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Observation of cerium isotope fractionation in ion-exchange chromatography of Ce(III)–malate complex

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Abstract

The cerium isotope fractionation between Ce(III)–malate complex in aqueous solution and cerium ions in a cation-exchange resin was conducted by displacement chromatography. The pH and the chemical composition of the eluent were optimized for maintaining the self-sharpening band boundaries and the 21 m chromatographic migration of the Ce band underwent. Graphite slurry was coated on the tantalum filament prior to sample loading for reducing the isobaric interferences in cerium isotopic ratio determination by mass spectrometry. From the experimental results, it was found that the heavier isotope was enriched in the front boundary part of the cerium adsorption band, which meant that the heavier isotope was preferentially fractionated into the Ce^{3+} malate complex rather than simply hydrated Ce^{3+} ions. The isotope separation coefficient for the $^{136}Ce/^{140}Ce$ and $^{142}Ce/^{140}Ce$ was 5.2×10^{-5} and -1.9×10^{-5}, respectively, at 298 K.

Keywords: Cerium isotopes; Malate complex; Displacement chromatography; Isotopic fractionation; Isotope abundance ratio

1. Introduction

Separation of isotopes by ion exchange is a chemical exchange method, which is based on the chemical equilibrium between isotopic species distributed between the stationary resin phase and the mobile solution phase. Equilibrium isotope effects in chromatographic isotope separation systems have been considered to arise from slight differences in vibrational frequencies of isotopically substituted species between the two phases [1], and their magnitude is expressed in terms of single-stage separation factor, α. The equation by which α is evaluated using experimental data had been derived by Spedding et al. [2] and Kakihana and Kanzaki [3]. Systematic investigation on the isotope effects in ion exchange, especially the one concerning isotope accumulating process, has been conducted experimentally and theoretically by Kakihana and Oi et al., by ion-exchange displacement chromatography [4–9]. Chromatography operated in the band displacement manner is an efficient process for obtaining enriched isotopes. This operation is characterized by maintaining self-sharpening band boundaries at both the migration band ends. During the operation, a band of the isotopic chemical species to be separated is eluted through the column by a displacing eluent solution and the rate of movement of the band is determined by the equilibrium between the solution phase and the resin phase as well as by the flow rate of the solution. The ion-exchange displacement chromatography has been applied successfully to the separation of isotopes of various elements in complex formation systems, in particular, those using hydroxycarboxylates as ligands. Oi and Kakihana carried out isotope fractionations covering the alkali and alkaline earth elements in lactate complex formation systems [10], and Fujii and coworkers investigated the isotope fractionations of transition elements including V, Cu and Zn in complex formation systems by displacement chromatography using strongly acidic cation-exchange resins [11–14].

Since isotope effects of heavy elements are in general small, the separations of isotopes of heavy elements, especially those of lanthanides and actinides, seem a big challenge. Aaltonen and coworkers performed several investigations related to isotope separations of heavy elements by elution

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chromatographic technique, including Nd, Sm, Gd as well as U using ammonium α-hydroxyisobutyrate as eluents [15–17]. However as to isotope separations related to heavy elements by the displacement chromatographic mode, only those of Gd, Eu and U were reported [18–20].

As a continuing effort toward observation of isotope effects of heavy elements in ion-exchange systems and their systematics, we attempted isotope separation of Ce. Cerium is a member of the lanthanides and of very unique and intriguing feature to study isotope effects, because it has four stable isotopes with only even mass numbers 136, 138, 140 and 142, whose natural isotope abundances are 0.1904, 0.253, 88.475 and 11.081%, respectively [21]. We employed the displacement chromatographic technique to carry out the cerium isotope fractionation between Ce(III)–malate complex in aqueous solution and cerium ions in cation-exchange resin. Experiments were carried out in two steps. In the first phase, we searched, using short columns, for the chromatographic conditions under which elution of a Ce band could be achieved in the band displacement manner. In the second phase, we tried to observe Ce isotope fractionation by long distance chromatography under the optimum condition found in the experiments with short columns.

