Calcium Isotope Effects in Ion Exchange Electromigration and Calcium Isotope Analysis by Thermo-Ionization Mass Spectrometry

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Calcium ions were made to electromigrate along a cation exchange membrane. The abundance ratios of the calcium isotopes (Ca-40, 42, 43, 44, 48) in the migrated bands were measured by thermo-ionization mass spectrometry. The lighter isotopes were enriched in the front part of the migrated band. The increments in the isotope abundance ratios were found to be proportional to the mass differences of the isotopes. The observed ε-values per unit mass difference ($\varepsilon/\Delta M$) were 1.26×10^{-4} (at 20 °C), 1.85×10^{-4} (at 25 °C) and 2.4×10^{-4} (at 40 °C). The mass spectrometry was improved by using a low temperature for the evaporation of CaI_2.

Introduction

Calcium-48 has been considered a useful material to synthesize superheavy elements [1]. Fusion reactors are anticipated to utilize various materials in the middle-heavy mass region, which should show low radioactivation. For these and other reasons mentioned in the literature [11], isotope separation of elements such as calcium is of continuing interest.

So far calcium isotope separation was studied on several processes: molten salt electromigration (Klemm [2, 3]), ion exchange chromatography (Heumann [4], Aaltonen [5], Klinskii [6], Okamoto [7], Lee [8], Gutsykov [9], Jepson [10]), macrocyclic polyether (Jepson [11]), cryptand (Heumann [12]), and amalgam (Honda [13], Drury [14], Klinskii [15]).

In a previous paper, Kobayasi et al. [16] studied the calcium isotope separation by electromigration using ion exchange resins packed in a column. In the present work an ion exchange membrane was chosen as the migration medium because of the ease in the experimental operations.

Experimental

Materials

The cation exchange membrane Aciplex CK-1, a homogeneous, strongly acidic type stylene divinylbenzene copolymer resin, was manufactured by Asahi Chemical Industry Co. Prior to use the membrane was converted to the H^+ form and cut into a strip (4 cm wide and 1 m long). Other chemicals were of reagent grade.

Procedure

The electromigration tube with the membrane strip was placed in a thermostated water bath (Figure 1). CCl_4 works as coolant for the membrane and also as electric insulator to separate the cathode from the anode compartment. In experimental Run 1, 0.5 mol/dm^3 (M) $CaCl_2$ was first fed into the anode compartment and then replaced by 0.5 M $SrCl_2$ after the formation of an appropriate width of a calcium adsorption band in the membrane by passing direct current. In Runs 2 and 3, a solution of 0.5 M $MgCl_2$ was first fed into the anode compartment and then replaced by 0.5 M $CaCl_2$ after the formation of an a few cm's wide magnesium band. 0.1 M HNO_3 was used throughout in the cathode compartment.

Part of the membrane was rolled up in the cathode compartment at the beginning of the migration. During the migration the membrane was con-

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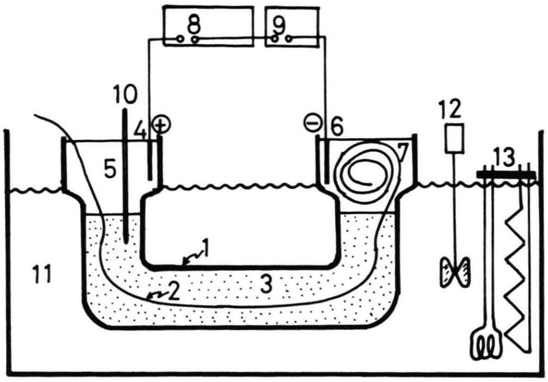

Fig. 1. The electromigration apparatus. 1. Migration tube. 2. Cation exchange membrane. 3. CCl_4. 4. Anode (Pt). 5. Anode solution. 6. Cathode (Pt). 7. Cathode solution. 8. Stabilized DC power supply. 9. Ammeter and voltmeter. 10. Thermometer. 11. Thermostated water bath. 12. Stirrer. 13. Heater and Cooler.

tinuously pulled out from the anode compartment to keep the migration band in a stationary position. The temperature was controlled with thermostated water at 20, 25, 40 °C, for Run 1, 2, 3, respectively. After the migration, the membrane was taken out through the cathode compartment and washed with deionized water. The front part of the migration band was made visible by UV light and cut into stripes of 2 mm length in Run 1, and 5 mm length in Runs 2 and 3. The calcium ions in the samples were leached out with 2 M HNO_3.

