Solvent Extraction of Zirconium and Hafnium as Homologues of Rutherfordium by Triisooctylamine from HCl Solutions

Aiko KINO,1 Yoshitaka KASAMATSU,1,* Takuya YOKOKITA,1 Takashi YOSHIMURA,2 Yukiko KOMORI,1,3 Yuki KIKUTANI,1 Naruto TAKAHASHI1 and Atsushi SHINOHARA1

1Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka, 560-0043, Japan
2Radioisotope Research Center, Osaka University, Yamadaoka 2-4, Suita, Osaka 565-0871, Japan
3Nishina Center for Accelerator-Based Science, RIKEN, Hirosawa 2-1, Wako, Saitama 351-0198, Japan

(Received November 17, 2014; Accepted February 2, 2015)

Solvent extraction of the group 4 elements Zr and Hf, homologues of Rf (Z = 104), by triisooctylamine (TIOA) from hydrochloric acid (HCl) was performed by batch method using carrier-free radioisotope tracers. The times required to reach equilibria were determined, and then variations of the equilibrium distribution ratios (D) were investigated against the TIOA and HCl concentrations. It was found that the chemical reactions involved in the extraction of the chloride complexes of Zr and Hf by 0.1–1.0 M TIOA from 7.4–10.4 M HCl reached equilibrium in 10–20 min. The D values increased as the concentrations of HCl and TIOA increased, suggesting the formation of anionic chloride complexes of Zr and Hf. We obtained comparison data to study Rf-chloride complex formation. Although the reaction time in the extraction needs to be shortened, the extraction behavior of Rf could be investigated by solvent extraction under the present experimental conditions.

1. Introduction

The chemical properties of transactinide elements (Z ≥ 104) are expected to deviate from the periodicity of their lighter homologues in the Periodic Table owning to the strong relativistic effects on valence electronic shells of these heavy atoms [1]. Thus, elucidating the chemical properties of these elements is one of the intriguing goals in inorganic chemistry research. The transactinide elements are produced by heavy-ion-induced nuclear reactions using accelerators, and the production rates are typically lower than several atoms per minute. Additionally, the half-lives of these nuclides are usually less than a few minutes. These conditions create the need for rapid chemical experiments on a one-atom-at-a-time basis [2]. Therefore, prior to carrying out chemical experiments with transactinide elements, we need to determine suitable conditions for these experiments to be successfully conducted. One common way of doing this is by performing chemical experiments using homologues of transactinide elements, and the comparative data to investigate the chemical properties of the transactinides in question are obtained through these experiments.
Owning to the difficulty in establishing experimental methods for the chemistry of transactinide elements, the results from those aforementioned experiments are not abundant. Notably, in solution chemistry, ion-exchange and solvent extraction experiments have been carried out for elements 104, 105, and 106 [1]. In some chemical separations, the behavior of these elements was reported to be similar to that of their homologues (d-block metal elements in the Periodic Table). Further detailed chemical study is desired to elucidate their chemical properties such as complex formation. However, although chemical properties are investigated on the basis of equilibrium data, it is very difficult for short-lived transactinides to reach equilibrium. For fluoride complexation, ion-exchange experiments of rutherfordium (Rf, Z = 104) were successfully performed under conditions such that the equilibrium distribution behavior was observed for the homologues of Rf [3–5]. In these anion- and cation-exchange chromatographic experiments involving Rf in HF and HF/HNO\textsubscript{3} solutions, intriguing results were obtained. For example, the distribution coefficients of Rf in anion-exchange chromatography were found to be at least one order of magnitude smaller than those of its homologues zirconium (Zr) and hafnium (Hf) [3,4]. In order to clarify the chemical properties of Rf, complex forming reactions of Rf with other ligand ions such as chloride and bromide are of great importance. The chemical behavior of Rf complexes in HCl was investigated [6–10] and reported to be similar to that of Zr and Hf [6–9], though different from that of the pseudo homologue thorium (Th) [7]. Although these pioneering Rf experiments using micro columns are important for deducing the chemical behavior of Rf in HCl, equilibration of the chemical reactions was not confirmed for either Zr or Hf. Because reaction kinetics should be different for each element, it is difficult to discuss chemical properties from the comparison of experimental data among some elements when chemical reactions do not reach the equilibrium.

