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The Synergistic Effect in Solvent Extraction—The Correlation of the Ionic Radius of Rare Earth Elements with the Stability Constants of Rare Earth Benzoyltrifluoroacetonate Adducts with *n*-Hexyl Alcohol, TBP and TOPO

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The synergistic effects of *n*-hexyl alcohol, TBP and TOPO on the extraction of rare earth ions with benzoyltrifluoroacetone in benzene have been studied. The stability constants of the adducts were determined by means of the curve-fitting method. The equation based on the shift of $\mathrm{pH}_{1/2}$ ($-\Delta\mathrm{pH}_{1/2}$) was also employed to analyse the data. The results were discussed in relation to the ionic radius of rare earth elements and summarized as follows: (1) The stability of rare earth benzoyltrifluoroacetonate decreases but that of the adducts increases, as the ionic radius increases. (2) The maximum number of base molecules bonding to one molecule of the metal chelate is 2, except that in the case of lutetium adduct with TOPO, where the formation of secondary adducts is not observed. (3) Although the overall stability constant of the adduct increases in the following order; lutetium < terbium < europium < lanthanum, as mentioned above, the first stability constant does not show such a distinct sequence. Therefore the contribution of the second stability constant seems to be an important factor. (4) Organic bases studied form stable adducts with rare earth benzoyltrifluoroacetonates in the following order; *n*-hexyl alcohol<TBP<TOPO. This order corresponds to the donating power of lone pair electrons of the oxygen atoms in these compounds.

The liquid-liquid distribution method, in which metal ions react with a suitable chelating reagent to form extractable metal chelate compounds, is very useful not only for the chemical separation of the metal but also for the determination of the stability constants of the metal chelates. Some metal chelates can often be extracted at a lower pH region by adding oxygen- or nitrogen-containing Lewis bases to the extraction system. Such phenomena have generally been called "synergistic effect" and may be caused by the adduct formation between the metal chelates and the active oxygen- or nitrogen-containing compounds.

The synergistic enhancement of metal chelate extraction has been found in various systems and the theoretical considerations of the reactions are also made by many investigators.

By applying the curve-fitting method$^{1,2)}$ to the synergistic solvent extraction, Sekine *et al.* determined the stability constants of the adducts of europium(III)$^{3)}$ or some tervalent metal β-diketone chelates with tri-*n*-butylphosphate (TBP), methylisobutylketone and dibutyl sulfoxide.$^{4)}$

In the previous paper,$^{5)}$ the authors reported the synergistic effect of many kinds of oxygen- or nitrogen-containing compounds on the solvent extraction of europium(III) benzoyltrifluoroacetonate, and discussed the usefullness of this effect in the extraction of rare earth(III) ions with β-diketones.

In the present investigation, the correlation between the ionic radii of rare earth(III) elements and the synergistic effect on the extraction of their benzoyltrifluoroacetonates was examined by using *n*-hexyl alcohol, TBP and tri-*n*-octylphosphine oxide (TOPO) as adduct-forming compounds; and the stability constants of the adducts were determined by means of the curve-fitting method.

Experimental

The radioisotopes, europium-152, 154 and lutetium-177 were supplied from The Radiochemical Centre, Amersham, England; lanthanum-140 was obtained from the Japan Atomic Energy Research Institute, and separated from barium-140 by solvent extraction; and neodymium-147 and terbium-160 were produced in the Research Reactor of Kyoto University. Specific activities of these isotopes were sufficiently high for this investigation.

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1) D. Dyrssen and L. G. Sillen, *Acta Chem. Scand.*, **7**, 663 (1953).

2) L. G. Sillen, *ibid.*, **10**, 186 (1956).

3) T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

4) T. Sekine and D. Dyrssen, private communication.

5) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, This Bulletin, **39**, 165 (1966).

Benzoyltrifluoroacetone was obtained from the Dojindo Co., Ltd., Research Laboratories. TBP was purified by washing with a diluted sodium hydroxide solution, a diluted hydrochloric acid and a saturated sodium chloride solution, and by centrifugation. All the other reagents were reagent-grade and used without further purifications.

