Influences of Nuclear Mass, Size, Shape and Spin on Chemical Isotope Effect of Titanium

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Titanium isotopes of Ti (III) or Ti (IV) were fractionated by liquid-liquid extraction system using dicyclohexano-18-crown-6. The nuclear size and shape effect and the nuclear spin effect resulted in the breakdowns of the linear dependency of the enrichment factors to the mass difference. The nuclear mass effect, the nuclear size and shape effect and the nuclear spin effect were calculated by the isotope pair evaluation method. The nuclear mass effects were 0.000634 for 48Ti-46Ti (III) and 0.000559 for 48Ti-46Ti (IV), where the total enrichment factor were 0.000989 and –0.000166, respectively. The nuclear size and shape effects were 0.000369 for 48Ti-46Ti (III) and –0.000725 for 48Ti-46Ti (IV). The nuclear spin effects were 0.000180 for 47Ti (III), 0.000369 for 48Ti (III), –0.000303 for 47Ti (IV) and –0.000526 for 49Ti (IV). The ratio of chemical effect given by the field shift of 3d-orbital to that of 4s-orbital was –1.54, which had same direction and quantity with the field shift ratio of 3d-orbital to 4s-orbital in Ti I atomic spectra. This showed that the nuclear size and shape effect on the chemical isotope effect directly reflected the field shifts of Ti I. The nuclear spin effect was the function of the number of the hyperfine splitting vibrational energy levels and the coordination number. This effect was found when the coordination numbers differ nonstoichiometrically between the aqueous phase and the organic phase.

1. Introduction

The mass dependence theory of the Bigeleisen-Mayer formulation [1] has believed since the publication of their article in 1947; i.e., isotope enrichment factors in a chemical exchange reaction are proportional to the isotopic mass difference $\Delta m$ and inversely proportionate to the product of masses $m$ and $m'$ of two isotopes. About forty years after the establishment of this rule, Fujii and co-workers [2] have discovered the anomalous isotope effect of 235U in U(IV)-U(VI) exchange reaction. Nishizawa et al. [3–5] have reported the isotope effects being contrary to the Bigeleisen-Mayer theory on the numerous elements in the solvent extraction using macrocyclic ligands. Since the anomalouness arising mainly on the odd atomic mass isotopes of the even atomic number elements, they named it the odd/even atomic mass effect. The rapid progress of the mass spectrometer has brought more accurate evaluation of the unusual isotope effects. We have reported on the odd/even atomic mass effects and on the breakdown of the Bigeleisen-Mayer theory of the even atomic mass isotopes for samarium, zirconium and zinc in the complex formation with the macrocyclic reagents [6–8].

In atomic spectra, the centroid of the lines of an odd atomic mass isotope deviates from the midway between the adjacent even ones: this effect has been recognized as the odd-even staggering for many years [9, 10]. Because of the analogouness of the odd/even atomic mass effects to the odd-even staggering, we have looked for some relationship between the chemical isotope effect and an isotope shift. The isotope shifts [9–11] represent the isotopic energy changes in atomic orbital, which result from the nuclear characteristics; the nuclear mass, the nuclear size and shape and the nuclear spin. Hence, the deformation of the nuclear charge distribution results in the additional isotope effect in the chemical exchange system [6–8].

In 1996, Bigeleisen [12, 13] theoretically verified the implication of a field shift, one of the isotope shifts, with the chemical isotope effects of uranium. He added the correction term of the field shift to the Bigeleisen-Mayer term, which makes the shift to the minimum in the electronic energy.

The influence of the field shift on the vibrational and rotational energy of diatomic molecules has been investigated by Tiemann [14] and Schlembach [15]. They denoted that the field shift dominantes the isotopic change of the vibrational frequency in lead or thallium compound. Titanium is a transition element belonging to the first long period, and is a rare element having different nuclear spin in the odd atomic mass isotopes: 47Ti and 49Ti have 5/2 and 7/2, respectively. Because of the Fermi contact interaction [16], these odd atomic mass isotopes have different hyperfine splitting levels in an electronic state. Thus, the study on the nuclear size and shape effects and the nuclear spin effects in the titanium isotope separation is of interest. In the present study, the isotope effects in titanium-crown isotopomers are investigated on Ti (III) or Ti (IV).

