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Isotope effects of europium in ligand exchange system and electron exchange system using ion-exchange displacement chromatography

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Abstract

The ion-exchange chromatography of europium has been carried out to study the europium isotope effects in a ligand exchange system (LXS) and an electron exchange system (EXS). In both cases highly acidic cation-exchange resin (AG-MP 50) with 100–200 mesh size particles was used. In the case of LXS, where EDTA was chosen as a ligand for Eu^{3+} ions, the heavier isotope ^{153}Eu has been enriched at the front boundary of the europium band. Such findings mean that the heavier isotope ^{153}Eu is preferentially fractionated into the EDTA complex form in the solution phase. In the EXS, where Eu(II)–Eu(III) exchange reaction takes place, the heavier isotope ^{153}Eu has been observed to be enriched in the front part of the europium band. The result shows that the heavier isotope is preferentially fractionated in the Eu(II) solution phase. The values of the single stage separation coefficients ($\varepsilon = S - 1$) of the $^{153}Eu/^{151}Eu$ isotopic pair have been calculated for LXS as $1.48 \cdot 10^{-5}$ at 80°C and for EXS as $2.13 \cdot 10^{-4}$ at 60°C. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many successful methods have been developed for the separation of isotopes utilizing slight differences in physical or chemical properties. The first successful separation of neon isotopes by Aston (gaseous diffusion, 1913, and mass spectroscopy, 1919) and the introduction of the separation cascade concept by Hertz in 1932 were milestones in the evolution of an entirely new industry devoted to the separation of the isotopes of elements ranging from hydrogen to uranium [1]. Taylor and Urey [2] were the first to investigate the isotope separation of lithium using an ion-exchange technique in 1938. That pioneer work was followed by the studying of the isotope effects in chemical exchange of light elements [3–8], medium elements [9–16], and heavy elements [17,18] etc. Europium (Eu) isotope effects have been studied using the liquid–liquid solvent extraction technique [1,19] and the precipitation method [1].

The aim of this work is to study the separation of Eu isotopes using ion-exchange displacement chromatography on both the ligand exchange system (LXS) and the electron exchange system (EXS). The separation of Eu isotopes by ion-exchange displacement chromatography is of interest since the isotope effects of other lanthanides elements have been studied [18,20]. Moreover, several practical applications are anticipated for separated Eu isotopes (e.g., ‘custom tailored‘ burnable poisons for research reactors) [1]. In a previous study on the isotope effects of uranyl complex-formation ion-exchange

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chromatography, the malic acid eluent system showed a large separation coefficient among some selected uranyl carboxylate complexes [21]. While in another study on the isotope effects of gadolinium in LXS [18], EDTA showed a larger separation coefficient than malic acid. In the present work we apply EDTA as the ligand for Eu(III) complex formation system.

The utilization of the redox system for the separation of uranium isotopes gives a relatively high separation factor compared to ligand systems [22]. Recently isotope effects in redox systems have been concerned from the view point of the nucleus–electron interactions [23,24]. As Eu has two ionic state of Eu(II) and Eu(III) in aqueous solutions, it is possible to find an isotope effect in the Eu(II)–Eu(III) exchange reaction. In the present work the isotope effects in the chemical exchange are determined by the ion-exchange displacement band chromatography in the case of LXS and by breakthrough chromatography in the case of EXS.

2. Experimental

2.1. Ion-exchange resin and reagents

The ion-exchange resin used in both LXS system and EXS system was a macroporous strongly acidic cation-exchange resin (Bio-Rad, AG-MP 50, 100–200 mesh size). Eu_2O_3 99.9% was supplied by Wako, and converted to $EuCl_3$ without further purification. All other reagents used were of analytical grade and employed without further purification.