Analysis

An aliquot of the leaching solution of each sample fraction was used to determine the amount of calcium ions by flame photometry at 554.0 nm. The pieces of the membrane from which the calcium ions were extracted, were rinsed with deionized water and dried at 40 °C for a few hours. The weight of the dried pieces was used to evaluate the concentration of the calcium ions in the membrane.

The remaining sample solutions were dried on a hot plate and contacted repeatedly with HI solution to obtain calcium iodide for the mass spectrometric analysis. A droplet of a CaI_2 solution (approx. 10 μg of Ca ions) was placed on a vaporization filament in the thermo-ionization cartridge of a mass spectrometer MAT CH-4. The optimum evaporation condition was found by observing the amount of ionized calcium at different heating currents.

Results and Discussion

Calcium mass spectrometry

In the standard method for calcium isotope analysis by surface-(thermo-)ionization one applies a very high temperature to both the vaporizing and ionizing filaments, CaI_2 being converted to CaO by strong heating [17]. This method is well applicable when the sample is extremely pure and the pressure in the vacuum system is extremely low. However, the sample taken from the ion exchange electromigration unavoidably contain some impurities which cause an instability in the calcium ionization at the high temperature and also a rise of the noise level of the mass spectra.

In the preliminary experiments aimed at finding the optimum conditions for the calcium mass spectrometry, we observed that there were two regions of calcium ionization in terms of the heating temperature. On using CaI_2 samples and tungsten filaments for both ionization and vaporization, the heating current of the ionizing filament was increased up to 5.5 A, and thereafter the heating current of the vaporizing filament was slowly increased. The ionization of Ca-40, detected by means of a Faraday-cup collector, first appeared at 0.5 A of vaporizing current. Above 1 A the calcium ion beam rapidly decreased, and it then increased again above 3 A. These observations are presented in Figure 2.

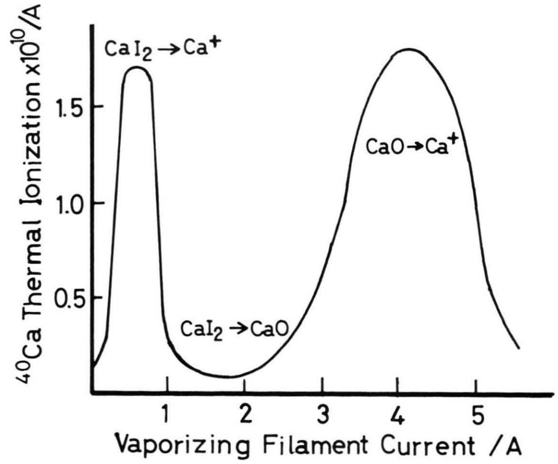

Fig. 2. Thermo-ionization of calcium in a mass spectrometer. Sample: CaI_2. Ionizing filament: tungsten (heating current 5.5 A). Vaporizing filament: tungsten. Mass spectrometer: MAT CH-4.

Samples taken after the tests in the low heating region showed a transparent glass-like state, being the same as the original state of the sample. When the glassy state sample was reheated in the ion source of the mass spectrometer, the same ion currents were obtained. On the other hand, a sample taken after a test at the higher heating condition had changed to a white solid. When this sample was reheated in the mass spectrometer, the calcium ion beam was only obtained in the higher heating region. These facts indicate that the sample CaI_2, which has a relatively high vapor pressure, evaporates in the low heating region and is directly ionized at the surface of the ionizing filament, while the sample is converted to CaO in the high heating region and gives a sufficient ion beam in the strong heating conditions of 4 A only, due to the low vapor pressure of CaO.

Test were conducted using rhenium filaments for ionization and tungsten filaments for vaporization. In these experiments basically the same pattern of the calcium ionization was observed, with 4.5 A on the rhenium filament. This tendency of calcium ionization was also observed in tests using the triple-filament cartridge mounted in a mass spectrometer MAT CH-5. In the present work all the measurements of the calcium isotopic ratios were carried out in the low heating region using rhenium filaments for ionization and tungsten filaments for vaporization.

