Separation of Am(III), Cm(III), and Cf(III) using capillary electrophoresis

By H. Kikunaga¹, T. Yoshimura^{1,*}, T. Kuribayashi¹, Y. Kitamoto¹, N. Takahashi¹, H. Haba², Y. Ezaki², S. Enomoto^{2,3}, T. Mitsugashira⁴ and A. Shinohara¹

¹ Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

² Nishina Center for Accelerator-Based Science, RIKEN, Wako, Saitama 351-0198, Japan

³ Graduate School of Medicine, Dentistry and Pharmaceutical Science, Okayama University, Tsushima-naka, Okayama 700-8530, Japan

⁴ International Research Center for Nuclear Materials Science, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan

(Received December 20, 2009; accepted in revised form November 12, 2010)

*Actinides / Lanthanides / Cesium / Strontium /
Capillary electrophoresis*

Summary. Trivalent actinides Am(III), Cm(III), and Cf(III) were successfully separated for the first time using capillary electrophoresis in 2-hydroxyisobutyric acid/acetic acid. It was found that the ionic radius was primarily important for separation of trivalent actinides as well as lanthanides in this condition. The stability constants of the Am(III) complexes with 2-hydroxyisobutyrate were estimated using the correlations between the molar fraction ratio of lanthanides and their ionic radii.

1. Introduction

Separation of trivalent actinides and lanthanides is one of the most difficult, because their physical and chemical properties are so similar [1, 2]. The separation of trivalent actinides and lanthanides is of current interest in the field of the reprocessing of spent nuclear fuel [3–13]. In solution chemistry, ion exchange chromatography and solvent extraction have been well studied for the separation of lanthanides and actinides [3–13]. Capillary electrophoresis (CE) also shows promise for the separation of trivalent actinides because the separation behavior of lanthanides using complex-forming agents is well established for CE [14–17], and the separation of all lanthanides has been accomplished within several minutes [14, 15]. Several studies on the separation of actinides using CE have been reported [18–21]. Timerbaev applied CE for separation of Th(IV), U(VI), and Ln(III) [18]. Kuczewski *et al.* reported separation of Np(V), U(VI), Th(IV), and La(III). Furthermore they reported separation of Pu and Np species with various oxidation states using a CE/ICP-MS system [19]. Separation of U(VI), Np(V), and Am(III) and that of Pu(III), Pu(V), and Pu(VI) were demonstrated by Ambard *et al.* [20]. Recently, separation of Am(III) from Eu(III) was achieved in an acidic aqueous solution containing thiocyanide by

Suganuma [21]. However, no study on the mutual separation of trivalent actinides using CE has been reported. In this study, we report on separation of Am(III), Cm(III), and Cf(III) using 2-hydroxyisobutyrate (HIB[−]) and acetate using CE. Moreover, the separation behaviors of trivalent actinides were compared with those of lanthanides, cesium, and strontium. It was found that the ionic radius was primarily important for separation of trivalent actinides as well as lanthanides. The species of Am(III) and stability constants with HIB[−] were estimated from the correlation between the ratio of the species of lanthanide in 2-hydroxyisobutyric acid (HIBA)/acetic acid and the ionic radius.

