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A Study on Zinc Isotope Fractionation in a Benzo Crown Resin/Acetone System

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Zinc isotope fractionation has been studied in different cavities of crown ether resins that were synthesized in porous silica beads. Displacement chromatography was performed, as a breakthrough manner, in glass columns by feeding in a zinc chloride solution. From the mass analysis of effluents, the heavier isotopes of zinc were enriched at the beginning of the zinc adsorption band. The front maximum enrichment (1.0168), separation coefficient (8.1×10^{-4}), and smaller HETP (0.205 cm) for the isotopic pair ^{68}Zn/^{64}Zn were obtained with the use of the benzo-15-crown-5 resin. Zinc isotope fractionation was obviously affected by the cavity size of the crown ethers.

Since Taylor and Urey applied a chromatographic adsorption method to the separation of lithium in 1938,[1] many studies involving isotope effects and separations by chemical-exchange processes ranging from hydrogen to uranium have been reported.[2] In our laboratory, starting from uranium,[3,4] the isotope effect and separation of transition-metal elements Cu[5] and V,[6,7] and of the lanthanides Eu[8] and Gd[9] were studied by ion-exchange chromatography. Recently, our attention has turned to the transition-metal element zinc, due to its ability to reduce the contamination of ^{60}Co in nuclear power plants.[10] The amount of ^{60}Co incorporated in an oxide film decreased in the presence of Zn ions in water.[11] Naturally occurring zinc contains five stable isotopes: ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn, of which their natural abundances are 48.6, 27.9, 4.1, 18.8, and 0.62%, respectively. From thermal neutron adsorption, ^{64}Zn in the vicinity of a reactor core can be converted to the radioactive isotope ^{65}Zn which has a relatively long half life of 245 days. Therefore, ^{64}Zn-depleted zinc is desirable to decrease the occupational radiation dose to workers who inspect and maintain the nuclear power plants.

After Pedersen synthesized crown ethers,[12] intensive studies have been performed concerning the complex formation reactions of crown ethers with various cations,[13,14] and a number of studies involving the isotope effects have been reported. Nishizawa et al. studied isotope effects in liquid–liquid extraction with crown ethers and determined isotope separation factors for many metal elements such as lithium,[15] nickel,[16] zinc,[17] strontium,[18] and barium.[19]

Liquid–liquid systems have been used in many reports to study the isotope effects of crown ethers. On the contrary, there has been only a limited number of works on chromatographic isotope separation using crown ether resins. Column chromatography is advantageous because it is a multi stage process. In the present work, four resins which have a benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, and dibenzo-18-crown-6 moiety were newly synthesized. The structures of these compounds are illustrated in Fig. 1. The synthesize methods for benzo crown resins were as follows: 3,3′-ethylenedioxydiphenol and benzo crown were added into trichloroacetic acid, and dissolved while stirring, paraformaldehyde was added to the mixture, and then the resin was precipitated from the mixture. The synthesis of crown ether resins will be reported elsewhere in detail. These resins seem very good based on the adsorption amount and velocity to equilibrium determined from batch testing. Therefore, these four resins were synthesized in small silica beads for chromatographic use. In the present paper, we experimentally study zinc isotope separation by using crown ether resins and, specifically, determine isotope front maximum enrichment (β), separation coefficient (ε), and the height equivalent to a theoretical plate (HETP). The effect of the cavity size of crown ethers on isotope separation is obviously related to zinc isotope separation.

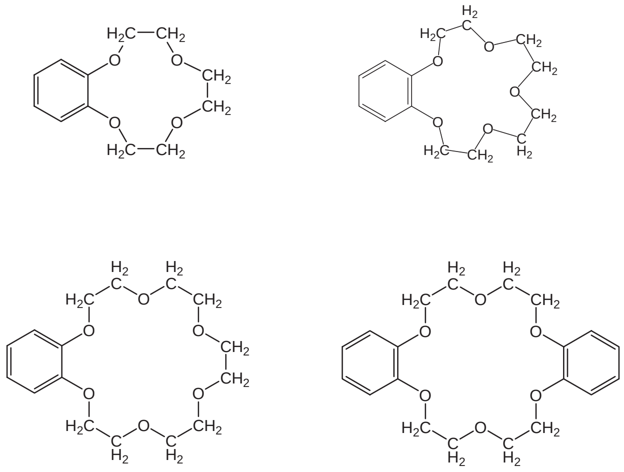

Fig. 1. Structure of benzo crown ethers.

