Polarity Effect of Organic Solvents on the Separation Factors across the Lanthanoid Series

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The extraction constants ($K_{\mathrm{ex}n}=[\mathrm{LnX_3}\cdot n\mathrm{E}]_o/[\mathrm{Ln^{3+}}][\mathrm{X^-}]^3[\mathrm{E}]_o{}^n$, $n=3$ and/or 4) were determined across the lanthanoid series, when lanthanoids(III) were extracted from a 1 M sodium thiocyanate (NaX) solution into benzene and chlorobenzene containing trioctylphosphine oxide (TOPO, E). The dominant species were $\mathrm{LnX_3\cdot 4E}$ for light lanthanoids and $\mathrm{LnX_3\cdot 3E}$ for heavy ones. Although both extraction constants increased along with the atomic number, the difference in the magnitude of $\log K_{\mathrm{ex_4}}$ from $\log K_{\mathrm{ex_3}}$ to a less-polar solvent, benzene, was larger than that to chlorobenzene. The separation factor was similar either in light lanthanoids or in heavy lanthanoids to both solvents, reflecting the similar variation of the constants across the series. However, in the middle of the series, it was smaller upon using less-polar solvents than polar solvents. One of the reasons was the larger proportion of $\mathrm{LnX_3\cdot 4E}$, of which extraction constant did not change much in the middle of the series. In addition, when the concentration of TOPO was not in a large excess of the lanthanoid(III) concentration it was due to a greater consumption of TOPO; that is, the heavier lanthanoid(III), which was extracted better, required more TOPO molecules to be combined with $\mathrm{LnX_3}$, and into less-polar solvents lanthanoids(III) were extracted better than into polar solvents. Consequently the separation factor when using less-polar solvents was smaller than expected from the extraction constants.

It has been found[1] that the extraction of lanthanoids(III) with the thiocyanate ion and trioctylphosphine oxide (TOPO) into chloroform should be much better along with increasing the atomic number, while extraction into hexane does not change much across the series. The properties of these solvents somewhat differ one from other; hexane is very inert, but chloroform has an active H atom capable of forming hydrogen bonding, and is rather polar. In addition, since extraction into hexane is much better than that into chloroform, the distribution ratio across the lanthanoid series between both solvents can not be compared under a same condition. Thus, in the present study benzene and chlorobenzene were used as organic solvents, because they are similar, except for their polarity. It may be easy to examine the effect of the polarity of the organic solvents on the separation factor of the respective lanthanoid(III) in more detail.

Experimental

Reagents: All of the reagents were of analytical grade. Benzene or chlorobenzene solution of 0.1 M (1 M = 1 mol dm^{-3}) TOPO (purchased from Dojindo Laboratories) was washed with a 0.1 M sodium hydroxide solution three times, and then with deionized water until the solution became neutral. Lanthanoid(III) stock solutions were prepared in a similar way as described elsewhere.[1] A sodium thiocyanate stock solution was prepared by weighing a portion of the saturated solution in the presence of solid salt, and then diluting it with deionized water. The concentration was determined by argentometry. 1,1,1-Trifluoro-4-(2-thienyl)-2,4-pentanedione (TTA) was obtained from Dojindo Laboratories. Chloroform was washed three times with deionized water prior to use.

Procedure: Two phases consisting of benzene or chlorobenzene containing TOPO and an aqueous solution containing 5×10^{-4} M lanthanoid(III) and sodium thiocyanate were shaken until they attained the extraction equilibrium. The extractability of the respective lanthanoid(III) into benzene or chlorobenzene at a constant TOPO concentration was measured while changing the concentration ratio between $\mathrm{SCN^-}$ and $\mathrm{Cl^-}$ at 1 M Na(SCN, Cl). Several lanthanoids(III) were distributed between 1 M Na(SCN, $\mathrm{ClO_4}$) or Na(Cl, $\mathrm{ClO_4}$) and chloroform containing 0.1 M TTA. The hydrogen-ion concentration at equilibrium was measured potentiometrically using a solution containing 1.00×10^{-2} M perchloric acid and 0.09 M sodium perchlorate as a standard of $-\log[\mathrm{H^+}]=2.00$.

