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Contributions of Nuclear Size and Shape, Nuclear Mass, and Nuclear Spin to Enrichment Factors of Zinc Isotopes in a Chemical Exchange Reaction by a Cryptand

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ABSTRACT

The isotope effect of zinc in the chemical exchange reaction using a macrocyclic ligand was not found to be ruled by the Bigeleisen–Mayer approximation, which suggested that the enrichment factor is proportional to the mass difference and is inversely proportional to the product of the masses of the isotopes. The separation factors of zinc isotopes in the chemical exchange reaction using cryptand(2B,2,1) polymer were precisely measured by means of an ICP mass spectrometer equipped with nine collectors as ion detectors. The liquid chromatography of a column packed with the cryptand polymer was used for the separation of the zinc isotopes. The enrichment factor $\epsilon_{67,66}$ for ^{67}Zn to ^{66}Zn was $-3.3329(3) \times 10^{-4}$. That for ^{68}Zn to ^{66}Zn was $1.846(1) \times 10^{-4}$ and that for ^{70}Zn to ^{68}Zn was $7.19(2) \times 10^{-4}$. They were not scaled with $\Delta m/mm'$, where Δm is the mass difference between the isotope pairs, and m and m' represent the masses of the isotopes. The isotope effect of zinc is implicated with the isotope shift, and the

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hyperfine structure shift in the isotopomer of the zinc isotopes. The sum contribution of the vibrational energy shift from one isotope to the other and the nuclear mass shift to the enrichment factor of ^{67}Zn was -1.05×10^{-3} , and the contribution of the field shift caused by the nuclear size and shape of the isotope was 5.26×10^{-4} . The contribution of the nuclear spin or the hyperfine structure shift to the enrichment factor of ^{67}Zn was small: 1.94×10^{-4} .

Key Words. Isotope separation; Even atomic mass; Odd atomic mass; Cryptand polymer; Zinc isotopes; Isotope shift; Field shift; Nuclear spin

INTRODUCTION

An isotope effect in a chemical exchange reaction has been believed to be proportional to the difference in the masses and to be inversely proportional to product of the masses of the isotopes since publication of an article by Bigeleisen and Mayer (1) in 1947. The theoretically induced equation for an isotope enrichment factor has been inconsistent with almost all experimental results (2), except for a little experimental evidence on uranium isotopes. Nishizawa and coworkers, in turn, found an unusual separation factor for an odd atomic mass isotope of zinc, ^{67}Zn , in a study of zinc isotope separation by liquid-liquid extraction using a crown ether (3). This work was followed by studies on the isotopes of other elements: magnesium (4), strontium (5), nickel (6), and barium (7), and by more precise measurements for zinc (8). All of the odd atomic mass isotopes in the even atomic number elements have shown different enrichment factors from the values scaled with $\Delta m/mm'$, where Δm is the mass difference between the isotopes and m and m' are their masses. The observed odd atomic mass effects have been large enough to be beyond experimental errors.

On the basis of the experimental evidences obtained by the use of a macrocyclic ligand, dicyclohexano-18-crown-6, Nishizawa et al. (3) first appreciated that the isotopic enrichment factor is subjected mainly to the isotope shift recognized in atomic spectra as early as 1927 (9). In particular, the even-odd staggering in the field shifts is responsible to the odd atomic mass effects in the chemical exchange reaction. Recently, Bigeleisen (10) theoretically verified the implication of the field shift in the fractionation factor, which is based on the experimental results (11) of the enrichment factors precisely measured in the U(IV)-U(VI) exchange reaction in column chromatography using an ion exchanger. He examined the following five effects on the fractionation factor: the vibrational energy shift, the anharmonic oscillation, the correction to the Born-Oppenheimer approximation, the hyperfine structure shift induced from a coupling of nuclear and electronic magnetic momenta, and the field shift. Consequently, he attributed an anomalous behavior of ^{235}U to the field shift and less effectively to the hyperfine structure shift.