Experimental

Apparatus. The apparatus used for chromatography of the

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Table 1. Chromatographic Experimental Conditions for Zinc Isotope Separation

	Benzo-12-crown-4	Benzo-15-crown-5	Benzo-18-crown-6	Dibenzo-18-crown-6
Capacity/mmol m^{-1}	13.5	12.6	12.0	13.8
Feed solution	0.5 ± 0.2 mol dm^{-3} $ZnCl_2$ in dehydrated acetone			
Temperature/K	298 ± 1			
Flow rate/mL h^{-1}	5.6	6.0	4.8	5.5
Band velocity/cm h^{-1}	12.9	11.3	10.5	10.5
Migration length/cm	500	500	400	500

zinc isotope separation consists of five ion-exchange columns equipped with water jackets (100 cm × 0.8 cm diameter made of pressure resistant Pyrex glass). A high-pressure pump was used for controlling the feeding solution at a constant flow-rate. To monitor the column pressure, a pressure gauge with a safety device was placed between the column and the pump. Flexible PTFE tubes with a diameter of 0.8 mm were used to connect the columns, valves, and pump. The temperature was set at 298 ± 1 K throughout the experiments by circulating thermostated water through extension water jackets on the columns. A fraction collector was used for collecting the effluent emerging from the bottom of the column.

Chromatographic Method and Analysis. The crown ether resins embedded in silica beads were put into the columns, which were rinsed with an amount of dehydrated acetone three times the total volume of the columns. A dehydrated acetone solution of zinc chloride was introduced into the top of the column to form a zinc adsorption band, of which the color was dark enough to distinguished from the straw yellow color of the original resin. The effluent was collected in small fractions (ca. 1.0 mL) by using a fraction collector. The fractions were used to analyze the zinc concentration and isotopic abundance ratios. The concentration of zinc was measured by flame analysis with an atomic absorption spectrophotometer (ANA-182F). The isotopic abundance ratio of the front band of the effluent was determined by using an inductively coupled plasma mass spectrometer (ICP-MS) with the zinc concentration diluted to 30 ppb. The dwell time for ^{64}Zn, ^{66}Zn, and ^{67}Zn was 10 ms and for ^{68}Zn and ^{70}Zn was 20 ms. For each isotope, the number of scans was 200, and the measurement error was within 0.2%. The experimental conditions for zinc chromatographic operation systems are shown in Table 1.

Results and Discussion

Four different benzo crown resins were used to study zinc isotope separation. The most obvious difference between these resins was the size of the macrocyclic cavity. Figure 2 shows the zinc adsorption capacities of the different crown ether resins. The total adsorption of zinc on the crown ether resin (Q_{tot}) was calculated by Eq. 1:

$$Q_{tot} = C_0(V_{FB} - V_d), \tag{1}$$

where C_0 is the concentration of zinc in the feed solution, V_{FB} is the breakthrough volume, which is defined as the volume when zinc starts coming out of the column, and V_d is the dead volume of the column. Benzo-15-crown-5 resin contains 12.6 mmol of the benzo crown moiety in a one meter column, and its zinc adsorption capacity Q_{tot} was 7.96 mmol. Therefore, only 63% of benzo crown moiety adsorbed zinc if zinc and benzo crown ether formed as 1:1 complex. The adsorption capacity of zinc does not depend on the cavity size of crown ethers. The adsorption mechanism for zinc seems to be very complicated, and the zinc adsorption capacity can not be determined only by the cavity size of crown ether. The ionic radii of Zn^{2+} is 0.74 Å (coordination number 6), and 0.60 Å (coordination number 4).[20] Therefore, zinc seems to enter into the cavity of 15-crown-5. The reaction of $ZnCl_2 \cdot 2H_2O$ with benzo-15-crown-5 in methanol gives rise to a polymer with the zinc ion located outside the macrocyclic cavity.[21] Therefore, water should be removed from the zinc solution to avoid formation of hydrogen bonds, which seem to affect adversely isotope separation. In the present work, dehydrated acetone and zinc chloride were used for preparation of the solutions. During chromatography, acetic anhydride (1.0% volume ratio) was added to the zinc chloride solution to remove water. The resin phase was dried by washing the mixture of dehydrated acetone and acetic anhydride. Various types of complexes may exist in this system even under dehydrated conditions. Further experiments are needed to clarify intra- and extra-cavity ionic complexes and their equilibria with zinc, crown ethers, and solvent as one of ligands.

