Mutual Separation of Rare Earth Elements by Extraction Chromatography Using Bis(1,1,3,3-tetramethylbutyl)phosphinic Acid as a Stationary Phase

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The extraction behavior of rare earth elements was systematically investigated by using bis(1,1,3,3-tetramethylbutyl)phosphinic acid (HMBP) in HNO3 medium. The extraction mechanism was evaluated through a log-log plot analysis, and the overall extraction equilibrium constant K was calculated for each rare earth element(III). The degree of mutual separation of adjacent pair of rare earth elements was discussed from the value of separation factor S.F. and explained by thermodynamic function—the relative free energy change of adjacent rare earth elements(III) Δ(AG°)Z+Z. The separation of scandium from lanthanoids and yttrium was achieved by a single HMBP extraction and the mutual separation of lanthanum, cerium and praseodymium was achieved by HMBP-extraction chromatography.

Keywords Rare earth elements, solvent extraction, extraction chromatography, thermodynamics

Rare earth elements form a special group in the periodical table in which the ionic radii of the elements decrease along with the increase in their atomic number because of preferential filling of 4f orbital. The mutual separation of this series is one of the most difficult problems in the field of inorganic separation and continues to be an interesting research subject. Among many kinds of extractants used for the separation of rare earth elements, acidic phosphorus extractants such as 2-ethylhexyl phenylphosphonic acid (HEHbP) and di(2-ethylhexyl)phosphoric acid (HDEHP) have been often used. On the other hand, bis(1,1,3,3-tetramethylbutyl)phosphinic acid (HMBP) which has recently been developed and applied to extract several metal ions. Because of two alkyl substituents contained in its structure, the acidity of this reagent is rather low due to higher electron density on the oxygen in HMBP molecule and it is expected to be used in a lower acidity medium than in the cases of the above extractants. In fact, similar extractants to HMBP such as bis(2,4,4-trimethylpentyl)phosphinic acid and di(2-ethylhexyl) phosphinic acid had been used in the separation of rare earth elements together with additives such as trioctylphosphine oxide (TOPO). Although the extractability was enhanced with the addition of additives, the selectivity to each rare earth element decreased.

In this paper, the extraction behavior of rare earth elements by using HMBP in HNO3 medium was systematically investigated, and the extraction mechanism was evaluated with a log-log plot analysis. The degree of separation of adjacent pairs of rare earth elements was explained through thermodynamic functions, the relative free energy change of adjacent rare earth elements Δ(AG°)Z+Z. The mutual quantitative separation of some adjacent pairs of lanthanoids including yttrium was performed with solvent extraction as well as extraction chromatography using HMBP.

Experimental

Apparatus
Extraction chromatographic column: a glass column with a water jacket, 6x170 mm, was used for separation. An Iwaki FRC-2100 automatic fraction collector was used to collect the effluent from the column. Separatory funnels were shaken by an Iwaki SHK-101B shaker and the temperature was controlled by an Iwaki CTR-320 thermo regulator. A Shimadzu ICP-1000III sequential ICP atomic emission spectrometer was employed for determining the contents of rare earth elements. A Horiba F-16 pH meter was used for pH measurement and correlation of pH and p[H+].

Reagents
Bis(1,1,3,3-tetramethylbutyl)phosphinic acid was obtained from Nippon Chemical Industrial Co. Ltd., the purity is greater than 99.99%. The standard solutions (1000ppm) of rare earth elements were from Wako Pure Chemical Industry, Ltd. and diluted to an appropriate concentration needed. Silica gel 60 silanized from Merck (0.149-0.063 mm) was used as the support of the stationary phase. All other chemicals used were of guaranteed grade; deionized distilled water was used throughout.
Procedure
Extraction experiment
At an appropriate temperature, known amount of rare earth elements(III) as well as the buffer solution of CH₂CICOOH-CH₂CICOOHNa or CHCl₂CICOOH-CHCl₂COONa were added in a separatory funnel, then the volume of the aqueous phase was kept to 20 cm³ with the deionized distilled water to which NaNO₃ was added to maintain the ionic strength constant. The mixture was shaken for 10 min after the addition of 20 cm³ of 5.0×10⁻² mol dm⁻³ (HMBP)₂/cyclohexane in spite of the extraction equilibrium being reached within 3 min. The contents of rare earth elements(III) in the aqueous phase were determined by ICP-AES. The distribution ratio D and extractability %E of rare earth element(III) were calculated using

\[
D = \frac{(w - w_{aq})V_{aq}/V_{aq}V_{org}}{D + V_{aq}/V_{org}}
\]

\[
%E = 100D/(D + V_{aq}/V_{org})
\]

in which w is the total amount of rare earth element(III) originally added to the aqueous phase, \(w_{aq}\) is the amount of rare earth element(III) left unextracted in the aqueous phase after extraction equilibrium, and \(V_{aq}\) and \(V_{org}\) denote the volume of the aqueous and organic phases, respectively.