2.2. The LXS

Eu isotope separation experiment based on the EDTA complex formation was carried out with a cyclic displacement chromatography system which was composed of three glass columns (100×0.8 cm I.D., with water jacket) connected in series with a PTFE tube (1 mm I.D.) so that they were repeatedly used in merry-go-round way for a total migration length of 7 m. These columns were packed uniformly with the above-mentioned resin. The resin was pretreated with 2 *M* HCl solutions to remove impurities and converted to H^+ form. This was followed by passing a solution of 0.1 *M* of $CuCl_2$ to convert the resin into Cu^{2+} form. Then a 0.1 *M* $EuCl_3$ solution was fed into the first column at a constant flow-rate by a peristaltic pump to form a Eu^{3+} adsorption band. When the Eu^{3+} ion adsorption band had grown to an appropriate length of 41 cm, the supply of the feed solution was stopped. The Eu^{3+} and Cu^{2+} adsorption bands were eluted by an eluent solution containing 0.05 *M* $(NH_4)_2EDTA$+ 0.1 *M* NH_4NO_3 adjusted to pH 7.5 with an NH_4OH solution. After adjusting the pH to 7.5, it is expected that the four carboxylic groups of the EDTA will be occupied by NH_4^{+1}. This was supported by a pH titration test of EDTA, of which the four carboxylic groups are in H^+ form, with NH_4OH. The eluent was fed at the same flow-rate as that of the feed solution. The adsorption band of Eu^{3+} was visible, white, in contrast with the preceding blue Cu band. When the Eu^{3+} adsorption band migration length reached seven meters, it was eluted out from the last column. The effluent was collected in small fractions which were, thereafter, subjected to the concentration analysis and the isotopic analysis.

2.3. The EXS

Two glass columns with the same type as used in the LXS experiment were packed with the same resin used in the LXS. The resin of these columns was converted into H^+ form by feeding a 2 *M* HCl solution to the columns. Then 0.1 *M* $FeCl_3$ solution was fed to the columns to convert them into Fe^{3+} form. A H-shaped electrolysis cell with cation-exchange membrane was used to reduce $EuCl_3$ to $EuCl_2$. The cathode of the cell was mercury highly purified by bubbling three times with HNO_3 solutions followed with pure water bubbling and finally by distillation under vacuum two times. The cathode compartment contained 0.1 *M* $EuCl_3$ at pH 0.9 covered with oxygen-free nitrogen. The anode was Pt wire and the anode compartment contained an acidic solution at the same pH as the cathode one. When almost 100% reduction was achieved, the Eu^{2+} solution was directly fed to the columns from the electrolysis cell while the cell was still activated to assure no reoxidation. When the Eu(II) adsorption band was eluted out from the second column, the

effluent was collected into small fractions, and the fractions were subjected to the concentration analysis and the isotopic analysis.

The temperatures of the columns were kept constant at 80±0.2°C in the LXS and at 60±0.2°C in the EXS by circulating the thermostatted water through the water jackets surrounding the columns. The set of apparatus for the chromatographic experiments in LXS and in EXS are illustrated in Figs. 1 and 2, respectively. The experimental conditions for LXS and EXS are summarized in Table 1.

2.4. Analysis

The concentration of Eu in each fraction of the effluents was determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) system Model SPS 1500VR, Seiko Instruments at a wavelength of 381.967 nm. The concentration of Eu^{2+} was measured by adding an excess amount of Fe^{3+} ions to the known volume of the sample. The reduced Fe^{2+} by Eu^{2+} was titrated against potassium permanganate solution. The end point was determined by drawing a curve between the solution potential and the volume of the added potassium permanganate solution. The $^{153}Eu/^{151}Eu$ isotopic ratios of Eu samples were measured by using a MAT 261 mass spectrometer with a thermal ionization method. The filament unit for sample ionization comprises two filaments made of rhenium ribbon; one is for sample vaporization and the other is for ionization. A 1-μg Eu sample was loaded on the surface of a vaporizing filament and dried by heating with an electric current about 1.7 A for 1 min. The filament unit loaded with a sample was inserted into the ion source of the mass spectrometer. Then the ion source system was pumped down to pressure of $2.7\sim4\cdot10^{-4}$ Pa. Liquid nitrogen was fed to the cold-trap which further reduced the pressure to $7\cdot10^{-5}\sim1.3\cdot10^{-4}$ Pa. A current of 1 A was applied to the ionization filament for heating. Then the ionization current was slowly increased by adding 0.5 A every 3 min in a stepwise manner. The vaporization filament current was increased to 0.6 A when the ionization current reached 2 A. Then the vaporization filament current was increased by 0.2 A every 3 min. Eu ion beam appeared when the ionization filament current reached ~4 A and the vaporization current reached ~1.4 A. After setting the magnetic field, ^{153}Eu and ^{151}Eu mass peaks were repeatedly recorded by a Faraday cup collector. For the measurement of isotopic ratio, the mass scanning of the