2. Experimental

2.1 Liquid-Liquid Extraction Procedure

Cis-dicyclohexano-18-crown-6 (DC18C6) was a product of Aldrich Chemical Company. Titanium powder and titanium (IV) chloride were reagent grades (Wako Pure Chemical Industries). Titanium metal was dissolved in concentrated hydrochloric acid for 7 days. Then 0.25 mol...
dm$^{-3}$ (M) titanium (III) in 11 M HCl was prepared. The titanium (IV) chloride was diluted with HCl to make 1.8 M titanium (IV) in 7.2 M HCl. These titanium chloride solutions were served for the aqueous phase of the liquid-liquid extraction. The organic phase was 0.2 M DC18C6 solution in chloroform.

Each 20 cm$^3$ solution of the aqueous solution of titanium chloride and the organic solution of DC18C6 was mixed in a flat-bottomed flask and stirred by a magnetic stirrer for 30 min. Then the mixed solution was transferred into a separating funnel and kept still 90 min. These procedures were carried out at 273.2±0.5 K. After the extraction procedures, two phases were separated. The separated organic phase was scrubbed with 0.1 M HCl. Titanium concentration in the stripping water was analyzed by ICP-AES (Shimadzu ICPS-7500).

### 2.2 Isotopic Analysis

The titanium chloride salt in the back-extraction solution was once dried by heating. In order to decompose residual organic substances, 3 cm$^3$ of 14 M HNO$_3$ was added to the dried salt and heated for 30 min on a hot plate at 423 K and, after that, 1 cm$^3$ of 30% H$_2$O$_2$ was added. Then the solution was heated to dryness at 373 K.

The turbid sample solution of 500 ppm titanium in 1.0 M HNO$_3$ was prepared for the analysis of isotopic composition. Each solution of 3 l (1.5 l g of Ti) was loaded onto a rhenium evaporation filament of double filament system. The isotopic analysis was performed using a mass spectrometer with a multicolonlector system (Finnigan MAT262).

The ionization filament was heated to the 100 mV (digital recorder output) of $^{187}$Re. The evaporation filament was heated until the $^{48}$Ti ion beam reached 100 mV, and this condition was maintained for 15 min. Then the temperature of the evaporation filament raised to attain the appropriate measurement range of 2 V for $^{48}$Ti. This condition was maintained again for 40 min, then the isotope ratio, $^{m}$Ti/$^{48}$Ti, was measured. The multicollector system made it possible to obtain accurate data of titanium isotope ratios. The precision of the measured isotope ratio was less than 0.018% (1 SD).

### 3. Results

#### 3.1 Definitions

The isotopic exchange reaction can be written

$$A'Yn_Y + AXn_X = A'Xn_X + AYN_Y,$$

where $A'$ or $A$ is the light or heavy isotope of an element $A$. Expressions of $X$ and $Y$ represent ligands coordinated to the isotope ions. $n_X$ or $n_Y$ is the number of ligands around the isotope. The equilibrium constant, $K$, of the isotope exchange reaction of Eq. (1) is equal to the single state isotope separation factor $a$. The single stage isotope separation factor for titanium in the present system is defined

$$a_{48,m} = ([^{m}$Ti$]/[^{48}$Ti$])_{org}/([^{m}$Ti$]/[^{48}$Ti$])_{aq},$$

where $([^{m}$Ti$]/[^{48}$Ti$])_{org}$ and $([^{m}$Ti$]/[^{48}$Ti$])_{aq}$ are the isotope ratios of $^{48}$Ti relative to $^{48}$Ti found in the organic and aqueous phases, respectively. The superscript $m$ means mass number 46, 47, 49 or 50. The isotope enrichment factor $e$ is defined as