A mass spectrum of the calcium isotopes is shown in Figure 3. A single scanning of the concerned isotopes takes about 1 minute. An example of the time variation of the isotopic ratios is presented in Figure 4. The standard errors of the isotopic ratios in Fig. 4 are approximately 0.3%. Because of the long time interval between the cyclic scannings, the standard error became somewhat large. This error, however, is well within the allowable level for the present purpose of isotope analysis. If the measurement were confined to a fixed pair of isotopes, e.g. Ca-40 and Ca-44, the errors would become smaller.

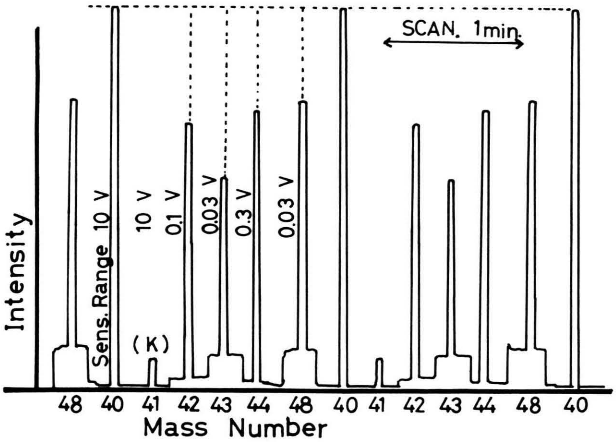

Fig. 3. Mass spectrum of calcium isotopes. The base-line is elevated to indicate the sensitivity ranges.

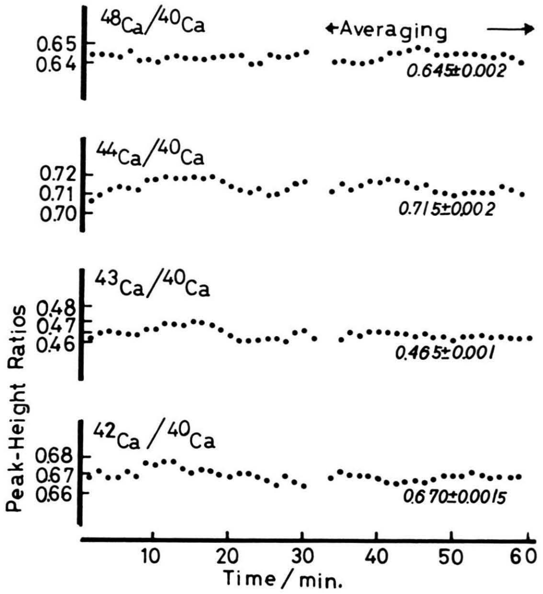

Fig. 4. Time variation of measured isotopic ratios. The isotopic ratios are obtained by multiplying the figures with the sensitivity factors 1×10^{-2}, 3×10^{-3}, 3×10^{-2}, 3×10^{-3} for Ca-42, 43, 44, 48, respectively, resulting in $r(42/40) = (0.670 \pm 0.002) \times 10^{-2}$, $r(43/40) = (1.395 \pm 0.003) \times 10^{-3}$, $r(44/40) = (2.145 \pm 0.006) \times 10^{-2}$, $r(48/40) = (1.935 \pm 0.006) \times 10^{-3}$. The errors indicate 2 σ.

Electromigration

The experimental conditions are summarized in Table 1. The profiles in the calcium bands after the migration are shown in Figures 5–7. The change in the isotopic ratios is expressed in terms of the local enrichment factor α defined as

$$\alpha = r(i/40)_x / r(i/40)_o, \tag{1}$$

where $r(i/40)_x$ is the abundance ratio of the isotope i and the reference isotope Ca-40 at a distance x from the starting position of migration, and the

Table 1. Experimental conditions and results.