Experimental procedure was almost the same as previously described.[5] Ten milliliters of aqueous sample solution, which contained rare earth ions (in the concentration of a few ppm), sodium perchlorate (0.1 M) and acetic acid (0.01 M*[1]) and was adjusted to a desired pH, was shaken with 10 m*l* of 0.05 M benzoyltrifluoroacetone-benzene for about one hour. Adduct-forming materials such as *n*-hexyl alcohol, TBP and TOPO were added to the organic phase. After organic and aqueous layers were separated, 2 m*l* of each of the two phases were pipetted into test tubes (14 mm in diameter) and the radioactivities were counted with a NaI(Tl) scintillation counter: The pH values of the aqueous phase were again measured with a glass electrode pH meter. The pH values obtained after the extraction were used to plot the curves shown in the following figures. The chemical procedures were all carried out at 20±1°C.

Theoretical

When tervalent rare earth ions, M^{3+}, react with β-diketone, HR, and are extracted as neutral chelate, MR_3, the distribution ratio of the metal may be written as follows:

$$D=\frac{[MR_3]_0}{\sum\limits_{m=0}[MR_m{}^{(3-m)+}]+\sum\limits_{i=1}[M(OH)_i{}^{(3-i)+}]+\sum\limits_{j=1}[MX_j{}^{(3-jN)+}]}\qquad(1)$$

where [ ] and $[\ ]_0$ designate the concentration in aqueous phase and in organic phase, respectively; and $M(OH)_i{}^{(3-i)+}$ and $MX_j{}^{(3-jN)+}$ indicate the metal hydroxocomplexes and water-soluble complexes formed with masking agents, *etc.*

The equation can be reduced to Eqs. (2) and (2′), if the following assumptions are fulfilled:

1) The metal concentration can be neglected in comparison with the total concentration of the β-diketone, C_{HR}.

2) The distribution coefficient of the β-diketone is fairly high. But the acid dissociation is considerably low in the pH region investigated.

3) The formation of hydroxocomplexes can be neglected in the pH region studied; and the contribution of complexes to the total metal concentration can also be negligible.

$$D=\frac{PK_3}{1+\sum\limits_{m=1}K_m[R^-]^m}\cdot\left[\frac{K_AC_{HR}}{K_D[H^+]}\right]^3\qquad(2)$$

or

$$\log D=3(pK_D-pK_A+\log C_{HR}+pH)+\log\frac{PK_3}{1+\sum\limits_{m=1}K_m[R^-]^m}\qquad(2)'$$

where K_A and K_D are the acid dissociation constant and the distribution coefficient of the β-diketone; K_m, the stability constant of the metal β-diketonate; and *P*, the distribution of the neutral chelate.

The pH value at half extraction, $pH_{1/2}$, can be given by

$$pH_{1/2}=pK_A-pK_D-\log C_{HR}-\frac{1}{3}\log\frac{PK_3}{1+\sum\limits_{m=1}K_m[R^-]^m}\qquad(3)$$

When a Lewis base, L, added in the organic phase reacts with the metal β-diketonate to form the adduct compounds, which are almost insoluble in the aqueous phase, and if the Lewis base does not give any changes in the acid dissociation and the distribution of β-diketone, the distribution ratio of the metal and the $pH_{1/2}$ value may then be given by the following equations;

$$D^*=\frac{PK_3(1+\sum\limits_{n=1}\beta_n[L]_0{}^n)}{1+\sum\limits_{m=1}K_m[R^-]^m}\cdot\left[\frac{K_AC_{HR}}{K_D[H^+]}\right]^3\qquad(4)$$

or

$$\log D^*=3(pK_D-pK_A+\log C_{HR}+pH)+\log\frac{PK_3(1+\sum\limits_{n=1}\beta_n[L]_0{}^n)}{1+\sum\limits_{m=1}K_m[R^-]^m}\qquad(4')$$

$$pH^*_{1/2}=pK_A-pK_D-\log C_{HR}-\frac{1}{3}\log\frac{PK_3(1+\sum\limits_{n=1}\beta_n[L]_0^n)}{1+\sum\limits_{m=1}K_m[R^-]^m}\qquad(5)$$

where β_n is the stability constant of the metal chelate adduct.