2. Experimental

2.1. Ion-exchange resin and reagents

The cation-exchange resin used in this study was a strongly acidic cation-exchange resin Asahi SQS-6 with sulfo groups as ion-exchange group (highly porous; diameter, 70–90 μm; degree of cross-linking, 8–12%; ion-exchange capacity, ca. 4 meq/dry g; developed by Asahi Chemical Industry, Japan). All the reagents were purchased from Wako (Japan) except $Ce(NO_3)_3{\cdot}6H_2O$ which was purchased from Kojundo Chemical Lab (Japan). They were of analytical grade and were used without further purification.

2.2. Chromatographic experiments

The chromatographic experiment system consisted of Pyrex columns (30, 100 or 150 cm long × 1 cm i.d.), pumps, a fraction collector and a water bath. A circulation-type low temperature thermostatic water bath (TRLN 11, Thomas) was used for controlling the operating temperature through water jackets attached to Pyrex columns, and a high-pressure pump (NPL-2100, Nihon Seimitsu) was used to feed the solution at a constant flow rate. The cation-exchange resin in the hydrogen form packed in the column was first loaded with the feed solution of cerium(III) nitrate, $Ce(NO_3)_3$, to form the Ce adsorption band of a suitable length, and the eluent solution of ammonium malate, which was prepared from D,L-malic acid ($COOH–CH_2CHOH–COOH$, abbreviated to H_2L) and $NH_3{\cdot}H_2O$, was then pumped onto the top of the column at a suitable flow rate to develop the Ce adsorption band. The effluent flowing out of the column was collected into small fractions by a fraction collector (CHF 100AA, Advantec, Japan). The above-stated pump, columns and fraction collector were connected in series with 1.0 mm i.d. PTFE tube. In experiments with a short column, various chromatographic parameters such as the pH and malate ion concentration of the eluent and the flow rate were varied, and the Ce concentration profiles were determined to obtain an optimum condition under which a band displacement chromatography was realized. In a long migration experiment, after the Ce adsorption band passed one column, the resin in this column was regenerated to the H^+ form so that a long distance migration of the Ce band ran continuously through the four packed columns (all 150 cm long) in a merry-go-round way. The schematic illustration of the setup for fractionating the cerium isotopes by cation-exchange displacement chromatography is depicted in Fig. 1.

The operating temperature was set at 298 K throughout all the experiments.

2.3. Measurements of Ce^{3+} concentration and pH

The Ce^{3+} concentration in the effluent fractions was measured after dilution by inductively coupled plasma-atomic emission spectrometry with a Seiko Instruments SPS 7700 ICP-atomic emission spectrometer, at the most sensitive wavelength 413.380 nm. Their pH values were measured with a pH meter (F-23, Horiba).

2.4. Mass spectrometric determination of Ce isotopes

The cerium isotopic ratios of the selected effluent fractions of the long-migration experiment were analyzed by mass spectrometry. The determination of cerium isotopic ratios was based on the measurement of the Ce^+ ion peaks by the surface ionization technique using Ta filaments with a Finnigan MAT 261 mass spectrometer (a single-focusing 23 cm radius, 90° magnetic sector field), equipped with a thermal-ionization ion source. It is known that Ce compounds contain small amounts of Ba, La and Nd, and Ba is also contained in Ta filament materials. Therefore, it was necessary to test the interference effects from Ba, La and Nd to Ce mass peaks, since the ^{136}Ba may make contributions (interferences) to signal of $^{136}Ce^+$, ^{138}Ba and ^{138}La to ^{138}Ce, and ^{142}Nd to $^{142}Ce^+$. Table 1 lists the cerium isotopes and the interfering isobars as well as their natural isotopic abundances expressed in at.%.

