Mass Dependence of Uranium Isotope Effects in the U(IV)−U(VI) Exchange Reaction

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Abstract: Isotope separation of ^{233}U by anion exchange chromatography based on the U(IV)−U(VI) exchange is studied. After long-distance migration, ^{233}U enrichment is observed at the rear band boundary. To examine the isotope effects of ^{233}U, ^{234}U, and ^{238}U, three-isotope plots of local enrichment factors are constructed for the isotopes contained in sample fractions of the eluted uranium band. The results clearly show an anomalous mass dependence for ^{233}U. We previously reported that the even-mass nuclides ^{232}U, ^{234}U, ^{236}U, and ^{238}U show a regular mass-dependence in their isotope separation behaviors, while ^{235}U does not fall on the same line. The isotope effects of the odd-mass nuclides ^{233}U and ^{235}U deviate from the linear mass dependence observed among the even-mass nuclides. The isotope effects observed in chemical exchange are shown to be closely related to the isotope shifts in the atomic spectra of uranium isotopes.

Introduction

Isotope effects in the U(IV)−U(VI) exchange system have been extensively studied in an attempt to develop a uranium enrichment process based on chemical exchange. Pioneering work on the chemical exchange system was first carried out in 1948 by Woodard et al.[1] using UCl_4 and UO_2Cl_2. They reported an isotopic equilibrium constant of 1.0012, where the lighter isotope ^{235}U was enriched in U(VI). In 1949, Twichell[2] investigated an electromigration process involving the U(IV)−U(VI) redox reaction and found that the lighter isotope ^{235}U was enriched in U(VI). The possibility of applying ion exchange chromatography to the U(IV)−U(VI) exchange system for uranium enrichment was studied by Shimokawa[3] using a cation exchange resin and by Gonda[4] using an anion exchange resin. Shimokawa reported depletion of ^{235}U at the uranium band boundary where uranium, U(IV), is oxidized by Fe(III) ions. Gonda found that the U(IV)−U(VI) electron exchange reaction rate increased in the presence of concentrated HCl. More recently, anion redox chromatography utilizing Ti(III) as a reducing reagent and Fe(III) as an oxidizing reagent was developed by Asahi Chemical Industries[5] and Tokyo Institute of Technolgy.[6] During the intensive development work, which lasted approximately 20 years, the Asahi R&D group developed the "Asahi Super Process" which enables recovery of the reducing and oxidizing reagents used in the process. These achievements are reported in refs 7−12. The experimental arrangements for the uranium redox chromatography used in the present work are based on the Asahi Super Process.

As mentioned above, it is well-known that the light isotope ^{235}U is enriched in U(VI), which is in the form of UO_2^{2+} ion in aqueous solution, rather than in U(IV), which is in the simple form of U^{4+}. Theoretically, ^{238}U should be enriched in UO_2^{2+} due to the strong bonds between U and two oxygen atoms. However, the experimental results have been puzzling. The origins of chemical isotope effects in the U(IV)−U(VI) exchange reaction on the mass dependence of isotope effects among ^{234}U, ^{235}U, ^{236}U, and ^{238}U[13,14] were therefore studied, and this work has recently been extended to ^{232}U.[15]

The results of these studies clearly show that the magnitude of isotope effects for even-mass isotopes, i.e., ^{232}U, ^{234}U, and ^{236}U, is linearly correlated to the mass difference between these isotopes and the reference isotope, ^{238}U. So far, only the odd isotope ^{235}U has been shown to deviate from the linear relationship observed for the even-mass nuclides. Therefore, the behavior of the remaining odd-mass nuclide, ^{233}U, is of great interest. This paper will discuss the isotope effect of ^{233}U in the U(IV)−U(VI) exchange system.

Experimental Section

Chromatography. Uranium redox chromatography was performed with the feed uranium containing ^{233}U in addition to the naturally occurring ^{234}U, ^{235}U, and ^{238}U. The feed uranium also contained a trace amount of ^{232}U. Four units of columns made of a titanium alloy, 2 cm i.d. and 1 m long, were connected in series and cyclically used. Each column was packed with Asahi-AR01, a highly-porous strongly-basic anion exchanger embedded in porous silica beads ca. 50 μm in diameter.

