]_o + [[LnA_2B]^+ClO_4^-]_o}{[Ln^{3+}]} \qquad (1)$$

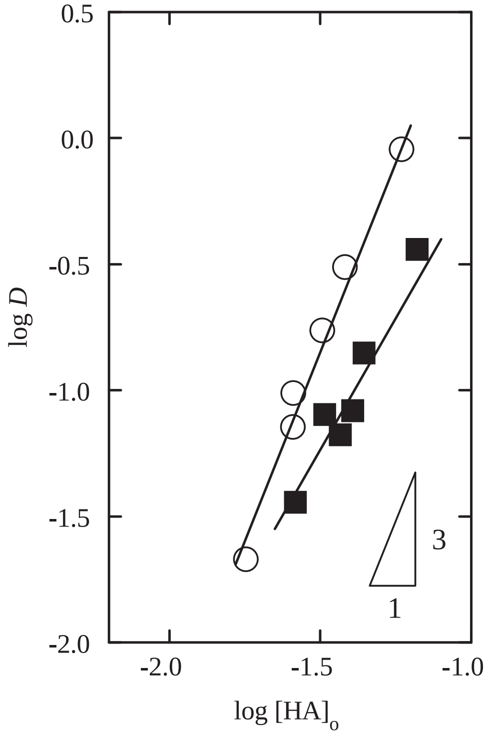

Fig. 4. Distribution ratio of Ln(III) as a function of log$[Hpta]_o$ in the extraction with Hpta and 2×10^{-4} M MePhPTA at pC_H = 3.5. ○ (Sm), ■ (Tm).

where the subscript “o” denotes the organic phase and no subscript shows the aqueous phase.

First, let’s look the extraction behavior of the light Lns(III). As seen in Fig. 2, the extraction of LnA_3 is much poorer than that of LnA_3B. Since the dominant extracted species for Pr(III) to Dy(III)

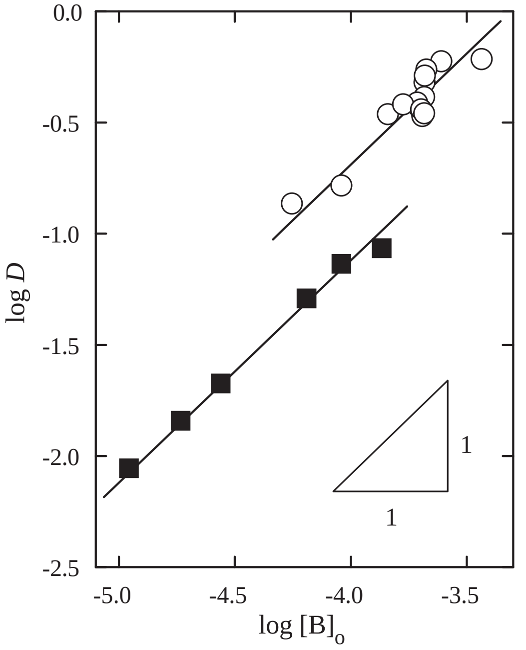

Fig. 5. Distribution ratio of Sm(III) (○) and Tm(III) (■) as a function of MePhPTA concentration in the extraction with 0.04 M Hpta and MePhPTA at pC_H = 3.5.

Table 1
Extraction constants of Ln(III) in the extraction from 0.1 M $NaClO_4$ into $CHCl_3$ containing Hpta and/MePhPTA, and stability constants of $Ln(pta)_3$ (MePhPTA).

Ln(III)	$\log K_{ex31}$[a] $\pm \sigma$	$\log \bar{\beta} \pm \sigma$[b]	$\log K_{ex21}$[c] $\pm \sigma$	$\log K_{ex30}$[d] $\pm \sigma$
Pr	-3.52 ± 0.06	8.26 ± 0.06	–	-11.78 ± 0.08
Nd	-3.24 ± 0.05	8.18 ± 0.05	–	-11.42 ± 0.05
Sm	-2.98 ± 0.05	7.63 ± 0.05	–	-10.61 ± 0.05
Eu	-3.13 ± 0.08	7.37 ± 0.08	–	-10.48 ± 0.05
Gd	-3.32 ± 0.04	7.26 ± 0.04	–	-10.58 ± 0.08
Tb	-3.43 ± 0.06	6.60 ± 0.08	–	-10.12 ± 0.09
Dy	-3.65 ± 0.03	6.57 ± 0.07	–	-10.04 ± 0.08
Ho	-3.85 ± 0.08	6.31 ± 0.08	-0.9 ± 0.1	-9.92 ± 0.06
Tm	–	–	-0.46 ± 0.06	-9.34 ± 0.04
Yb	–	–	-0.36 ± 0.04	-9.07 ± 0.03