A portion of a selected sample fraction of the effluent was placed on a small column packed with a cation-exchange resin in the H^+ form, and washed first with 0.1 mol dm^{-3} HNO_3 to remove organic matters, and then eluted with 7 mol dm^{-3} HNO_3. The resulting effluent sample containing cerium was collected in a sample vial and was evaporated to dryness on a hot plate. The evaporation residue was dissolved with diluted HNO_3 solution, resulting in 10 mg/cm^3 cerium(III) nitrate solution for sample loading on a filament.

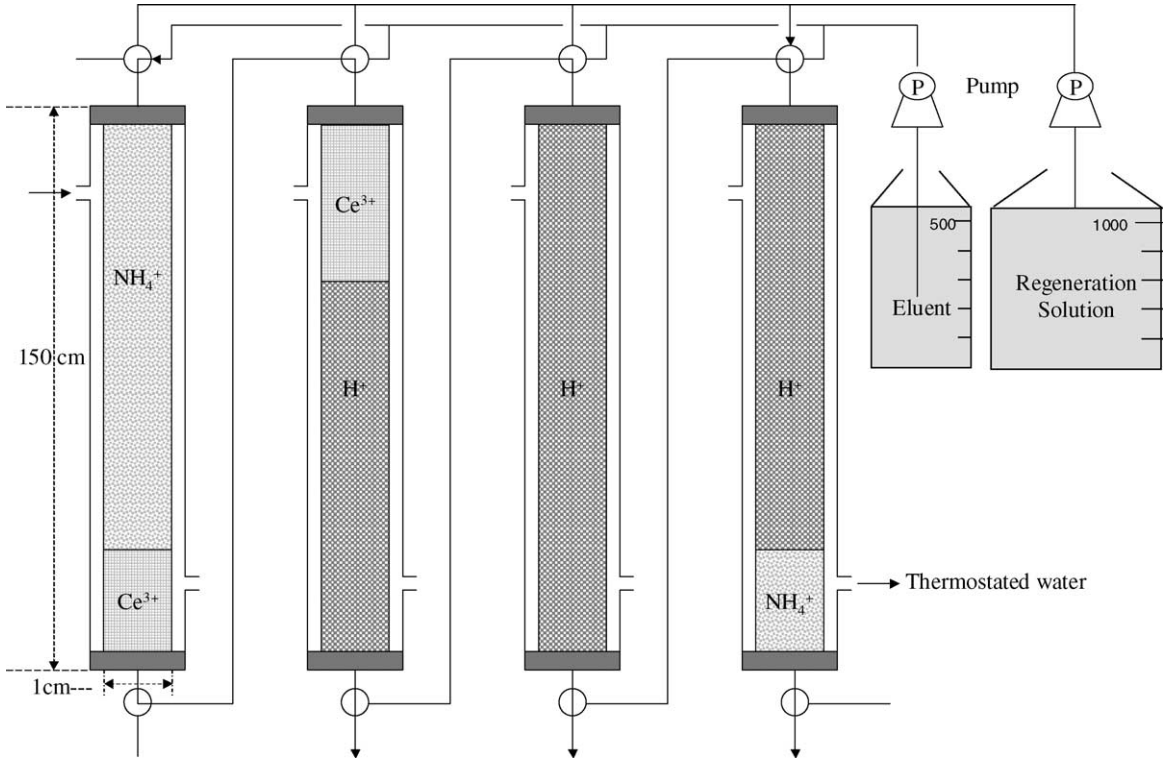

Fig. 1. The illustration of experimental setup for the long migration chromatographic experiment.