2. Experimental

All reagents were analytical grade, unless otherwise specified. Methanol for high-performance liquid chromatography was supplied by Kishida Chemical Co., Ltd. HIBA was supplied by Sigma-Aldrich Co., with a purity of 99%. Creatinine was supplied by Sigma-Aldrich Co. An(III) (Am(III), Cm(III), and Cf(III)) tracers were purified as follows. The mixture of An(III) in 12 mol/dm³ of HCl was passed through an anion exchange resin column (Muromac 1 × 8 200–400 mesh). The resin was washed with 12 mol/dm³ of HCl to elute An(III) from the column. This eluate was evaporated to dryness, dissolved in 13.5 mol/dm³ of HNO₃, and then evaporated to dryness. The residue was dissolved in 90% methanol–10% HNO₃ solution. The solution was passed through an anion exchange resin column (Muromac 1 × 8 200–400 mesh) to adsorb An(III). The resin adsorbing An(III) was washed with 90% methanol–10% HNO₃ solution. An(III) were eluted from the column with 0.1 mol/dm³ of HCl. The eluate was evaporated to dryness, and then the residue was dissolved in water; this procedure was repeated for five times. The residue was dissolved in water to adjust to pH 3.0. A radioactive multitracer solution in hydrochloric acid (pH 3) containing ⁸⁵Sr(II), ¹³⁷Ce(III), ¹⁴³Pm(III), ¹⁴⁵Sm(III), ¹⁴⁶Eu(III), ¹⁵³Gd(III), ⁸⁸Y(III), and ¹⁷³Lu(III), which was prepared by nuclear spallation reaction of ¹⁹⁷Au(¹⁴N, X) at the E3b course of the RIKEN

* Author for correspondence
(E-mail: tyoshi@chem.sci.osaka-u.ac.jp).

Ring Cyclotron, was obtained by separation from the target material like used for purification of An(III). The Yb(III) tracer was prepared by the reaction of $^{169}\text{Tm}(p, n)^{169}\text{Yb}$. The product was dissolved in 3 mol/dm^3 of HNO_3 . The solution was chromatographed on a Ln resin column to separate from the target material. The $^{169}\text{Yb(III)}$ fraction eluted with 8 mol/dm^3 of HNO_3 was collected, and then evaporated to dryness. The following purification procedure was almost the same as mentioned above. The $^{137}\text{Cs(I)}$ tracer was used as purchased. The Am(III), Cm(III), Cf(III), Yb(III), and Cs(I) tracers were added to the multitracer solution at pH 3.

A fused silica capillary (GL Science) was filled with an electrolyte solution (12 mmol/dm^3 of HIBA, 10 mmol/dm^3 of creatinine, and varying concentration of acetic acid). The mixture of An(III) tracers in hydrochloric acid (pH 3) was injected into the anode side of the capillary by a hydrostatic method (10 cm for 10 s), followed by the electrolyte solution. The electrodes were platinum wires, and a voltage of +30 kV was applied with Matsusada Precision HCZE 30PN power supply at room temperature (Fig. 1). The separation behaviors using inactivated capillary (inner diameter $100 \mu\text{m}$) were investigated at pH = 3.10, 3.55, and 3.94 by adjusting the concentration of acetic acid in the electrolyte (0.35 mol/dm^3 at pH = 3.10, 0.087 mol/dm^3 at pH = 3.55, and 0.017 mol/dm^3 at pH = 3.94). At the pH = 3.10, the inactivated or untreated silica capillaries with 150, 100, and $75 \mu\text{m}$ inner diameter were also investigated. Separation of trivalent actinides with rare earths, cesium, and strontium in HIBA/acetic acid at pH = 3.07 was performed using an inactivated silica capillary (60 cm (length) $\times$ $100 \mu\text{m}$ (i.d.)) with applied voltage +30 kV.

To record the electropherogram, alpha-particle and gamma-ray spectroscopies were used to detect trace amounts of the trivalent actinides, rare earths, strontium, and cesium since detection of radioactivity provides high sensitivity. A tailor-made cartridge covering the capillary at the cathode end was provided to fractionalize the sample solution. The cartridge is composed of a Pt electrode and an electrolyte flowing path to adequately flush the electrophoretically separated samples from the capillary (Fig. 1). In the case of separation of Am, Cm, and Cf, each drop of electrolyte with a flow rate of 1.2 ml/min was fractionally collected. In the case of the separation of trivalent actinides, rare earths, strontium, and cesium, the electrolyte with a flow rate of 1.0 ml/min was fractionally collected at 5 s. The alpha-particle spectrometry was performed with a silicon

semiconductor detector *in vacuo*, after the electrolyte solution containing actinides was fractionalized on aluminum plates and was dried by heating. For gamma-ray spectrometry, each fraction was collected into plastic tubes, and the radioactivity was measured using a Ge semiconductor detector. The electrophoretic mobility was calculated from the peak position of the eluted ion in elapsed time.

