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Isotope Effects of Hafnium in Solvent Extraction Using Crown Ethers

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Hafnium isotopes were fractionated in a liquid–liquid extraction system by using seven types of crown ethers, tributyl phosphate, or *o*-diethoxybenzene. The largest isotope effect was observed in the isotope pair of ^{177}Hf–^{179}Hf with dibenzo-24-crown-8; the isotope enrichment factor was observed to be 0.0129 ± 0.0032.

The latest knowledge of isotope chemistry is that the isotope effect has two origins: one is an energy shift in vibrational levels of the bond between the isotope and ligands; and the other is a shift in the energy level of the molecular orbital. The well-known Bigeleisen–Mayer theory[1] elucidates the nuclear mass effect in the vibrational energy. The isotopic difference in the energy level of the molecular orbital leads to a change in the minimum potential energy of the vibrational energy curve. Isotope shifts in the atomic spectra[2] are appropriate references which account for the isotopic shifts in the energy level of the molecular orbital. The isotope shifts are composed of mass shifts, a field shift and a hyperfine splitting shift. The mass shift results from a coupling of the motions of the nucleus and the orbital electrons. The field shift is caused by a difference in the nuclear size and shape. The hyperfine splitting shift is due to an interaction between the orbital electrons and the electromagnetic moments of the nucleus. The conventional mass-dependent theory of the isotope effect has been extended to include the nuclear size and shape effect and the nuclear spin effect as the mass-independent isotope effects.[3] In the case of the energy level of the molecular orbital, the mass-independent isotope effects in the vibrational energy have received considerable attention.[4–6]

We discuss the isotope effects of hafnium in this note. In a previous study on titanium isotope separation,[7] we pointed out that the nuclear spin effect is characterized by the number of hyperfine splittings in the vibrational energy via a Fermi contact interaction. Hafnium has two odd atomic mass isotopes, ^{177}Hf and ^{179}Hf, in naturally occurring abundances, which have specific nuclear spins, $I = 7/2$ for ^{177}Hf and $I = 9/2$ for ^{179}Hf. Thus, regarding the isotope pair of ^{177}Hf–^{179}Hf, an isotope effect due to the difference in the nuclear spins can be expected to appear. The isotope effects of hafnium were studied using seven types of crown ethers: benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), 4′-nitrobenzo-18-crown-6 (NB18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6), and dibenzo-24-crown-8 (DB24C8) (Chart 1). Tributyl phosphate (TBP) and *o*-diethoxybenzene (DEB) were also used as non-macrocyclic extractants for a comparison.

The single stage isotope separation factor,[8,9] $\alpha_{\mathrm{m}',\mathrm{m}}$, for hafnium is defined as

$$\alpha_{\mathrm{m}',\mathrm{m}} = ([^{\mathrm{m}}\mathrm{Hf}]/[^{\mathrm{m}'}\mathrm{Hf}])_{\mathrm{org}}/([^{\mathrm{m}}\mathrm{Hf}]/[^{\mathrm{m}'}\mathrm{Hf}])_{\mathrm{aq}}, \tag{1}$$

where m′ and m mean the light isotope and the heavy isotope, respectively. Subscripts aq and org mean the aqueous phase and the organic phase, respectively. The isotope enrichment factor,[8,9] $\varepsilon_{\mathrm{m}',\mathrm{m}}$, is defined as

$$\varepsilon_{\mathrm{m}',\mathrm{m}} = \alpha_{\mathrm{m}',\mathrm{m}} - 1. \tag{2}$$

The isotope enrichment factor, $\varepsilon_{177,179}$, is obtained for a pair of odd atomic mass isotopes, ^{177}Hf–^{179}Hf, and $\varepsilon_{178,180}$ for a pair of even atomic mass isotopes, ^{178}Hf–^{180}Hf.

The obtained isotope enrichment factors are given in Table 1. The distribution ratios of extraction are also given. A correlation of the distribution ratio to the size fitness can be seen; the orders of the ionic diameter of Hf^{4+} and the cavity diameters of crown ethers[10] are B15C5 < Hf^{4+} < B18C6 and Hf^{4+} < DB18C6 < DB24C8. The largest isotope effect was observed in $\varepsilon_{177,179}$ with DB24C8, while it has the most unfitted cavity size for hafnium extraction: $\varepsilon_{177,179} = 0.0129 \pm 0.0032$. In Table 1, NR (not recognized) is used when the absolute value of the isotope enrichment factor is smaller than the experimental error of 1 SD. Neither $\varepsilon_{177,179}$ nor $\varepsilon_{178,180}$ can be recognized in

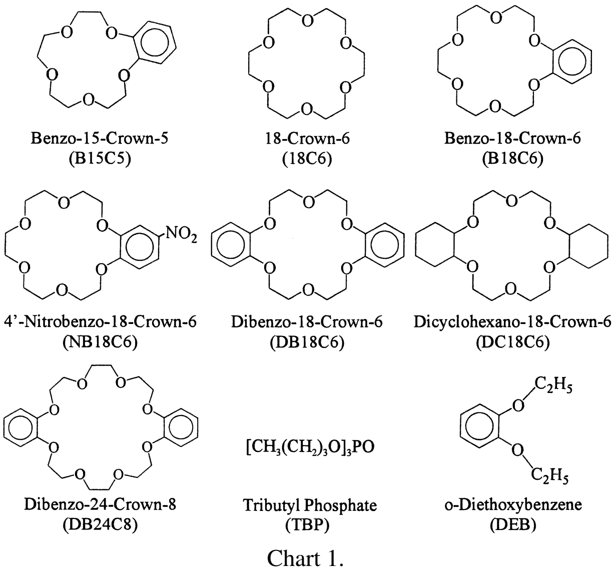

Chart 1.