The concentration of lanthanoid(III) distributed between the two phases was determined as follows. Upon extraction with TTA, those lanthanoids(III) were back-extracted into 0.1 M perchloric acid and followed with ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry); the concentration, which remained in the aqueous phase, was obtained from the balance between the initial concentration and the concentration in the organic phase at equilibrium. Upon extraction with TOPO, the metal(III) in the organic phases was determined after back extraction into 10^{-3} M nitric acid, and that in the aqueous phases after diluting with 10^{-3} M nitric acid as much as 10 times was determined by ICP-AES. The concentration ratio between both phases was defined as the distribution ratio.

Results and Discussion

Figure 1 shows the variation in the distribution ratio of the respective lanthanoid(III) (initial concentration is 5×10^{-4} M) between a 1 M sodium thiocyanate solution and chlorobenzene or benzene solution of 5×10^{-3} M TOPO across the series. The distribution ratio seems to increase along with the atomic number in these organic solvents. However,

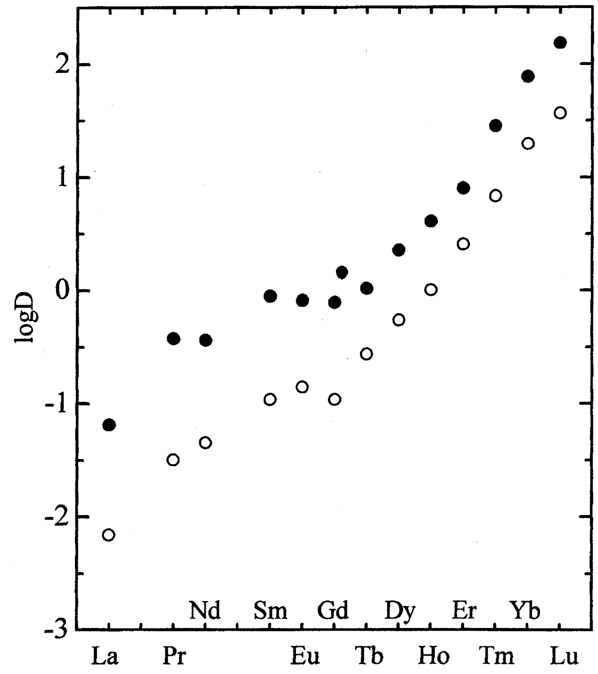

Fig. 1. Distribution ratio against atomic number when $\mathrm{Ln^{III}}$ (initially 5×10^{-4} M) was extracted from 1 M NaSCN into benzene (●) or chlorobenzene (○) containing 5×10^{-3} M TOPO.

in the benzene system Sm, Eu, Gd, and Tb show a similar distribution ratio. It was observed in the hexane system that the distribution ratio did not change among Sm, Eu, Gd, Tb, Dy, and Ho when lanthanoids(III) (initial concentration is 1.3×10^{-4} M) were extracted with 1.5×10^{-3} M TOPO.

To examine the effect of organic solvents on the separation factors more quantitatively, the extraction constants of lanthanoids(III) upon using benzene and chlorobenzene containing TOPO and the stability constants of the aqueous complexes with thiocyanate ion were determined.

1) Extraction Equilibria of Lanthanoids(III) with the Thiocyanate Ion and TOPO. When lanthanoids(III) are extracted with the thiocyanate ion (X^-) and a solvating ligand, TOPO (E), as $LnX_3{\cdot}nE$, and form aqueous complexes, such as LnX^{2+}, the distribution ratio can be represented as

$$D=\frac{\sum[LnX_3{\cdot}nE]_o}{[Ln^{3+}]+[LnX^{2+}]+\cdots}, \tag{1}$$

where subscript "o" denotes the organic phase and no subscript means the aqueous phase. By introducing the extraction constants ($K_{ex_n}=[LnX_3{\cdot}nE]_o/[Ln^{3+}][X^-]^3[E]_o{}^n$) and the stability constants of the aqueous complexes with thiocyanate ions ($\beta_m=[LnX_m^{3-m}]/[Ln^{3+}][X^-]^m$) into Eq. 1, the following equation can be obtained:

$$D=\frac{\sum K_{ex_n}[X^-]^3[E]_o{}^n}{1+\sum\beta_m[X^-]^m}. \tag{2}$$

To confirm that the extracted species are accompanied with 3 molecules of SCN^-, the dependence of the distribution ratio on the thiocyanate-ion concentration was measured. Figure 2 shows the correlation between the distribution ratio and the thiocyanate-ion concentration when lanthanoids(III) were extracted into solvents containing a given concentration of TOPO. To prevent any change in the activity coefficients, the total cation concentration was kept at 1 M by adding a sodium chloride solution, 1 M Na(SCN, Cl). The plot shows straight lines having a slope of +3 in the low-concentration region. This may suggest that the extracted species were accompanied by three molecules of SCN^-, and that the dominant species in the aqueous phases was Ln^{3+} in the low $[SCN^-]$. However, the chloride ion as well as the thiocyanate ion may form aqueous complexes with lanthanoids(III).

2) Determination of the Stability Constants of Lanthanoid(III) Complexes with Chloride and Thiocyanate Ions. To check aqueous-complex formation, the distribution ratio of lanthanum(III), europium(III), and ytterbium(III) between chloroform solution of 0.1 M TTA and 1 M Na(SCN, ClO_4) or 1 M Na(Cl, ClO_4) was measured as a function of the thiocyanate or chloride ion concentration. The distribution ratio decreased slightly when $[Cl^-]$ or $[SCN^-]$ increased, as can be seen from Fig. 3. When the perchlorate ion is assumed to be completely inert for lanthanoids(III), the decrease can be regarded as being complex formation in the aqueous phase, i.e.,

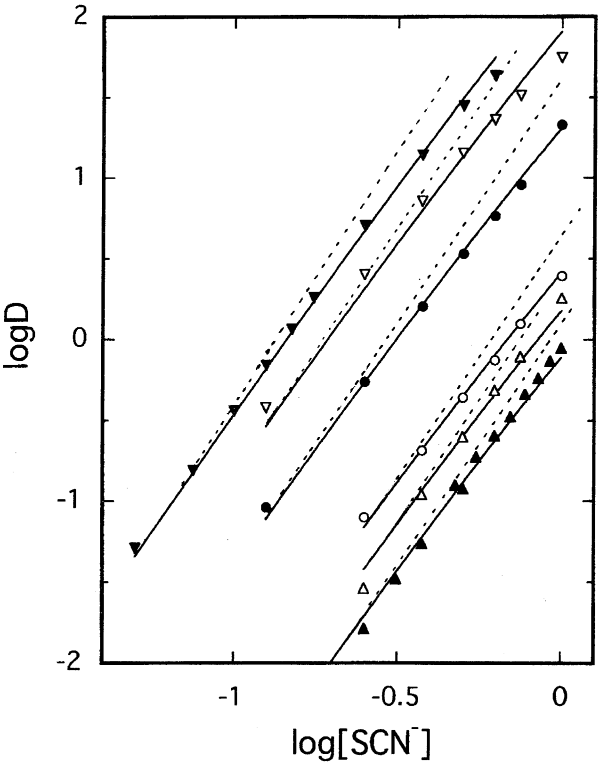

Fig. 2. Distribution ratio as a function of NaSCN concentration at 1 M Na(SCN, Cl). TOPO concentration is for benzene 8×10^{-3} M (La (▲), Eu (●)), and 4×10^{-3} M (Yb (▼)), and for chlorobenzene 0.02 M (La (△)), 0.01 M (Eu (○)), and 5×10^{-3} M (Yb (▽)). The solid curves are calculated from $D=\frac{\sum K_{ex_n}[X^-]^3[E]_o{}^n}{1+\beta_1^{Cl}(1-[X^-])+\beta_1^{SCN}[X^-]}$ using the constants in Tables 1 and 2. The dotted lines are straight lines having slope of +3.