Here, if it can be assumed that tervalent metal ions, M^{3+} are dominant species in the aqueous phase, the pH drift, $\Delta pH_{1/2}$, which serves as a measure of the synergistic effect, can now be calculated from Eqs. (3) and (5):

$$\Delta pH_{1/2}=pH^*_{1/2}-pH_{1/2}=-\frac{1}{3}\log(1+\sum_{n=1}\beta_n[L]_0^n)\qquad(6)$$

On the other hand, from Eqs. (2) and (4) the fundamental equations of the curve-fitting method are obtained as follows;

$$D^*/D=1+\sum_{n=1}\beta_n[L]_0^n\qquad(7)$$

or

$$\log D^*/D=\log(1+\sum_{n=1}\beta_n[L]_0^n)\qquad(7')$$

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*[1] One hundredth molar acetic acid hardly gave the influence on the distribution ratio of metals, *D*, and on the slope of log *D* *vs.* pH plot.

Results and Discussion

Figure 1 shows the log D *vs.* pH plot on the extraction of rare earth benzoyltrifluoroacetonates, which was obtained in the absence of any adduct-forming organic bases. The logarithm of the distribution ratio is linearly related with pH when the concentration of benzoyltrifluoroacetone is kept at constant. But the slope of the straight lines slightly deviates lower from 3, theoretical value. This may be caused by the formation of a small amount of water-soluble complexes such as intermediate chelate complexes or hydroxocomplexes.

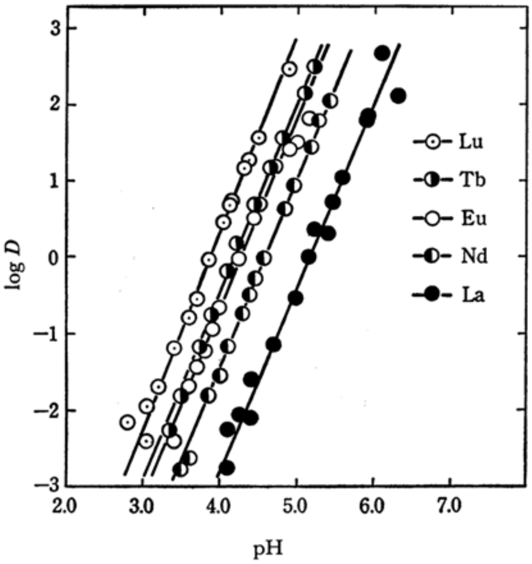

Fig. 1. Logarithm of the distribution ratio of rare earths as a function of the pH value.
Organic phase: 5×10^{-2} M BFA in benzene
Aqueous phase: 10^{-1} M $NaClO_4$

As shown in the figure, the extraction of rare earth benzoyltrifluoroacetonates is enhanced in the following order; lutetium > terbium > europium > neodymium > lanthanum. The sequence of $pH_{1/2}$ is, therefore, of the same; in other words, the value of $pH_{1/2}$ rises as the ionic radius of the central rare earth metal increases, and this can be seen more evidently in Fig. 2. Equation (3) indicates that the $pH_{1/2}$ value is a measure of the stability of metal chelates. The lower $pH_{1/2}$ value, the more stable the chelate. Accordingly, the stability of rare earth benzoyltrifluoroacetonate decreases with the increase of the ionic radius of rare earth element.

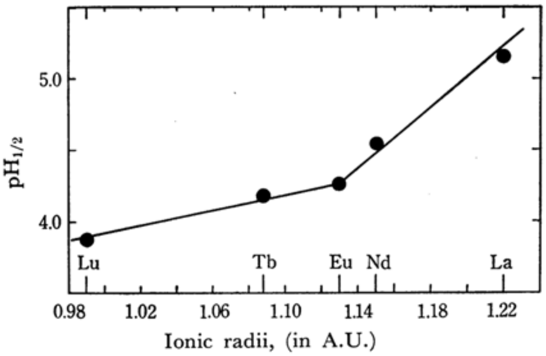

Fig. 2. $pH_{1/2}$ in the extraction of rare earth benzoyltrifluoroacetonate as a function of the ionic radius.