At the beginning of the chromatographic operation, the column system was divided into two groups: each consists of two columns

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connected in series. A uranium solution, 0.1 M U(VI) in 3.6 M HCl, was fed into the columns of the first group to form a uranium adsorption band. The band was eluted with an eluent containing 3.5 M HCl, 0.6 M trivalent vanadium, V(III), which is a reducing reagent, and 1 M Fe(II), which is a catalyst of the U(IV)−U(VI) electron exchange reaction. The effluent was fed into the columns of the second group, where the packed anion exchange resin was initially loaded with an oxidizing-reagent solution consisting of 0.6 M oxovanadium ion, V(IV), 1.58 M ferrous ion, Fe(II), and 5.2 M HCl. When the uranium band was completely eluted out of the first column group and sent to the second column group, all the columns were connected in a closed cycle manner. Then the effluent was recycled as an eluent by a pump set in the column system at the flow rate of 32 cm^3/min (0.53 cm^3/s).

To detect the U(VI) and Fe(III) ion bands, a photoanalyzer was set in the column system. When the oxidizing Fe(III) ion band was consumed, almost every hour, the column system was opened and the redox-reagent solutions were fed into the columns. Then the close mode recycling operation was continued. In the present experiment, approximately 50% of the redox reagents were recovered and recycled. Column temperature was controlled by a circulating oil bath maintained at 433 K (160 °C). The uranium adsorption band, which was 1.4 m long, was eluted at a rate of 90.3 m/day (1.05×10^{-3} m/s). The total migration length was 192.6 m.

After migration, the effluent was collected in fractions of approximately 5 or 10 cm^3 each and purified with small ion exchange columns to remove V and Fe ions and other impurities. The concentration of uranium in each sample fraction was measured by colorimetry at 390 nm.

Mass Spectrometry. The isotopic abundance ratios among ^{233}U, ^{234}U, ^{235}U, and ^{238}U were measured by mass spectrometry using a MAT-261 mass spectrometer equipped with a thermal ionization ion source. The minor isotopes ^{233}U and ^{234}U were determined relative to ^{235}U using a secondary electron multiplier (SEM) collector. The major isotopic pair ^{235}U/^{238}U was detected by a Faraday Cup collector. The isotopic ratios of minor isotopes were determined from the observed peak heights, after multiplying the peak height ratios by the square root of the isotope mass ratios in the conventional manner used for the correcting the isotopic abundance ratio meausurements made with a SEM type collector.[13,14]

Results and Discussion

The chromatographic operation was conducted using the “Super Process” developed by Asahi Chemical Industries. The eluting solution initially contained V(III) as the reducing reagent and highly concentrated Fe(II). When the solution contacted the uranium band, U(VI) was reduced to U(IV) and released to the solution phase, and V(III) was oxidized to V(IV). In the solution phase of the uranium band, redox equilibrium was attained between the U(IV), V(IV), and Fe(II) ions. At the front boundary of the uranium band, where the Fe(III) chloro-complex ion had been adsorbed in the anion exchange resin, U(IV) was oxidized by Fe(III) to U(VI) and adsorbed in the resin. After uranium was removed from the solution, the solution contained mainly Fe(II) and V(IV).

According to the Nernst equation, both the Fe(III)/Fe(II) pair and the V(IV)/V(III) pair can coexist in an equilibrium state, although the concentration of Fe(III) is very small compared to that of Fe(II). Although V(IV) is not usually regarded as an oxidizing reagent for Fe(II) from the viewpoint of standard electrode potentials, some amount of Fe(III) is generated in the presence of V(IV). Vanadium(IV) is reduced to V(III) in the presence of a large excess of Fe(II):

$$\mathrm{V(IV)} + \mathrm{Fe(II)} = \mathrm{V(III)} + \mathrm{Fe(III)} \qquad (1)$$

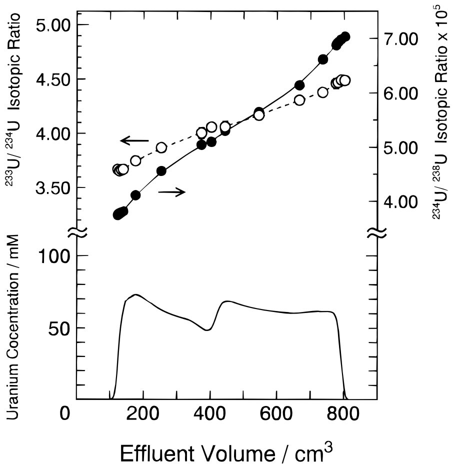

Figure 1. Uranium concentration profile and isotope separation observed in the uranium band: (○) ^{233}U/^{234}U; (●) ^{234}U/^{238}U.