3. Results and discussion

3.1 Separation of Am, Cm, and Cf

Fig. 2 shows the electropherogram of An(III) at pH 3.10. The three trivalent actinides were separated in less than 6 min at +30 kV, and moved in order of the atomic number; Am(III) eluted first, followed by Cm(III), and then Cf(III). This order was also observed both at pH 3.55 and 3.90. The degree of separation of Am(III) and Cm(III) decreased with increasing electrolyte pH, since pronounced tailing appears as pH and acetate concentration of the electrolyte increase. At pH 3.10, the peak positions of Am(III) and Cm(III) were well resolved and Cf(III) was separated completely from Am(III) and Cm(III). At pH 3.10, separation of Am(III), Cm(III), and Cf(III) was performed using three types of capillaries 75, 100, and $150 \mu\text{m}$ in inner diameter. The separation of Am(III), Cm(III), and Cf(III) using $150 \mu\text{m}$ of the capillary was lesser compared with those using 75 and $100 \mu\text{m}$.

3.2 Separation of trivalent actinide, lanthanide, strontium, and cesium

Table 1 shows the electrophoretic mobility of actinides, rare earths, strontium, and cesium ions. In the separation, cesium ions were eluted at first, followed by strontium, and then lanthanides and trivalent actinides. The lanthanides were eluted in the order of the atomic number as reported in the literature [14]. Am(III), Cm(III), and Cf(III) was eluted within the range of the rare earths. The mobility values of Am(III) and Cm(III) were between that of Pm(III) and Sm(III), and these

Fig. 1. A schematic of the capillary electrophoresis apparatus (left) and the cartridge attached at the end of the capillary (right).

Fig. 2. Electropherogram of Am(III), Cm(III), and Cf(III) in HIBA (12 mmol/dm^3)/acetic acid at pH 3.10 (Am: filled square, Cm: filled circle, Cf: filled triangle). The applied voltage is +30 kV.

Table 1. Electrophoretic mobility values of trivalent actinides, lanthanides, strontium, and cesium in HIBA (12 mmol/dm³)/acetic acid at pH 3.07.

Metal ion	Electrophoretic mobility $\times 10^5$ /cm ² V ⁻¹ s ⁻¹	
	Experimental	Simulated
Am(III)	44.0 $\pm$ 0.8	
Cm(III)	43.2 $\pm$ 0.8	
Cf(III)	37.8 $\pm$ 0.6	
Cs(I)	94.0 $\pm$ 3.7	
Sr(II)	67.5 $\pm$ 1.9	
Y(III)	38.4 $\pm$ 0.6	
La(III)		51.2
Ce(III)	49.6 $\pm$ 1.0	47.9
Pr(III)		46.5
Nd(III)		45.4
Pm(III)	44.4 $\pm$ 0.8	
Sm(III)	42.6 $\pm$ 0.8	42.8
Eu(III)	41.7 $\pm$ 0.7	41.9
Gd(III)	41.2 $\pm$ 0.7	41.4
Tb(III)		39.4
Dy(III)		38.0
Ho(III)		37.0
Er(III)		35.9
Tm(III)		34.6
Yb(III)	29.4 $\pm$ 0.4	33.4
Lu(III)	28.0 $\pm$ 0.3	32.6

values were so larger than those of 4f congeners Eu(III) and Gd(III). The mobility value of Cf(III) was smaller than that of Gd(III) and similar to that of Y(III). The mobility of lanthanides decreases with decreasing its ionic radius. This is attributed to the difference of effective charge by formation of the metal complex with HIB⁻ and acetate, since the stability constant of the complex with HIB⁻/acetate increases with decreasing the ionic radius of the metal ion [22–26]. These results suggest that the main contribution to separation of the trivalent actinides under these conditions is the difference of the ionic radius of the metal ion, which affects the stability constants and molar fraction of the complexes existing in the electrolyte. In our experiment, Cs(I) and Sr(II) were eluted faster than trivalent lanthanide and

actinides. The trend that alkali metal and alkali-earth metal ions showed larger mobility than lanthanides is consistent with the results in the literature [15]. The smaller charge and larger ionic radius of Cs(I) and Sr(II) as compared to trivalent lanthanides and actinides may result in the larger effective charge by formation of the metal complex with HIB⁻ and acetate.