$$e_{48,m} = a_{48,m} - 1 \approx \ln a_{48,m} (|\ln a_{48,m}| \ll 1).$$

#### 3.2 Unusual Isotope Effect

The isotope enrichment factors of titanium are illustrated as a function of mass number in Fig. 1 for Ti (III) and Fig. 2 for Ti (IV) together with the experimental errors. The enrichment factors shown in Fig. 1 are obtained under the condition of 0.25 M titanium (III) in 11 M HCl as the initial aqueous phase and those in Fig. 2 are of 1.8 M titanium (IV) in 7.2 M HCl. These curves of the enrichment factor to the mass number for both Ti (III) and Ti (IV) show obvious breakdown from the old Bigeleisen theory. Suppose the isotope effects are ruled by the mass difference, we can delineate a straight line for the enrichment factors versus mass numbers. Nonlinear dependencies of the enrichment factors to the mass numbers point out necessarily to make modification onto the Bigeleisen-Mayer formulation.

### 4. Discussion

#### 4.1 Isotope Pair Evaluation

The Bigeleisen-Mayer approximation [1] chooses the zero of the energy scale at the minimum in the potential energy curve which is appropriate since it is the same for
the two isotopic molecules. The isotope effect in Eq. (1) is derived as [1, 7]

$$\ln a_0 = \frac{\langle r^2 \rangle^2}{m'} \frac{m_Y}{m_X} \omega_X^2 - m_X \frac{m_Y}{m_X} \omega_X^2 \Delta m/(24mm')^2,$$

where $m_X$ and $m_Y$ are the masses of the ligands X and Y, respectively. $m'$ is the mass of the lighter isotope, $m$ is that of heavier one and $\Delta m$ is the mass difference of them. The wave number of the harmonic oscillation of stretching motion between the ligand X and the isotope is represented as $\omega_X$, and $\omega_Y$ is that between the ligand Y and the isotope. $h$, $c$, $k$ and $T$ have usual meaning.

The field shift effect in the vibrational frequency of the diatomic molecule is investigated by a precise laser and microwave spectroscopy [14]. The field shift is referred to be predominant on the isotopic frequency shift of the vibrational-rotational energy [14, 15]. The change in mean square radii, $\delta\langle r^2 \rangle$, is theoretically verified to be proportional to the isotopic change of force constants, $\delta k$ [14, 15]. The changes in mean square radii $\delta\langle r^2 \rangle$, of titanium [11, 17] from $^{48}$Ti are given in Table 1. The correlation of $\delta\langle r^2 \rangle$ versus atomic mass shows similar characteristics to the enrichment factors shown in Figs. 1 and 2.

We try to reappraise the formulization of the isotope effect in Eq. (1) introducing the isotopic change in force constant, $\delta k$,

$$\ln a_0 = \frac{\langle r^2 \rangle^2}{m'} \frac{m_Y}{m_X} \omega_X^2 - m_X \frac{m_Y}{m_X} \omega_X^2 \Delta m/(24mm')^2$$

$$+ \frac{hc}{2\pi kT} \left( \frac{\delta k_Y}{2m_Y} m_Y \frac{m_Y}{m_X} \omega_X^2 \right) \Delta m/(24mm') + \frac{hc}{2\pi kT} \left( \frac{\delta k_X}{2m_X} m_X \frac{m_Y}{m_X} \omega_X^2 \right) \Delta m/(24mm'),$$

where $\delta k_Y$ or $\delta k_X$ is the isotopic change of force constant in the system AX/A$'$X or that in A$'$Y/A$'$Y. We can simplify the second term in Eq. (5) by substituting $\delta k$ to $\delta\langle r^2 \rangle$,

$$\ln a_0 = \frac{\langle r^2 \rangle^2}{m'} \left( \frac{m_Y}{m_X} \omega_X^2 - m_X \frac{m_Y}{m_X} \omega_X^2 \right) \Delta m/(24mm')^2 + \frac{hc}{2\pi kT} \left( \frac{\delta k}{2m} \frac{m_Y}{m_X} \omega_X^2 \right) \Delta m/(24mm'),$$

where $\delta k_Y$ or $\delta k_X$ is the isotopic change of force constant in the system AX/A$'$X or that in A$'$Y/A$'$Y. We can simplify the second term in Eq. (5) by substituting $\delta k$ to $\delta\langle r^2 \rangle$,
The nuclear spin effects are 0.000180 for \(^{48}\text{Ti}\) (III), 0.000369 for \(^{49}\text{Ti}\) (III), –0.000303 for \(^{47}\text{Ti}\) (IV) and –0.000526 for \(^{49}\text{Ti}\) (IV). We can see that the nuclear size and shape effect and the nuclear spin effect are also significant as in the case with the nuclear mass effect.