Our works (3–8) mentioned above were carried out by means of an ICP quadrupole mass spectrometer or a surface ionization mass spectrometer equipped with a single collector for the measurement of the isotope ratios. As a consequence, the precision of the separation factor was not always as accurate as desired because of the fluctuation of the total ion current during the peak-to-peak interval of each isotope. In the present study we used a double focusing ICP mass spectrometer equipped with nine collectors, and the results are about 4000 times more precise than in our earlier work.

Cryptand($2_B, 2, 1$) polymer, a macrocyclic ligand containing two nitrogen atoms as an electron donor group, is known to be effective for the separation of the isotopes (12). It is suitable for chromatographic use as a column packing reagent because of its resistivity to various solvents. Multistage use of the ligand makes the separation factor of zinc isotopes accurate.

By examining the enrichment factors determined from this mass spectrometer and column chromatography, we found that isotopes of even atomic mass are not scaled with $\Delta m/m$: the enrichment factors of the even atomic mass isotopes do not show a linear relationship to the mass numbers. The zinc isotopes show individual separation factors for each isotope pair, even if there is the same mass difference between the isotopes. Differences in the sizes and shapes of the isotopes give rise to the field shifts which are the major causes of isotope fractionation rather than the vibrational energy shift in the chemical exchange reaction of a macrocyclic ligand. Besides contributions of the vibrational energy shift, isotope shifts resulting from nuclear mass differences, from nuclear sizes and shapes, and from hyperfine structure shifts to the isotope enrichment factors will be discussed as we develop a modified Bigeleisen theory.

EXPERIMENTAL

Zinc chloride (reagent grade, guaranteed to be 99.99%) was purchased from Wako Pure Chemical and used without further purification. Hydrochloric acid and acetone were of reagent grade from Wako Pure Chemical. Cryptand($2_B, 2, 1$) polymer was a product of Merck (named Kryptofix 221B polymer). The particle size of the cryptand was stated to be 250–500 μm .

The cryptand polymer was packed into a glass tube (diameter = 5.0 mm, length = 1000 mm) with filters at both ends. A liquid chromatographic system was composed of a flowing pump (Eyela VSP-3050) for an eluting solution, a valve for sample injection, a chromatographic column, an electroconductometer, and a fraction collector. The solvent was degassed continuously before flowing into the column by a pump.

The solvent was composed of water (50%), acetone (50%) and hydrochloric acid of $0.002 \text{ mol}\cdot\text{dm}^{-3}$ (M). A sample solution of 0.1 M ZnCl_2 was prepared by dissolving ZnCl_2 into the solvent. A zinc chloride band was created on the

top of the column by injecting the sample solution of 1.0 cm^3 . Then the band was eluted with a $0.4 \text{ cm}^3/\text{min}$ flow of the solvent. An eluted mixture was introduced into the electroconductometer to measure the conductivity of the eluted solution. It was automatically registered and then collected fractionally into vials as 5.6 cm^3 stepwise specimens. All these procedures were carried out at 298 K (room temperature). The concentration of ZnCl_2 in each vial was analyzed by an atomic absorption spectrometer (Shimadzu AA-640-12).

In order to determine the chromatography stage number, a batch experiment was also carried out. Cryptand polymer (1.0 g) and the sample solution dissolved in 0.2 M ZnCl_2 in the solution (identical with that used in the liquid chromatography) were placed in a flat-bottomed flask. This mixture was stirred by a magnetic stirrer for 30 minutes at room temperature. Then the cryptand polymer was filtered and washed with ethanol (100 mL). The zinc chloride in the polymer was eluted by a 0.002 M HCl solution. The solution was measured for the ZnCl_2 concentration and for the isotopic composition in a way similar with the chromatograph samples.

