



Chromatographic separation of neodymium isotopes by using chemical exchange process

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ABSTRACT

The neodymium isotope effects were investigated in Nd–malate ligand exchange system using the highly porous cation exchange resin SQS-6. The temperature of the chromatographic columns was kept constant at 50 °C by temperature controlled water passed through the columns jackets. The separation coefficient of neodymium isotopes, ϵ 's, was calculated from the isotopic ratios precisely measured by means of an ICP mass spectrometer equipped with nine collectors as ion detectors. The separation coefficient, $\epsilon \times 10^5$, were calculated and found to be 1.4, 4.8, 5.4, 10.6, 16.8 and 20.2 for ¹⁴³Nd, ¹⁴⁴Nd, ¹⁴⁵Nd, ¹⁴⁶Nd, ¹⁴⁸Nd and ¹⁵⁰Nd, respectively.

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1. Introduction

Different researches in the isotopes separation field indicated that the isotopes of a given element may show some quantitative differences in chemical exchange systems [1–7]. Urey, as early as 1942 [2], found that, chemical exchange is a promising method for isotopic separation of nitrogen, carbon and sulfur. On a laboratory scale, Urey achieved production capacities of the order of one gram per day of enriched material from natural abundance feed, typically one atom percent of the desired isotope. Chemical exchange can generally be carried out with established industrial technology.

Separation of isotopes by ion exchange displacement chromatography is one of the chemical exchange methods, which is based on the chemical equilibrium between isotopic species distributed between the stationary resin phase and the mobile solution phase. This operation is characterized by maintaining self-sharpening band boundaries at both the migration band ends. During this 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 [1]. Since the publication of

the molecular vibration theory by Bigeleisen and Mayer [6] in 1947, isotope effects in a chemical exchange reaction has been believed to be proportional to the difference in the masses and inversely proportional to product of the masses of the isotopes. However, the theoretically induced equation for an isotope enrichment factor has been inconsistent with some of the experimental results [7]. Nishizawa and his coworkers [8], in turn, found an unusual separation factor for an odd atomic mass isotope of zinc in a study of zinc isotope separation by liquid–liquid extraction using crown ether. This work was followed by studies on the isotopes of other elements: magnesium [9], strontium [10], nickel [11], and barium [12], and by more precise measurements for zinc [13]. The enrichment factor of the odd atomic mass isotopes, as compared to the even atomic mass isotopes, have shown deviation from the values scaled with, 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.

Based on the experimental results of the uranium isotopic exchange reaction equilibrium, which was precisely measured in the $U(IV)$ – $U(VI)$ exchange reaction studied by ion exchange chromatography [14,15], Bigeleisen [16] attributed this anomalous odd-even phenomena to the field shift. Nishizawa et al. [17] reported the anomalous mass effects in the isotope separation of the odd-mass ⁶⁷Zn from the even-masses ⁶⁴Zn, ⁶⁶Zn, and ⁶⁸Zn. They attributed this anomaly to the isotope shift in the orbital energy.

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Lanthanides and actinides are known to have deformed nuclei, which cause the charge distribution effects in the isotope shifts of the atomic emission spectral lines. Although almost all of the lanthanides have more than one isotope, only few investigations have been reported on the isotope effects of these elements. Uranium was the only exception as it was the subject of an extensive research due to the importance of ^{235}U isotope, the ligand exchange system was applied to Gd [18], Eu [19] and U [20] isotopes separation.

Neodymium has several odd and even isotopes: ^{142}Nd , ^{143}Nd , ^{144}Nd , ^{145}Nd , ^{146}Nd , ^{148}Nd and ^{150}Nd . They are used in a variety of applications. Among them, the use of ^{146}Nd for the production of ^{147}Pm , which can be used as a source of radio isotopic power generation. Fujie et al. have studied the fractionation of these Nd isotopes by single stage solvent extraction technique using crown ether [21]. The change in the mean square radii of Nd isotopes have been measured by G. Lalazissis et al. [22]. Studying the isotope effects of Nd with the help of the current available data of the change in the mean square radii of Nd isotopes is possible and would enhance our knowledge of the nuclear size and shape effects in chemical isotope effects. The chromatographic technique allows the utilization of several theoretical stages, by increasing the migration distance, which increases the final separation effect. The difference between the isotope ratios of the samples at the band boundaries and the middle samples, which represents the original feed, is enlarged to be much more than the expected error in the isotope ratio measurements. This increases the confidence in results obtained by long chromatography.