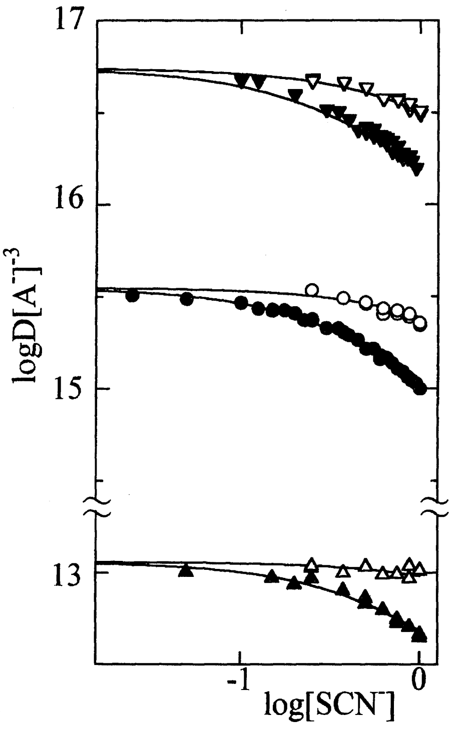

Fig. 3. Decrease in the extraction of Ln^{III} into 0.1 M TTA–$CHCl_3$ from 1 M Na(X, ClO_4).
X: SCN (▲), Cl (△) for La; SCN (●), Cl (○) for Eu; SCN (▼), Cl (▽) for Yb. The solid curves are calculated from $\log D[A^-]^{-3} = \log K_{ex_{30}} - \log(1+\beta_1[X^-])$ using the constants in Table 1.

$$D = \frac{[LnA_3]_o}{[Ln^{3+}]+[LnX^{2+}]+\cdots} = \frac{K_{ex_{30}}[A^-]^3}{1+\sum\beta_m[X^-]^m}, \tag{3}$$

where $K_{ex_{30}}=[LnA_3]_o/[Ln^{3+}][A^-]^3$ (A^- is TTA anion: the concentration was calculated from the total TTA concentration and the proton concentration at equilibrium using the distribution constant ($10^{1.89}$) and pK_a (6.28) when the aqueous solution was 1 M $NaClO_4$ and the organic solvent was chloroform.2)) Since the limiting slope of the distribution curves is much smaller than unity, the extraction data in Fig. 3 were analyzed by only assuming the formation of the first complexes of lanthanoids(III) with chloride and thiocyanate ions without higher complexes, and the first stability constants were determined. The constants are listed in Table 1 together with the extraction constants ($K_{ex_{30}}$). The solid curves in Fig. 3 were calculated on the basis of Eq. 3 using the equilibrium constants. Although all parts of sodium perchlorate were replaced with either sodium thiocyanate or chloride, the curves fit well the experimental data. The first stability constants of the other lanthanoid(III) complexes were then determined on the basis of Eq. 3 using the distribution ratio at 1 M NaCl or at 1 M NaSCN and $K_{ex_{30}}$ determined separately, assuming that the differences in the distribution ratio in 1 M NaX (X=Cl or SCN) from that in 1 M $NaClO_4$ resulted from the chloro or thiocyanato complexes. The stability constants obtained for other lanthanoids(III) are also listed in Table 1.

The values of $K_{ex_{30}}$ in the present work (1 M $NaClO_4$) are smaller than those in 0.1 M $NaClO_4$.3) The trend is not special, because it was reported that the extraction constants of copper(II) and zinc(II) with several β-diketones from 1 M $NaClO_4$ media into carbon tetrachloride were also smaller than from 0.1 M media.4)

Table 1. Stability Constants of Thiocyanato and Chloro Lanthanoids(III) Complexes in 1 M NaX and the Extraction Constants of the TTA Chelates at 298 K
aq. phase: NaX containing 5×10^{-4} M La^{III}
org. phase: $CHCl_3$

Ln^{III}	$\log\beta_1^{SCN}$ a)	$\log\beta_1^{Cl}$ a)	$\log K_{ex_{30}}$ b)
La	0.1_4	-0.7_0	13.0_6
Pr	0.3_4	-0.4_7	14.3_4
Nd	0.4_3	-0.0_6	14.5_8
Sm	0.3_4	-0.6_6	15.3_8
Eu	0.3_5	-0.3_4	15.5_5
Gd	0.4_0	-0.1_6	15.3_7
Tb	0.4_4	-0.1_8	15.8_6
Dy	0.4_5	-0.1_2	16.0_5
Ho	0.4_5	-0.1_5	16.0_5
Er	0.4_5	-0.1_3	16.2_2
Tm	0.4_2	-0.1_4	16.3_9
Yb	0.4_1	-0.1_4	16.7_4
Lu	0.4_5	-0.1_4	16.4_6

a) $\beta_1^X = \frac{[LnX^{2+}]}{[Ln^{3+}][X^-]}$ (X=SCN or Cl). b) $K_{ex_{30}} = \frac{[LnA_3]_o}{[Ln^{3+}][A^-]^3}$ (A^-=TTA anion, ionic medium : 1 M).