The ZnCl_2 solutions collected and analyzed for the zinc concentrations were placed into Teflon vials together with dilute nitric acid and heated to dryness: the residue in the vial was zinc nitrate. Then a 0.1 M HNO_3 solution was poured into the vial to obtain a zinc nitrate solution of the nitric acid solvent. About 5 cm^3 of the nitric acid base solution adjusted to be 1.5 ppm zinc was prepared as a sample for mass spectrometric analysis.

The isotope ratio was determined by a mass spectrometer (VG Element Plasma-54) with an ICP ion source. It was equipped with a double focusing system and nine Faraday cup ion collectors. The precision of the zinc isotope ratio measurement is less than $\pm 0.05\%$ for the isotopic enrichment factor of ^{68}Zn to ^{66}Zn . This figure is very small relative to the quadrupole ICP-MS of a single collector type whose precision was checked by the present authors to be $\pm 90\%$ for measurement of a similar enrichment factor of zinc isotopes.

RESULTS AND DISCUSSION

Zinc has five naturally occurring isotopes. The isotopic abundances of ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn are 48.89, 27.81, 4.11, 18.56, and 0.62%, respectively. In the present study we measured the isotope enrichment factors of ^{67}Zn , ^{68}Zn , and ^{70}Zn to ^{66}Zn . We did not measure the enrichment factor of ^{64}Zn to ^{66}Zn because it has a fairly large experimental error resulting from the ion current of $^{64}\text{Ni}^+$ which is emitted from the ion drawing cones made of nickel metal in the ion source of the ICP mass spectrometer.

The isotope fractionation factors α^n of ^{67}Zn , ^{68}Zn , and ^{70}Zn based on chromatographic separation are illustrated in the upper part of Fig. 1 the elution curve of zinc chloride is presented in the lower part. The experimental errors of fractionation factors ascribed to mass spectrometric analysis are not shown

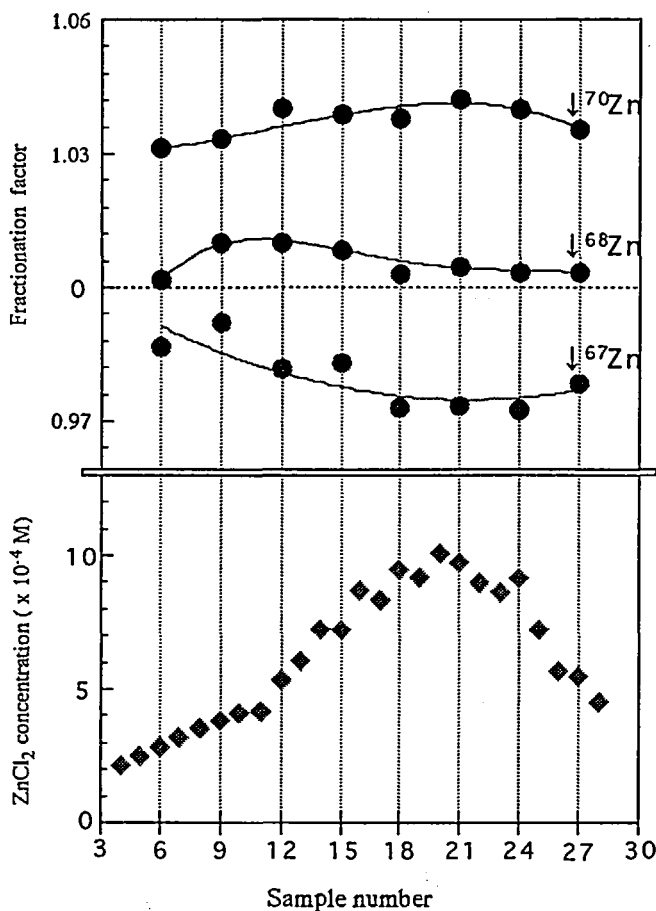


FIG. 1 Fractionation factors of ^{70}Zn , ^{68}Zn and ^{67}Zn to ^{66}Zn and elution curve. The fractionation factor is defined as the ratio of the isotope ratio in the eluted solution to that in the untreated natural zinc. The isotope ratios were measured intermittently in accordance with the corresponding sample numbers in the eluted solutions fractionally collected. ^{64}Zn was not measured because of the disturbance of $^{64}\text{Ni}^+$ ions emitted from the ion source of the mass spectrometer.