To achieve an effective isotopic separation process by displacement chromatography, a band of the isotopic chemical species is to be eluted through the column by a displacing eluent solution. As the isotopes fractionation is observed at the band boundaries, it is essential to maintain an ideal chromatogram with self-sharpening boundaries during the whole band migration. This can be achieved by the best selection of the ion exchanger affinity, chemical compositions, and the pH value. Besides, it is very important to select the suitable complexing agent to form complexes with neodymium(III) ions. Although EDTA is well known to be used in refining of rare earth elements, its complexes have low solubility in aqueous solutions especially at higher temperatures. Therefore, the EDTA complexing ligand was not selected for our system. 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 copper and uranyl isotope effect studies, the malate has shown large separation coefficient [23,24]. As displacing cation, the ammonium ion is mostly 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.

Therefore, the aim of this work is to study the isotope effects of neodymium in ligand exchange system using malic acid as ligand. Due to the presence of several odd and even isotopes of Nd this study will not only investigate the possibility of neodymium isotope separation, but it will also give more information that may help in understanding the theory of isotope effects.

2. Experimental

2.1. Ion exchange resins and reagents

Naturally occurring neodymium composed of seven isotopes was used in this work. The abundance of these isotopes are 27.13%, 12.18%, 23.8%, 8.3%, 17.19%, 5.76% and 5.64% for ^{142}Nd , ^{143}Nd , ^{144}Nd , ^{145}Nd , ^{146}Nd , ^{148}Nd and ^{150}Nd , respectively [25]. It was supplied by Alfa-Aesar in the form of Nd_2O_3 of purity 99.99% and was con-

verted to NdCl_3 by dissolving in 2 M HCl solution followed by a well gentle evaporation to dryness and the obtained residue was washed several times with distilled water followed by evaporation till neutrality, and was used without further purification. The ion exchange resin mainly used in the ligand exchange system, LXS, was macroporous strongly acidic cation exchange resin, (SQS, 100–200 mesh size) obtained from Asahi Chemical Co. Asahi, Japan. All other reagents used were of analytical grade and employed without further purification.

2.2. Columns preparation

To avoid any irregular packing of the resin inside the column, the ion-exchanger was stirred with hot distilled water in a beaker and the slurry was poured into the column, which was originally half filled with hot distilled water. As air bubbles are not allowed to exist in the column, the column was heated, through its jacket, to a higher temperature than the operational temperature while it was filled by the resin. The solution level was kept at 2–3 cm above the top of the bed in this work.

2.3. Chromatographic system

Three ion-exchange glass columns (0.8 cm I.D. \times 100 cm) were connected in series with Teflon tubes 1 mm inner diameter, in a cyclic displacement chromatographic system, so that they were repeatedly used in merry-go-round way for the desired migration length. The small inner diameter of the connecting tubes does not allow for back mixing of band, while it migrates from one column to another. Besides, a re-sharpening of the band boundaries takes place during the band moving from one column to another. The columns were packed uniformly with the above-mentioned resin. Thermo stated water was circulated through the jacket to maintain the temperature at $50 \pm 0.2^\circ\text{C}$. Then, 2 M, mol/dm³, HCl solution was fed into the column to convert the resin into H^+ form. Solution of 0.1 M CuCl_2 was fed to convert the working resin into Cu^{2+} form. Then, 0.05 M NdCl_3 solution was fed into the first column at a constant flow rate by a peristaltic pump to form Nd^{3+} adsorption band. When the Nd^{3+} ion adsorption band had grown to an appropriate length, the supply of the feed solution was stopped. The Nd^{3+} and Cu^{2+} adsorption bands were eluted by an eluent solution containing 0.2 M $(\text{NH}_4)_2$ malate + 0.1 M NH_4NO_3 + 0.0002 M NaN_2 adjusted to pH 4.6 with NH_4OH solution. The adsorption band of Nd^{3+} was visible, pink, in contrast with the preceding green Cu band. When the Nd^{3+} adsorption band migration length reached to the desired length, it was eluted out from the last column. The effluent was collected in small fractions of 2 cm³ that were, thereafter, subjected to the concentration analysis and the isotopic analysis. The set of apparatus for the chromatographic experiment is illustrated in Fig. 1, and the experimental conditions are summarized in (Table 1).

