

Synergistic extraction of lanthanoids(III) with thenoyl-trifluoroacetone and aromatic carboxylic acids and the hydration of the extracted species

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Abstract : In order to study how and why the stabilities of lanthanoid(III) complexes in solutions vary across the series, the formation constants of the adducts of tris(2-thenoyltrifluoroacetono)lanthanoids(III) with seven carboxylic acids in chloroform have been determined by solvent extraction technique at 298K. The formation constants with carboxylic acids generally decrease with increasing the atomic number, but in the middle of the series, they change only slightly. Such trends have been interpreted as related to a change of the coordination number in the middle of the series. It has been attempted to determine the number of water molecules coordinated to the adducts as well as $\text{Eu}(\text{TTA})_3$ in chloroform by measuring the fluorescence life time of europium(III), to ensure the assignment of the coordination number.

Keywords : Adduct Formation, Carboxylic Acids, Lanthanoids(III), Relative Stability, Solvent Extraction, Synergistic Effect.

1. Introduction

Synergistic extraction for lanthanoids(III) has been widely studied since Cuninghame, et al.(1) reported the remarkable enhancement of extractability of europium(III) compared to using the respective extractant when 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (hereafter abbreviated as TTA) and tributylphosphate(TBP) was used as extractants. The interest in the studies seems mainly

to have been directed in the synergists. Partially it may depend on the troublesome methods to determine lanthanoids(III)(Ln^{III}), and partially the worse selectivity in the synergistic extraction of Ln^{III} .

However, it is useful to elucidate the factors affecting the synergistic enhancement, or the stabilities of the adducts of lanthanoid(III) chelates with a Lewis base across the series, in order to improve the efficiency of the separation as well as the fundamental chemistry of

lanthanoids(III) in solutions.

2. Experimental

1) Solvent extraction of lanthanoids(III) with TTA and a carboxylic acid. The procedures were carried out in a thermostatted room at 298K. The total anion concentration was adjusted to 0.1 M (1 M = 1 mol dm⁻³) with sodium perchlorate. The proton concentration at equilibrium was measured potentiometrically. Chloroform containing 0.1 M TTA and/or various amounts of an aromatic carboxylic acid and aqueous solution containing Ln^{III} were shaken for an hour. The Ln^{III} extracted was back-extracted into 0.1 M perchloric acid and the concentration in this stripping solution was measured by ICP-AES. The concentration in the aqueous phase was determined as the balance between the initial concentration added and the concentration in the organic phase at equilibrium. The concentration ratio between the two phases was defined as the distribution ratio of Ln^{III}.

2) Measurement of fluorescence lifetime of europium(III) Chloroform containing 0.01M TTA was shaken with sodium hydroxide solution. After then europium(III) perchlorate was added (3×10⁻² M). The two phases were shaken for an hour to ensure equilibrium. At -log[H⁺] = ca. 5, europium(III) of 1×10⁻³ M was extracted. A portion of the chloroform was transferred into another glass tube and there an equal volume of 1-naphthoic acid solution ((0.1-1)×10⁻² M) was added. Europium(III) in the chloroform was excited to ⁵L₆ state by a pulsed laser beam with a XeCl excimer-dye laser. Subsequently, the emission light (⁵D₀→⁷F₂ (615nm)) was measured. The signal was fed into a digitizing oscilloscope installed on a personal computer. The similar experiments were performed using D₂O and CDCl₃. The fluorescence decay constants k_{obs} (ms⁻¹) were determined.

3. Data Treatment

When Ln^{III} is extracted from 0.1 M sodium perchlorate medium into chloroform containing TTA

(HA) and a carboxylic acid(HB), the distribution ratio (D) can be represented as follows,

$$D = \frac{[\text{LnA}_3]_o + [\text{LnA}_3 \cdot \text{HB}]_o + \dots}{[\text{Ln}^{3+}] + [\text{LnB}^{2+}] + [\text{LnB}_2^+]}$$

$$= \frac{K_{\text{ex}}[\text{A}^-]^3(1 + \bar{\beta}_1[\text{HB}]_o + \bar{\beta}_2[\text{HB}]_o^2 + \dots)}{1 + \beta_1[\text{B}^-] + \beta_2[\text{B}^-]^2} \quad (1)$$

where the organic phase is denoted by the subscript "o", $K_{\text{ex}}(=[\text{LnA}_3]_o/[\text{Ln}^{3+}][\text{A}^-]^3)$ is the extraction constant of the TTA chelate, $\bar{\beta}_m(=[\text{LnA}_3 \cdot m\text{HB}]_o/[\text{LnA}_3]_o \times [\text{HB}]_o^m)$ is the m-th adduct formation constants, and $\beta_n(=[\text{LnB}_n^{3-n}]/[\text{Ln}^{3+}][\text{B}^-]^n)$ is the n-th stability constant of the aqueous complexes with these carboxylic acids. The carboxylic acids form dimers in chloroform and dissociate in aqueous solutions. Then from the mass balance of these acids, the concentrations of the monomer in chloroform and the dissociated acid, B⁻, in Eq. (1) were calculated using these equilibrium constants, as follows;

$$[\text{HB}]_o = \frac{-\left(1 + K_d + \frac{K_a}{[\text{H}^+]}\right) + \sqrt{\left(1 + K_d + \frac{K_a}{[\text{H}^+]}\right)^2 + 8K_{\text{dim}}K_dB_T}}{4K_{\text{dim}}K_d}$$

where K_d, K_a, and K_{dim} are the distribution, dissociation, and dimerization constants, respectively, and B_T is the total concentration of the carboxylic acid added.