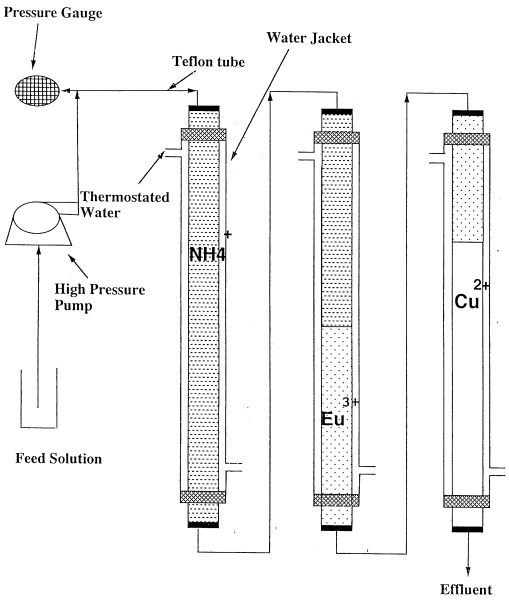

Fig. 1. Schematic of separation column system in the LXS for Eu isotope separation.

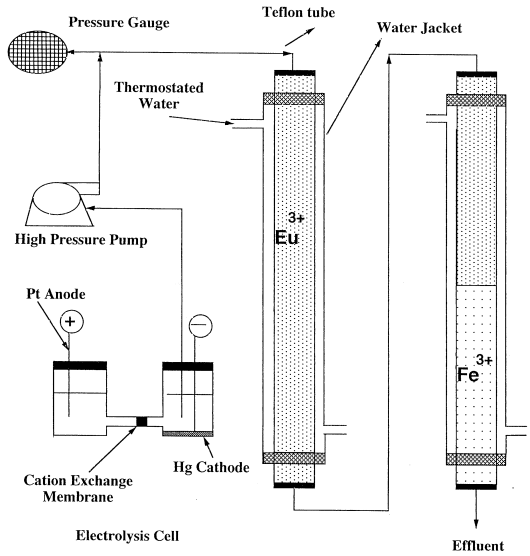

Fig. 2. Schematic of separation column system in EXS for Eu isotope separation.

Table 1
Experimental conditions in the LXS and the EXS

System	LXS	EXS
Resin	Strongly acidic cation-exchange resin (AG MP 50, 100–200 mesh size)	Strongly acidic cation-exchange resin (AG MP 50, 100–200 mesh size)
Pretreatment	2 *M* HCl followed by 0.1 *M* $CuCl_2$ to convert resin into Cu^{2+} form	2 *M* HCl followed by 0.1 *M* $FeCl_3$ to convert resin into Fe^{3+} form
Feed solution	0.1 *M* $EuCl_3$	0.1 *M* $EuCl_2$
Eluent	0.05 *M* EDTA·$4NH_4$ + 0.1 *M* NH_4NO_3 at pH 7.5	
Column size	100 cm×0.8 cm I.D.	100 cm×0.8 cm I.D.
Eu band length	70 cm	–
Migration length	7 m	2 m
Temperature	80°C	60°C
Flow-rate	0.32 ml/min	0.226 ml/min
Band velocity	0.06 cm/min	0.08 cm/min

pair of the isotopes was repeated six times in a block, and, in all cases, four blocks were recorded as one measurement. The isotopic ratios of a block were calculated by averaging all the peak height ratios of the recorded peaks of ^{153}Eu and ^{151}Eu. The measuring time was approximately 1 h and the total time for one measurement was about 2 h.

3. Results and discussion

3.1. LXS

The chemical exchange reactions involved in the LXS first takes place at the interface between NH_4^+ and Eu^{3+} adsorption bands. When $(NH_4)_4$EDTA reached the front boundary of Eu^{3+} adsorption band, the EDTA ligands are transferred to Eu^{3+} because of the large stability constant of the Eu–ligand complex formation compared to that of ammonium ion (Eq. (1)). During the moving down of the Eu–ligand complex species through the Eu^{3+} adsorption band in the column, the isotopic exchange reaction takes place between Eu^{3+} ions in the resin phase and Eu–ligand complex species in the solution phase (Eq. (2)). After that the Eu–ligand complex reaches the Cu^{2+} ion band, where ligand are transferred to Cu^{2+} ions and Eu^{3+} ions are adsorbed in the resin phase (Eq. (3)). The relating chemical reactions could be expressed, in the most simple form, as