[a] $K_{ex31} = [LnA_3B]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3}[B]_o^{-1}$.
[b] $\bar{\beta} = [LnA_3B]_o[LnA_3]_o^{-1}[B]_o^{-1}$.
[c] $K_{ex21} = [[LnA_2B]^+X^-]_o\,[H^+]^2[Ln^{3+}]^{-1}[HA]_o^{-2}[B]_o^{-1}[X^-]^{-1}$.
[d] $K_{ex30} = [LnA_3]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3}$ taken from Ref. [7].

should be the ternary complex, LnA_3B, the distribution ratio can be given by the following equation instead of Eq. (1):

$$D = \frac{[LnA_3B]_o}{[Ln^{3+}]} \tag{2}$$

Therefore, the synergistic extraction equilibrium and the extraction constant (K_{ex31}) can be written as

$$\begin{aligned} &Ln^{3+} + 3HA(o) + B(o) \rightleftharpoons LnA_3B(o) + 3H^+ \\ &K_{ex31} = [LnA_3B]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3}[B]_o^{-1} = D[H^+]^3[HA]_o^{-3}[B]_o^{-1} \end{aligned} \tag{3}$$

Accordingly,

$$\log K_{ex31} = \log D - 3(pC_H + \log [HA]_o) - \log [B]_o \tag{3'}$$

The values of K_{ex31} were calculated according to Eq. (3′) using all the extraction data obtained; for $\log D$ *vs.* $\log[HA]_o$, $\log D$ *vs.* pC_H, and $\log D$ *vs.* $\log[B]_o$. The values determined are listed in Table 1. The value of K_{ex31} increases clearly from Pr(III) to Sm(III), and thereafter decreases with increasing Ln atomic number.

When the synergistic extraction is treated separately with two steps, the extraction of Ln^{3+} ion with HA from aqueous phase into organic phase and the complexation between LnA_3 and B in the organic phase, the former can be represented as

$$\begin{aligned} &Ln^{3+} + 3HA(o) \rightleftharpoons LnA_3(o) + 3H^+, \\ &K_{ex30} = [LnA_3]_o[H^+]^3[Ln^{3+}]^{-1}[HA]_o^{-3} \end{aligned} \tag{4}$$

and the latter is

$$\begin{aligned} &LnA_3(o) + B(o) \rightleftharpoons LnA_3B(o), \\ &\bar{\beta} = [LnA_3B]_o[LnA_3]_o^{-1}[B]_o^{-1} \end{aligned} \tag{5}$$

It then follows that the synergistic extraction constant (K_{ex31}) is the product of the extraction constant of LnA_3 (K_{ex30}) and the stability constant of LnA_3B ($\bar{\beta}$):

$$K_{ex31} = \bar{\beta} \times K_{ex30} \text{ or } \log \bar{\beta} = \log K_{ex31} - \log K_{ex30} \tag{6}$$

The value of $\bar{\beta}$ was determined using Eq. (6) and are listed in the second column in Table 1.

Since the value of K_{ex30} generally increases with increasing Ln atomic number because of the higher charge density of heavier Lns(III), it was expected that the largest distribution ratio of Sm(III) should be caused by the formation of the most stable complex between MePhPTA and SmA_3. However, as seen in Table 1, contrary to expectation, the stability constant simply decreases along with increasing Ln atomic number. The largest K_{ex31} for Sm(III) may ascribe to the β-diketone side.

3.2. Variation pattern of extraction of Lns(III) with β-diketones alone across the Ln series

Fig. 6 shows the extraction constants, $\log K_{ex30}$, in the extraction of Lns(III) with several β-diketones alone across the Ln series. Although $\log K_{ex30}$ with β-diketones which do not have F atoms such as acetylacetone(Hacac) and benzoylacetone(Hbza) [10] simply increases along with increasing Ln atomic number, the increase in $\log K_{ex30}$ with β-diketones having trifluoromethyl group [2,7,9–11] is different between light and heavy Lns(III). The slope in the plot of $\log K_{ex30}$ *vs.* Ln atomic number (AN) is smaller in the heavy Ln group than that in the light ones. Further the slope always seems to change in Sm(III).