because they are too small to exhibit as error bars. The curve of the fractionation factor of ^{67}Zn has a maximum at margin of the figure, and the curves of ^{68}Zn and ^{70}Zn have maximums at positions made shifts to right side in order. The fractionation factors of ^{70}Zn to ^{66}Zn and ^{68}Zn to ^{66}Zn have maximums at sample numbers 21 and 12, respectively, and their values are more than unity within the region in which mass spectrometric analysis performed: both isotopes are

TABLE 1
Separation Factors by a Single Process

α (67/66)	α (68/66)	α (70/66)
1.00122 ± 0.00004	1.00004 ± 0.00006	1.00088 ± 0.00001

enriched in that range. The depleted isotopic composition in ^{70}Zn or ^{68}Zn is assumed to be observed at the left-hand side of the elution curve. The fractionation factor is defined as

$$\alpha^n = (^A\text{Zn}/^{66}\text{Zn})_{\text{elut}} / (^A\text{Zn}/^{66}\text{Zn})_{\text{nat}} \quad (1)$$

where $(^A\text{Zn}/^{66}\text{Zn})_{\text{elut}}$ and $(^A\text{Zn}/^{66}\text{Zn})_{\text{nat}}$ denote the isotope ratios of the isotope of atomic mass A to that of atomic mass 66 found in the eluted solution and in the untreated solution of naturally occurring isotopic abundance, respectively. The single-stage separation factor is represented by α , which is defined as the ratio of the isotope ratio of zinc in the cyptand complex to that in the fluid which makes contact with the complex. The stage number is shown as n , which is determined by comparison between the experimentally determined fractionation factor α^n by chromatography and a rough value of the single-stage separation factor estimated from batch experiment. The separation factors obtained by the batch experiment are shown in Table 1 together with the errors, and in these the separation factor of ^{70}Zn to ^{66}Zn , $\alpha = 1.0008$, is used to determine the stage number because of its smaller error. The stage number can be calculated by using the fractionation factor of sample number 12, $\alpha^n = 1.0497$ for ^{70}Zn to ^{66}Zn , as $n = 55.14$. It is rounded off to 55 for every isotope pair in order to simplify further calculations. Consequently, the single-stage enrichment factors, ϵ 's ($\epsilon = \alpha - 1$), of sample number 12 in the

TABLE 2
Enrichment Factors (ϵ_{12}) Observed in Sample Number 12, $\Delta m/mm'$, and Field Shifts

	Isotope pair		
	66-68	68-70	66-67
Enrichment factor ($\times 10^{-4}$) ^a	1.846 ± 0.001	7.19 ± 0.02	-3.3329 ± 0.0003
$\Delta m/mm'$ ($\times 10^{-4}$)	4.46	4.20	2.26
Field shifts (GHz) ^b	-0.602	-0.712	-0.140

^a The enrichment factor, ϵ_{12} is determined by $\epsilon_{12} = \alpha_{12} - 1$, where α_{12} represents the single-stage separation factor of the sample number 12 which has the stage number 55.

^b Reference 16.

fractional collected solutions are determined as shown in Table 2, which are revised into those of ^{67}Zn to ^{66}Zn , ^{68}Zn to ^{66}Zn , and ^{70}Zn to ^{68}Zn .