$$(NH_4)_4 - L + \underline{Eu^{3+}} + H^+ \rightarrow 4\underline{NH_4^+} + Eu - L - H \quad (1)$$

$$^{153}\underline{Eu^{3+}} + {}^{151}Eu - L - H \leftrightarrow {}^{151}\underline{Eu^{3+}} + {}^{153}Eu - L - H \quad (2)$$

$$Eu - L - H + \underline{Cu^{2+}} + H^+ \rightarrow \underline{Eu^{3+}} + Cu - L - 2H \quad (3)$$

where the underlines represent the species in the resin phase and L represents ligand. The concentration of Eu in the plateau region of the chromatogram, 0.04 mol, and the concentration of EDTA in the eluent feed, 0.05 mol, were used to perform a charge balance analysis for Eu–L complex. The analysis shows that only 60% of the carboxylic groups in EDTA are coordinating with Eu. The rest is assumed to be coordinating with H^+ initially sorbed mixing with Cu and Eu ions in the band [18]. This is supported by the low pH value of the plateau region of the chromatogram as shown in Fig. 3. In fact, the chemistry of the system may be much more complicated than that represented by Eqs. (1)–(3). The exact complex structure and the different possibilities of Eu and/or water hydrolysis are out of the scope of the present work.

The chromatogram of Eu in the LXS after 7 m long migration and the isotope abundance ratio observed in the displacement band are shown in Fig. 3. The dotted line shows the isotopic abundance ratio in the feed solution. It can be seen that the heavier isotope ^{153}Eu is enriched into the front part, or preferentially fractionated in the complex form in the solution phase. This tendency is the same as that observed in the chromatographic isotope separation

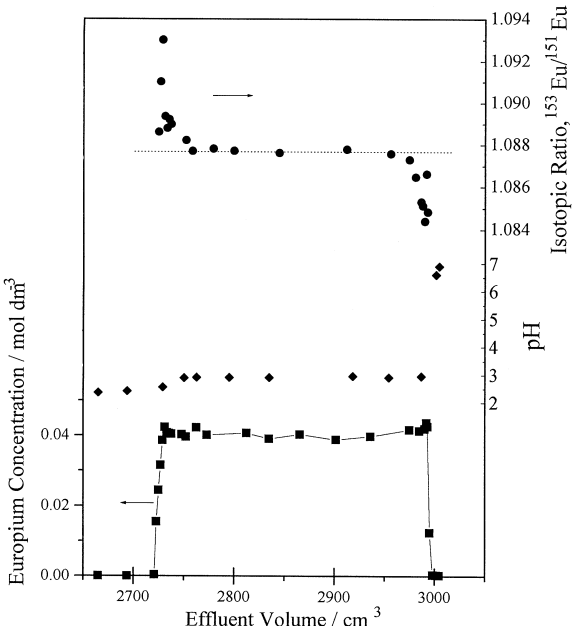

Fig. 3. Concentration profile, pH profile and the isotopic distribution in Eu band displaced by EDTA (LXS).

of calcium [9–11], magnesium [12] strontium [13], gadolinium [18] and copper [16]. Since the heavier isotope is enriched in the complex species, the observed isotopic enrichment tendency accords with the theoretically expected direction of the isotopic effects in chemical exchange.

The single stage separation factor, $S=(1+\varepsilon)$ for the ^{153}Eu/^{151}Eu isotopic pair is defined here as:

$$S=([^{151}\underline{Eu}]/[^{153}\underline{Eu}])/([^{151}Eu]/[^{153}Eu]) \quad (4)$$

where the underlines represent the species in the resin phase. The separation coefficients, ε, were calculated using the isotopic enrichment curves of the front and rear boundaries according to the equation developed by Spedding et al. [25], and Kakihana and Kanzaki [26]. The mathematical average of the two values obtained from the front and rear boundaries was taken to calculate the process separation coefficient ε. The calculated value of ε from the front part of the chromatogram is $1.59\cdot10^{-5}$ and that from the rear part is $1.36\cdot10^{-5}$, giving an average value of $(1.48\pm0.11)\cdot10^{-5}$.