Table 1. Isotope Enrichment Factors of Hafnium

Extractant	Concn of extractant /M	Distribution ratio	Isotope enrichment factor	
			Odd-odd pair ^{177}H–^{179}Hf	Even-even pair ^{178}Hf–^{180}Hf
B15C5	0.02	2.9×10^{-4}	0.0044(13)	NR
B18C6	0.02	3.2×10^{-4}	0.0037(17)	NR
DB18C6	0.02	1.5×10^{-3}	0.0062(30)	NR
DB24C8	0.02	4.9×10^{-4}	0.0129(32)	−0.0054(35)
NB18C6	0.02	4.6×10^{-5}	NR	NR
DEB	2.5	1.0×10^{-5}	−0.0042(20)	NR
18C6	0.2	5.1×10^{-5}	0.0050(12)	NR
DC18C6	0.2	1.1	−0.0045(32)	NR
TBP	0.2	220.2	−0.0049(31)	NR

NR: Not recognized. Values in bracket are errors of 1SD.

extraction with NB18C6. In a system with the non-macrocyclic ligand TBP, although an isotope effect can be seen in the isotope pair of ^{177}Hf–^{179}Hf, it is small within the experimental error of 2 SD. *o*-Diethoxybenzene was used as a reference of a decomposed substance of benzo- and dibenzo- crown ethers. It is of interest that $\varepsilon_{177,179}$'s of the macrocyclic compounds substituted by the benzene group show positive values, whereas $\varepsilon_{177,179}$'s of the non-macrocyclic ligands show negative values.

As shown in Table 1, the isotope effect can not be recognized for the isotope pair of ^{178}Hf–^{180}Hf, except for extraction with DB24C8; the observed absolute values of $\varepsilon_{178,180}$ were smaller than the 30% of those of $\varepsilon_{177,179}$. The isotope enrichment factors, $\varepsilon_{177,179}$ and $\varepsilon_{178,180}$, can be written as[7]

$$\varepsilon_{177,179} = (\delta m/mm')_{177,179}\, a + (\delta\langle r^2\rangle)_{177,179}\, b + \{(ln\ K_{\mathrm{hf}})_{179} - (ln\ K_{\mathrm{hf}})_{177}\}, \tag{3}$$

$$\varepsilon_{178,180} = (\delta m/mm')_{178,180}\, a + (\delta\langle r^2\rangle)_{178,180}\, b, \tag{4}$$

where δm is the difference in mass of the isotopes and $\delta\langle r^2\rangle$ is the isotopic change in the mean-square radius; a and b are scaling factors of the nuclear mass effect term and the nuclear size and shape effect term, respectively. The third term in Eq. 3 is the nuclear spin effect term. Since the nuclear spins of ^{178}Hf and ^{180}Hf are zero, the nuclear spin effect term is excluded from Eq. 4. The detailed meanings of the terms in Eqs. 3 and 4 can be seen elsewhere.[3,7] Because $\delta m = 2$, the nuclear mass effect of ^{177}Hf–^{179}Hf is equal to that of ^{178}Hf–^{180}Hf. From literature data,[11] $(\delta\langle r^2\rangle)_{177,179} = 0.068$ fm^2 and $(\delta\langle r^2\rangle)_{178,180} = 0.069$ fm^2 can be obtained, and hence the nuclear size and shape effect of ^{177}Hf–^{179}Hf is also identical to that of ^{178}Hf–^{180}Hf. Thus, the following equation can be deduced:

$$\varepsilon_{177,179} = \varepsilon_{178,180} + \{(ln\ K_{\mathrm{hf}})_{179} - (ln\ K_{\mathrm{hf}})_{177}\}. \tag{5}$$

Since most of $\varepsilon_{178,180}$'s were negligibly small in the present study, only the difference in the nuclear spin effects should be observed as $\varepsilon_{177,179}$.

Experimental

The crown ethers used were products of Aldrich Chemical Co. (18C6, DC18C6), Nakarai Tesque (B15C5, DB18C6), and Tokyo Kasei Kogyo Co., Ltd. (B18C6, NB18C6, DB24C8). The chemical reagents used were all of analytical grade. The aqueous phase was 0.03 mol dm^{-3} (M) hafnium in 10 M HCl. Each extractant was dissolved in chloroform to be 0.02 M (B15C5, B18C6, DB18C6, NB18C6, DB24C8), 0.2 M (18C6, DC18C6, TBP), or 2.5 M (DEB). These were served as the organic phase. Liquid–liquid extraction was performed at 273 K. The detailed procedure can be found in previous papers.[7,12,13]

The concentration of hafnium was analyzed by an ICP-atomic emission spectrophotometer (Shimadzu, ICPS-7500). The isotopic composition of hafnium was measured with an ICP-multiple collector mass spectrometer (VG Elemental, Plasma-54). Before mass spectrometry, all samples were converted into the diluted nitric acid solutions of ca. 10 ppb hafnium. The precision of the measured isotope ratio was 0.3% (1SD) or better.

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