$$[\text{B}^-] = \frac{K_a[\text{HB}]_o}{K_d[\text{H}^+]}$$

4. Results and Discussion

Figure 1 shows several typical extraction data used to determine the formation constants of the adducts. As seen in Fig. 1, the extraction of lanthanoids(III) is enhanced with the increase in the monomer concentration of the carboxylic acid in the organic phase. The data were analyzed by assuming the formation of the adducts involved two as well as one molecule of the carboxylic acids, similar to earlier reports(2). The solid curves in Fig. 1 are drawn using these constants.

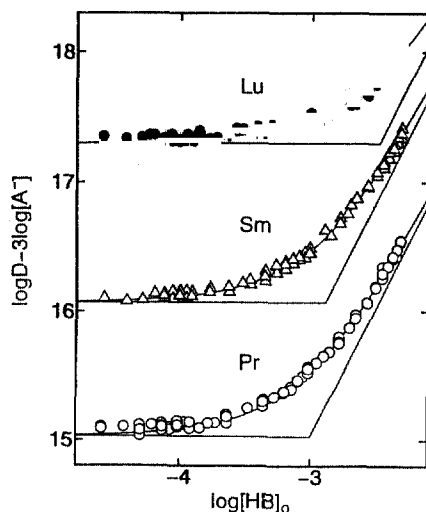


Fig. 1. Enhancement of the extraction of Pr^{III} , Sm^{III} , and Lu^{III} with TTA in the presence of 2-naphthoic acid.

Figure 2 shows the correlation between the formation constants and the atomic number. The variation of the constants against atomic number is classified into three groups. The first and the second groups consist of the light(La-Sm) and the heavy(Ho-Lu) lanthanoids, respectively, for which the constants decrease with increasing atomic number. The third group is the lanthanoids(III) in the middle of the series(Eu-Dy) which

show little decrease with increasing atomic number. When lanthanoids(III) are extracted with TTA and acetophenone or benzofuran, no enhancement of the extractability is observed.

The trend in the variation of the adduct formation constants with carboxylic acids against atomic number is not observed among the formation constants of the adducts with stronger base such as TBP(3), but it is observed

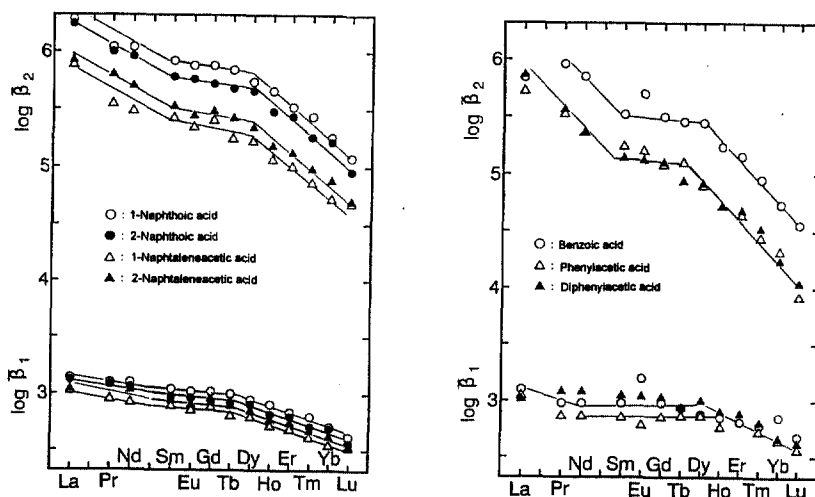


Fig. 2. The adduct formation constants of Ln^{III} -TTA chelates as a function of atomic number.

among those with weaker base such as triphenylphosphine oxide(4). The variation of the adduct formation constants may be influenced by many factors such as basicity of the donor atom in the synergists. One of the factors must be the change in the coordination number of lanthanoids(III), because the pattern of the variation corresponds to the change in the coordination number for which 9 is assigned for the lighter lanthanoids(III), and 8 for the heavier ones, with an equilibrium mixture of 8 and 9 in the middle of the series.

