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Complex formation of lanthanides(III) and actinides(III) with dicarboxylates containing soft donor groups

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Abstract

In order to investigate the design concept of highly ion selective extractants for f-element series, some stability constants of trivalent f-element/dicarboxylate complexes were determined by solvent extraction method in 0.1 M $NaClO_4$ at 25 °C. The negatively charged oxygen donors in terminal carboxyl groups can mainly contribute to stabilize the metal complex. On the other hand, secondary amine groups in the dicarboxylic acid enhance stabilization of a series of metal complexes. Especially, the soft donor atom such as nitrogen, which can coordinate covalently to 5f-elements, shows the higher selectivity of 5f elements from 4f ones than the harder oxygen atom. The role of nitrogen donor atoms in the carboxylic acid is also discussed with the well-known multidentate ligand EDTA.

Keywords: Stability constant; Soft donor; Dicarboxylic acid; f-Element; Selectivity

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1. Introduction

Group separation recovering minor actinides such as Np, Am and Cm is useful to transmute them in advanced nuclear fuel cycle, which can reduce the volume of radioactive wastes. For this purpose, a variety of new reagents and processes has been developed and/or are being developed around the world [1–5]. It has been recognized that the most efficient group separation is accomplished through the agency of donor atoms softer than oxygen, and extensive efforts are being devoted to design more powerful and useful extractants having soft donor atoms [6]. For practical use, however, not only the higher An/Ln selectivity but also the other requirements of the stability to degradation, the incinerability, and so on are to be considered, and it is quite difficult task to design the extractants which meet all these requirements. Systematic investigation is thus needed for the best selection.

In the present study, complexation behavior of trivalent An/Ln with dicarboxylates containing nitrogen of soft donor was investigated by solvent extraction method, in which the distribution ratios determined as a function of ligand concentration evaluate complexation constants. The results obtained show the role of the soft donor atoms in the complex formation of f-elements and the impact of multiple soft donor atoms on An/Ln selectivity.

2. Experimental

For the preparation of ^{242}Cm, ^{241}Am nitrate solution, 4.0 μg as americium, was dried up and converted to the oxide form in a quartz test tube. The sample tube was sealed in vacuo. Then, the tube was inserted into a larger quartz tube with a small amount of quartz glass wool as a retardant, and sealed again. Finally, the double sealed tube was packed in a thin aluminum tube. The tube was inserted into a solid aluminum capsule and irradiated in a hydraulic transferring system (Hyd) at Kyoto University Reactor. The thermal neutron flux at Hyd was reported to be $8.15 \times 10^{13}\,n\,cm^{-2}\,s^{-1}$. The sample was irradiated for 10 h and left for 10 days to reduce the radioactivity of short-lived nuclides. The oxide was dissolved in 5 mL of 2 mol dm^{-3} (M) HNO_3, filtrated

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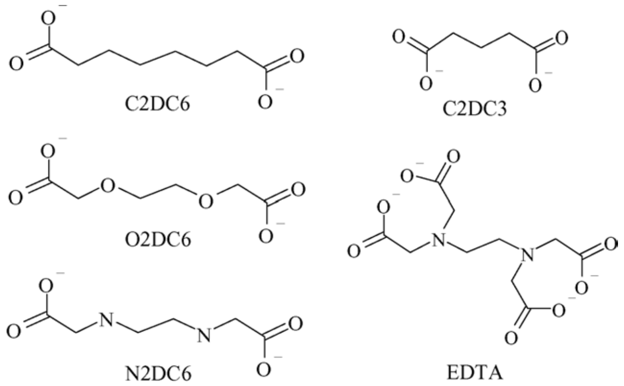

Fig. 1. Chemical structure of four carboxylic acids as anion forms; C2DC6, O2DC6, N2DC6 and C2DC3, and EDTA for discussion.

from broken pieces of tube, and dried up. The standard mixture solution of ^{241}Am and ^{242}Cm for solvent extraction was prepared by dissolving into 20 mL of 1 M $HClO_4$. Each radioactivity after the quantitative coprecipitation with SmF_3 on Nuclipore filter (25 mm in diameter, Whatman) was determined by α-ray spectrometry which was consisted of SOLOIST alpha spectrometer (EG&G ORTEC) with a silicon surface detector (BU-016-300-100) [7].