In order to understand Rf-chloride complex formation, equilibrium extraction data for Rf are needed and equilibrium extraction data for Zr and Hf are also important for comparison purposes. In the work presented herein, solvent extraction of Zr and Hf was performed by batch method using TIOA as the extractant and HCl as the aqueous solution. The ion-association extractant, TIOA, was selected because of the rapid extraction of the anionic species [11]. In a previous solvent extraction experiment using TIOA [12], macro amounts of Zr and Hf were used and thus these data are not suitable for comparison purposes with those of the transactinides. In another experiment in the TIOA/HCl system using carrier-free Zr and Th tracers [13], it is unclear whether the data were obtained under extraction equilibrium conditions because the mixing time of the 2 phases was fixed at 2 min (most likely in an attempt to obtain data directly comparable with that of short-lived Rf). Herein, we have examined the dependence of the distribution behavior in solvent extraction on the shaking time for Zr and Hf in the TIOA/HCl system. By investigating variations of the distribution ratios (D) in equilibria against the TIOA and HCl concentrations, the chloride complex formation of Zr and Hf and their extracted species into the organic phase have been studied. Based on the obtained results, we propose suitable experimental conditions for Rf experiments.

2. Experimental

2.1 Preparation of mixed solutions of \( ^{88}\text{Zr} \) and \( ^{175}\text{Hf} \)

The \( ^{88}\text{Zr} \) \((T_{1/2} = 83.4 \text{ d} [14]) \) and \( ^{175}\text{Hf} \) \((T_{1/2} = 70.0 \text{ d} [14]) \) nuclides were produced in the \( ^{89}\text{Y}(p,2n)^{88}\text{Zr} \) and \( ^{178}\text{Lu}(p,n)^{175}\text{Hf} \) reactions, respectively. About 1 \( \mu \text{A} \) proton beams with an energy of 22
MeV for Zr and 14 MeV for Hf were delivered by the AVF cyclotron at the Research Center for Nuclear Physics, Osaka University. After the production, the product nuclides were purified by anion-exchange method. The procedures in these production and purification are described in the literature \cite{15}. The purified Zr and Hf tracers were mixed and stored in 6 M HCl solutions in a polypropylene (PP) tube.

2.2 Solvent extraction

TIOA and HCl solutions of the desired concentrations were prepared by dilution with benzene and distilled water, respectively. Before the extraction, the organic and aqueous phases were mixed using a vortex mixer for about 1 h at 25 ± 1 °C in order to prepare the solutions for the extraction. After separating the phases by centrifuging the mixture, the densities of both phases were determined. For the extraction experiments, 5 mL of the organic phase and 5 mL of the aqueous phase containing the $^{88}$Zr and $^{175}$Hf tracers were mixed in a PP tube for 2–180 min using a vortex mixer at 25 ± 1 °C and then the solution was centrifuged for 1 min. Samples (4 mL) of both the phases were pipetted into other tubes and subjected to γ-ray spectrometry. For the γ-ray spectrometry, counts of the peaks at 392.9 keV \cite{14} for $^{88}$Zr and 343.4 keV \cite{14} for $^{175}$Hf were measured using a planar-type Ge semiconductor detector with a distance between the detector and the samples of typically 1–3 cm. The volume of each solution was precisely determined from its weight and density. After γ-ray measurement, the concentration of the HCl solution was determined by titration with a standardized NaOH solution. To examine the time required to equilibrium in the extraction, the time dependence of the $D$ value was investigated under following two conditions: (1) The HCl concentration after the extraction was held constant at 7.4 M, and the TIOA concentration was varied to be 0.10, 0.50, and 1.0 M. (2) The TIOA concentration was held constant at 0.10 M, and the HCl concentration was varied to be 7.4, 8.1, and 10.4 M.

