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Separation of calcium-48 isotope by crown ether chromatography using ethanol/hydrochloric acid mixed solvent

Shin Okumura [a], Saori Umehara [b], Yasuhiko Fujii [a,*], Masao Nomura [a], Toshitaka Kaneshiki [a], Masaki Ozawa [a], Tadafumi Kishimoto [c]

[a] Tokyo Institute of Technology, Research Laboratory for Nuclear Reactors, O-okayama, Meguroku, Tokyo 152-8550, Japan
[b] Osaka University, Research Center for Nuclear Physics, Ibaraki, Osaka 567-0047, Japan
[c] Osaka University, Graduate School of Science, Toyonaka, Osaka 567-0043, Japan

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ABSTRACT

Benzo-18-crown-6 ether resin embedded in porous silica beads was synthesized and used as the packing material for chromatographic separation of ^{48}Ca isotope. The aim of the present work is to develop efficient isotope enrichment process for double β decay nuclide ^{48}Ca. To this end, ethanol/HCl mixed solvent was selected as the medium for the chromatographic separation. Adsorption of calcium on the resin was studied at different HCl concentrations and different ethanol mixing ratios in batch-wise experiments. A very interesting phenomenon was observed; Ca adsorption is controlled not by the overall HCl concentration of the mixed solvent, but by the initial concentration of added HCl solution. Calcium break-through chromatography experiments were conducted by using 75 v/v% ethanol/25 v/v% 8 M HCl mixed solvent at different flow rates. The isotope separation coefficient between ^{48}Ca and ^{40}Ca was determined as 3.8×10^{-3}, which is larger than that of pure HCl solution system. Discussion is extended to the chromatographic HETP, height equivalent to a theoretical plate.

1. Introduction

Calcium isotope ^{48}Ca is a double β nuclide with the high decay energy of 4.27 MeV. The 0 neutrino decay of ^{48}Ca shows a sharp peak of β-ray spectrum, which is quite different from the normal β-ray spectrum. The measurement of double β decay of ^{48}Ca gives the very important information for nuclear physics. Two of the present authors, Kishimoto and Umehara have been conducting the measurement of double β decay of ^{48}Ca using natural calcium [1,2]. However the abundance of ^{48}Ca in natural calcium is very low, 0.187%. Enrichment of ^{48}Ca has been anticipated.

Chemical isotope separation methods have been applied to the stable isotope separation of light elements such as hydrogen, lithium, boron, carbon, nitrogen, oxygen, etc. The isotopically enriched products of these elements are commercially available. The commercial processes for the isotope separation of these elements are distillation, chemical exchange, electrolysis, etc.

Chromatographic methods with packed columns have been also applied for the research work on isotope effects and isotope separation. Boron isotope separation has been studied by using anion exchange resins [3]. Nitrogen isotope separation has been studied by using cation exchange resins [4,5]. Even in the case of uranium, chromatographic separation of isotope ^{235}U was studied by using anion exchange resin in the laboratory scale [6,7]. Calcium isotope separation by chemical exchange is based on the isotopic fractionation occurring in the chemical exchange reactions. Calcium isotope fractionation has been observed in several chemical exchange processes. Kobayashi et al. studied calcium isotope separation by using ion exchange chromatography [8] and by electro migration using ion-exchange resin [9]. The ion exchange process of calcium shows so small isotope separation coefficient that calcium isotope enrichment process is regarded to be difficult. Heumann et al. [10,11] have observed the calcium isotope fractionations in the adsorption processes of ion exchange, crown ethers and criptand. Jepson et al. [12,13] studied the calcium isotope separation by using crown ether resin. Criptand and crown ether resin show larger isotope separation coefficients and they are regarded as promising materials. In our previous papers, we have also developed benzo-18-crown-6-ether resin, depicted in Fig. 1, synthesized by the phenol condensation type polymerization. The resin has been applied to calcium isotope separation using concentrated HCl solutions [14,15]. Oi et al. also reported Ca isotope separation by using our type of resin [16,17].

* Corresponding author.
E-mail address: yfujii@nr.titech.ac.jp (Y. Fujii).

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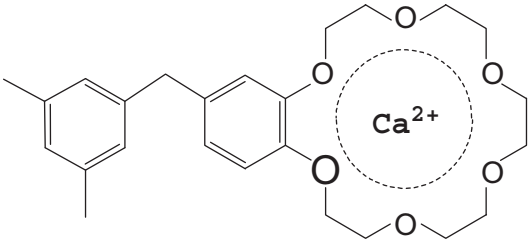

Fig. 1. Calcium ion adsorption on the benzo-18-crown-6 ether resin.

The principle of chemical isotope separation of calcium is based on the isotope fractionation occurring in the following exchange reaction,

$$^{40}Ca^{2+}{}_{aq} + {}^{48}Ca^{2+}CE = {}^{48}Ca^{2+}{}_{aq} + {}^{40}Ca^{2+}CE, \quad (1)$$

where CE represents crown ether in the resin phase and $Ca^{2+}{}_{aq}$ is aqua-complex of calcium in the aqueous phase. Because of the molecular vibration in the Ca complexes, the light isotope is fractionated in the loosely coordinated species, which is crown ether complex in this case. On the other hand the heavy isotope is fractionated in aqua-complex where Ca^{2+} ions are strongly coordinated with water molecules. Usually, Ca^{2+} aqua-complex in aqueous solution is so strong that Ca^{2+} ion does not form complex with the crown ether resin. In the present work, concentrated HCl solutions are examined as media for Ca^{2+} ion adsorption by crown ether resin.