A combination glass electrode (Horiba, D-50) was used for pH measurement and its reference electrode was filled with 3.6 M NaCl + 0.4 M $NaClO_4$ to avoid precipitation of $KClO_4$ at the junction of electrode and solution. The correction of the pH value (the observed readings) into pHc (the negative logarithms of hydrogen ion concentrations) was followed by the literature [8].

For the solvent extraction to obtain the distribution ratio of metal ion D, an aqueous phase, containing 10^{-1} to 10^{-8} M carboxylic acid (see Fig. 1) and ca. 0.1 kBq ^{241}Am and ^{242}Cm ions in each, was adjusted to the desired pHc with sodium hydroxide, perchloric acid and buffer reagents (a mixture of 5×10^{-3} M MES and MOPS (Dojindo)). Four carboxylic acids used in this study were shown in Fig. 1; suberic acid (C2DC6), 3,6-dioxaoctanedioic acid (O2DC6), ethylenediamine-*N*,*N*′-diacetic acid (N2DC6) and glutaric acid (C2DC3). The ionic strength was also adjusted to 0.1 M with $NaClO_4$. Organic solution, containing 1×10^{-3} M TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; Dojindo) as extractant and TBP (tributyl phosphate; Wako) as a synergist in xylene, was pre-equilibrated with 5×10^{-3} M MES and MOPS and 0.1 M $NaClO_4$ aqueous solution. The aqueous (3.5 mL) and organic (2.5 mL) phases were contacted in a 13 mL borosilicate glass vial with a screw cap, and were shaken horizontally and gently with the aid of a mechanical shaker (Taitec VBR-36) at 25 ± 1 °C. A shaking time of 6 h was found to be long enough to attain the extraction equilibrium. For comparison, non-radioactive europium was extracted in the same procedure. The total recovery of these elements usually were more than 95% and even for worse case more than 85%, it was considered that a serious unexpected reaction such as precipitation did not occur. After phase separation, the pHc of aqueous phase was measured and taken as the equilibrium pH.

Alpha radioactivity of Am and Cm in both phases was measured by α-ray spectrometry after the coprecipitation with SmF_3 as described above, where the organic phase was determined after stripping with 0.1 M HNO_3 solution. The concentration of Eu was determined by ICP-AES (Shimadzu, ICPS-5000). All reagents were of analytical grade and used without further purification.

3. Results and discussion

The extraction reaction of trivalent actinides and lanthanides can be described as

$$M + 3(HT)_o + l(B)_o \rightleftarrows (MT_3B_l)_o + 3H^+ \tag{1}$$

$$K_{ex} = \frac{[MT_3B_l]_o[H^+]}{[M][HT]_o^3[B]_o^l} \tag{2}$$

where the square brackets denote the concentration, and subscript o, M, HT and B are the species in the organic phase, trivalent metal ions (Am, Cm, Eu), undissociated form of TTA, and TBP, respectively. When the complex formation of M by TTA is negligible in the aqueous phase, the distribution ratio of M, D_0, in the absence of a complexation ligand can be expressed simply by

$$D_0 = \frac{[M]_o}{[M]} \tag{3}$$

On the other hand, the distribution ratio, D, in the presence of a complexation ligand (L) is expressed by

$$D = \frac{[M]_o}{[M] + [ML] + [ML_2] + \cdots} \tag{4}$$

where [ML] and $[ML_2]$ are the concentrations of metal complexes in the aqueous phase. The formation constant of 1:n complex ML_n can be expressed by

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \tag{5}$$

Therefore, Eq. (4) is replaced to Eq. (6):

$$D = \frac{D_0}{1 + \sum [L]^n \beta_n} \tag{6}$$

where n is the number of ligand molecules in the complex. When it is unlikely to occur that more than three molecules coordinate together to one metal ion, n is considered to be equal to one and two.