Figure 3 shows the correlation between the formation constants of the second adducts($\text{LnA}_3\cdot 2\text{HB}$) with benzoic and 1-naphthoic acids and the reciprocal of the ionic radii which were calculated by Shannon(4). For the closed symbols, the values of ionic radii for the coordination number(CN) of 9 are assigned, and for the open symbols, the radii of CN = 8 are employed. The plot given with the closed symbols(Pr-Sm) and the open symbols(Er-Lu) shows straight lines with negative slopes, although in the middle of the series, the lines have much

smaller negative slopes. Then using the formation constants estimated from the extension of the two lines and the experimental constants, it was attempted to calculate the proportion of the constants assigning to the coordination number of 8, x . The formation constant of an adduct of a certain lanthanoid(III), consisting of the mixture of the species of CN= 8 and 9, can be represented as,

$$\bar{\beta}_{2(\text{obs})} = \bar{\beta}_{2(8)}x + \bar{\beta}_{2(9)}(1 - x). \text{ Then,}$$

$$x = (\bar{\beta}_{2(\text{obs})} - \bar{\beta}_{2(9)})/(\bar{\beta}_{2(8)} - \bar{\beta}_{2(9)}).$$

Table 1 shows the estimated formation constants as well as the observed constants together with the proportion of the species of CN = 8.

According to Table 1, europium(III) seems essentially to be the CN = 9. If it is correct, the water should coordinate 3 molecules to $\text{Eu}(\text{TTA})_3$ at maximum. It has been attempted to determine the number of water molecules coordinated by measuring the fluorescence life

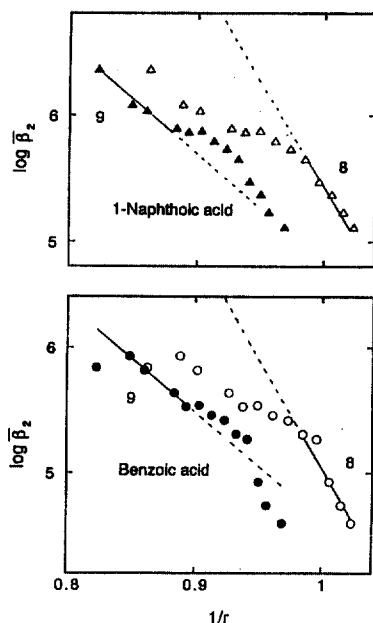


Fig. 3. Formation constants of the second adducts of Ln^{III} -TTA chelates with benzoic(circles) and 1-naphthoic acids (triangles) as a function of ionic radii(CN = 9(closed symbols), CN = 8(open symbols)).

Table 1 Proportion of CN=8 (x) in the adducts of Ln(TTA)₃ with carboxylic acids estimated from $\bar{\beta}_2$ for CN=8 and 9

$$x = (\bar{\beta}_{2(\text{obs})} - \bar{\beta}_{2(9)}) / (\bar{\beta}_{2(8)} - \bar{\beta}_{2(9)})$$

Ln ³⁺	1/r ₍₉₎	1/r ₍₈₎	Benzoic acid				1-Naphthoic acid			
			log $\bar{\beta}_{2(9)}$	log $\bar{\beta}_{2(8)}$	log $\bar{\beta}_{2(\text{obs})}$	x	log $\bar{\beta}_{2(9)}$	log $\bar{\beta}_{2(8)}$	log $\bar{\beta}_{2(\text{obs})}$	x
Eu	0.8929	0.9381	5.53	7.18	5.53	0	5.76	6.72	5.87	0.04
Tb	0.9132	0.9615	5.36	5.83	5.46	0.13	5.58	6.26	5.80	0.17
Dy	0.9234	0.9737	5.27	5.60	5.42	0.36	5.50	6.02	5.74	0.32

time. Since the fluorescence of Eu^{III} decays exponentially, to determine the decay constant, the decay curve was analyzed by non-linear least square method based on $I = I_0 e^{-kt}$. As the decay constants, k_{obs} (in units of msec⁻¹) obtained with the extraction from H₂O solutions are around 9.0 either for 100% Eu(TTA)₃ or for the mixture of 6% Eu(TTA)₃, 24% Eu(TTA)₃·HB, and 70% Eu(TTA)₃·2HB, although the constants are qualitatively going to smaller with increasing of the proportion of the adducts. The numbers obtained from H₂O as well as D₂O solution are larger than those reported for benzene(5), i.e. 5.1 and 1.9, respectively, because in the present work, for the former it is 9, and for the latter, 6. It may be due to the higher solubility of water in chloroform or to the function of chloroform which accelerates fading of the fluorescence of europium(III). The number of water molecules, n, was calculated using the equation, $n = 1.05(k(\text{H}_2\text{O}) - k(\text{D}_2\text{O}))$, offered by Choppin, et al.(6). Then, as the number of n, 3 was obtained, that is, the number of the water molecules may be 3. It seems to support that the coordination number of europium(III) is 9. When the proportion among

Eu(TTA)₃, Eu(TTA)₃·HB, and Eu(TTA)₃·2HB is altered from 14%, 33%, and 53%, to 54%, 33% and 13%, the observed decay constants do not change within the experimental accuracy. This may suggest that the respective species coordinate 3, 2, and 1 water molecules, or that 3, 1, and 0. It must wait to offer the conclusion till the more accurate results can be obtained.

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