Extraction chromatographic separation
A mixture solution (0.20 cm³) containing 50 µg each of La⁺, Ce⁺⁺, and Pr⁺⁺, respectively, was applied to the top of a 6x170 mm extraction chromatographic column containing 3 g silica gel silanized and 0.84 g HMBP after the column was pre-equilibrated with a suitable mobile phase. And then La⁺, Ce⁺⁺, and Pr⁺⁺ were eluted by a HNO₃ solution used as a mobile phase. The effluent was collected in fractions of 0.5 cm³ each, and determined by ICP-AES.

Results and Discussion
Extraction behavior
If the extractant HMBP existed in the organic phase as a dimer of \((HA)₂\) (\(A' = MBP'\)), the extraction reaction of rare earth elements(III) \(RE\) with HMBP can be expressed as following

\[
RE_{aq} + n(HA)_{org} \rightleftharpoons RE(HA₂)_{n org} + nH^+_{aq}
\]

Thus, the extraction equilibrium constant \(K_{ex}\) can be written as

\[
K_{ex} = \frac{[RE(HA₂)_{n org}] y_{RE} y_{HA₂}[H^+]_{aq} y_{H^+}}{[(HA)_{2 org}] y_{HA} \times [RE]_{aq} y_{RE}} \quad (1)
\]

where \(γ\) refers to the activity coefficient of the species in organic and aqueous phases. Because the ionic strength was kept constant (0.1 mol dm⁻³) and the extractant concentration employed was very low, the activity coefficient can be considered being constant during the extraction process, \(γ = γ_{RE(III)} y_{RE} y_{HA₂} y_{H^+} y_{HA} y_{H^+}\). And assuming only \(RE(HA₂)_{n}\) exists in the organic phase, the distribution ratio \(D\) of \(RE\) may be expressed as

\[
D = \frac{[RE(HA₂)_{n org}] y_{RE}}{[RE]_{aq} y_{RE}} \quad (2)
\]

where \(α\) is the side-reaction coefficient of \(RE\) with CH₂CICOO⁻ or CHCl₂COO⁻, \(α = 1 + β_1[L] + β_2[L]² + \cdots\), \(L\) indicates CH₂CICOO⁻ or CHCl₂COO⁻. Combining eqs. (1) and (2), and taking logarithm, we obtain

\[
\log Dα = \log K_{ex} + n \log([HA]_{aq}) + n \log[H^+]_{aq}
\]

Both plots of \(\log Dα\) vs. \(p[H^+]\) and \(\log Dα\) vs. \(\log([HA]_{aq})\) showed slopes of 3 (Figs. 1). Thus, the extraction goes in the way of

\[
RE_{aq} + 3(HA)_{2 org} \rightleftharpoons RE(HA₂)₃_{org} + 3H^+_{aq}
\]

Fig. 1 Plots of \(\log Dα\) vs. \(p[H^+]\) (a) or \(\log([HA]_{aq})\) (b)

If the product of \(K_{ex}K_{r}\) is defined as an overall equilibrium constant \(K^*\), this can be calculated from the following equation

\[
\log K^* = \log α - 3 \log([HA]_{aq}) - 3 \log[H^+]_{aq} \quad (3)
\]

in which \([H^+]_{aq}\) is the \(H^+\) concentration as the distribution ratio \(D\) equals to 1. The values of \(K^*\) for rare earth elements were listed in Table 1. The data of the overall extraction equilibrium constants of rare earth elements in Table 1 show that \(K^*\) increases along with the increase in the atomic number of this series, the \(K^*\) of yttrium is just between holmium and erbium, and that of scandium is beyond lutetium. Scandium was quantitatively extracted in the acidic range studied. Plots of \(\log K^*\) against the atomic number of this series show a
typical tetrad effect\(^{11,12}\) (Fig. 2). The shape of the plots was similar to those of other acidic phosphorus extractants.

Moreover, the separation factor \(S\text{-}F\)\(_{z+1/z}\) of adjacent pair of rare earth elements can be evaluated from the distribution ratios or overall extraction equilibrium constants of the adjacent pair,

\[
S\text{-}F\text{-}z+1/z = D_{z+1}/D_z = K_{z+1}^*/K_z^* 
\]

in which \(z\) is the atomic number of lanthanoids. Yttrium is placed between holmium and erbium considering its \(K^*\) value. The data are listed in Table 1. The \(S\text{-}F\) values in Table 1 indicate that the pair of europium(III) and gadolinium(III) was the most difficult to be separated, and the pair of lanthanum(III) and cerium(III) is the easiest among the adjacent pairs of this series.

**Thermodynamics**

The standard enthalpy change \(\Delta H^o\) of the extraction process of rare earth elements(III) can be obtained by the temperature coefficient method,

\[
d\ln K^*/d(1/T) = -\Delta H^o/R 
\]

where \(T\) is the absolute temperature and \(R\) the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). \(\Delta H^o\) for individual rare earth element(III) in Table 1 indicated that the extraction processes of all the rare earth elements(III) were very endothermic, and the \(\Delta H^o\) value decreased along with the increase in the atomic number. The \(\Delta H^o\) value of yttrium fell between holmium and erbium, and that of scandium could not be determined.