Run No.	1	2	3
Temperature/°C	20	25	40
Migration length/cm	70	64	80
Migration velocity/ cm h^{-1}	4	2	4
Applied voltage/V	440 ~ 550	600 ~ 1200	600 ~ 800
Current density/ mA cm^{-2}	228	114	228
$\varepsilon(42/40) \times 10^4$ (cf. (2))	2.85	3.96	5.22
$\varepsilon(43/40) \times 10^4$	4.44	6.14	7.36
$\varepsilon(44/40) \times 10^4$	5.04	7.02	8.46
$\varepsilon(48/40) \times 10^4$	10.2	16.9	19.2
Av. $\varepsilon/\Delta M \times 10^4$	1.26	1.85	2.4

The experimental errors of ε are estimated to be 10% of each values (1 σ).

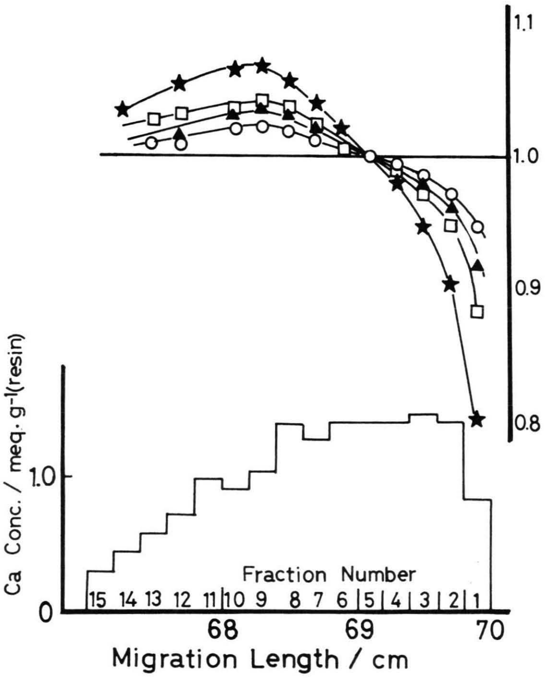

Fig. 5. Profiles of the calcium concentration and the local enrichment factor of the calcium isotopes in the band (Run 1). ○: $\alpha(42/40)$. ▲: $\alpha(43/40)$. □: $\alpha(44/40)$. ★: $\alpha(48/40)$.

subscript o indicates the original value before the migration.

It is seen that the shape of the calcium profile depends on the leading and following ions. In Run 1, H^+ is leading and Sr^{2+} is following. In Runs 2 and 3, Mg^{2+} is leading and Ca^{2+} is following (breakthrough type). A sharp leading boundary was only attained in Run 1. This is because the mobility of

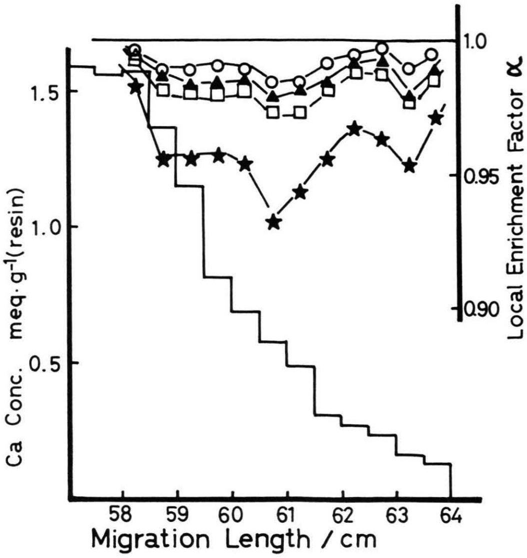

Fig. 6. Profiles of the calcium concentration and the local enrichment factor of the calcium isotopes in the band (Run 2). Symbols are the same as in Figure 5.

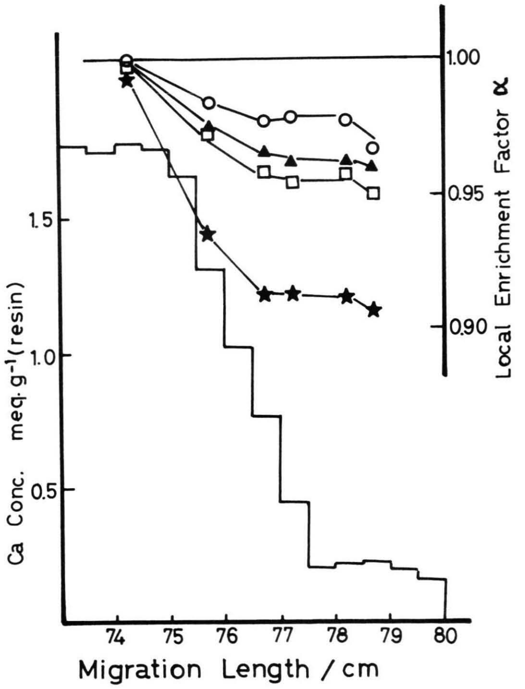

Fig. 7. Profiles of the calcium concentration and the local enrichment factor of the calcium isotopes in the band (Run 3). Symbols are the same as in Figure 5.