2.4. Analysis

Some selected samples of the chromatographic band fractions besides the feed sample were analyzed for ion concentration and isotopic distribution ratios. The UV–vis spectra of lanthanides were scanned from 500 nm by means of UV–vis spectrophotometer. The instance pink color solution of Nd is the basis for the determination of Nd concentration by photometry at wavelength 576 nm after dilution with 0.1 M HCl. The neodymium isotopic ratios of some selected samples were measured using a Joel high-resolution inductively coupled plasma mass spectrometer JMS–plasma x2 ICP–MS. At first, the Nd selected effluent samples were transferred to neodymium nitrate form by several cycles of gentle evaporation and treatment with nitric acid to decompose malic acid and to

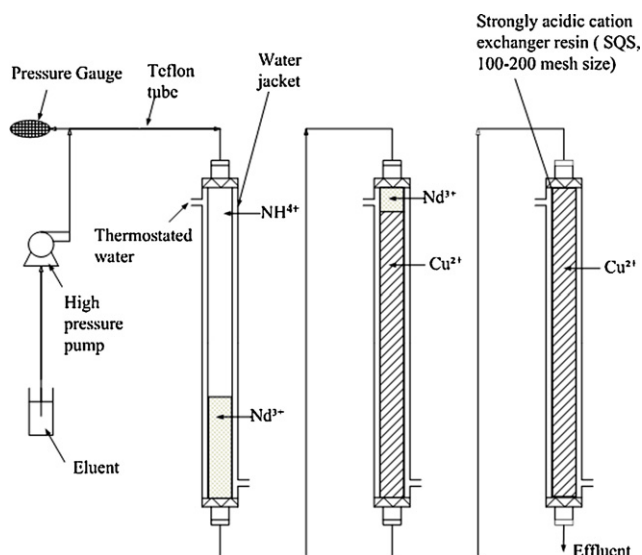


Fig. 1. Schematic of separation system used.

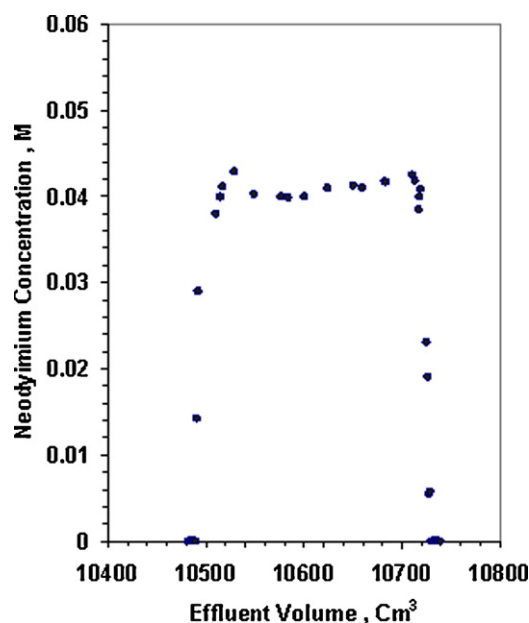


Fig. 2. The chromatogram for Nd–malate system at 50 °C.

remove ammonia from the solution. After dilution of the samples to ppm range, they were introduced to the peristaltic sample inlet of the ICP-MS. The dwell time for ¹⁴²Nd, ¹⁴⁴Nd and ¹⁴⁶Nd was 10 ms and for ¹⁴³Nd, ¹⁴⁵Nd, ¹⁴⁸Nd and ¹⁵⁰Nd was 20 ms. For each isotopic peak, three points were measured and the number of scans was 100 for each run. Each sample was measured for 30 s for five runs. The measurements error was within 0.4%.