The stability constants obtained in the present work do not change much across the series, except for lanthanum(III). The stability constants of thiocyanatocomplexes are similar to those previously reported,5) where the concentration of ionic media was not kept constant, although those in light lanthanoids are slightly larger in the present results. The constants given in the literature are also similar to the present results. As the values of $\log\beta_1$ of thiocyanate complexes, 0.1 (La) and 0.2 (Tb) in 1 M $NH_4ClO_4$6) or 0.24±0.06 (La), 0.32±0.09 (Eu), and 0.45±0.09 (Lu) in 5 M Na(ClO_4) are reported.7) However, the constants of chlorocomplexes are slightly scattered in the literature (−0.05 (La), −0.05 (Ce), −0.05 (Pr), −0.10 (Eu), −0.10 (Tm), −0.23 (Yb), −0.40 (Lu) in 1 M ionic media,8) and −0.22±0.11 (La), −0.15±0.10 (Eu), −0.35±0.07 (Lu) in 4 M Na(ClO_4)9)). In the present work, the proton concentration in 1 M NaSCN or 1 M NaCl was determined potentiometrically using a salt bridge at 1 M $NaClO_4$, while neglecting the difference in the activity coefficients. Accordingly, the stability constants obtained in the present work may imply some inaccuracy.

Using the stability constants of the lanthanoid(III) complexes with chloride ion as well as thiocyanate ion, Eq. 2 should be rewritten as

$$D = \frac{\sum K_{ex_n}[X^-]^3[E]_o^n}{1+\beta_1^{Cl}(1-[X^-])+\beta_1^{SCN}[X^-]}. \tag{4}$$

The distribution ratio in Fig. 2 can thus be represented by Eq. 4 instead of Eq. 2. The solid curves in Fig. 2 were calculated from Eq. 4 using the values of the stability constants and the extraction constants of lanthanoid(III) with the thiocyanate ion and TOPO (K_{ex_n}) described later. The calculated curves fit well the expelimental data.

3) Trend of the Variation in the Extraction Constants across the Lanthanoid Series. Figure 4 shows a plot of $\log D$ vs. $\log\,[\mathrm{E}]_{\mathrm{total}}$ when several lanthanoids(III) are extracted with TOPO from 1 M NaSCN into benzene (a) and chlorobenzene (b). The slopes of the extraction curves seem to be almost 4 for the light lanthanoids, and they gradually decrease from light to heavy lanthanoids. The slopes also seem to change with changing in TOPO concentration for a given lanthanoid. The TOPO concentration at equilibrium is not always equal to the concentration added, because

$$\begin{aligned}[\mathrm{E}]_{\mathrm{org,total}} &= [\mathrm{E}]_{\mathrm{o}} + 3[\mathrm{LnX_3{\cdot}3E}]_{\mathrm{o}} + 4[\mathrm{LnX_3{\cdot}4E}]_{\mathrm{o}} \\ &= [\mathrm{E}]_{\mathrm{o}} + 3K_{\mathrm{ex_3}}[\mathrm{Ln^{3+}}][\mathrm{E}]_{\mathrm{o}}^3 + 4K_{\mathrm{ex_4}}[\mathrm{Ln^{3+}}][\mathrm{E}]_{\mathrm{o}}^4 \qquad (5)\end{aligned}$$

and

$$\begin{aligned}[\mathrm{Ln^{III}}]_{\mathrm{total}} &= [\mathrm{Ln^{3+}}] + [\mathrm{LnX^{2+}}] + [\mathrm{LnX_3{\cdot}3E}]_{\mathrm{o}} + [\mathrm{LnX_3{\cdot}4E}]_{\mathrm{o}} \\ &= [\mathrm{Ln^{3+}}](1 + \beta_1^{\mathrm{SCN}} + K_{\mathrm{ex_3}}[\mathrm{E}]_{\mathrm{o}}^3 + K_{\mathrm{ex_4}}[\mathrm{E}]_{\mathrm{o}}^4). \qquad (6)\end{aligned}$$