3.3. Selective separation of a particular Ln(III) by the synergistic extraction

The separation factor between two Lns(III), *X* and *Y*, is represented as:

$$SF_{X/Y} = \frac{D_X}{D_Y} = \frac{D_X([H^+]/[HA]_o)^3[B]_o^{-1}}{\{D_Y([H^+]/[HA]_o)^3[B]_o^{-1}\}} \tag{7}$$

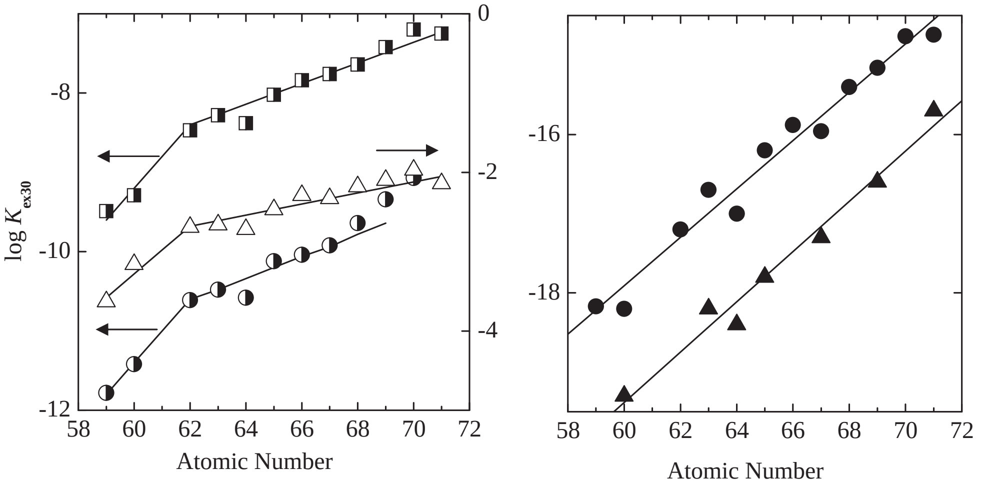

Fig. 6. Variation of the extraction constants of tris(β-diketonato) Ln(III) as a function of Ln atomic number in the extraction of Ln(III) with Hhfa (△), Htta (◨), Hpta (◑), and Hbza (●), and Hacac (▲).

Then,

$$\mathrm{SF}_{X/Y} = \frac{K_{\mathrm{ex31},X}}{K_{\mathrm{ex31},Y}} = \frac{K_{\mathrm{ex30},X}\bar{\beta}_X}{K_{\mathrm{ex30},Y}\bar{\beta}_Y} \tag{7'}$$

Accordingly, the separation factor, $\mathrm{SF}_{X/Y}$, for the synergistic extraction can be represented as,

$$\log \mathrm{SF}_{X/Y} = (\log K_{\mathrm{ex30},X} - \log K_{\mathrm{ex30},Y}) + (\log \bar{\beta}_X - \log \bar{\beta}_Y) \tag{8}$$

In the synergistic extraction with Hpta and MePhPTA, for Sm(III) and Nd(III), the value in Eq. (8) is plus while for Sm(III) and Eu(III) it is minus. The relation can be visually observed. The first term on the right-hand side in Eq. (8) is equivalent to the slope of the plot in Fig. 6. The second term is the slope when $\log \bar{\beta}$ in Table 1 is plotted against AN. When the plot is performed in the same scale to the plot for $\log K_{\mathrm{ex30}}$, the absolute number of the slope of the plot for $\log \bar{\beta}$ is smaller than that for $\log K_{\mathrm{ex30}}$ in the light Lns(III) (Pr to Sm), however, for post-Sm(III), the slope of the plot of $\log \bar{\beta}$ *vs.* AN is larger than that of $\log K_{\mathrm{ex30}}$ *vs.* AN. Accordingly, the distribution ratio of Sm(III) is the largest among all Lns(III).