3. Results and discussions

3.1. Chromatographic system

The neodymium band was formed and eluted as explained in the experimental part described above. The neodymium band was visible through the glass columns, which allow the measurement of the band length by a ruler. The band displacement chromatography was carried out at 50 °C, which is the best temperature based on our previous experience with Eu, U and Gd. In general the higher the temperature, the sharper the band boundaries due to the higher reactions rate at the boundaries, the faster the isotope exchange reaction, the smaller the height equivalent to theoretical plate, the plate height, and the higher the separation degree. However, higher temperatures than 50 °C create some air bubble problems in the column, which badly affect the band boundaries. The profile of Nd concentration in the effluent fractions, which corresponds to the neodymium band profile in the column after 50 m migration, is shown in Fig. 2. The sharp boundaries of the band indicate that the chromatographic displacement was

almost ideal at both boundaries. The chemical reactions involved in the ligand exchange system (LXS) takes place at the interface between NH_4^+ and Nd^{3+} adsorption bands, rear boundary. When ammonium malate reached the rear boundary of Nd^{3+} adsorption band, the ligands are transferred to Nd^{3+} because of the large stability constant of the Nd–malate complex compared to that of ammonium malate complex. During moving down of the solution phase, which contains Nd–malate complex species through the Nd^{3+} adsorption band in the column, the isotopic exchange reaction takes place between Nd^{3+} ions in the resin phase and Nd–malate complex species in the solution phase. After that the Nd–malate complex reaches the Cu^{2+} ion band, where the ligands are transferred to Cu^{2+} ions and Nd^{3+} ions are adsorbed in the resin phase. The related chemical reaction for the carboxylic acid (malate) ligand can be expressed, in the simplest form, as:



where the underlines represent the species in the resin phase, L represents the ligand species and ^HNd and ^LNd represent the heavy

Table 1
Experimental conditions of the ligand exchange system of neodymium at 50 °C.

Ligand (carboxylic acid)	Malic acid
Resin	Strongly cation exchange resin (SQS-6, 100–200 mesh size)
Pretreatment	2 M HCl followed by 0.1 M CuCl_2 to convert the resin into Cu^{2+} form
Column size	0.8 cm I.D. and 100 cm length
Eluent	0.2 M ammonium malate + 0.1 M NH_4NO_3 + 0.0002 M NaN_2 at pH 4.6
Feed solution	0.05 M NdCl_3
Nd-band length, cm	48.0
Migration length, m	50
Flow rate, cm^3/min	0.183
Band velocity, cm/min	0.072
Total effluent volume, cm^3	10,730.0

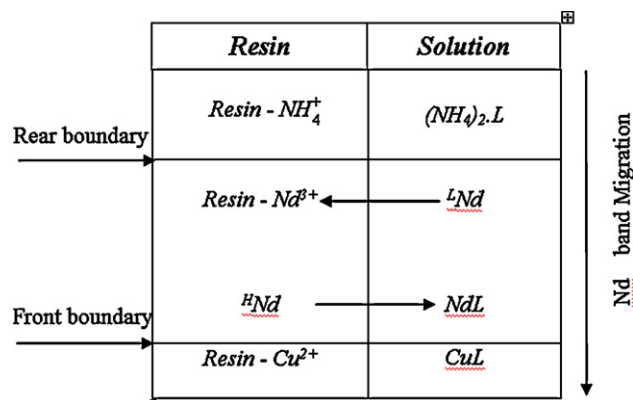


Fig. 3. Schematic diagram of the ion exchange mechanism.