Since the thiocyanate-ion concentration is kept at 1 M in the present system, $[\mathrm{X^-}]$ is abbreviated in Eqs. 5 to 7. Accordingly,

$$[\mathrm{E}]_{\mathrm{org,total}} = [\mathrm{E}]_{\mathrm{o}} + \frac{[\mathrm{Ln^{III}}]_{\mathrm{total}}\{3K_{\mathrm{ex_3}}[\mathrm{E}]_{\mathrm{o}}^3 + 4K_{\mathrm{ex_4}}[\mathrm{E}]_{\mathrm{o}}^4\}}{1 + \beta_1^{\mathrm{SCN}} + K_{\mathrm{ex_3}}[\mathrm{E}]_{\mathrm{o}}^3 + K_{\mathrm{ex_4}}[\mathrm{E}]_{\mathrm{o}}^4}. \qquad (7)$$

The extraction data were analyzed by a nonlinear least-squares method (the computer program (MULTI2) developed by Dr. K. Yamaoka, Kyoto Univ. 1986), using Eqs. 2 and 7. The determined extraction constants are listed in Table 2. The solid curves in Fig. 4 were calculated using the obtained constants.

As can be seen from Table 2, the dominant extracted species in light lanthanoids are $\mathrm{LnX_3{\cdot}4E}$, that of the heavy ones is $\mathrm{LnX_3{\cdot}3E}$, and in the middle of the series they are

Table 2. The Extraction Constants of Lanthanoids(III) as Thiocyanates with TOPO at 298 K

Solvent	Benzene		Chlorobenzene	
$\mathrm{Ln^{III}}$	$\log K_{\mathrm{ex_3}}$	$\log K_{\mathrm{ex_4}}$	$\log K_{\mathrm{ex_3}}$	$\log K_{\mathrm{ex_4}}$
La	—	8.47±0.01	—	7.38±0.01
Pr	—	9.43±0.01	—	8.32±0.03
Nd	—	9.70±0.01	—	8.51±0.01
Sm	—	9.95±0.01	—	8.84±0.01
Eu	—	10.04±0.01	—	8.93±0.01
Gd	—	9.98±0.01	—	8.95±0.01
Tb	7.19±0.04	10.14±0.02	6.38±0.03	9.31±0.01
Dy	7.78±0.01	10.39±0.01	7.06±0.04	9.51±0.03
Ho	8.32±0.01	—	7.71±0.01	—
Er	8.72±0.01	—	8.12±0.02	—
Tm	9.19±0.01	—	8.57±0.01	—
Yb	9.83±0.01	—	9.11±0.02	—
Lu	9.96±0.01	—	9.34±0.01	—