4.2 Nuclear Size and Shape Effect

In atomic spectra, the isotopic change of the nuclear size and shape is observed as a field shift [9–11]. Different isotopes have the same number of protons, but they do not have the same distribution of protons in space; the charge distribution is affected by the number of neutrons in the nucleus. A change in the energy of a level arising from the difference is called the field shift.

Because of the largest electron density at the nucleus, it is regarded that the field shift occurs only in the s-orbital. The field shifts of non-s orbital are, however, measurable large in some elements [11, 19, 20]. In the recent works on the isotope shifts of Ti I, the isotope shifts of 3d\(^2\)4s\(^2\)-3d\(^2\)4s\(^4\)4p transitions [21] and those of 3d\(^4\)s\(^3\)-3d\(^4\)s\(^4\)p transitions [22] are precisely measured. Applying those data of the isotope pair \(^{46}\text{Ti}-^{48}\text{Ti}\) to the King-plot method [11], we can obtain the field shift ratio of 3d-orbital to 4s-orbital (it is regarded the field shifts in 4p-orbital to be negligible small comparing to those of 3d-orbital and 4s-orbital): the field shift ratio, \(\delta E_{3d}/\delta E_{4s} = -1.64\), where \(\delta E\) means the isotopic energy shift due to the field shift. This shows that the field shift of 3d-orbital is inverse in sign and larger than that of 4s-orbital. Thus, we should also pay attention to the field shift effects of d-orbital in titanium-crown complexes.

In the previous paper on zirconium isotope effects, we have reported that the scaling factors are strongly affected by the conditions of the initial aqueous phase, but the scaling factor ratios indicate the constant values [7]. We have used the field shifts of s-orbital and d-orbital of Zr, and showed that the scaling factor ratios (the nuclear mass effect versus the field shift effects) are invariant [7].

The scaling factor ratios of titanium however show inverse direction and different quantities for Ti (III) and Ti (IV) as shown in Table 2: \(y_{III}/x_{III} = 0.562\) and \(y_{IV}/x_{IV} = -1.30\), respectively. The titanium 3+ ion is made by liberation of one electron from 3d-orbital and two from 4s-orbital, while titanium 4+ lacks two electrons from 3d-orbital and two from 4d-orbital, so the difference between Ti (III) and Ti (IV) is one electron rest in 3d-orbital. Because of the large field shift of d-orbital, the disparate number of valence electrons of 3d-orbital should result in the difference of the field shift ratios. Considering the number of valence electrons, we can rewrite the field shift effect terms in Eqs. (9) for an isotope pair \(^{46}\text{Ti}-^{48}\text{Ti}\),

\[
\begin{align*}
\delta(r^2)_{48,46}y_{III} & = 2\delta(r^2)_{48,46}y_{IV} + \delta y_{d48,46}z_{III}, \\
\delta(r^2)_{48,46}y_{IV} & = 2\delta(r^2)_{48,46}y_{IV} + 2\delta y_{d48,46}z_{IV},
\end{align*}
\]

where \(\delta y_d\) means the frequency change of the field shift of the 3d-orbital, \(y^r\) is the scaling factor of the field shift effect on the vibrational levels or that on the minimum in the electronic energy [12, 13], \(\hbar c\Delta E/\kappa T\), is calculated to be \(4\times10^{-3}\) or smaller for the isotope pair of \(^{46}\text{Ti}-^{48}\text{Ti}\) [18, 22], if the field shift gives directly change to the minimum in the potential curve.