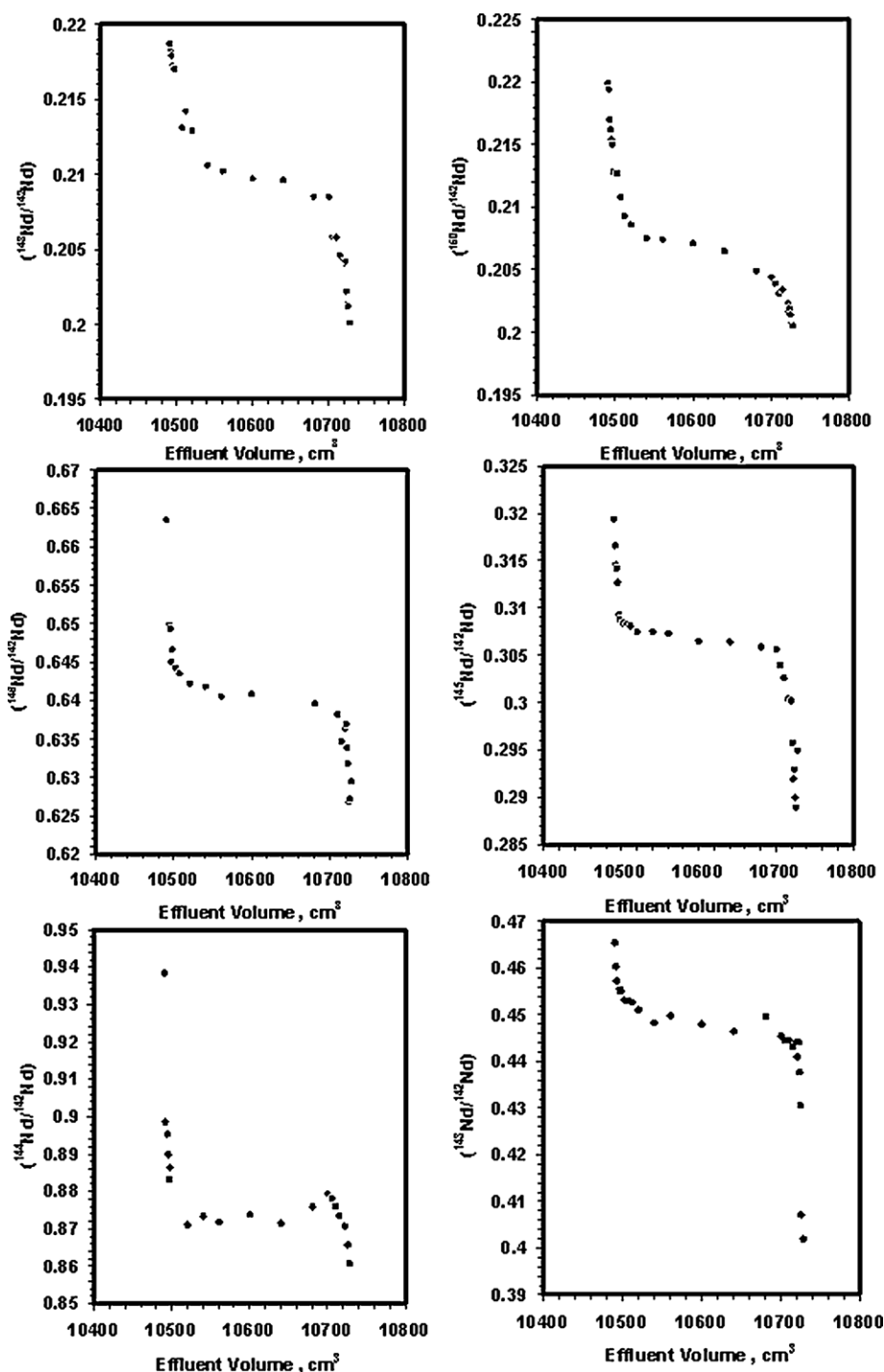


Fig. 4. Isotopic distribution ratio of different Nd isotopes against ^{142}Nd in Nd–malate system at 50 °C.

and the light neodymium isotopes, respectively. The schematic diagram of the expected ion exchange mechanism under the above-mentioned conditions, in the simplest form, is represented in Fig. 3. The chemistry of the system may be more complicated than that represented by the above equations. The exact complex structure and the different possibilities of Nd and/or H_2O hydrolysis are out of the scope of the present work.