The enrichment factor ϵ is almost equal to the logarithm of the separation factor because the absolute value of ϵ in the chemical exchange separation of isotopes is small compared with unity; $\epsilon = \ln \alpha$. The enrichment factors of ^{66}Zn to ^{66}Zn ($\epsilon_{66,66}$), ^{67}Zn to ^{66}Zn ($\epsilon_{67,66}$), ^{68}Zn to ^{66}Zn ($\epsilon_{68,66}$), and ^{70}Zn to ^{66}Zn ($\epsilon_{70,66}$) are illustrated in the solid symbols in Fig. 2. The experimental

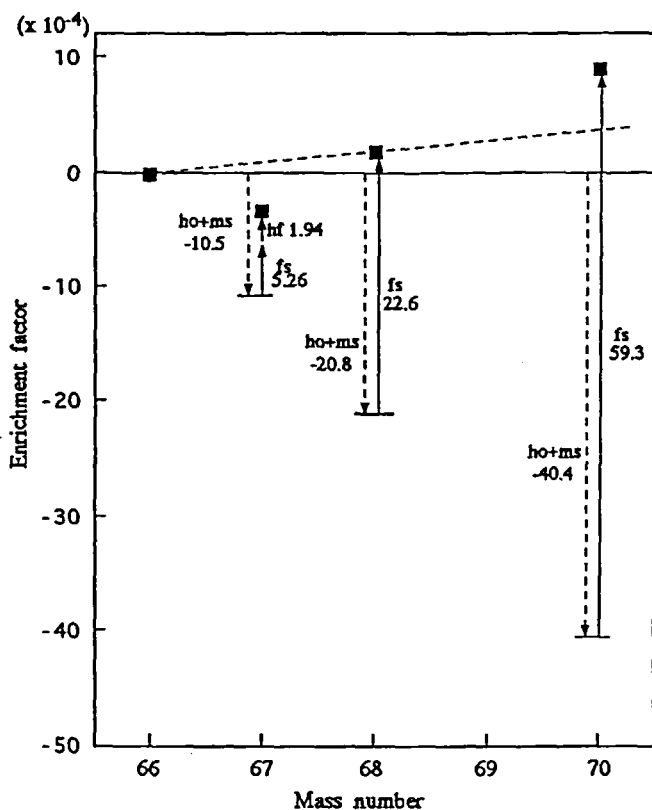
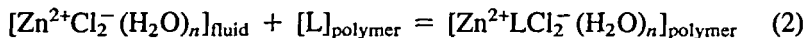


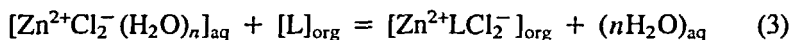
FIG. 2 Contributions of sum of vibrational energy shift and mass shift, field shift, and hyperfine structure shift. Measured enrichment factors are shown in squares for the corresponding mass number. The straight line joining ϵ_{66} and ϵ_{68} is shown as a dashed line. The contribution of the sum of harmonic oscillation and mass shift (ho + ms) is shown as a vertical dashed line, and that of field shift (fs) is shown as a vertical solid line for each mass number. The magnitude of these are shown numerically besides the lines. The arrows represent the direction of enrichment. ^{67}Zn has a contribution from the hyperfine structure shift (hf).

errors are not shown because of their small values. The characteristic feature of Fig. 2 is that enrichment factors of both ^{67}Zn to ^{66}Zn and of ^{70}Zn to ^{66}Zn deviate greatly from a straight line (shown as dashed lines in Fig. 2) joining the enrichment factors of ^{66}Zn and ^{68}Zn . The enrichment factor of ^{67}Zn , $\epsilon_{67,66}$, is negative, whereas $\epsilon_{68,66}$ and $\epsilon_{70,66}$ are both positive.

The single-stage separation factors of the present experiment are quite small compared with those observed in liquid-liquid extraction (8) using, dicyclohexano-18-crown-6. The enrichment factor for ^{68}Zn to ^{66}Zn was reported to be negative and large; $\epsilon = -0.036$. This is assumed to be produced from two causes. The first is that the zinc ion is caught on the cryptand polymer which has hydrated some water molecules, whereas in liquid-liquid extraction the ion prevents them from being transported into the organic phase. These different ways of complexation are described in separate equilibrium equations:



and



where $[\text{Zn}^{2+}\text{Cl}_2^- (\text{H}_2\text{O})_n]$ shows the chloro complex of zinc with n water molecules, and L is the ligand of the cryptand or the crown ether. The "fluid" or "polymer" suffix indicates that the chemical species in brackets is in the fluid phase or in the polymer of the chromatography, and "aq" or "org" indicates that the chemical species is in the aqueous phase or in the organic phase, respectively. Consequently, the chemical exchange reactions of isotopes are represented by different equations, and the resultant equilibrium constants must also differ. This is similar to the inference of Jepson (13) in his study on calcium isotope fractionation using a crown ether suspended on resin.