4.3 Nuclear Spin Effect

<table>
<thead>
<tr>
<th>(y')</th>
<th>(z)</th>
<th>(\rho_{3d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (III)</td>
<td>0.767×10(^{-3})</td>
<td>-1.178×10(^{-3})</td>
</tr>
<tr>
<td>Ti (IV)</td>
<td>0.676×10(^{-3})</td>
<td>-1.039×10(^{-3})</td>
</tr>
</tbody>
</table>

\(^{a}\) \(\rho_{3d} = y_{III}/x_{III} = y_{IV}/x_{IV}\).  
\(^{b}\) \(\rho_{3d} = z_{III}/x_{III} = z_{IV}/x_{IV}\).
Titanium-47 and -49 have nuclear spin of \( I = \frac{5}{2} \) and \( \frac{7}{2} \), respectively. Because of the coupling of angular momentum \( F = \hbar + J, J - \hbar - 1, J - \hbar - 2, \ldots, \lfloor J - \hbar \rfloor \), an energy level of atomic orbital splits into hyperfine levels [16], where \( F \) is the total angular momentum and \( J \) is the total angular momentum of electrons; i.e., the lower level of \( 3d^34s^5 \) configuration \((J = 2)\) splits into 5-sub levels for each of those isotopes [18]. The nuclear spin effects on the minimum in the electronic energy [12] at 273.2 K can be calculated theoretically by means of these hyperfine splitting energies [18]; \((\ln K_{\text{hfs}})_{47} = 2.3 \times 10^{-8}\) and \((\ln K_{\text{hfs}})_{49} = 2.7 \times 10^{-8}\), which are small to be neglected.

In the recent works on the spectroscopic analysis of ro-vibrational lines [23, 24], the vibrational levels are known to have the hyperfine structure as in the case with the orbital energy. The hyperfine splitting vibrational levels should give the nuclear spin effect to the chemical isotope enrichment. We refer the nuclear spin effect on the vibrational levels to \( K_{\text{hfs}} \).

In general, the chemical isotope effect can be denoted via the partition function ratio, \( Q/Q' \). The isotope separation factor due to the vibrational motion, \( a_0 \), in the chemical equilibrium shown in Eq. (1) can be written

\[
\ln a_0 = n_Y \ln (Q/Q)_{AY'/AY} - n_X \ln (Q/Q)_{AX'/AX} \quad (12)
\]

We set the minimum in the ground energy of the isotope \( A' \) as the absolute zero. The vibrational partition function \( Q \) is

\[
Q = \sum_i \exp (-E_i/kT),
\]

where \( E_i \) is the energy of \( i \)th vibrational level. If the vibrational levels of isotope \( A \) have the hyperfine structure, the hyperfine splitting vibrational levels deviate \( \delta E_i \) from their center of gravity \( E_i \), where suffix \( j \) means \( j \)th hyperfine splitting vibrational level of the \( i \)th vibrational level. The vibrational partition function, \( Q_{\text{hfs}} \), having the hyperfine structure, is

\[
Q_{\text{hfs}} = \sum_i [\exp (-E_i/kT) + \sum_j \exp \{- (E_i + \delta E_i)/kT \}] = \sum_i \exp (-E_i/kT) \cdot \sum_j \exp (-\delta E_i/kT). \quad (14)
\]

Since the energy difference of \( \delta E_i \) should be negligible small compared with \( E_i \), \( \exp (-\delta E_i/kT) \) turns into unity. We can obtain the partition function \( Q_{\text{hfs}} \)

\[
Q_{\text{hfs}} = g \sum_i \exp (-E_i/kT) = gQ, \quad (15)
\]

where \( g \) is the number of hyperfine splitting levels in every vibrational level.

We can rewrite Eq. (12) as

\[
\ln a_0 = n_Y \ln (gQ/Q)_{AY'/AY} - n_X \ln (gQ/Q)_{AX'/AX} = \{n_Y \ln (Q/Q)_{AY'/AY} - n_X \ln (Q/Q)_{AX'/AX} \} + (n_Y \ln g_Y - n_X \ln g_X). \quad (16)
\]

Hence, we can obtain the nuclear spin effect, \( \ln K_{\text{hfs}} \), as

\[
\ln K_{\text{hfs}} = n_Y \ln g_Y - n_X \ln g_X. \quad (17)
\]