Table 1. Uranium Isotopic Abundance Ratios in Sample Fractions[a]

sample	^{233}U/^{235}U	^{234}U/^{235}U	^{235}U/^{238}U	ln $\beta_{(233/234)}$	ln $\beta_{(234/238)}$
12	0.02596(12)	0.007070(33)	0.005299(4)	−0.1120	−0.3557
13	0.02601(10)	0.007113(32)	0.005318(4)	−0.1160	−0.3458
14	0.02613(9)	0.007124(23)	0.005331(6)	−0.1130	−0.3419
15	0.02610(11)	0.007106(33)	0.005369(7)	−0.1117	−0.3374
22	0.02700(5)	0.007198(21)	0.005709(9)	−0.0907	−0.2632
30	0.02817(6)	0.007278(35)	0.006272(5)	−0.0592	−0.1579
42	0.02947(33)	0.007356(11)	0.006864(18)	−0.0249	−0.0572
45	0.02974(14)	0.007323(34)	0.006967(9)	−0.0113	−0.0467
49	0.03012(9)	0.007415(74)	0.007150(12)	−0.0110	−0.0083
59	0.03108(10)	0.007452(39)	0.007581(15)	0.0155	0.0551
71	0.03223(13)	0.007480(40)	0.008210(34)	0.0480	0.1386
81	0.03347(10)	0.007642(46)	0.008660(11)	0.0644	0.2134
89	0.03420(16)	0.007663(48)	0.008975(17)	0.0831	0.2520
90	0.03431(6)	0.007670(37)	0.009034(12)	0.0854	0.2594
92	0.03445(7)	0.007664(29)	0.009113(8)	0.0903	0.2673
94	0.03454(6)	0.007691(29)	0.009145(12)	0.0894	0.2743
feed	0.03048(19)	0.007421(49)	0.007204(6)		

[a] Standard deviation σ is indicated in parentheses following the last significant figure.

Since the anion exchange resin has a strong affinity for Fe(III) chloride complexes, Fe(III) ions generated in the process are adsorbed in the anion exchange resin and an Fe(III) adsorption band is created in front of the uranium adsorption band. After most of the V(IV) has been consumed by reaction 1, the effluent contains mainly Fe(II) and V(III). This means that the oxidizing reagent, Fe(III), and the reducing reagent, V(III), are regenerated from Fe(II) and V(IV). The effluent containing V(III) is recycled to the top of the next column as the eluent for the uranium band. As mentioned in the Experimental Section, approximately 50% of the redox reagents were recovered by this process in the present work.

The chromatographic profile of the uranium band is shown in Figure 1 together with the enrichment curve for ^{233}U/^{234}U and ^{234}U/^{238}U. The measured isotopic abundance ratios of uranium isotopes (^{233}U/^{235}U, ^{234}U/^{235}U, and ^{235}U/^{238}U) in the sample fractions are listed in Table 1. The separation coefficient is defined as,

$$\epsilon = S - 1 \qquad (2)$$

where S is the unit-stage isotope separation factor of the experimental system determined from the observed isotope enrichment profile in the chromatogram. As seen in Figure 1, however, there is no plateau between the enrichment portion and the depletion portion in the uranium band. Remixing has aparently taken place between the enrichment and depletion portions, and consequently the separation coefficients cannot be determined from the isotope enrichment profile. However, the relative magnitude of the separation coefficients for all coexisting isotopes can be determined using three-isotope plots, as explained in the previous papers.[13,14]

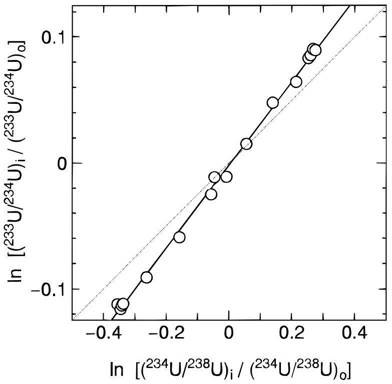

Figure 2. Three-isotope plot of local isotopic enrichment factors between isotopes of ^{233}U, ^{234}U, and ^{238}U for eluted uranium samples: subscripts i and o refer to eluate fraction number and feed, respectively. Dotted line indicates relation of normal mass dependence with slope of 1/4.