The $D$ values were determined using the equation:

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \frac{A_{\text{org}} V_{\text{aq}}}{A_{\text{aq}} V_{\text{org}}}$$

(1),

where $[M]_{\text{org}}$ and $[M]_{\text{aq}}$ are the concentrations of $^{88}$Zr or $^{175}$Hf in the organic and aqueous phases, respectively. The symbols $A_{\text{org}}$ and $A_{\text{aq}}$ represent the radioactivities (Bq) of $^{88}$Zr or $^{175}$Hf in the organic and aqueous phases, respectively, and $V_{\text{org}}$ and $V_{\text{aq}}$ are the volumes (mL) of the organic and aqueous phases, respectively. Only the statistical error in the γ-ray counts was taken into consideration for the error in the $D$ value.

Based on these results, the $D$ values at equilibrium were determined in 5.7, 8.7, and 9.4 M HCl at a constant TIOA concentration of 0.10 M with shaking times of 120, 60, and 45 min, respectively. The $D$ values in 0.17, 0.20, 0.29, 0.35, and 0.47 M TIOA were also obtained in 7.4 M HCl by shaking for 50 min.

3. Results and Discussion

The dependences of the $D$ values of Zr and Hf on the shaking time in 0.10, 0.50, and 1.0 M TIOA are shown in Figures 1(a) and 1(b). All of the HCl concentrations after the extraction were found to be almost identical (7.4 ± 0.1 M). From these results, it is clear that the $D$ values of Zr and Hf become constant after 10–20 min in all of the TIOA concentrations studied. This suggests that the chemical reactions in the
extraction reach equilibrium within 20 min. Figure 2 shows the variations of the logarithm of the equilibrium distribution ratio (log\(D\)) as a function of the logarithm of the TIOA concentration (log\[TIOA\]) in 7.4 M HCl. The log\(D\) values increase linearly as log\[TIOA\] increases with slope values of 1.7 ± 0.2 and 1.8 ± 0.3 for Zr and Hf, respectively. The extraction equilibrium can be described by the following equation:

\[
n \ (R_3N)_{org} + n \ H^+_{aq} + [MCl_{n+1}]^{n^-}_{aq} \rightarrow (R_3NH)_n[MCl_{n+1}]_{org}
\]  

(2),

where M\(^{4+}\) is the metal ion of a group 4 element, and R\(_3\)N represents TIOA. The equilibrium constant (\(K_{ex}\)) derived from eq. (2) is given by the following equation:
Here, on the assumption that a single chemical species, \([\text{MCl}_{n+4}^n]^{m-}\), is dominantly present in the aqueous phase at constant HCl concentration, the \(D\) value for the extraction is expressed by the following equation:

\[
D = \frac{[(\text{R}_3\text{NH})_n\text{MCl}_{n+4}]_{\text{org}}}{[\text{MX}_{\text{total}}]_{\text{aq}}} \approx \frac{[(\text{R}_3\text{NH})_n\text{MCl}_{n+4}]_{\text{org}}}{[(\text{MCl}_{n+4})^m]_{\text{aq}}}
\]  

(4),

where \([\text{MX}_{\text{total}}]_{\text{aq}}\) represents the total concentration of the M species in the aqueous phase. From eqs. (3) and (4), the following equation is obtained:

\[
\log D = n \log [\text{R}_3\text{N}]_{\text{org}} + \log K_{\text{ex}} + n \log [\text{H}^+]_{\text{aq}}
\]  

(5).