Fig. 4 shows the isotope distribution ratios for neodymium isotopes for malate ligand at the constant temperature, 50 °C. It can be seen that the heavier isotopes are enriched into the front part, or preferentially fractionated in the complex form in

the solution phase. The degree of fractionation takes the order $^{143}\text{Nd} \leq ^{144}\text{Nd} \leq ^{145}\text{Nd} \leq ^{146}\text{Nd} \leq ^{148}\text{Nd} \leq ^{150}\text{Nd}$. This tendency is the same as that observed in the chromatographic isotope separation of calcium [26,27], magnesium [28], strontium [7], gadolinium [18], copper [23], and europium [19]. Since the heavier isotope is enriched in the complex species, the observed isotopic enrichment tendency in accordance with the theoretically expected direction of the isotopic effects in chemical exchange. 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.

Table 2
The average values of the separation coefficients, ϵ 's, of Nd isotopes against ^{142}Nd .

	Separation coefficient, ϵ ($\times 10^5$)					
	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
Rear boundary	1.6	5.1	5.7	9.8	17.2	19.6
Front boundary	1.2	4.5	5.1	11.4	16.4	20.8
Average	1.4	4.8	5.4	10.6	16.8	20.2

3.2. Separation factor

Isotopic fractionation in this study is expressed by reaction (2). It is possible to assume that only neodymium hydrated species exist in resin phase and only neodymium malate complex species exist in solution phase and the values of the isotopic equilibrium constant K is equal to the value of the single stage isotope separation factor, $\alpha = 1 + \epsilon$. Moreover, due to the fact that the separation coefficient of heavy isotopes is a small value, the separation coefficient, ϵ , will be equal to the logarithm of the equilibrium constant $\ln K$.

The separation factor of the current system, based on reaction (2) can be expressed as:

$$\alpha = 1 + \epsilon = \frac{[L\text{Nd}/H\text{Nd}]_r}{[L\text{Nd}/H\text{Nd}]_s} \quad (4)$$

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 'L' and 'H' represent the light and heavy isotopes. 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 given in Fig. 4, using the method developed by Spedding et al. [29] and Kakihana and Kanzaki [30].

The mathematical averages of the two separation coefficient values obtained from the front and rear boundaries were taken to calculate the process separation coefficient (ϵ) similar to the case of Gd [18]. Table 2 shows the calculated separation coefficients for the rear boundary, front boundary and their average values.

From the data shown in Table 2, it can be easily noticed that the separation coefficient increases with the increase of the mass number. This trend agrees with the previous findings in case of uranium [31] and gadolinium [18].

The separation coefficients ϵ of neodymium isotopes shown in (Table 2) are of higher values than those of cerium in cerium–malate system, where 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 [1]. They are also almost three times the values of the isotope separation coefficients ϵ of ^{155}Gd , ^{156}Gd , ^{157}Gd and ^{158}Gd against ^{160}Gd in gadolinium–malate system, which were found to be 6.1×10^{-5} , 5.2×10^{-5} , 4.4×10^{-5} and 2.7×10^{-5} , respectively [18]. On the other hand, they are much less than the isotope separation coefficients ϵ of $^{63}\text{Cu}/^{65}\text{Cu}$ in copper–malate system, which were found to be equal to 28.7×10^{-5} , 28×10^{-5} , 23.9×10^{-5} and 21.3×10^{-5} at 15 °C, 40 °C, 60 °C and 80 °C, respectively [32]. These higher values for copper isotope separation coefficients could be attributed to its lower mass number, according to the molecular vibration theory.