$$\frac{D_0}{D} = 1 + [L]\beta_1 + [L]^2\beta_2 \tag{7}$$

$$\log\ D = \log\ D_0 - \log(1 + [L]\beta_1 + [L]^2\beta_2) \tag{8}$$

From the plots of $\log D$ versus log[L], free parameters of β_1, β_2 and D_0 can be obtained by a least-square fitting

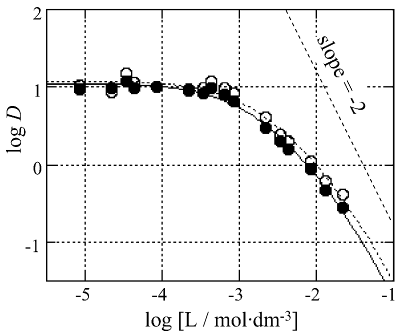

Fig. 2. Distribution ratios of Am(III) (open) and Cm(III) (solid) in the presence of various concentration of C2CD6. $I = 0.1$ M $NaClO_4$.

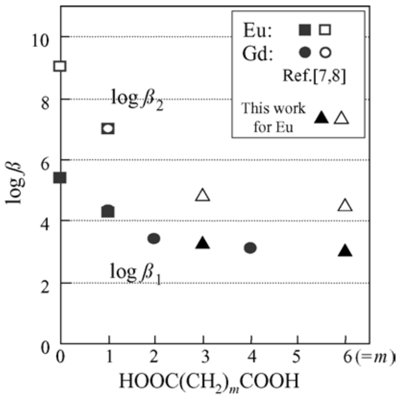

Fig. 3. Dependence of alkyl chain length in dicarboxylic acids on the stability constants of Eu-, or Gd-complex [7,8] and this work for Eu.

analysis [9]. Fig. 2 shows a typical example for determining $\log \beta_n$. The values of $\log D$ for Am and Cm in the presence of C2DC6 are plotted against log[L]. The $\log D$ value decreases with an increase of the C2DC6 concentration. This indicates that Am(III) and Cm(III) form the 1:1 and 1:2 complexes in the aqueous phase ($n = 1$ and 2 in Eq. (5)).

In Fig. 3, the logarithms β_1 and β_2 for Eu-C2DC6 and -C2DC3 complexes are plotted with the reference data of dicarboxylic acids containing a different alkyl length ($m = 0$, 1, 2 and 4), which have been obtained by other experimental techniques such as titration method [10,11]. Although some reference data are for not Eu(III) but Gd(III), the values change continuously over all alkyl chain length. The results support the applicability of our experimental technique to determine a series of stability constants. These values decrease with an increase of alkyl length, significantly at the shorter length, and leached to almost constant value around 3 and 4.5 for $\log \beta_1$ and $\log \beta_2$ respectively, at the longer length. On the other hand, the reference values for monocarboxylic acids, such as acetic acid and propionic acid, are to be 2.1–2.2 (β_1) and 3.4–3.6 (β_2) [10]. Comparing different kinds of ligands with the same number of carboxyl groups, the $\log \beta_1$ (3.24) for C2DC3 ($m = 3$ in Fig. 3) is found to be comparable to the $\log \beta_2$ (3.4–3.6) for monocarboxylic acids. However, in the case of longer chain ligand C2DC6 ($m = 6$), the $\log \beta_1$ (2.96) is obviously smaller than the $\log \beta_2$ for monocarboxylic acids. In the view of the charge of negative oxygen atoms in C2DC3 and C2DC6, these apparent charges are considered to be the same since the acid dissociation constants are quite similar. Consequently, the decrease of β may be due to a longer alkyl chain, which is a disadvantage in conformational energy when the ligand coordinates to a metal ion.