When Lns(III) are extracted with Hbza and MePhPTA, $\log K_{\mathrm{ex31}}$ should be similar across the Ln series, because the degree of the variation of $\log K_{\mathrm{ex30}}$ is similar to that of $\log \bar{\beta}$, however, when Hhfa is used instead of Hpta, the selectivity of Sm(III) should be improved, because as seen from Fig. 6, the variation of $\log K_{\mathrm{ex30}}$ with Hhfa for post-Sm(III) is much smaller than that with Hpta. Similar tendency is observed in the extraction of Ln(III) with several β-diketones having -$\mathrm{CF_3}$ group [11] and also by Imur et al.[2]. As a result, it will be realized that the selection of β-diketone is important for the selective separation of Sm(III), and β-diketones possessing more F atoms seem to be more favorable.

Similarly, the selection of a Lewis base is also important for the separation of a particular Ln(III), because the increase or the decrease of the stability constant of the complex across the Ln series depends on Lewis bases. When the decrement of $\log \bar{\beta}$ is similar to the increment of $\log K_{\mathrm{ex30}}$, $\log K_{\mathrm{ex31}}$ should not change much across the Ln series. Such examples are often observed in the synergistic extraction of Ln(III) with β-diketone and monodentate Lewis base such as tributylphosphate [12], triphenylphosphine oxide [13] and carboxylic acids [13–15]. When $\log \bar{\beta}$ as well as $\log K_{\mathrm{ex30}}$ increases, $\log K_{\mathrm{ex31}}$ increases with increasing Ln atomic number, and the separation factor should be improved, as already shown in the extraction with Hpta and bpy [7]. Thus, although the balance between the decrement of $\log \bar{\beta}$ and the increment of $\log K_{\mathrm{ex30}}$ is important for the selective separation of a particular Ln(III), the most significant factor will be the size-matching effect. The stability constants of the complex formed between $\mathrm{Ln(pta)_3}$ and phen have not reported across the Ln series. However, since the constants of several $\mathrm{Ln(pta)_3}$ complexes with phen ($\log \bar{\beta}$ is 6.5 ± 0.1 for La(III) [16], 7.61 ± 0.06 for Eu(III) [17], and 7.6 ± 0.1 for Lu(III) [16]) agreed with those of $\mathrm{Ln(tta)_3phen}$ [9] where Htta is 2-thenoyltrifluoroacetone, $\log D$ was calculated using the stability constants for $\mathrm{Ln(tta)_3phen}$ [9] and $\log K_{\mathrm{ex30}}$ for $\mathrm{Ln(pta)_3}$ [7]. As shown in Fig. 2, on the comparison of the variation of $\log D$ using phen to that using MePhPTA, $\log D$ in the presence of MePhPTA (●) is larger than that of phen (chain line) from Pr to Sm, for post-Sm, $\log D$ decreases in the presence of MePhPTA, while in the presence of phen it still increases. The difference of the variation pattern can be related to the difference of the size-matching effect and the stability constants of the ternary complex with MePhPTA from that with phen. Tris(β-diketonato)Ln(III) in light Lns forms very stable two five-membered ring using the amide O as well as the phenanthroline N of MePhPTA, as similar as the complexation in aqueous solutions [8]. However, the stability of the ternary complex rapidly decreases along with increasing Ln atomic number. Since the distance between donor atoms, O and N, in MePhPTA matches to the size of light Ln(III), Pr(III) will form most stable complex with the Lewis base, however, the heavier Ln(III) will be too small to form stable complex with the three donor atoms. The size-matching effect is also observed in the formation of the ternary complexes consisting of Ln(III), HA, and bpy [7], that is, the stability constants increase along with increasing Ln atomic number to Dy or Ho, and then decrease, because the distance between two donor atoms of bpy, that is, N-N, matches to the size of Dy(III) or Ho(III).

For the formation of the most stable ternary complex, it is important to find a Lewis base having two donor atoms separated by a distance that matches the size of the target Ln(III) as well as having a side group that obstructs the formation of a stable complex with $\mathrm{LnA_3}$. Consequently, a selective separation of a particular Ln(III) other than Sm(III) could also be performed.