The standard free energy change \(\Delta G^o\) of the extraction processes of rare earth elements(III) can be calculated from the overall extraction equilibrium constant \(K^*\). And the relative standard free energy change \(\Delta\Delta G^o\text{-}z+1/z\) of the adjacent pair of this series indicates the difference in the tendencies of the extraction processes of the two adjacent rare earth elements(III), and controls the degree of separation between the two adjacent rare earth elements(III). It can be calculated by

\[
\Delta(\Delta G^o)^{z+1/z} = -RT\ln(K^*_z/K^*_{z+1}) 
\]

The values were listed in Table 1 and plotted together with \(S\text{-}F\text{-}z+1/z\) against the adjacent pairs of rare earth elements(III) in Fig. 3. The greater the value of \(\Delta(\Delta G^o)^{z+1/z}\), the easier the mutual separation is, as expected from equation (6).

The standard entropy change \(\Delta S^o\) of the extraction processes of rare earth elements(III) was evaluated by the following thermodynamic equation as

\[
\Delta S^o = (\Delta H^o - \Delta G^o)/T. 
\]
scandium(III) was quantitatively extracted as the acidity in the aqueous phase was greater than 1 mol dm$^{-3}$ while all the lanthanoids(III) and yttrium(III) left in the aqueous phase (Fig. 4). Thus, the quantitative separation of scandium(III) from them could be achieved by only a single extraction.

Extraction chromatographic separation of lanthanum(III), cerium(III) and praseodymium(III)

According to the results of solvent extraction experiments of rare earth elements(III), the mutual separation of the adjacent pairs of lanthanoids(III) including yttrium(III) was unfeasible by employing a single extraction using HMBP as an extractant. Thus, extraction chromatography, which inherently has not only the high selectivity of solvent extraction but also the high efficiency of chromatography, was applied to the mutual separation of La$^{III}$, Ce$^{III}$ and Pr$^{III}$. The result is shown in Fig. 5. Quantitative mutual separation among those three cations can be achieved as shown in the figure 5. hence, the HMBP-extraction chromatography may be applied to the mutual separation of other rare earth elements(III) in HNO$_3$ medium.

Table 1 pH, logK*, S.F., log12, AH*, AS* and A(AG °)2+1/z of rare earth elements in HMBP-HNO$_3$ system

<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>logK*</th>
<th>S.F.</th>
<th>log12</th>
<th>AH*</th>
<th>AS*</th>
<th>A(AG °)2+1/z</th>
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<td>La</td>
<td>3.30</td>
<td>-5.24</td>
<td>10.7</td>
<td>23.19</td>
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<tr>
<td>Ce</td>
<td>2.75</td>
<td>-4.81</td>
<td>12.4</td>
<td>18.10</td>
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<tr>
<td>Pr</td>
<td>2.58</td>
<td>-5.70</td>
<td>17.0</td>
<td>16.12</td>
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<tr>
<td>Nd</td>
<td>2.50</td>
<td>-4.47</td>
<td>15.5</td>
<td>15.07</td>
<td>-14.20</td>
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<tr>
<td>Sm</td>
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<td>13.44</td>
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<td>Eu</td>
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<td>11.0</td>
<td>11.00</td>
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<tr>
<td>Ho</td>
<td>1.75</td>
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<td>12.00</td>
<td>-13.50</td>
<td>-1.67</td>
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<tr>
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<tr>
<td>Yb</td>
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<td>13.6</td>
<td>11.51</td>
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<tr>
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<td>3.04</td>
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<td>6.04</td>
<td>97.57</td>
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| a the average value of three duplicate runs, RSD less than 5%; b KJ mol$^{-1}$; c J mol$^{-1}$ K$^{-1}$.

Fig. 4 Extractive separation of Sc$^{III}$ from Y$^{III}$ and lanthanides(III)

Extraction chromatographic separation of lanthanum(III), cerium(III) and praseodymium(III)

According to the results of extraction experiments of rare earth elements(III), the mutual separation of the adjacent pairs of lanthanoids(III) including yttrium(III) was unfeasible by employing a single extraction using HMBP as an extractant. Thus, extraction chromatography, which inherently has not only the high selectivity of solvent extraction but also the high efficiency of chromatography, was applied to the mutual separation of La$^{III}$, Ce$^{III}$ and Pr$^{III}$. The result is shown in Fig. 5. Quantitative mutual separation among those three cations can be achieved as shown in the figure 5. hence, the HMBP-extraction chromatography may be applied to the mutual separation of other rare earth elements(III) in HNO$_3$ medium.

Fig. 5 Separation of La$^{III}$, Ce$^{III}$ and Pr$^{III}$

Stationary phase: 28 % HMBP silica gel, 100-200 mesh mobile phase: pH2.16 HNO$_3$
Sample: 50μg La$^{III}$ + 50μg Ce$^{III}$ + 50μg Pr$^{III}$
Column size: 6 x 170 mm; Temperature: 50°C
Flow rate: 0.1 ml/min cm$^{-2}$

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References