Table 1 shows the local enrichment factors for ^{233}U and ^{234}U calculated from the measured isotopic ratios. The isotopic local enrichment factor β is defined as

$$\beta_{(j/k)} = r/r_o \tag{3}$$

where r is the isotopic ratio of the isotopic pair j and k and the subscript o denotes the feed. The correlation between the enrichment behavior for different isotopes can be determined by plotting the local enrichment factor of an isotopic pair against that of another isotopic pair. This is known as the three-isotope plot method which as been used mainly in geochemistry and cosmochemistry to analyze isotopic fractionation in minerals.

The three-isotope plots made for ^{233}U, ^{234}U, and ^{238}U in the present work are shown in Figure 2. The circles of plotted data in Figure 2 cover their error ranges which are calculated from the values of σ listed in Table 1. Since the mass difference of the ^{233}U/^{234}U isotopic pair is unity and that of the ^{234}U/^{238}U pair is four, the slope of the plots in Figure 2 should be equal to 1/4 (dotted line in the figure), if the normal mass effect were to hold for the isotopic enrichment in the U(IV)−U(VI) exchange system. However, it is apparent from Figure 2 that the slope is larger than 1/4; the actual value is 0.330. This means that the odd nuclide ^{233}U does not show the same linear mass dependence observed among the even-mass nuclides, ^{232}U, ^{234}U, ^{236}U, and ^{238}U. This confirms that the "anomaly" previously observed for ^{235}U is also present with ^{233}U, another odd-mass nuclide in the uranium isotope family.

The slope of the three-isotope plot is equal to the ratio of the separation coefficients ϵ of the isotopic pairs. In order to compare the slopes of all isotopic pairs, the ^{235}U/^{238}U pair is taken as a reference pair. The slope θ calculated for each pair is listed in Table 2 and plotted in Figure 3.

The apparent mass difference effect (AMDE) is defined as the relative ratio of the separation coefficient ϵ and consequently as the relative ratios of θ for each isotope pair. The AMDE's have been calculated and are listed in Table 2, where the AMDE value for the ^{234}U/^{238}U pair is set to 4.0 to equate to the mass difference. Thus, AMDE values for the other isotopes are normalized against ^{234}U. Previously observed results for ^{232}U, ^{234}U, ^{235}U, and ^{236}U have also been included in Table 2. It is clear from the table that the AMDE's of ^{233}U and ^{235}U are higher than the values that would be predicted from the normal mass dependence. The deviation in AMDE for ^{235}U corresponds to 0.5 atomic mass units. In the present work, the deviation in AMDE for ^{233}U corresponds to 0.3 atomic mass units. Thus AMDE is expressed by

Table 2. Summary of Uranium Isotope Effects in U(IV)−U(VI) Exchange

isotopic pair	$\theta^a \pm \sigma$	AMDE^b	ΔM	remarks
^{236}U/^{238}U	0.5684 ± 0.0064	2.0	2.0050	ref 14
^{235}U/^{238}U	1	3.5	3.0068	control
^{234}U/^{238}U	1.1392 ± 0.0030	4.0	4.0098	ref 13
	1.1447 ± 0.0023	4.0		ref 14
	1.1421 ± 0.0049	4.0		this work
^{233}U/^{238}U	1.5188 ± 0.0055	5.3	5.0113	this work
^{232}U/^{238}U	1.6932 ± 0.0463	6.0	6.0136	ref 15 (α-spectrometry)

[a] θ = slope of the three-isotope plot relative to the ^{235}U/^{238}U pair defined by the following: $\theta = \ln \beta_{(j/238)}/\ln \beta_{(235/238)}$, where j = 232, 233, 234, 235, and 236. [b] AMDE (apparent mass difference effect) is the ratio of separation coefficient, ϵ, calculated to evaluate the mass difference effects with a reference value of 4.0 for the ^{234}U/^{238}U isotopic pair which appears in all experiments reported by the authors.

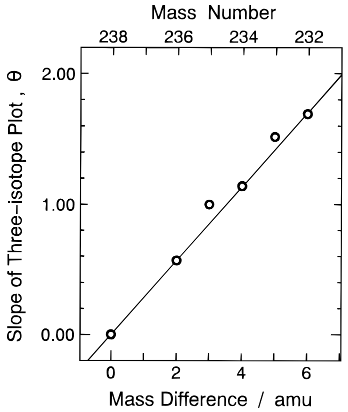

Figure 3. Correlation between the mass difference, ΔM, and the slope of the three-isotope plot, θ, relative to the ^{235}U/^{238}U pair.

$$\mathrm{AMDE} = \Delta M + \delta \tag{4}$$

$$\delta_{235} = 0.5, \quad \delta_{233} = 0.3, \quad \delta_{\mathrm{even}} = 0$$

where δ is the anomaly term and the subscript is the isotope. The anomaly suggests that there is an interaction between the bound electrons and nuclei. Such interactions have been well-known as the isotope shifts in the atomic spectral lines.