The separation coefficients of the LXS have been found to be much smaller than those of gadolinium [27] and samarium [20] previously reported by Aaltonen. However, they accord with separation coefficients of gadolinium reported by Chen et al. [18].

3.2. EXS

The Eu(II)–Eu(III) system has a very low standard electrode potential of −0.429 V. This indicates the fact that Eu(II) ions are easily oxidized to Eu(III) by Fe(III) ions. As the selectivity of the cation-exchange resins generally increase with the cation valence, Fe(III) ions are reduced to Fe(II) and released from the cation-exchange resin, when Eu(II) eluent reaches the rear boundary of the Fe(III) adsorption band. The redox reaction, taking place at the interface between Fe(III) adsorption band and Eu(II) eluent, is given by:

$$\underline{Fe^{3+}}+Eu^{2+}\rightarrow Fe^{2+}+\underline{Eu^{3+}} \quad (5)$$

The feed Eu(II) ions flow down through the Eu(III) adsorption band in the chromatographic column. During the passing down of Eu(II) ions through the adsorption band, the isotopic electron exchange reaction takes place between Eu(II) and Eu(III) ions. The reaction is given by Eq. (6):

$$^{153}\underline{Eu^{3+}}+{}^{151}Eu^{2+}\leftrightarrow{}^{151}\underline{Eu^{3+}}+{}^{153}Eu^{2+} \quad (6)$$

The observed concentrations and isotopic abundance ratios of Eu are plotted in Fig. 4. Apparently ^{153}Eu is enriched in the front boundary region. The results clearly indicate that the lighter isotope of ^{151}Eu is fractionated into Eu(III) adsorbed in the resin phase. This fact means that the isotopic equilibrium constant of Eq. (6) is larger than unity or the equilibrium shifts slightly to the right hand side. The irregular decrease in the isotopic ratio in the first eluted samples is due to the channelling on the surface of the column wall, wall effect. Accordingly, a small amount of Eu solution from the Eu band bulk, with smaller isotopic enrichment, passed by the wall and preceded the boundary. When the band started to elute from the column, these amount came first and shown a lower values for Eu concentration and isotopic ratio. From our experience with chroma-

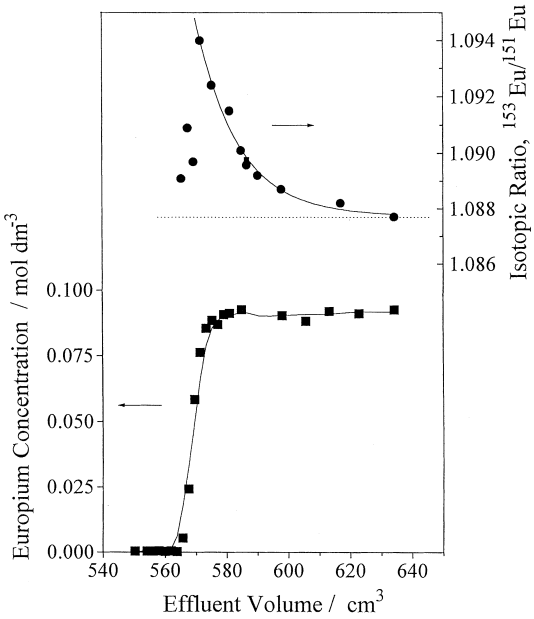

Fig. 4. Concentration profile and isotopic distribution in Eu breakthrough chromatography (EXS).

tography, decreasing the band velocity and/or increasing the column diameter reduces such an effect.

From the data presented in Fig. 4, separation coefficient ε of the EXS is calculated in the same way as previously described for the LXS. The calculated separation coefficient is $(2.13\pm0.2)\cdot10^{-4}$ in the present EXS.