The identical relation between the ionic size or the basicity of rare earth element and the stability of the β-diketonate has already been reported,[6-8] and the similar extraction tendency was found in rare earth - acetylacetone system.[9]

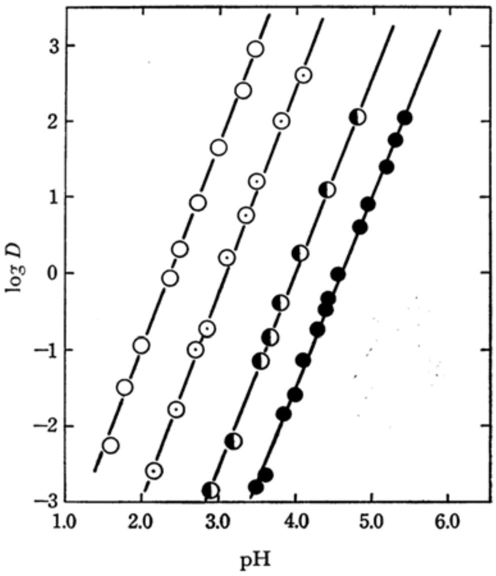

Fig. 3. Logarithm of the distribution ratio of neodymium(III) as a function of pH.
Solvent: benzene BFA: 5×10^{-2} M
Molarity of added organic base: —●— none, —◐— 10^{-1} M *n*-Hexyl alcohol, —⊙— 10^{-2} M TBP, —○— 10^{-3} M TOPO

Figure 3 shows the log$D$ *vs.* pH plots on the extraction of neodymium benzoyltrifluoroacetonate in the presence of 0.1 M *n*-hexyl alcohol, 0.01 M TBP and 0.001 M TOPO, respectively. The $pH_{1/2}$ shift becomes large in the following order; *n*-hexyl alcohol < TBP < TOPO.

As described above, the $pH_{1/2}$ value must shift

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[6] N. K. Dutt and P. Bandyopadhyay, *J. Inorg. Nucl. Chem.*, **26**, 729 (1964).

[7] R. M. Izatt *et al.*, *J. Phys. Chem.*, **59**, 80, 170 (1955).

[8] I. Grenthe and W. C. Fernelius, *J. Am. Chem. Soc.*, **82**, 6258 (1960).

[9] W. B. Brown, J. F. Steinbach and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **13**, 119 (1960).

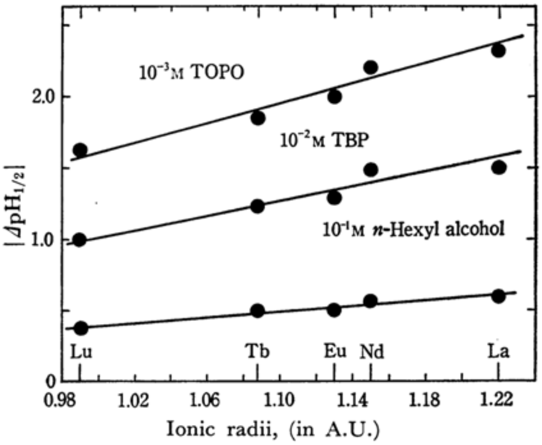

Fig. 4. Shift of $pH_{1/2}(-\Delta pH_{1/2})$ in the synergistic extraction as a function of the ionic radius of rare earth.

to lower, when Lewis bases added to the extraction system form the metal chelate adducts. In Fig. 4, are plotted as a function of the ionic radius, the absolute values of the $pH_{1/2}$ shift, $|\Delta pH_{1/2}|$ which was obtained in the presence of 0.1 M *n*-hexylalcohol, 0.01 M TBP and 0.001 M TOPO, respectively. The $|\Delta pH_{1/2}|$ value rises linearly with the increase in the ionic radius of rare earth element. Equation (6) suggests that the $\Delta pH_{1/2}$ value correlates directly with the logarithm of the overall stability constants of metal chelate adducts, $\log\beta_n$, under the constant concentration of adduct-forming materials. Therefore, it can be expected that the stability of rare earth chelate adducts increases with the increase in the ionic radius of rare earth element, just in contrast with the stability of the chelates.