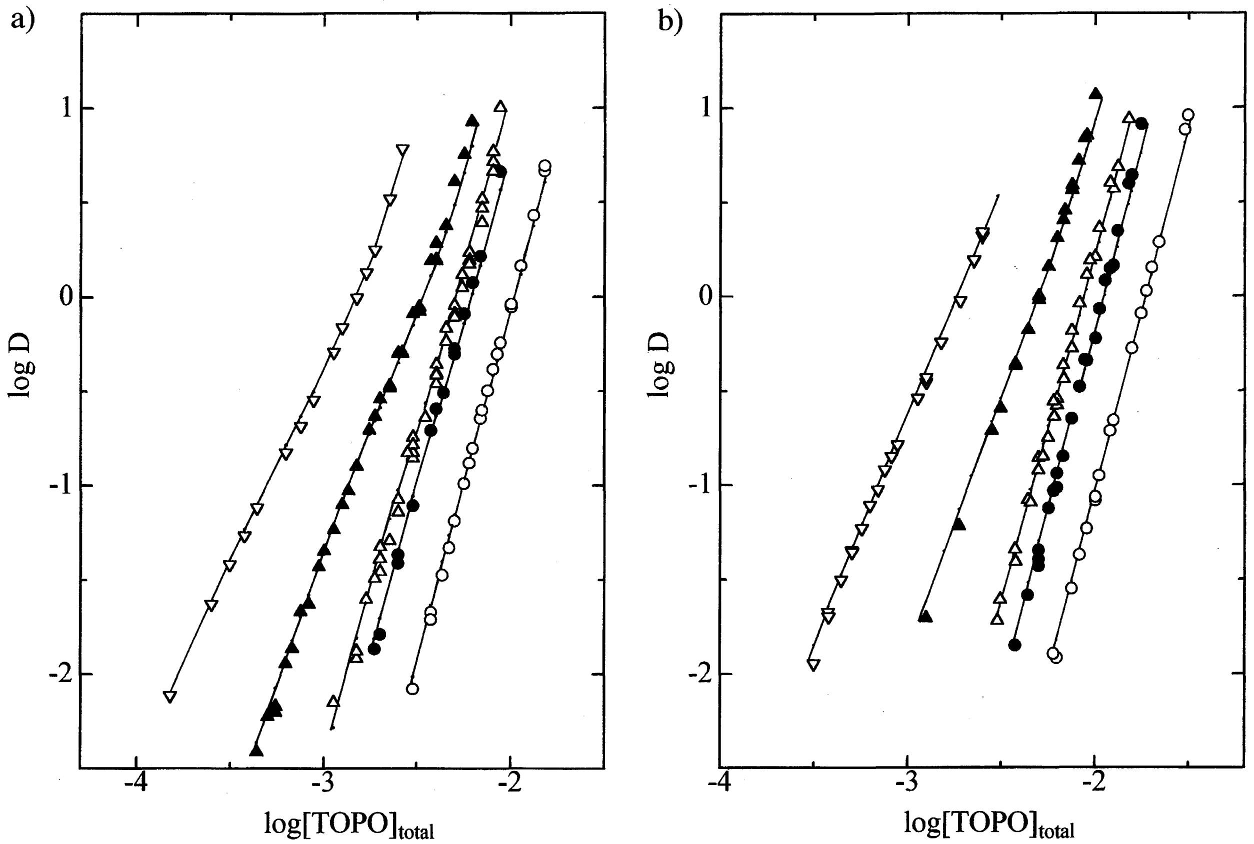

Fig. 4. Distribution ratio against TOPO concentration when $\mathrm{Ln^{III}}$ (initially 5×10^{-4} M) was extracted from 1 M NaSCN with TOPO. a: benzene, b: chlorobenzene, ○ (La), ● (Nd), △ (Eu), ▲ (Ho), ▽ (Lu). The solid curves are calculated from $D=\frac{\sum K_{\mathrm{ex}_n}[\mathrm{X^-}]^3[\mathrm{E}]_{\mathrm{o}}^n}{1+\beta_1[\mathrm{X^-}]}$ introducing $[\mathrm{X^-}]=1$ M and the constants in Tables 1 and 2.

a mixture of $LnX_3 \cdot 3E$ and $LnX_3 \cdot 4E$ when the organic solvents are benzene and chlorobenzene. It has already been reported[1,10] that the dominant species is $LnX_3 \cdot 4E$ when light lanthanoids(III) are extracted and that in heavy lanthanoids is $LnX_3 \cdot 3E$.

The extraction constants obtained in the present work agree well with those of lanthanum(III) as well as lutetium-(III) in the extraction with TOPO into toluene from a 1 M NH_4SCN solution[10] when the term of the stability constants of the aqueous complexes is considered. They describe that the solvation number of the metal ions with TOPO is in general 4 for the lighter lanthanoids and 3 for the heavier ones. However, the present results as well as our previously reported results[1] show that across the series the respective lanthanoid(III) may have both solvation numbers. Since heavy lanthanoids(III) are extracted much better than light ones, as can be seen from Fig. 1, a similar distribution ratio can be obtained, with a lower TOPO concentration than that required for the light lanthanoids(III). As a result, in heavy lanthanoid(III) complexes the proportion of $LnX_3 \cdot 3E$ is much larger than that of $LnX_3 \cdot 4E$, and the extraction constants of $LnX_3 \cdot 4E$ can not be determined within the experimental accuracy. On the other hand, since the extraction of light lanthanoids(III) is poorer, it is experimentally difficult to determine the extraction constant of $LnX_3 \cdot 3E$, which would dominate in the lower concentration region of TOPO.