The $\log \beta_1$ and $\log \beta_2$ values for other two ligands containing oxygen or nitrogen donors were also obtained. These values are summarized in Table 1. For each metal ion, the stability constants increased in the order of C2DC6 < O2DC6 ≪ N2DC6. This tendency depends on the additional neutral donor atoms, which can donate to the metal ion when the terminal carboxylates bind to that ion. Especially, the lone pair electron on the secondary amines shows a highly nucleophilic and basic character due to its high electron density.

The stabilization by nitrogen is more significant for the trivalent actinides than lanthanides, as $Eu(N2DC6)^+ < Am(N2DC6)^+ \sim Cm(N2DC6)^+$ and $Eu(N2DC6)_2^- < Am(N2DC6)_2^- \sim Cm(N2DC6)_2^-$. The stability constants of 1:1 and 1:2 complexes for Am and Cm are 10 and 100 times higher than for Eu, in spite of similar ionic radii each other [12]. Although these ions are still hard Lewis acids, Am and Cm prefer to bind softer Lewis bases more strongly than Eu.

The difference of $\log \beta_1$ between Am- and Cm-Eu, $\Delta\log \beta_{1,\mathrm{Am-Eu}}$ and $\Delta\log \beta_{1,\mathrm{Cm-Eu}}$, for N2DC6, EDTA, C2DC6 and O2DC6 are summarized in Table 2. The traditional nitrogen-containing ligand EDTA (ethylenediaminetetraacetic acid) consists of four carboxyl groups and two tertiary amines. The structural frame of EDTA can be considered as the addition of two extra carboxyl groups to the frame of N2DC6 as shown in Fig. 1. The literature values of $\log \beta_1$ for EDTA are to be 17.29 (Eu), 17.8 (Am) and 18.1 (Cm) [10]. These values for EDTA are much larger than for N2DC6. However, $\Delta\log \beta_1$s for EDTA and N2CD6 are close to each other, while that for C2DC6 and O2DC6 are rela-

Table 1
Summary of stability constants of Am(III), Cm(III) and Eu(III)–dicarboxylate complexes and the values of pH_c after equilibrium

	C2DC6			O2DC6			N2DC6		
	$\log \beta_1$	$\log \beta_2$	pH_c	$\log \beta_1$	$\log \beta_2$	pH_c	$\log \beta_1$	$\log \beta_2$	pH_c
Am	2.92 ± 0.12	4.49 ± 0.27	5.35	5.39 ± 0.12	8.59 ± 0.18	5.55	10.21 ± 0.58	19.59 ± 0.23	5.60
Cm	3.00 ± 0.08	4.66 ± 0.14	5.35	5.55 ± 0.12	8.90 ± 0.57	5.55	10.76 ± 0.71	20.09 ± 0.38	5.60
Eu	2.96 ± 0.05	4.47 ± 0.16	5.30	5.18 ± 0.13	8.90 ± 0.08	5.30	9.78 ± 0.10	17.90 ± 0.05	5.55

$I = 0.1$ M $NaClO_4$, 25 °C.

Table 2
Comparison of the difference of $\log\beta_1$ between Am–Eu, Cm–Eu and Cm–Am for N2DC6, EDTA, C2DC6 and O2DC6

	$\Delta\log\beta_1$			
	N2DC6	EDTA [7]	C2DC6	O2DC6
Am-Eu	0.43	0.51	−0.04	0.21
Cm-Eu	0.98	0.81	0.04	0.37
Cm-Am	0.55	0.30	0.08	0.16

tively smaller than for N2CD6. Thus, the negatively charged oxygen donor in terminal carboxyl group can mainly contribute to stabilize the metal complex. On the other hand, the neutral nitrogen donors in alkyl amine groups have the lone pair electrons, which can donate covalently to a cation. Thus, it can account for the stabilization of 5f-element/carboxylate complexes.

In detail of our results, each β value for Cm is slightly larger than Am as shown in Table 2 described as $\Delta\log\beta_{1,\mathrm{Cm-Am}}$. The reason of its selectivity has not been understood yet. More systematic study of ligands with neutral donors such as nitrogen, oxygen and sulfur, with different frames such as alkyl chains and aromatic rings, are now in progress.

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