Table 1
The natural abundances (at.%) of Ce isotopes and the related isobars over the mass number range from 136 to 143

Element	Mass number						
	136	137	138	139	140	142	143
Ba	7.85	11.23	71.70				
La			0.090	99.91			
Ce	0.185		0.251		88.450	11.114	
Nd						27.2	12.2

Due to severe isobaric interferences mostly from Ba, it was very difficult to analyze less abundant Ce isotopes, ^{136}Ce and ^{138}Ce. Hence, based on the results by Xiao et al. [22], the addition of graphite or carbon has been applied to the isotopic measurement of cerium prior to sample loading to reduce the interferences from Ba. A single Ta filament (7.5 mm × 0.76 mm × 0.025 mm) was used in the mass analysis. The Ta filament was first degassed at 4.0 A for 1 h to expel barium impurities, and then coated with ca. 3 μl graphite slurry containing 100 μg graphite, which was made by mixing the spectroscopic-grade graphite with an ethanol–water (80:20, v/v) solution. The slurry was allowed to evaporate to near dryness. Thereafter an aliquot of the above-prepared Ce sample (containing ca. 20 μg of cerium) was added on the filament and dried for 3 min with a current of 1.4 A passed through the filament. The Ce-loaded filament was introduced into the ion source of the mass spectrometer and an isotopic analysis was initiated when the base pressure in the instrument reached (2–3) × 10^{-7} Torr (1 Torr = 133.322 Pa). The filament current was increased to 2.7 A in 10 min. The $^{140}Ce^+$ ion beam was adjusted to (1.5–2.0) × 10^{-11} A by adjusting the filament current, which was typically 2.8–3.1 A. The ion peak height data were collected by switching magnetically over mass range from 136 to 143 after 1 h from the start of heating the filament, because the isobaric interference of Ba^+ decreased with time and usually could be ignored after a period of 60 min. In this study, fortunately, the Nd^+ was found negligible probably due to retardation in the columns after the long chromatographic migration and sample pretreatment for purification. The total time for the mass spectrometric measurement of one sample was approximately 3 h.

3. Results and discussion

3.1. Preliminary considerations

In a displacement chromatographic process, a band of the isotopic chemical species is eluted through the column

by a displacing eluent solution, which has to meet strict demands concerning the stationary phase affinity, chemical compositions, and the pH value to maintain an ideal chromatogram with self-sharpening boundaries during the whole band migration. Therefore, the very important thing is to select the suitable complexing agent to form complexes with cerium(III) ions. EDTA is well known to be used in refining of rare earth elements. In preliminary experiments of the cerium isotopic fractionation, EDTA was first selected as a ligand to prepare the eluent for developing the cerium adsorption band which was formed by feeding the cerium(III) nitrate onto the top of resin bed packed in a column. Due to the very low solubility of cerium–EDTA complex at room temperature, however, the large amount of precipitate deposited in the column during migration. We thus abandoned the Ce(III)–EDTA complex system. Then the ligand was changed to malate because malic acid was also widely used in the rare earth element technology as complexing agents in their group analysis, separation and final purification. Furthermore, in uranyl and copper isotope effect studies, the malate has shown the large separation coefficient [13,20]. As displacing cation, the ammonium ion was selected because it has relatively large selectivity and relatively low stability constant with the malate anion. Besides, the ammonium solution has a high buffer capacity, which is of important role in keeping the desired pH value constant during migration in the displacement chromatography.

3.2. An appropriate condition for long distance migration

In the cerium–malate complex formation system, short chromatographic columns of 30, 100 and 150 cm (all with 1 cm i.d.) were first used for searching for suitable conditions under which the ideal band displacement chromatography could be realized. We tried the various chemical compositions of the eluent solution and various other operating parameters. At too low pH, the Ce band could not be eluted out from the column due to insufficient complexation, resulting in tailing phenomenon. At too high pH, precipitation occurred in the column due to hydrolysis or polymerization of cerium complexes. Fig. 2 shows the chromatograms of the selected experiments with the column size: (a) 30 cm, (b) 30 cm, (c) 150 cm, and their experimental conditions are summarized in Table 2. In the case of (a), the concentration of ammonium malate was high and its pH value was a little too low so that the malate ligand in the solution pulled Ce^{3+} ions from the resin and released them into the solution phase and went down the column relative fast, resulting in short retention on the resin bed, and thus tailing phenomenon was observed. On the contrary, in the case of (b), the concentration of ammonium malate was too low to form the cerium–malate complex sufficiently, resulting in the leading phenomenon. It can be seen that even the subtle differences in composition of the eluent brought out the distinct consequences, which suggests that suitable condition for ideal displacement chromatography of cerium–malate complex system is very narrow. In the experiment (c) shown in Fig. 2, the chromatogram registered relatively sharp at the both edges of the band. We regarded this chromatogram as an ideal one, and decided the composition of solution containing 0.12 mol dm^{-3} $NH_3 \cdot H_2O$ and 0.060 mol dm^{-3} H_2L with pH 5.5, as our appropriate displacing eluent.