3.3 Speciation of Am(III) in HIBA/acetic acid

We discuss at first about the relation between the separation behavior of trivalent actinides and lanthanide and the eight- or six-coordination ionic radius. The six-coordinate ionic radius decreases in the order Am (0.975 Å) > Pm (0.97 Å) = Cm (0.97 Å) > Sm (0.958 Å) [27]. On the other hand, the eight-coordinate ionic radius is decreased in the order Pm (1.093 Å) > Am (1.09 Å) > Sm (1.079 Å) [27]. The eight-coordinate ionic radius of Cm(III) and nine-coordinate ionic radii of Am(III) and Cm(III) are not determined [27]. The mobility value of our results in electrophoresis decreased in the order Pm > Am > Cm > Sm. Accordingly, a trend for the order of the mobility values is in good agreement with the order of the values of the eight-coordinate ionic radius. In the single-crystal X-ray study of the lanthanide complexes with HIB⁻, the lanthanide atoms are eight-coordinate structures [28]. It is premature to conclude that the complex in the present experimental condition is eight-coordinate structure, since in the case of the Cm(III) complexes with glycolate, the estimated coordination numbers of Cm(III) is between 8 and 9 [29].

Hirokawa *et al.* reported the information on the mobility of lanthanides using isotachopheresis and stability constants of the individual complexes having HIB⁻ and acetate [30]. We applied for the method to derive stability constants of the complexes for Am(III) with HIB⁻. At first, the ratio of the eight lanthanide complexes [Ln(HIB)₃], [Ln(acetate)₃], [Ln(HIB)₂]⁺, [Ln(HIB)(acetate)]⁺, [Ln(acetate)₂]⁺, [Ln(HIB)]²⁺, [Ln(acetate)]²⁺, and [Ln]³⁺ was calculated along with our experimental condition (pH 3.07) using the parameters reported in the literature [30]. Fig. 3 shows the

Fig. 3. The molar fraction of lanthanide complexes vs. reciprocal ionic radius of lanthanide ion (CN = 8) in HIBA (12 mmol/dm³)/acetic acid at pH 3.07.

Fig. 4. The plot of electrophoretic mobility against reciprocal ionic radius (CN = 8). The solid line is simulated electrophoretic mobility.

Table 2. Calculated stability constants of Am(III) and Pm(III) complexes, respectively, with HIB⁻.

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Am(III)	3.36	5.87	7.46
Pm(III)	3.35	5.84	7.41

ratio of each complex vs. reciprocal ionic radius of eight coordinate trivalent lanthanides. Fig. 4 exhibits the observed and simulated electrophoretic mobilities of lanthanides together with the observed mobility values of Am(III) and Pm(III). The simulated mobility for each lanthanide includes a constant value ($9.466 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which relate to electroosmotic flow, as the simulated line is in good agreement with the data points of the observed mobility values of lanthanides. It should be noted that the mobility value of Am(III) lies on the simulated line for those of lanthanides. Therefore, we suppose that the molar fraction ratio and stability constant of the Am(III) complex is calculated by interpolation of the plot of molar fraction of the Nd(III) and Sm(III) complexes against reciprocal ionic radius. Table 2 showed that the calculated stability constants of the Am(III) and Pm(III) complexes, respectively, with HIB⁻. The values of calculated stability constants are quite reasonable as compared to the trend that the stability constants of Am(III) and Pm(III) in the literature are similar [27].

Acknowledgment. The present study includes the results of the efficient separation and analysis of nuclear fission products for reprocessing systems entrusted to Osaka University by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

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