H^+ is much larger than that of Ca^{2+}, while Mg^{2+}, Ca^{2+}, Sr^{2+} have similar mobilities.

In the case of the sharp leading band boundary between H^+ and Ca^{2+} (Run 1), the isotope accumulation in the leading part of the band follows an exponential curve. In the other cases (Runs 2 and 3), the isotope distribution is complicated; the maximum enrichment is not always obtained at the extreme front of the band. In chromatographic isotope separation, the maximum enrichment is expected to appear at the extreme front of the band even if chemically resembling ions form a broadening boundary (Glueckauf's theorem [18]). The present results suggest that the electromigration process may involve some different mechanisms.

The ε-values as defined for an isotopic binary system is determined by the equation [19]

$$\varepsilon = \sum_j f_j (R_j - R_o)/Q\, R_o (1 - R_o)\,, \qquad (2)$$

where f_j is the total amount of isotopes in sample fraction j, R_j the isotopic atom fraction in j, Q the total ion exchange capacity consumed in the migration, and the subscript o indicates the unchanged value. The summation is to be taken to one side of the unchanged R-value only. Since isotope Ca-40 is the predominant species and the other isotopes are minor components of Ca, this system can, with a good approximation, be regarded as an isotopically binary system where (2) is applicable. By marking pairs of Ca-40 and one of the other isotopes i, the ε-values were determined for each isotopic pair. The results are listed in Table 1.

The results clearly show that the value of ε is proportional to the isotopic mass difference $\Delta M (= M_i - 40)$. The ε-value per unit mass difference, $\varepsilon/\Delta M$, is also presented in Table 1. To examine the mass difference effect on the local enrichment factor α, the net increment of the local enrichment factor, $\ln \alpha$, is plotted in Fig. 8 against the isotopic mass difference using the experimental data for the sample fractions in Run 1. It is ascertained in Fig. 8 that the value of $\ln \alpha$, is proportional to the mass difference. A similar tendency of isotopic enrichment has been reported in other systems, e.g. the molten salt electromigration for zinc isotope separation [20] and calcium isotope separation by ion exchange chromatography [10].

The ε-value increases with temperature (cf. Table 1). This tendency is opposite to the normal temperature effect on equilibrium isotope effects and suggests that the present isotope effects originate partly from kinetic processes in the ion exchange membrane.

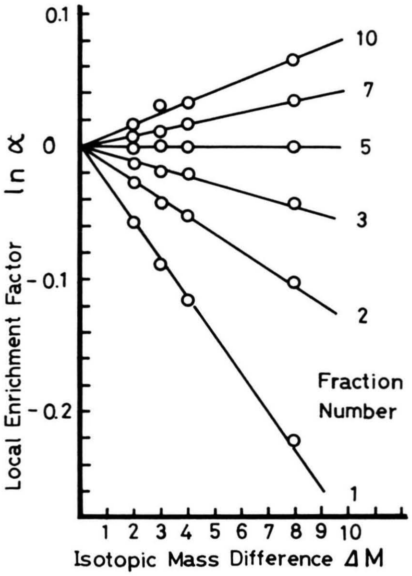

Fig. 8. The relation between local enrichment factor α and the isotopic mass difference, observed on the sample from Run 1.

Conclusions

A low temperature heating condition in calcium mass spectrometry was found to be convenient and specifically useful when the samples contain impurities.

The isotopic distribution in the calcium migration band strongly depends on the shape of the band boundary.

Both the ε-value and the increment $\ln \alpha$ in the local enrichment factor are proportional to the isotopic mass difference of the considered isotopes.

The ε-values correlates positively with the experimental temperature.

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