In order to make the phenomena clearer and to obtain the stability constants of the chelate adducts, the data were analysed by the curve-fitting method in two different ways. One was a commonly employed method based on Eq. (7'), but the other was based on Eq. (6), with the use of $\Delta pH_{1/2}$.

The analysed curves in each method are shown in Fig. 5 and Fig. 6, and the stability constants are summarised in Table 1. Although the values obtained from $\Delta pH_{1/2}$ are somewhat larger in general, there are satisfactory agreements between the results of the two methods.

Here come the following conclusions.

(1) Both the stabilities of rare earth benzoyltrifluoroacetonates and of the adducts formed between the chelates and some organic Lewis bases are related with the ionic radii of rare earth elements. However, the relation appears quite reversely; that is, the stability of the former decreases but that of the latter increases, as the ionic radius increases.

(2) The maximum number of base molecules bond to one molecule of the metal chelates is 2, except that in the case of lutetium adduct with TOPO, where the formation of secondary adducts is not observed. Similar information was reported in thulium-TTA-TOPO system.[10]

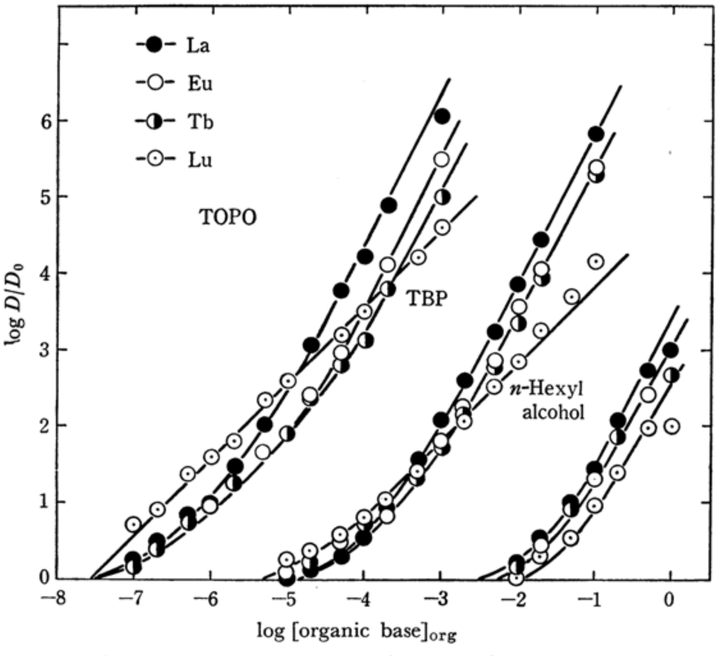

Fig. 5. Variation of the distribution ratio as a function of the organic base concentration.

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10) T. Y. Healy, *J. Inorg. Nucl. Chem.*, **19**, 314 (1961).