In the chromatographic process, it is expected that the light isotope of ^{40}Ca is trapped in the resin phase, and the heavier isotope ^{48}Ca, fractionated in the aqueous solution, appears in the front adsorption band boundary of the chromatogram. The separation coefficient observed in the present work corresponds to the isotopic equilibrium constant of the above-mentioned exchange reaction.

The most important factors to develop chromatographic isotope separation processes are the separation coefficient between two isotopes and the HETP of chromatography. The large values of the separation coefficients and the small value of HETP enhance the productivity of enriched isotopes. The separation coefficient depends on the difference in chemical states between the solution phase and the resin phase. We have to check different types of solution to obtain the better chemical system with larger separation coefficients. In the present paper, attention has been placed on the effects of ethanol/HCl mixed solvent and also on the effects of the feed flow rates.

2. Experimental

2.1. Calcium adsorption

Prior to ^{48}Ca isotope separation experiments, we tested the Ca adsorption on benzo-18-crown-6 ether resin in HCl and also in ethanol/HCl mixed solution. Adsorption capability is numerically expressed as the distribution coefficient, K_d. The value of K_d is a constant at infinitely low concentration of the ions in question in outer solution. At rather high concentration, the K_d value is changeable depending on the concentration of the ions in the outer solution. For the practical purpose of the present experiments, it is useful to measure the K_d values both at the very low concentration and also at the practically usable concentration of calcium ions in the mixed solution. Thus the distribution coefficients were measured at two different initial concentrations of Ca ion, 50 ppm and 4000 ppm in the present work.

2.1.1. Adsorption at low Ca concentration

Calcium adsorption on crown ether resin was studied using two types of solution; pure HCl solutions and ethanol/HCl mixed solutions. The concentration of pure HCl solutions and the compositions of ethanol/HCl mixed solutions are presented in Fig. 3. In both cases, calcium chloride 50 ppm (50 mg/l) solution was prepared, by dissolving $CaCl_2$ in HCl and ethanol/HCl mixed solutions. All chemicals, HCl, ethanol, $CaCl_2$ used in the present work were reagent grade supplied by Wako Pure Chemical Industries Ltd.

The crown ether resin 2 g, which contains crown ether 0.21 g as monomer, was immersed in 25 ml HCl solution or ethanol/HCl mixed solution in a 50 ml bottle and was vibrated in a shaker at the vibrational frequency of 160 rpm for 24 h at 298 K (25 °C). After the shaking, a portion of the solution was sampled and diluted with water. Ca concentrations in the diluted sample solutions were determined by flame photometry with the emission spectral line 622 nm. In the present work, calcium concentration was determined by an atomic absorption spectrophotometer ANA-182F, made by Tokyo Photoelectric Co. Ltd., with the mode of flame photometry. Radiation source of hollow cathode lamp was not used. The sensitivity, or the lowest measurable concentration, of flame photometry is approximately 1 ppm for Ca ions. This sensitivity is appropriate for calcium concentration measurement in the present work.

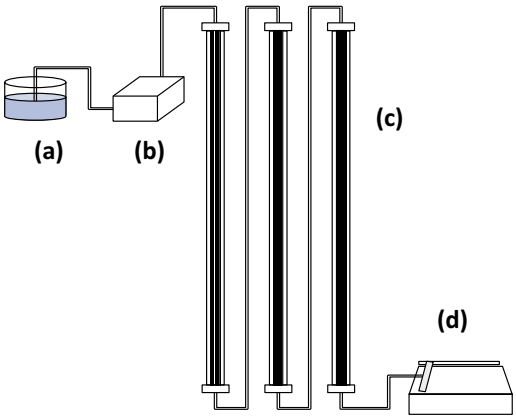

Fig. 2. Chromatographic apparatus. (a) Feed solution, (b) pump, (c) columns, (d) fraction collector.

2.1.2. Adsorption at high Ca concentration

Using the same type resin as mentioned above, we measured the distribution coefficients of Ca ions at rather high Ca concentration; the initial concentration of Ca was 4000 ppm. The ethanol/HCl mixed solutions were prepared by mixing 50 ml ethanol with 50 ml HCl solution. The concentrations of the added HCl were 1 M, 3 M, 6 M, 9 M and 12 M. The distribution coefficients of Ca in HCl aqueous solutions were also measured using solutions of 1 M, 3 M, 6 M, 9 M and 12 M HCl as reference solutions.

In each measurement, 8 g crown ether resin was put into 20 ml of above mentioned solution and left in a shaker in the same way as mentioned earlier. After 1 day, a portion of solution, 0.2 ml, was sampled and diluted with water of 19.8 ml. The concentration of Ca in the sample solution was measured by flame photometry at 622 nm.

2.2. Chromatographic experiments

The experimental arrangement of chromatographic apparatus is shown in Fig. 2. The synthesized benzo-18-crown-6 ether resin was packed in 3 units of glass column of which inner diameter is 8 mm each and the length is 100 cm. The packed columns were washed first with 2 M HCl solution, then with 0.1 M HCl solution and finally with ethanol (75 v/v%)/8 M HCl (25 v/v%) mixed solvent. Chromatographic isotope separation of calcium was conducted by

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