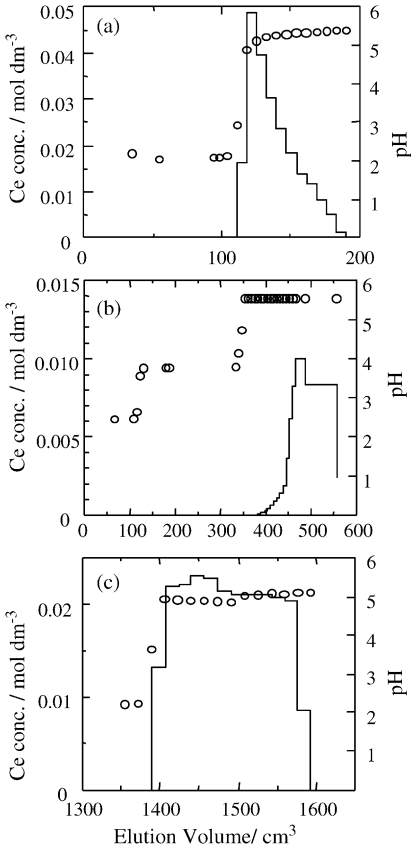

Fig. 2. Chromatograms of the selected experiments with (a) 30 cm, (b) 30 cm, (c) 150 cm column. (–) Ce concentration; (◯) pH.

3.3. Processes of cerium isotopic fractionation

Under the condition stated above, we realized the 21 m long distance migration of Ce band displaced by the eluent in the column through three and a half circles. The effluent of the Ce band was fractionated at 20 min intervals. The detailed experimental conditions are collected in Table 3. The Ce concentration profile of the effluent, which corresponds to the Ce band profile in the column, is shown in Fig. 3 together with pH values. Both the sharp boundaries of Ce chromatogram and the sudden changes of pH values in the Ce band, especially that at the frontal part, indicate that the nearly ideal displacement chromatography was performed successfully.

The reactions occurring in the ion-exchange column can be expressed in the following simple forms, by abbreviating malic acid as H_2L and the malate ion as L^{2-}:

Table 2
Experimental conditions of the selected short migration experiments

Run number	Eluent composition	Band length (cm)	Band velocity (cm h^{-1})	Flow rate (cm^3 h^{-1})	Migration length (cm)
(a)	0.30 mol dm^{-3} $NH_3{\cdot}H_2O$ + 0.15 mol dm^{-3} H_2L, pH 5.4	4	–	12.4	27
(b)	0.06 mol dm^{-3} $NH_3{\cdot}H_2O$ + 0.03 mol dm^{-3} H_2L, pH 5.6	3	0.5	25	25
(c)	0.12 mol dm^{-3} $NH_3{\cdot}H_2O$ + 0.06 mol dm^{-3} H_2L, pH 5.5	9	25	29	138.5

Note: Resin, SQS-6, porous, strongly acidic, 70–90 μm; H_2L, malic acid; operating temperature, 298 K.