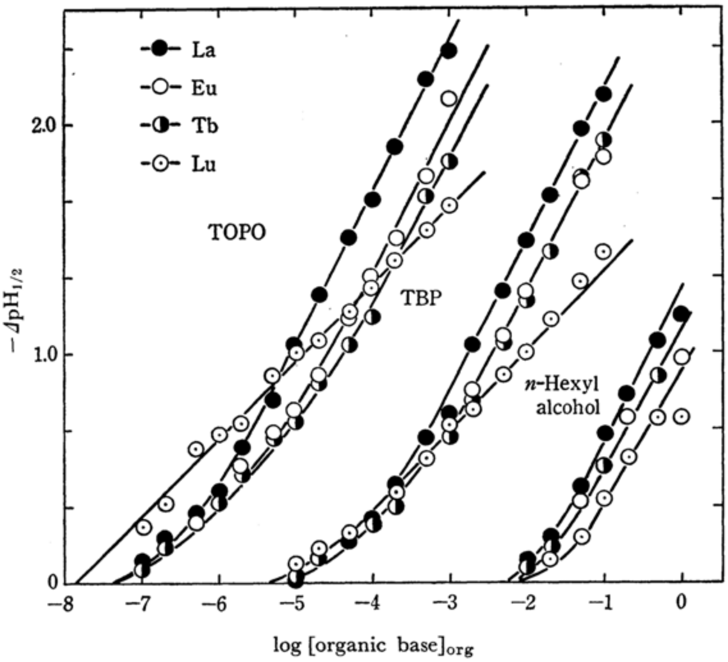

Fig. 6. Shift of $pH_{1/2}(-\Delta pH_{1/2})$ in the synergistic extraction as a function of the organic base concentration.

TABLE 1. STABILITY CONSTANTS OF RARE EARTH BENZOYLTRIFLUOROACETONATES AND THEIR ADDUCTS

	La		Eu		Tb		Lu	
log K_3	−11.6		−8.9		−8.8		−7.7	
log β_n	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2
n-Hexyl alcohol	1.95 (1.90)	3.30 (3.80)	1.85 (1.75)	3.10 (3.50)	1.85 (1.75)	3.10 (3.50)	1.65 (1.55)	2.70 (3.10)
TBP	4.38 (4.55)	7.80 (8.50)	4.55 (4.60)	7.40 (7.80)	4.50 (4.58)	7.30 (7.76)	4.70 (4.90)	6.00 (6.40)
TOPO	7.00 (6.80)	12.30 (13.00)	6.85 (6.93)	11.70 (11.86)	6.90 (7.18)	11.20 (11.76)	7.50 (7.83)	*

* Formation of the second adduct, MR_3L_2 was not observed. The values in the bracket were determined by analysing the curves of Fig. 6.

(3) Although the overall stability constant of the adducts increases in the following order; lutetium > terbium > europium > lanthanum, as just mentioned above, the first stability constant does not show such a distinct sequence. Therefore the contribution of the second stability constant seems to be an important factor, even when lutetium chelate-TOPO adduct is considered. It has been observed in the study on the vapour pressure of hydrates of rare earth acetylacetonates, that the lighter rare earth element could hold the second molecule of water more tightly.[11]

(4) Organic bases studied form stable adducts with rare earth benzoyltrifluoroacetonates in the following order; *n*-hexyl alcohol < TBP < TOPO. This order corresponds to the donating power of lone pair electrons of the oxygen atomes in these compounds.

In this research, the stability constants of the chelate adducts were obtained also from the $pH_{1/2}$ drift. The use of the $pH_{1/2}$ has an essential disadvantage that the values must be taken over one or two unit pH range, and therefore there is a fear of the change in the acid dissociation and consequently, the change in the distribution of the chelating reagent. In this respect, the use of the log D values at a settled pH is very attractive, because it is almost unnecessary to pay the regard to such a dissociation, unless the presence of a

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[11] G. M. Pope, J. F. Steinbach and W. F. Wagner, *ibid.*, **20**, 304 (1961).

Lewis base gives the influence. However, if the K_D value of the reagent is sufficiently large (*i. e.* 100 or more) and if all the $pH_{1/2}$ values measured to obtain $\Delta pH_{1/2}$ are smaller than the pK_A value, there is not detectable change in the concentration of the reagent in the organic phase, which is approximately equal to the total concentration. For benzoyltrifluoroacetone, pK_A is 6.3 (at 25°C)[12] and $\log K_D$ is expected to be nearly 2 from $\log K_D$ of benzoylacetone and TTA, although the value has not been reported. Therefore, about 99% of the reagent is present in the organic phase, at pH 5.3 which is the $pH_{1/2}$ of lanthanum benzoyltrifluoroacetonate, and this percentage hardly change below the pH. Then the $pH_{1/2}$ value could be utilized as same as the $\log D$ value in the present experiment.

From the results of the present investigation, it was impossible to reveal whether organic bases coordinated directly to the central metal ions or bonded to the coordinated chelating reagent molecules.

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[12] J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).