The second cause is the conformation of the zinc ion in the macrocyclic ligand. The mixed donor ring (14), like the cryptand, may have so large a stability constant with the transition metal ions that they have not been eluted from the ring-conformed zinc complex. Therefore, the zinc ion is assumed to be outside the ring with some donor atom rather than inside the ring.

Bigeleisen (10) suggested the enriching mechanism of isotopes in the chemical exchange reaction to be as follows. Consider the isotopic exchange reaction



where A and A' are the heavy and light isotope of the element A, respectively, and X and Y represent polyatomic groups. The logarithm of the complete isotope fractionation factor for this reaction is

$$\ln \alpha = \ln \alpha_0 + \ln K_{\text{anh}} + \ln K_{\text{BOELE}} + \ln K_{\text{hf}} + \ln K_{\text{fs}} \quad (5)$$

where

$$\ln \alpha_0 = \ln(s/s')f(\text{AY/A'Y}) - \ln(s/s')f(\text{AX/A'X}) \quad (6)$$

is the Bigeleisen–Mayer [1] approximation to the logarithm of the separation factor and $(s/s')f$ is the reduced partition function ratio. It is caused by the energy difference of the intramolecular vibration in the isotopomer and is a function of $\Delta m/mm'$. The correction terms are the anharmonic vibration correction (K_{anh}), the correction to the Born–Oppenheimer approximation, the isotope mass shift (K_{BOELE}), the nuclear spin effect (K_{hf}), and the nuclear field shift effect (K_{fs}).

The magnitude of the anharmonic oscillation depends on the vibrational amplitude and its change with isotopic substitution. It is a smaller correction for isotope effects in heavy elements (15) such as zinc. Although the nuclear mass shifts of zinc isotopes are given in the literature (16) for various transitions, changes of energy levels between the isotopes are not given but only the isotope shifts of transition energies. We can not estimate the orbital energy of a particular isotope from these data of the nuclear mass shift as optically measured, even if the orbital is related to the bond strength between the ligand and the isotope. In nuclear mass shifts, however, both the normal mass shift and the specific mass shift are proportional to $\Delta m/mm'$, where m or m' means the mass of each isotope and Δm is their mass difference. In turn, the Bigeleisen–Mayer approximation, $\ln \alpha_0$, is also proportional to $\Delta m/mm'$. Thus, the contributions of the mass shift and the difference of the vibrational energy dealt with as the harmonic oscillation to the logarithm of the separation factor can be collected into a single term if the experiment is carried out under constant temperature.

The field shift originates from the change of the finite size and angular shape of the nuclear charge distribution when neutrons are added to the nucleus. Consequently the binding energies of electrons that penetrate the nucleus differ for different isotopes (17). The field shift (18), δT , can be written as

$$\delta T = |\Psi(0)|^2 \pi a_0^3 C/Z \quad (7)$$

where $|\Psi(0)|^2$ is the electron density at the nucleus, the nuclear factor C is proportional to the mean square of the charge distribution radii, $\delta\langle r^2 \rangle$, and a_0 is the Bohr radius. The electron density at the nucleus, $|\Psi(0)|^2$, has a finite magnitude only for s-electrons and is zero for the other orbital. The field shift, therefore, occurs only in s-electrons, and the transition of $sp-s^2$ is reduced to the energy shift of the s-level. The isotope shift is commonly represented by a positive sign if the frequency of the line of the heavier isotope shows a

larger shift. The field shifts presented in Table 2 have negative signs, meaning the s-electron of the heavier isotope is in a higher energy level.