Fig. 5 shows the relationship between the separation coefficient and the reduced mass change from ^{142}Nd , $\delta m/mm'$. If the isotope effects of the current Nd–malate system is attributed to the conventional molecular vibration theory, the separation coefficients should be proportional to $\delta m/mm'$. It is clear that there is a negative deviation from the linearity for isotopes 143 and 145, while isotope 148 shows a positive anomaly. These deviations cannot be explained in the light of the molecular vibration theory or the odd-even phenomena. Similar to our discussion for Gd isotope effects [18] and Fujii et al. [21] discussion for Nd isotope effects in sol-

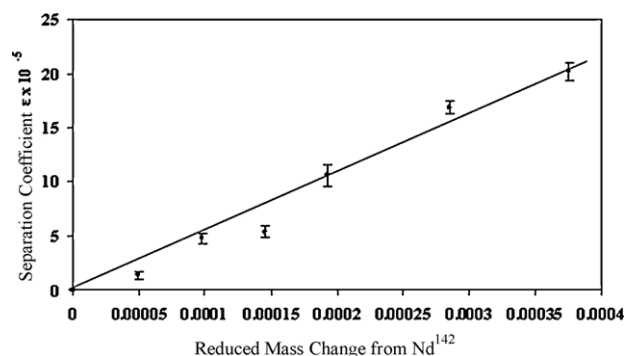


Fig. 5. The separation coefficient versus the reduced mass change from ^{142}Nd .

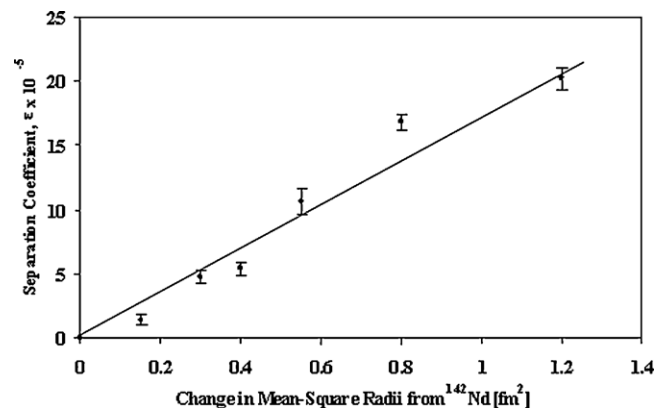


Fig. 6. The separation coefficient versus the change in the mean square radii of Nd isotopes from ^{142}Nd .

vent extraction system, the isotope effects of the current Nd–malate system can be attributed to the advanced theory according to the following relation:

$$\epsilon = \ln \alpha = \left(\frac{\delta m}{mm'} \right) a + (\delta \langle r^2 \rangle) b + \ln k_{\text{hf}} \quad (5)$$

where α is the separation factor and $\delta \langle r^2 \rangle$ is the mean square radii. The first term of Eq. (5) represents the molecular vibration. The second term represents the field shift, while the last term represents the nuclear spin. The changes in mean square radii of Nd isotopes have been measured by G. Lalazisis et al. [22]. A plot of the separation coefficient versus the change in the mean square radii of Nd isotopes is given in Fig. 6. A strong similarity can be easily notice between Fig. 5 and Fig. 6, which suggest that the field shift has a large contribution to the Nd–malate isotope exchange system. The odd isotopes 143 and 145 have a nuclear spin of 7/2, therefore the last term of Eq. (5) cannot be neglected and the nuclear spin contribution to the isotope effects of these two isotopes should be considered.

4. Conclusions

The displacement chromatogram of Nd ligand exchange system LXS was obtained at constant temperature, 50 °C, using malic acid as a complex reagent for a relatively long migration. The neodymium adsorption band underwent 50m of migration distance using four packed columns in a merry-go-round way. The degree of fractionation takes the order, $^{143}\text{Nd} \leq ^{144}\text{Nd} \leq ^{145}\text{Nd} \leq ^{146}\text{Nd} \leq ^{148}\text{Nd} \leq ^{150}\text{Nd}$. The heavier neodymium isotopes were clearly found to be enriched at Nd–ligand complex species side, and the lighter isotopes were enriched at the rear boundary in the LXS. The val-

ues of the neodymium isotope separation coefficients, ε , in neodymium–malate system were calculated and compared with those of cerium in cerium–malate system and with those of gadolinium in gadolinium–malate system, and those of copper in copper–malate system. The discussion was extended to the new advanced theory of isotope effects. It was shown that both field shift and nuclear spin contribute to the isotope effects of Nd–malate system.

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