

Solvent extraction of Zr and Hf in trioctylamine/ H_2SO_4 systemT. Yokokita*¹ and H. Haba*²

The chemical properties of superheavy elements (SHEs) with atomic number $Z \geq 104$ are expected to deviate from the periodicity of their lighter homologues in the periodic table. Thus, chemical studies on SHEs are interesting. SHEs are produced at accelerators using heavy-ion-induced nuclear reactions. The production rates of SHEs are low, and their half-lives are short ($T_{1/2} \leq 1$ min). Thus, the chemical studies of SHEs are conducted on a single-atom basis, which makes it difficult to perform chemical experiments with SHEs. Thus far, the chemical properties of SHEs have been discussed by comparing their behavior with those of homologous elements.¹⁾

We performed anion-exchange experiments of Rf and its homologous elements, Zr and Hf, to study its sulfate complexation.²⁾ From the previous study, we obtained the distribution coefficients of Rf, Zr and Hf in 0.060–0.46 M H_2SO_4 .²⁾ We need to identify the chemical species of the sulfate complexes of Zr and Hf under the studied conditions to discuss the sulfate complexation of Rf based on the comparison of the anion-exchange behavior of Rf and its homologous elements. In this work, we performed solvent extraction with an anion-exchanger, trioctylamine (TOA), from H_2SO_4 and ESI-MS spectroscopy to deduce the anionic sulfate complexes of Zr and Hf under the experimental condition of Rf.

Radiotracers ^{88}Zr and ^{175}Hf were produced in $^{89}\text{Y}(d, 3n)^{88}\text{Zr}$ and $^{175}\text{Lu}(d, xn)^{175}\text{Hf}$ reactions, respectively, using the RIKEN AVF cyclotron. Then, these tracers were purified by an anion-exchange method. The solvent extractions of Zr and Hf were performed by employing the batch method with 1.6–20 mM trioctylamine in CH_2Cl_2 from 0.11 M H_2SO_4 . The distribution ratios (D) were obtained according to $D = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}$; here, $[\text{M}]_{\text{org}}$ and $[\text{M}]_{\text{aq}}$ denote the metal concentration in the organic and aqueous phases, respectively.

For ESI-MS spectroscopy, Zr and Hf samples in the organic phases were obtained in the solvent extraction of 9.4 mM Zr and 7.6 mM of Hf, respectively, from 0.15 M H_2SO_4 into 3.6 mM TOA- CH_2Cl_2 solutions. Further, we made blank samples, *i.e.*, TOA- CH_2Cl_2 solutions without Zr and Hf. They were the organic phases obtained in the solvent extraction of 0.15 M H_2SO_4 without the metal ions and 3.6 mM TOA- CH_2Cl_2 solutions. All samples were diluted with CH_2Cl_2 before ESI-MS measurement using LTQ Orbitrap XL mass spectrometer (Thermo Fisher Scientific).

The slopes of $\log D$ and $\log [\text{TOA}]$ of Zr and Hf were obtained: the slope is related to the number of the protonated TOA cation (HTOA^+) of the extracted species. The slope values of both Zr and Hf were 1.9 ± 0.1 , which implies two HTOA^+ cations are paired with the anionic

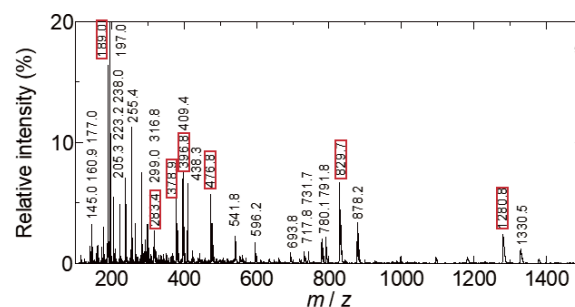


Fig. 1. ESI-MS spectrum (negative mode) of the Zr sample. The m/z values marked by the squares are the distinguishable peaks of the Zr sample.

sulfate complexes of Zr and Hf with a net charge -2 to be extracted into the organic phase from the aqueous phase.

In ESI-MS spectroscopy, the peaks of the ionized Zr and Hf species in the organic phase were assigned by comparing the mass spectra of Zr and Hf samples in the organic phase with those of the blank samples. The mass spectrum of the Zr samples is shown in Fig. 1. 7 distinguishable peaks were observed at $m/z = 189.0$, 238.0, 378.9, 396.8, 476.7, 830.0, and 1280.8, which corresponded to $[\text{Zr}(\text{SO}_4)_3]^{2-}$, $[\text{Zr}(\text{HSO}_4)_2(\text{SO}_4)_2]^{2-}$, $[\text{Zr}(\text{HSO}_4)(\text{SO}_4)_2]^-$, $[\text{Zr}(\text{OH})(\text{HSO}_4)_2(\text{SO}_4)]^-$, $[\text{Zr}(\text{HSO}_4)_3(\text{SO}_4)]^-$, $(\text{HTOA})[\text{Zr}(\text{HSO}_4)_2(\text{SO}_4)_2]^-$, and $(\text{HTOA})_2[\text{Zr}(\text{HSO}_4)_3(\text{SO}_4)_2]^-$, respectively. The extracted Zr species in organic phase contains the two HTOA^+ cations, and therefore, the Zr species before ionization are $(\text{HTOA})_2[\text{Zr}(\text{SO}_4)_3]$, $(\text{HTOA})_2[\text{Zr}(\text{HSO}_4)_2(\text{SO}_4)_2]$, $(\text{HTOA})_2[\text{Zr}(\text{OH})(\text{HSO}_4)(\text{SO}_4)_2]$, and $(\text{HTOA})_2[\text{Zr}(\text{OH})(\text{HSO}_4)_3(\text{SO}_4)]$.

For the Hf sample, 4 distinguishable peaks were observed at $m/z = 234.0$, 486.8, 919.6, and 1371.2, which correspond to $[\text{Hf}(\text{SO}_4)_3]^{2-}$, $[\text{Hf}(\text{OH})(\text{HSO}_4)_2(\text{SO}_4)]^-$, $(\text{HTOA})[\text{Hf}(\text{HSO}_4)_2(\text{SO}_4)_2]^-$, and $(\text{HTOA})_2[\text{Hf}(\text{HSO}_4)_3(\text{SO}_4)_2]^-$, respectively. The extracted Hf species in organic phase contains the two HTOA^+ cations, and therefore, the Hf species before ionization are $(\text{HTOA})_2[\text{Hf}(\text{SO}_4)_3]$, $(\text{HTOA})_2[\text{Hf}(\text{OH})(\text{HSO}_4)(\text{SO}_4)_2]$, $(\text{HTOA})_2[\text{Hf}(\text{OH})(\text{HSO}_4)_3(\text{SO}_4)]$, and $(\text{HTOA})_2[\text{Hf}(\text{HSO}_4)_2(\text{SO}_4)_2]$.

These results indicate that the proposed Zr and Hf species at 0.1 M H_2SO_4 are $[\text{M}(\text{SO}_4)_3]^{2-}$, $[\text{M}(\text{HSO}_4)_2(\text{SO}_4)_2]^{2-}$, $[\text{M}(\text{OH})(\text{HSO}_4)(\text{SO}_4)_2]^{2-}$, and $[\text{M}(\text{OH})(\text{HSO}_4)_3(\text{SO}_4)]^{2-}$ ($\text{M} = \text{Zr}$ and Hf). However, the main species of Zr and Hf in this studied condition cannot be determined from the present study. A combination of other analytical methods must be performed to identify the main chemical species.

References

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