It is obvious that the nuclear spin effect is the temperature-independent effect, and is the function of the coordinated numbers of ligands and the numbers of the hyperfine splitting vibrational energy levels. Suppose the numbers of hyperfine splitting lines, \( g_X \) and \( g_Y \), and the coordinate numbers, \( n_X \) and \( n_Y \), are stoichiometrically identical, the nuclear spin effect should not take place. The nuclear spin effects of \( ^{47}\text{Ti} \) and \( ^{49}\text{Ti} \) in the present study are

\[
(\ln K_{\text{hfs}})_{47} = (n \ln g_{47})_{\text{org}} - (n \ln g_{47})_{\text{aq}}, \quad (\ln K_{\text{hfs}})_{49} = (n \ln g_{49})_{\text{org}} - (n \ln g_{49})_{\text{aq}}, \quad (18)
\]

Eqs. (18) indicate if the numbers of the hyperfine splitting levels are same in both phases, \( g_{47} = g_{49} \) \((\leq \frac{5}{2})\), the magnitude of nuclear spin effect of \( ^{49}\text{Ti} \) must be equal to that of \( ^{47}\text{Ti} \), \((\ln K_{\text{hfs}})_{47} = (\ln K_{\text{hfs}})_{49}\). The absolute values of \((\ln K_{\text{hfs}})_{49}\) are larger than those of \((\ln K_{\text{hfs}})_{47}\) as shown in Table 2. Thus, \( g_{47} \) and \( g_{49} \) should be the different numbers in the aqueous phase and/or the organic phase. The difference of \( \ln K_{\text{hfs}} \)'s is

\[
(\ln K_{\text{hfs}})_{49} - (\ln K_{\text{hfs}})_{47} = \{n \ln (g_{49}/g_{47})\}_{\text{org}} - \{n \ln (g_{49}/g_{47})\}_{\text{aq}}. \quad (19)
\]

Applying \( \ln K_{\text{hfs}} \)'s in Table 2 and \( g \)'s into Eq. (19), we can obtain the change in coordination numbers, \( \Delta n = n_{\text{org}} - n_{\text{aq}} \). The calculated \( \Delta n \)'s are given in Table 4 together with the number of the hyperfine splitting vibrational energy levels. In the case of the invertable total angular momentum of electrons \( J_{\text{aq}} = J_{\text{org}} \geq 3 \), \( \Delta n \) has the appropriate solution in Eq. (19) as the nonstoichiometric deviation of the coordination numbers due to the concentrated aqueous phase of the present study. From Table 4, we can see that the small amount of the nonstoichiometric change in the coordination numbers, \( \Delta n \), result in the nuclear spin effects for \( \text{Ti (III)} \) and \( \text{Ti (IV)} \).

<table>
<thead>
<tr>
<th>( J )</th>
<th>( g_{47} )</th>
<th>( g_{49} )</th>
<th>( \Delta n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ti (III)} )</td>
<td>3</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>7/2~</td>
<td>6</td>
<td>8</td>
<td>6.57×10^{-4}</td>
</tr>
<tr>
<td>( \text{Ti (IV)} )</td>
<td>3</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>7/2~</td>
<td>6</td>
<td>8</td>
<td>-7.75×10^{-4}</td>
</tr>
</tbody>
</table>
5. Conclusions

The enrichment factors of titanium isotopes by liquid-liquid extraction using DC18C6 show breakdown of the Bigeleisen-Mayer approximation. The nuclear size and shape effect and the nuclear spin effect are responsible to these failures.

The scaling factors of mass effect, \( x' \), and field shift effect, \( y' \), and the nuclear spin effect, \( \ln K_{\text{hfs}} \), are calculated by the isotope pair evaluation method. The scaling factor ratio, \( y'/z = -1.54 \), is the same with the field shift ratio, \( \delta E_{3d}/\delta E_{4s} \). This shows that the ratio of the field shift effects (3d-orbital versus 4s-orbital) directly results from that of the field shifts of Ti I. The nuclear spin effect is the function of the number of the hyperfine splitting vibrational energy levels and the coordination number. It takes place when the coordination numbers of ligands deviate nonstoichiometrically between the aqueous phase and the organic phase.

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