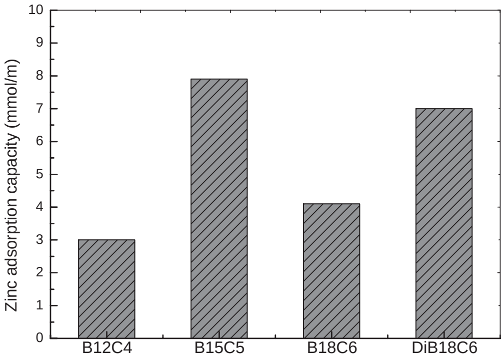

Fig. 2. Zinc adsorption capacity for different crown ether resins.

Figure 3 is an example of chromatographic profile obtained by using four different resins including benzo-18-crown-6 resin. The front maximum enrichment (β) for zinc isotope separation for the four resins is given in Fig. 4. Here, β is defined as Eq. 2:

$$\beta = ({}^{i}\mathrm{Zn}/{}^{64}\mathrm{Zn})_{\mathrm{sample}}/({}^{i}\mathrm{Zn}/{}^{64}\mathrm{Zn})_{\mathrm{original}}, \quad \text{where } i = 66 \text{ and } 68. \tag{2}$$

β values larger than 1.000 mean that the heavier isotope of zinc is preferentially enriched in the eluted samples in the front band region and lighter isotope is enriched in the resin phase. Benzo-15-crown-5 resin has the largest β for the isotopic pairs ^{68}Zn/^{64}Zn and ^{66}Zn/^{64}Zn among these four benzo crown resins. The value of each front maximum enrichment for isotopic pair ^{68}Zn/^{64}Zn is nearly twice than that for ^{66}Zn/^{64}Zn. This

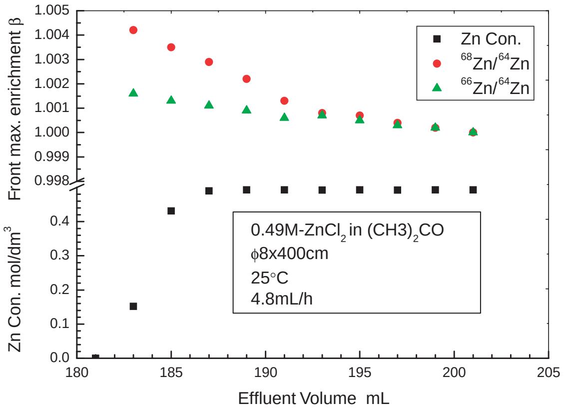

Fig. 3. Zinc isotopic enrichment and effluent concentration profile separated using benzo-18-crown-6 resin.

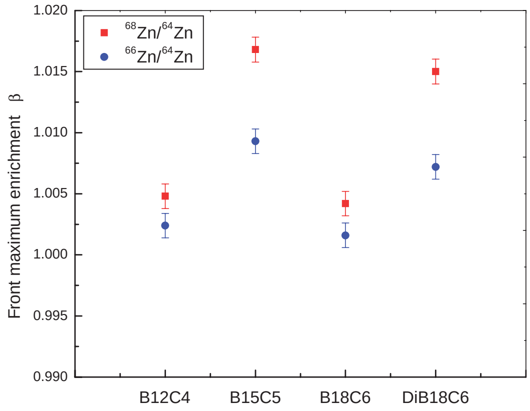

Fig. 4. Zinc isotopic front maximum enrichment of different crown ether resins.

can be attributed to the difference in mass difference.

In this study, the total zinc isotopic fractionation was analytically studied at the breakthrough point of the chromatography. Single-stage isotope separation factor, α, is defined in the Eq. 3 as the ratio $[^{H}Zn]/[^{64}Zn]$:

$$\alpha = 1 + \mathcal{E} = ([^{H}\mathrm{Zn}]/[^{64}\mathrm{Zn}])_{r}/([^{H}\mathrm{Zn}]/[^{64}\mathrm{Zn}])_{s}, \tag{3}$$

where ^{H}Zn denotes heavy zinc ^{66}Zn or ^{68}Zn. $([^{H}Zn]/[^{64}Zn])_r$ and $([^{H}Zn]/[^{64}Zn])_s$ are ratios for the resin and for the solvent phase, respectively. Separation factor indicates the deviation of the isotopic abundance ratios between two different phases at equilibrium. $\mathcal{E}$ in the equation denotes the separation coefficient. The value of the separation coefficient can be evaluated from the isotopic enrichment curves of the front and/or rear boundary according to Eq. 4 which was developed by Spedding et al.,[22] and by Kakihana and Kanzaki.[23] HETP (height equivalent to a theoretical plate), which was developed for isotope separation by ion-exchange chromatography, was calculated by Eq. 5:[24,25]