Table 3
Experimental conditions of the 21 m long distant migration of cerium adsorption band

Feed	0.02 mol dm^{-3} $Ce(NO_3)_3$ 800 cm^3
Eluent composition	0.12 mol dm^{-3} $NH_3{\cdot}H_2O$ + 0.06 mol dm^{-3} H_2L, pH 5.5
Band length (cm)	41
Band velocity (cm h^{-1})	3.1
Flow rate (cm^3 h^{-1})	33.3
Migration length (cm)	2100

Note: Resin, SQS-6, porous, strongly acidic, 70–90 μm; H_2L, malic acid; operating temperature, 298 K.

At the rear boundary of the Ce^{3+} adsorption band, the ion-exchange reaction occurs between Ce^{3+} ions in the resin phase and ammonium ions in the solution phase:

$$\overline{Ce^{3+}} + (NH_4)_2L \Rightarrow \overline{2NH_4^+} + (CeL)^+ \quad (1)$$

At the frontal boundary of the Ce^{3+} adsorption band, the ion-exchange reaction occurs between H^+ ions in the resin phase and Ce^{3+} ions with solution phase:

$$(CeL)^+ + \overline{2H^+} \Rightarrow H_2L + \overline{Ce^{3+}} \quad (2)$$

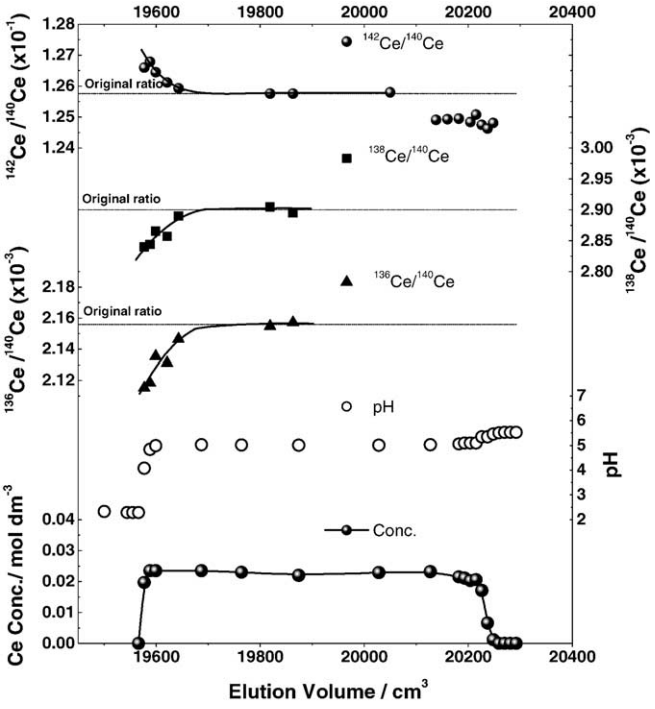

Fig. 3. Ce chromatogram and pH change, Ce isotopic ratio profile in the Ce adsorption band after 21 m long distance migration.

In the Ce adsorption band, cerium isotope exchange reactions occur between cerium–malate complexes in the external solution phase and the cerium(III) ion in the resin phase:

$$(^{140}CeL)^+ + \overline{^xCe} \Leftrightarrow (^xCeL)^+ + \overline{^{140}Ce} \quad (3)$$

In Eqs. (1)–(3), the overbar "–" denotes the resin phase, and superscript *x* the mass number 136, 138 or 142.

In this displacement chromatography, the column was first equilibrated with cerium(III) nitrate feed solution containing cerium isotopes to be separated. Ce^{3+} ions had a high affinity for the resin phase and saturated the resin phase in the upper region of the column forming the Ce adsorption band. Then the displacing eluent of ammonium malate was introduced into the column and its front traveled behind the Ce band. As the ammonium malate solution front traversed the column, the Ce^{3+} ion was coordinated with malate ions supplied by the eluent solution due to larger stability constant of the Ce–malate complex compared with that of the ammonium malate complex [23]. This reduced the charge of Ce^{3+} under the pH value 5.5, namely reduced the selectivity of the Ce^{3+} ion, and consequently, Ce^{3+} ions were displaced by NH_4^+ ions from the resin phase and released into solution phase (Eq. (1)).