The observed odd−even nuclide effects in the chemical isotope effects are very similar to the "odd−even staggering" of the isotope shift in the atomic spectra. The isotope shift in atomic spectra of ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U has been reported by Smith et al.[17] and Gagné et al.[18−20] Correlation between the isotope shift and observed AMDE is shown in Figure 4.

Gagné et al.[18−20] studied isotope shift in the atomic spectra of uranium and showed that the relative values of the shifts are the same for each of the different transition lines. This phenomenon is due to the volume and deformation effects of the nuclei, and the relative isotope shifts can thus be expressed in terms of the relative mass effect (RME), in the same way as with AMDE mentioned above. The RME of even-mass isotopes is almost equal to the mass difference between an isotope and the ^{238}U standard. However, the values of RME deviates from the mass difference in the cases of odd-mass isotopes. The reported isotope shifts and calculated RMEs are summarized in Table 3.

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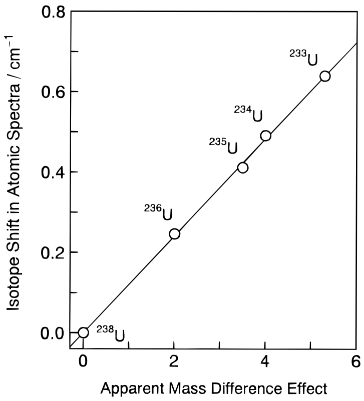

Figure 4. Correlation between chemical effects (AMDE) and isotope shifts in atomic spectra at 502.7 nm (UI) for isotopes ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U.

Table 3. Isotope Shifts in Atomic Spectra of Uranium Isotopes[17−20]

	line at 502.7 nm (UI)[a]		line at 424.4 nm (UII)[b]	
isotope	isotope shift/cm^{-1}	RME	isotope shift/cm^{-1}	RME
^{238}U	0		0	
^{236}U	0.2460	2.008	0.82	2.0
^{235}U	0.4104	3.350	1.39	3.35
^{234}U	0.4900	4.000	1.66	4.0
^{233}U	0.6387	5.213		

[a] References 18−20. [b] Reference 17.

Based on field shift effects of nuclei, Bigeleisen[21] developed a new theory for isotope effects. According to this theory, ϵ should have the following temperature dependence:

$$\epsilon = a/T + b/T^2 \qquad (5)$$

where a and b are constants and T is temperature. The first term in the right-hand side of eq 5 is related to the electronic state and the second term is related to molecular vibration. If we can apply this theory to the present system, ϵ for each isotope can be calculated by the following equation,

$$\begin{aligned} \epsilon &= A(\mathrm{RME})/T + B\Delta M/T^2 \\ &= C(\mathrm{AMDE}) \qquad (6) \end{aligned}$$

Substituting the values of RME, ΔE, and AMDE at 433 K and $\epsilon = 1.3 \times 10^{-3}$ at 308 K reported for the pair ^{235}U and ^{238}U[16] into eq 6 yields the values of constants A and B as $A = 0.192$ and $B = -25$. Then the value of ϵ for the pair ^{235}U and ^{238}U at 433 K is calculated as 1.08×10^{-3} and constant C at 433 K in eq 6 is given as 3.1×10^{-4}. This discussion suggests that the temperature dependence of ϵ is very important to confirm the theoretical relations. The experimental study on the temperature dependence will be presented in a subsequent paper.

Conclusion

The isotope effect for ^{233}U in the U(IV)−U(VI) exchange system has been experimentally studied using anion exchange redox chromatography. The isotope effect of ^{233}U has been found to deviate from the normal mass dependence observed among the even-mass nuclides of uranium. This deviation corresponds to an effective mass of 232.7 for ^{233}U on the scale for even-nuclide mass dependence. The results suggest that the isotope effects seen in the U(IV)−U(VI) exchange system arise mainly from the interaction between the nuclei and electrons in the isotopes.

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