3.4. *Extraction behavior of heavy Lns(III) as cationic species in the extraction with Hpta and MePhPTA.*

As shown in Fig. 2, $\log D$ for the heavy Lns(III) gradually again increases. As already explained by using the data in Figs. 3 and 4, the extracted species may not be $\mathrm{LnA_3B}$ but rather ion pairs such as $\mathrm{[LnA_2B]^+X^-}$ where $\mathrm{X^-}$ is $\mathrm{ClO_4^-}$, because the ionic medium 0.1 M $\mathrm{NaClO_4}$ is used. With increasing Ln atomic number, the ion pairs may also be extracted together with $\mathrm{LnA_3B}$. When both $\mathrm{LnA_3B}$ and $\mathrm{[LnA_2B]^+X^-}$ are extracted, D is given by,

$$D = \frac{[\mathrm{LnA_3B}]_\mathrm{o} + [[\mathrm{LnA_2B}]^+\mathrm{X}^-]_\mathrm{o}}{[\mathrm{Ln}^{3+}]} \tag{9}$$

The extraction equilibrium and the extraction constant of the ion pairs can thus be written as

$$\begin{gathered}\mathrm{Ln^{3+} + 2HA(o) + B(o) + X^- \rightleftharpoons [LnA_2B]^+X^-(o) + 2H^+},\\ K_{\mathrm{ex21}} = [[\mathrm{LnA_2B}]^+\mathrm{X}^-]_\mathrm{o}[\mathrm{H}^+]^2[\mathrm{Ln}^{3+}]^{-1}[\mathrm{HA}]_\mathrm{o}^{-2}[\mathrm{B}]_\mathrm{o}^{-1}[\mathrm{X}^-]^{-1}\end{gathered} \tag{10}$$

By introducing K_{ex31} and K_{ex21} into Eq. (9), the following equation is obtained:

$$\begin{aligned}&\log D[\mathrm{H}^+]^3[\mathrm{HA}]_\mathrm{o}^{-3}[\mathrm{B}]_\mathrm{o}^{-1}\\ &\quad = \log K_{\mathrm{ex31}}(1 + K_{\mathrm{ex21}}K_{\mathrm{ex31}}^{-1}[\mathrm{X}^-][\mathrm{H}^+][\mathrm{HA}]_\mathrm{o}^{-1})\end{aligned} \tag{11}$$

When the dominant extracted species is $\mathrm{LnA_3B}$, the plot of $\log D[\mathrm{H}^+]^3[\mathrm{HA}]_\mathrm{o}^{-3}[\mathrm{B}]_\mathrm{o}^{-1}$ *vs.* $-(\mathrm{p}C_\mathrm{H} + \log\,[\mathrm{HA}]_\mathrm{o})$ should give a flat line with slope of 0 being parallel to the *X*-axis. When the dominant extracted species is an ion pair, the plot should be a straight line having slope of unity. When both species are extracted, the plot should show a curve changing in the slope of 0 to +1. Fig. 7 shows typical examples of the plots. The plot for Sm(III) (open circle) is parallel to the *X*-axis except for the highest MePhPTA concentration region, and the value agrees well with $\log K_{\mathrm{ex31}}$ in Table 1 within experimental uncertainty. Similar results were obtained from the plot for Pr(III) to Dy(III). The plot for Yb(III) in Fig. 7 gives a straight line having slope of +1. The value of K_{ex21} was calculated using all extraction data of Yb(III). The slope of the plot for Ho(III) changes from 0 to +1. The values of K_{ex31} and K_{ex21} for Ho(III) were obtained by a successive approximation method. The obtained extraction constants are also listed in Table 1.

Hence, the distribution ratio first increases, reaches a maximum value at Sm(III), via decreasing thereafter, and in the heaviest Lns(III) increases again, in the extraction with Hpta and MePhPTA as seen in Fig. 2.

It has been reported that when Ln(III) is extracted with Htta (HA) and crown ethers (B) such as 18-crown-6 and cyclohexyl-18-crown-6 from 0.1 M $\mathrm{NaClO_4}$ into 1,2-dichloroethane, the extracted species is an ion pair of $\mathrm{[LnA_2B]^+X^-}$ for light Lns(III) while the ternary complex of $\mathrm{LnA_3B}$ is extracted for heavy Lns(III) [1]. In