When the cerium–malate complex species in the external aqueous solution phase reached the frontal boundary and contacted the preceding H^+ zone, due to relatively large concentration of H^+ and the high selectivity of Ce^{3+} to the resin phase, the cerium–malate complexes were dissociated, despite a little lower dissociation constant of malic acid (pK = 4.78) than stability constant of cerium–malate complex (pK_1 = 5.0) [23], and cerium ions were readsorbed into the resin phase, making the Eq. (2) proceed to right hand side.

Within the Ce band, the pH was kept constant (ca. 5.0). As a result, the cerium–malate complex species were constrained and the concentration of cerium was kept unchanged (ca. 0.02 mol dm^{-3}), as just reflected in the plateau region of the chromatogram shown in Fig. 3. Potentiometric study of the rare earths malate in aqueous solution showed that, in the acidic region, the cerium formed the 1:1 complex with malate ligand and assumed that the one complex, ML^+ was formed predominantly [24–28].

During the migration of the Ce band, the isotope exchange reaction took place repeatedly between Ce^{3+} ion in the resin

phase and cerium(III)–malate complex in external solution phase within the band (Eq. (3)). The cerium isotopes (initially with an original isotope abundance ratio in the band) are rearranged in the order of the distribution coefficients and consequently the fractionation of cerium isotopes took place on either side of the band because in the central region of the band there were no concentration gradients of Ce isotopes.

In Fig. 3 also were depicted the profiles of cerium isotopic ratio in the band for isotopic pairs of $^{136}Ce/^{140}Ce$, $^{138}Ce/^{140}Ce$ and $^{142}Ce/^{140}Ce$. It is obviously seen that the lighter cerium isotope was fractionated in the rear boundary region of the Ce adsorption band and the heavier was fractionated in the front boundary region. This fractionation tendency is in accord with the general conclusion that the heavier isotope is preferentially fractionated into the more strongly-bonded chemical species in the solution phase, based on the theory of isotope effects due to molecular vibration [1]. In this study, the Ce^{3+} ion in the resin phase may be taken to be in the analogous situation to that in the perchlorate solution, because the functional groups of the SQS-6 cation-exchange resin used was sulfo groups bound to benzene rings of divinylbenzene [29].

3.4. Separation factors and their evaluation

In this study, measurements were made of the total cerium isotopic fractionation which occurred when a band of cerium was eluted through a column of SQS-6 resin with an aqueous solution of ammonium malate. Isotopic fractionation in this study resulted from the reaction (3). If the reaction (3) is a solo isotope exchange reaction, the equilibrium constant, K, of this isotope exchange reaction is equal to the single-stage isotope separation factor, $\alpha(=1+\varepsilon)$, which is the ratio of the distribution coefficient of isotopic species between two phases and defined in the present system for the $^{x}Ce/^{140}Ce$ isotopic pair as:

$$\alpha = 1 + \varepsilon = \frac{[^{x}Ce/^{140}Ce]_{r}}{[^{x}Ce/^{140}Ce]_{s}} \tag{4}$$

where the brackets denote the abundance ratio of given isotopic pairs, the subscripts r and s represent the resin and solution phases, respectively, the superscript x is either value of the mass number 136, 138 or 142, and ε is the separation coefficient. The value of the separation coefficient ε is much less than unity especially for heavy elements and can be evaluated from the experimental data using the isotopic enrichment curves of the front or rear boundary according to Eq. (5) developed by Spedding et al. [2] and Kakihana and Kanzaki [3]:

$$\varepsilon = \frac{1}{Q} \times \frac{1}{R_{o}(1-R_{o})} \sum (R_{i} - R_{o}) q_{i} \tag{5}$$

$$Q = C_{av} V_{t}, \qquad q_{i} = C_{i} V_{i}, \qquad R_{i,o} = \frac{r_{i,o}}{1 + r_{i,o}}$$

where q is the amount of cerium, Q the total exchange capacity of the resin bed, C the concentration of cerium in the band in the effluent, V the effluent volume, r the $^{x}Ce/^{140}Ce$ isotopic ratio, and R the isotope atomic fraction, subscripts i, o, av, t the sample fraction number, the original feed, average value, total effluent volume, respectively, and the summarization in Eq. (5) is taken over all the fractions in which isotope fractionation is observed.