If only the electronic contribution of the isotope to the separation factor is considered in the chemical exchange reaction (e.g., Eq. 4), the contribution of the electronic levels to the equilibrium constant, K_{fs} , of the chemical exchange reaction is represented by

$$K_{fs} = [(s/s')f_e(AY/A'Y)/(s/s')f_e(AX/A'X)] \exp(-\Delta E_0/kT) \quad (8)$$

where ΔE_0 is the energy difference in the ground state of the electronic configurations between the isotopes. Both the electronic partition function ratios $(s/s')f_e(AY/A'Y)$ and $(s/s')f_e(AX/A'X)$ are unity at the moderate temperature used in the present experiment. Thus, the energy difference between the isotopes is identical with the nuclear field shift as for the s-orbital. The logarithm of the electronic contribution to the field shift is rewritten as

$$\ln K_{fs} = -v_{fs}/kT \quad (9)$$

where v_{fs} represents the field shift of the isotope pair.

We can then rewrite Eq. (6) at constant temperature to be

$$\ln \alpha = av_{fs} + b\Delta m/mm' + hf \quad (10)$$

where a and b are the weight of contributions of the field shift and that of the sum of the vibrational energy shift and the mass shift, respectively, and each has a particular constant value for every isotope of an element. The contribution of the hyperfine structure shift is shown as hf . It is induced from the coupling of the nuclear and electronic spin angular momenta, and it is a mechanism which concerns only the odd atomic mass isotope ^{67}Zn in even atomic numbered nuclides.

We can obtain three equations for isotope pairs of mass numbers 66–67, 66–68, and 68–70. The left-hand term of Eq. (10) is the enrichment factor determined from the chromatographic separation of each isotope pair, shown in Table 2 as ϵ_{12} , which is evaluated from data of sample number 12 and stage number 55, together with the measurement errors of mass spectrometric analysis. The field shift, v_{fs} , of the sp–s² transition of each isotope pair of zinc can be obtained from the literature (15) as shown in Table 2. The term concerning the nuclear mass, $\Delta m/mm'$, can easily be calculated.

Thus, the three unknown quantities in Eq. (10) are a , b , and hf . We can then obtain the contributions of the field shift (av_{fs}), the sum of the vibrational energy shift and the mass shift ($b\Delta m/mm'$), and the hyperfine structure shift (hf) to the enrichment factor observed, while we can not separate the contributions of the vibrational energy shift (ho) and the mass shift (ms). The values of a and b are calculated to be -3.757×10^{-3} and -4.658×10^{-4} , respectively. The contribution of the hyperfine structure shift to ^{67}Zn is $hf = 1.94$

$\times 10^{-4}$. The contributions of these three unknown quantities as calculated using a and b are schematically illustrated in Fig. 2. The effect of the vibrational energy shift, including the nuclear mass shift, is in the opposite direction to that of the nuclear field shift, and so they counteract each other, resulting in the small enrichment factors observed in the present experiment. The hyperfine structure shift enhances the effect of the field shift in ^{67}Zn .

CONCLUSIONS

The field shift is a major determinant in the separation factors of zinc isotopes in chemical exchange reactions which use cryptand(2_B,2,1) polymer. The sum contribution of the vibrational energy difference and the nuclear mass shift to the enrichment factors is in the opposite direction to that of the field shift. These two effects counteract each other, and the observed separation factor results in a small value in the present experiment. The nuclear spin effect, also referred to the hyperfine structure shift, is less effective as an enrichment factor of ^{67}Zn . This makes the odd atomic mass isotope more likely to be in the cryptand polymer than in the solvent in the chromatograph, but it is a smaller effect than the field shift effect. The negative and large enrichment factor of ^{67}Zn relative to the even atomic mass isotope is ascribed to the smaller field shift effect.

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