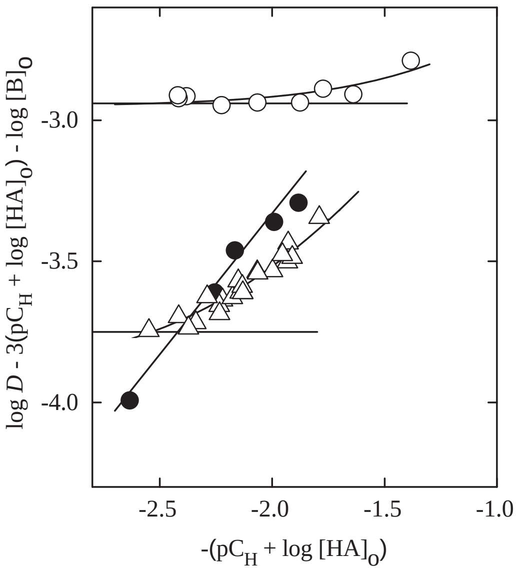

Fig. 7. The influence of $[H^+][HA]_o^{-1}$ on the variation of D of Ln(III). (see Eq. (11)). ○ (Sm), △ (Ho), ● (Yb).

contrast with our results, in the past work it was reported that because of the extraction of ion pairs as $[LnA_2B]^+ClO_4^-$, the extraction of light Lns(III) became much more efficient than that of heavy Lns(III). It is not easy to understand why extraction of the ion pairs is much better than extraction of the ternary complex, considering that the molecular volume of LnA_3B should be larger than that of $[LnA_2B]^+$, and also that the organophilic property should be better for the ternary complex than the ion pairs. However, extraction of La(III) as a cationic ternary-complex has been reported to be better than that of Eu(III) and Lu(III) for the case where Lns(III) were extracted with Htta and 18-crown-6 from 0.1 M LiCl into ionic liquid, namely, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [2]. The size-matching effect for the formation of ion pairs was invoked in those papers [1,2]; this effect is that since the cavity size of 18-crown-6 is closer to the ionic size of lighter Lns(III), the lighter Lns(III) can form a more stable complex with 18-crown-6 than the heavier Lns(III), although Ln(III) is not always incorporated into the cavity of crown ethers. For the present results, the different types of extracted species between the light and heavy Lns can be also explained as follows; the size and coordination number of light Lns(III) are larger than those of the heavy ones. Since the coordination number of light Lns(III) is generally nine and that of heavy ones is eight in solutions [18], the light Lns(III) could accept three pta^- anion and one MePhPTA, whereas heavy Lns(III) do not accept these four ligands. The large stability constant for light Lns(III) may support that 9 coordination sites of light Lns(III) are occupied by two N and one O donor atoms in addition to three pta^- ions, i.e., MePhPTA forms two 5-membered rings with $Ln(pta)_3$. Furthermore, Hpta forms one 6-membered ring with Ln(III), while MePhPTA may form 5-membered ring. Generally, a chelate consisting of 5-membered ring is more stable than one consisting of a 6-membered ring[18]. Accordingly it is reasonable that since one pta^- may be more easily released from Ln(III) than MePhPTA, the heavier Lns(III) are extracted as the ion pair such as $[LnA_2B]^+X^-$.

As seen in Fig. 2, owing to the extraction of ion pairs, the distribution ratio was enhanced among heavier Lns(III). This should be unfavorable for the selective extraction of a particular Ln(III). Although when perchlorate ionic medium was used in the extraction of Ln(III), light Lns(III) have been extracted as ion pairs consisting of Ln(III), pta^-, 18-crown-6 and ClO_4^- as already described [1], when NO_3^- ionic medium was used, such ion pair was not extracted, but the ternary complex was extracted [19]. This suggests that NO_3^- is too hydrophilic to serve as counter ion. Hence when NO_3^- ionic medium is used instead of ClO_4^-, the ion pair may not be extracted but the extraction of Sm(III) should be more effective among all Lns(III) and the extraction of the lighter and the heavier Lns(III) should be much worse than that of Sm(III) in the synergistic extraction with Hpta and MePhPTA.

4. Conclusion

In the present work, using synergistic extraction with Hpta and MePhPTA from 0.1 M sodium perchlorate medium into $CHCl_3$, the selective separation of Sm(III) among all Lns(III) was found. It is very important for a selective extraction of a particular Ln(III) to select a suitable combination of β-diketone, Lewis base, ionic medium, and organic solvent. Especially, Lewis base having a structure of rigid type and being strong base is effective for the separation of particular Ln(III).

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