In this work, the isotope separation coefficients ε of ^{142}Ce, ^{138}Ce and ^{136}Ce against ^{140}Ce were calculated as -1.9×10^{-5}, 5.2×10^{-5} and 5.2×10^{-5}, respectively, by using the data of the lighter isotope accumulated zone, i.e., the frontal part of the Ce band, which is much sharper than that of the rear part of the Ce band.

Comparing the present results with those of the Gd isotope effects, which was also carried by the band displacement technique [15], the separation coefficients ε of cerium isotopic pair in the malate complex formation system are on the same order of magnitude and little larger than those of Gd isotope effects. This is reasonable since the Gd isotopes are slightly heavier than Ce isotopes.

From these experimental results, the separation coefficient for isotopic pair $^{138}Ce/^{140}Ce$ seems too large compared with those of the other isotopic pairs, since ε is usually proportional to the mass difference between the isotopes. At this point of the research progress, we cannot specify the reason for it. Although the interference resulting from ^{136}Ba could be eradicated within the experimental uncertainty in the cerium isotope ratio analyses, the contribution of ^{138}Ba to the ion peak at mass number of 138 was not eradicated. This is because the abundance of ^{138}Ba is about seven times as large as that of the ^{137}Ba (shown in Table 1).

Although we admit some of data are not precise enough, we claim that this is the first observation of cerium isotope effects in ion-exchange systems. We expect the present observation will substantiate the theory of isotope effects and will contribute to systematics of isotope effects of heavy elements.

Certainly we need more efforts to enhance cerium isotope fractionation more substantially and to look for more precise method for analyzing cerium isotopic ratios in order to obtain ε values with small uncertainty. A longer chromatographic development of cerium adsorption band is in progress. Since the nature of the isotopic species involved determines the magnitude of the separation factor, the influence of various physico-chemical parameters upon the separation factor of cerium isotopes in ion-exchange systems needs to be studied. Other complexing agents are also under consideration.

4. Conclusions

The present work has been the first application of displacement chromatography to cerium isotope separation. The method may have even more interesting possibilities for isotopes of elements which form a variety of complexes.

From an academic standpoint, the separation of isotopes by displacement chromatography presents a useful tool for studying isotopic species in solution. The nature of the species may sometimes be elucidated by determining small variations in the single-stage separation factor if isotope separation is promoted by certain physico-chemical parameters. These parameters may include the p*K* of the complex, pH of the aqueous solution, temperature, concentration, the nature of the isotopic species involved in the aqueous phase and other factors depending on the chemistry of the particular isotope.

Major findings of the present study may be summarized as follows:

(1) The nearly ideal band displacement chromatogram in the Ce(III) complex formation system was achieved using malate as a complexing reagent. The optimal eluent found was: $0.012\,\mathrm{mol\,dm^{-3}}$ $NH_3{\cdot}H_2O + 0.06\,\mathrm{mol\,dm^{-3}}$ malic acid with pH 5.5.
(2) The cerium adsorption band underwent 21 m of migration distance using four packed columns in a merry-go-round way. The heavier isotope was enriched in the front boundary part of the band, which means that the heavier isotope was preferentially fractionated into the cerium complex in aqueous solution.
(3) The isotope separation coefficients of ^{136}Ce, ^{142}Ce against ^{140}Ce in the malate system were 5.2×10^{-5} and -1.9×10^{-5}, respectively.

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