$$\mathcal{E} = \frac{\sum q_i |R_i - R_o|}{Q_{tot} R_o (1 - R_o)}, \tag{4}$$

$$\mathrm{HETP} = \frac{\mathcal{E}}{|k_s|} + \frac{1}{{k_s}^2 L}, \tag{5}$$

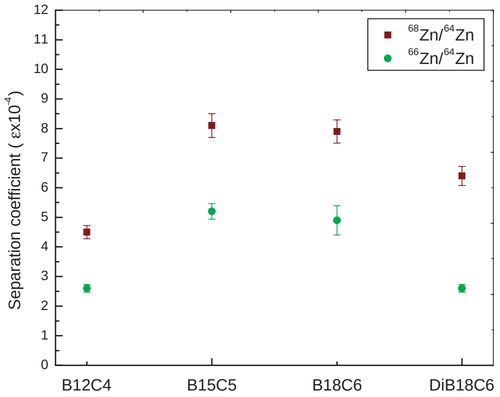

Fig. 5. Separation coefficient for the zinc isotopes by using different crown ether resins.

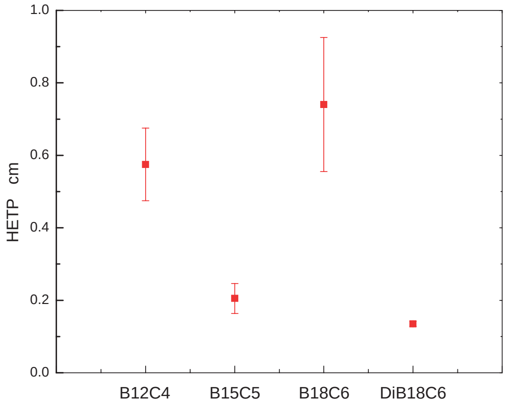

Fig. 6. HETP values against different crown ether resins.

where q_i is the amount of zinc in each fraction sample, Q_{tot} is the total amount of adsorbed zinc on the resin, L is the total migration length, R_i is the isotopic percentage of ^{H}Zn, and the subscripts i and o denote the fraction number and the original sample, respectively. k_s is the coefficient of the slope and can be obtained by Eq. 6:

$$\ln |R_i - R_o| = k_s (L - x_i). \tag{6}$$

In the above equation, $(L - x_i)$ is the distance from the boundary to the position x in the zinc adsorption band. Figures 5 and 6 show $\mathcal{E}$ and HETP values of different crown ether resins, respectively.

In this work, the isotope separation coefficients $\mathcal{E}$ of ^{68}Zn against ^{64}Zn were calculated as: 4.5×10^{-4}, 8.1×10^{-4}, 7.9×10^{-4}, and 6.4×10^{-4} for benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, and dibenzo-18-crown-6 resin, respectively, by using the data of the heavier isotope accumulation in the front adsorption boundary zone. Benzo-15-crown-5 resin has the largest separation coefficient for the isotopic pairs $^{68}Zn/^{64}Zn$ and $^{66}Zn/^{64}Zn$. HETP values for these four resins were 0.58, 0.21, 0.74, and 0.14 cm, respectively. Although for isotopic pair $^{68}Zn/^{64}Zn$, benzo-18-crown-6 resin has a separation coefficient similar with that of benzo-15-crown-5 resin, benzo-18-crown-6 resin has very large HETP value. Table 2 summarize the results of zinc isotope separation by using these four types of benzo crown resins.

Table 2. Chromatographic Experimental Results for Zinc Isotope Separation

Resin	Zn adsor. capacity /mmol m^{-1}	Front max. enrichment ^{68}Zn/^{64}Zn	Separation coefficient $\varepsilon \cdot 10^{-4}$	HETP /cm
Benzo-12-crown-4	3.00	1.0048	4.50	0.575
Benzo-15-crown-5	7.96	1.0168	8.10	0.205
Benzo-18-crown-6	4.05	1.0042	7.90	0.740
Dibenzo-18-crown-6	7.00	1.0150	6.40	0.135

Conclusion

Four kinds of benzo crown ether embedded into silica beads resin were synthesized and tested to study the effect of cavity size of crown ethers on zinc isotope fractionation. The results show that the lighter isotope ^{64}Zn was enriched in each crown ether resin. The isotope effect of zinc has been shown to be relate to the cavity size of crown ethers. Good enrichment at the front band boundary was observed in the benzo-15-crown-5 and dibenzo-18-crown-6 resins.

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