Figure 5 shows the variation in the extraction constants for benzene and chlorobenzene across the lanthanoid series. The extraction constants of $LnX_3 \cdot 4E$ as well as $LnX_3 \cdot 3E$ increase with increasing atomic number, although the variation in K_{ex_4} does not sharply change in a comparison with that of K_{ex_3}. The different tendency between K_{ex_3} and K_{ex_4} across the series would be caused by a different number of TOPO to solvate; with a greater number of TOPO, the property of the lanthanoids themselves would be concealed, as previously suggested.[1]

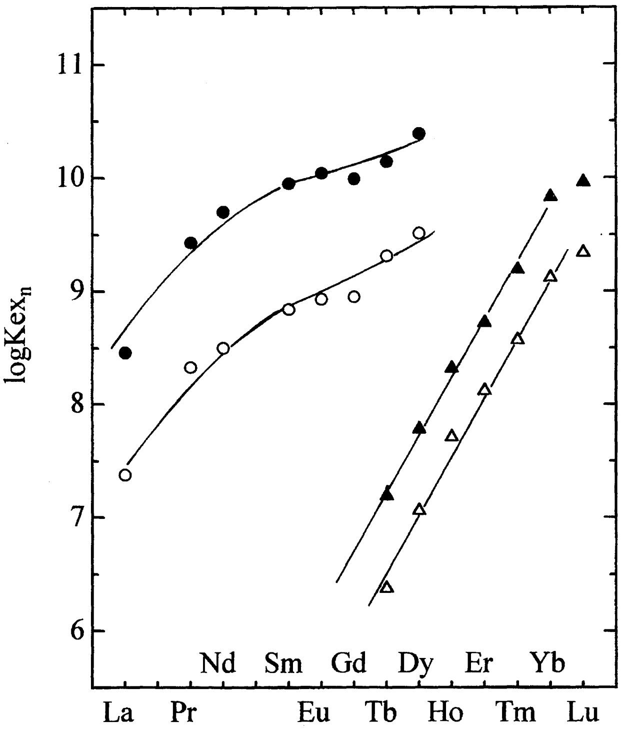

Fig. 5. Extraction constants against atomic number. ▲ (K_{ex_3}), ● (K_{ex_4}) for benzene, △ (K_{ex_3}), ○ (K_{ex_4}) for chlorobenzene. $K_{exn} = [LnX_3 \cdot nE]_o / [Ln^{3+}][X^-]^3[E]_o^n$.

The values of the extraction constants for a proper lanthanoid are larger in benzene than in chlorobenzene; also, the difference in K_{ex_4} between benzene and chlorobenzene would be larger than that of K_{ex_3}, although the pattern of the plot of the constants vs. the atomic number (AN) is similar between benzene and chlorobenzene. The larger difference of $\log K_{ex_4}$ between both solvents than that of $\log K_{ex_3}$ would be ascribed to a difference in the polarity between the organic solvents: The higher complexes, the more hydrophobic, and nonpolar solvents can accept the hydrophobic species.

We now compare the variation in the extraction constants shown in Fig. 5 with that of the distribution ratio under the constant experimental condition given in Fig. 1. The difference in the variation of the distribution ratio between both solvents is larger in the light lanthanoids than in the heavy ones, corresponding to the larger difference of $\log K_{ex_4}$ between both solvents. The similar distribution ratio in the middle of the series upon using benzene can be explained as follows. Although the total concentration of TOPO can be regarded as the free concentration in the large excess of the extractant to metal(III) extracted, when TOPO is not in large excess (in the present study, when $\log D$ is less than -0.5, the initial TOPO concentration was essentially same that at equilibrium), the heavier lanthanoids(III), which give a higher distribution ratio, would result in a larger decrement of the extractant due to the greater formation of $LnX_3 \cdot nE$. The proportion of TOPO combined with LnX_3 to the free (in other words, uncombined) TOPO increases along with the larger distribution ratio when a metal(III) is extracted with the same concentration of TOPO. However, in a sense that the heavier lanthanoids(III) may be extracted while accompanied by a smaller number of TOPO, the decrement in the extractant is not large. Even if the extracted species is only $LnX_3 \cdot 3E$, the heavier lanthanoids(III), which is extracted better, requires more TOPO molecules to be combined with LnX_3. Consequently, upon using less-polar organic solvents, into which the extraction is better, the distribution ratio over a wider range of lanthanoid does not change, as pointed out in "Introduction" in the present paper; that is, a smaller separation factor is observed than expected from the extraction constants.

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