The amount of Fe^{2+} ion in the effluent solution was measured by titration and found to be about 66% of the total Fe in effluent solution on mole basis. Since Fe^{2+} ions are practically not sorbed in the Fe^{3+} ion type resin, Fe^{3+} ions in the solution phase are regarded as being released from the resin by Eu^{3+} ions existing in the solution phase. Eu^{3+} ions, which is originally produced by Eq. (5) and sorbed by resin, was partially eluted by Eu^{2+} ions fed to the column. When this amount of Eu^{3+}, eluted by Eu^{2+} and exists in the solution phase, reaches the interface between Eu band and Fe band, it replace Fe^{3+} ions according to Eq. (7):

$$\underline{Fe^{3+}} + Eu^{3+} \rightarrow Fe^{3+} + \underline{Eu^{3+}} \tag{7}$$

This means that both Eu^{3+} and Eu^{2+} can coexist in both resin and solution phases. Since the concentration of Fe^{3+} in the solution phase corresponds to the concentration of Eu^{3+} in the solution phase, the Eu(II) and Eu(III) mole fraction in the solution phase are estimated as 0.66 and 0.34, respectively.

The sorption of Eu^{2+} ions in the resin phase was also supported by the analysis of the exchange capacity of the ion-exchange resin in the column under the condition of Eu(II) feeding. Since the total capacity of the amount of the resin in the column and the total feed of Eu^{2+} ions are known, the amount of sorbed Eu^{2+} ions is calculated from the ion balance in the column. The analysis suggests 30.02% of the Eu ions sorbed by the resin is in the form of Eu(II). Then, the average mole fraction of Eu(II) and Eu(III) in the resin phase are estimated as 0.3 and 0.7, respectively.

This is presumably the reason why the separation coefficient of EXS ε is smaller than the reported value of $7\cdot10^{-4}$ by Dembinski and Mioduski [19], who used the solvent extraction method where Eu(III) was contained in di-(2-ethylhexthyl) phosphoric acid (HDEHP), and Eu(II) was contained in hydrochloric acid solution. The separation coefficient of EXS was also smaller than the value reported by Schneider [1], $6.4\cdot10^{-4}$. In his work a seven-stage extraction cascade was employed using a solvent of HDEHP–$C_{12}H_{26}$ (1:1). In addition, he reported the separation coefficient of $6\cdot10^{-4}$ for the Eu^{2+}/Eu^{3+} exchange system in the precipitation of Eu(II) in sulfate form.

In solvent extraction system, Eu(III) practically exists only in the solvent phase and Eu(II) only exists in the solution phase. In such a case the separation factor becomes equal to the isotopic equilibrium constant K of Eq. (6). On the other hand, when concerned two chemical species coexist in both phases, the calculated separation factor is not equal to the equilibrium constant K of Eq. (6). In this case the isotopic equilibrium constant is given by Eq. (8) [28]:

$$\varepsilon = (K-1)(\chi_{II} - \chi_{\underline{II}}) \tag{8}$$

where χ_{II} and $\chi_{\underline{II}}$ are the mol fractions of Eu(II) in the solution phase and the resin phase, respectively. As we can express $K-1=\varepsilon_0$, the theoretical separation coefficient, ε_0, is derived from Eq. (8). Based on the above mentioned values of $\chi_{II}=0.66$ and $\chi_{\underline{II}}=0.3$ the calculated theoretical separation coeffi-

cient ε_0 is $(6\pm1.1)\cdot10^{-4}$ which agrees with the separation coefficients reported by Dembinski and Mioduski [19] and by Schneider [1] within the experimental errors.

The results show that the EXS has much larger isotope effect than the LXS has. This makes the study of the process mechanism is of great interest to find out the most appropriate process for Eu isotopes separation. Moreover, the separation coefficient of EXS would be improved by using the resin which is much more selective towards Eu(III).

4. Conclusions

(1) The ideal displacement chromatogram in the LXS was obtained using EDTA as a complex reagent for a relatively long migration.

(2) The heavier isotope ^{153}Eu was clearly found to be enriched at the front boundary of Eu adsorption band and lighter isotope ^{151}Eu was enriched at the rear boundary in the LXS.

(3) The isotope effect between Eu(II) and Eu(III) was measured in the EXS. The heavier isotope ^{153}Eu was found to be enriched at the Eu(II) side and lighter isotope ^{151}Eu was enriched at the Eu(III) side.

(4) The observed separation coefficient for LXS is $1.48\cdot10^{-5}$ at 80 ± 0.2°C and is $2.13\cdot10^{-4}$ at 60 ± 0.2°C in the case of EXS.

(5) The theoretical separation coefficient is estimated for EXS as $(6\pm1.1)\cdot10^{-4}$ which well accords with the reported one.

(6) The results show that the EXS has much larger isotope effect than the LXS.

Acknowledgements

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