The decrease in the hydrogen ion concentration by protonation of the TIOA is very small compared with the initial hydrogen ion concentration of the aqueous phase, and thus the value of \([\text{H}^+]_{\text{aq}}\) is assumed to be almost constant through the extraction. Therefore, as expressed in eq. (5), the slopes in the linear fits in Figure 2 correspond to the number of protonated TIOA ions in the extracted neutral metal complex, \((\text{R}_3\text{NH})_n[\text{MCl}_{n+4}]\) \((n \geq 1)\) [16,17]. The presently obtained result indicates that the species extracted from 7.4 M HCl solution is \((\text{R}_3\text{NH})_2[\text{MCl}_6]\), in which two protonated TIOA ions assemble with the anionic Zr or Hf chloride complex, as indicated in the literature [16,17]. Accordingly, protonation of TIOA, chloride-metal complex formation, ion-pair complex formation, and the extraction reaction of the ion-pair complex take place in the present extraction process as described in the literature [13,18,19].

Transactinides are identified by the detection of their \(\alpha\) decays and the samples for \(\alpha\) detection are typically prepared by evaporation of the solution. When a solution sample contains some salts: for example, an organic phase containing TIOA, the residual salt after evaporation might disturb the \(\alpha\) detection. For this problem, it has been reported that the residue prepared from lower concentration TIOA solutions (such as a 0.1 M TIOA-benzene solution) is a suitable sample for \(\alpha\)-spectroscopy with sufficiently high energy resolution [13]. As seen in Figures 1(a) and 1(b), the time to reach equilibrium was virtually constant regardless of the TIOA concentration. For these reasons, we investigated the dependences of the \(D\) values of Zr and Hf on the concentration of HCl at 0.10 M TIOA. Figures 3(a) and 3(b) show the dependences of the \(D\) values of Zr and Hf, respectively, on the shaking time in 7.4, 8.1, and 10.4 M HCl. We found that the chemical reactions reached equilibrium within 20 min for both Zr and Hf at all HCl concentrations studied. The variations of the equilibrium \(D\) values against HCl concentration obtained for 0.10 M TIOA are shown in Figure 4. The \(D\) values increased as the concentration of HCl increased, indicating that the abundance of the anionic chloride complexes of Zr and Hf increases at higher concentrations of HCl and that these complexes are extracted into a 0.10 M TIOA-benzene solution from 6–11 M HCl. The \(D\) values of Zr were higher than those of Hf at all HCl concentrations presented in Figure 4, suggesting that the anionic chloride complexes of Zr would be more stable than those of Hf as reported in the literature [20].

As shown in Figures 2 and 4, the \(D\) values of Zr and Hf obtained under the present experimental conditions lie in the range of 0.01–100 which is not too low or too high, and it is preferable to determine the \(D\) values of transactinides with a relatively small number of events. Therefore, we can conclude
that the concentrations of the TIOA-benzene (0.1–1.0 M) and HCl (7–11 M) solutions in this experiment are suitable for the extraction of Rf. It is worth noting that the times required to reach equilibria in the present liquid-liquid extraction study are relatively slow compared with the half-life of the $^{261}$Rf nuclide (68 s). Thus, a method to shorten the reaction time is required in order to investigate the chloride complex formation of Rf through solvent extraction. We are developing a rapid extraction apparatus equipped with a “micro-chemical chip” that has micro-scale flow channels [21,22]. Indeed, we demonstrated the possible shortening of the shaking time required to reach equilibrium from 20 min to tens of seconds by using the micro-chemical chip for extraction by TBP which extracts neutral species. By performing the solvent extraction for Rf by TIOA from HCl, we expect to investigate the properties of the anionic Rf-chloride complex in addition to the neutral complexes. The presently obtained $D$ values are also important to check the performance of these newly developed chemistry apparatuses which can rapidly obtain the equilibrium $D$ value. In addition, if the time to reach equilibrium could be shortened into a few minutes by applying

Figure 3. Distribution ratios of (a) $^{88}$Zr and (b) $^{175}$Hf for different shaking times in 0.10 M TIOA. The data for 7.4, 8.1, and 10.4 M HCl are denoted by circles, squares, and triangles, respectively.

Figure 4. Distribution ratios of $^{88}$Zr (circles) and $^{175}$Hf (squares) as a function of the HCl concentration at a constant TIOA concentration of 0.10 M.
such a device, the present extraction system would be suitable to investigate the reaction kinetics of Rf in comparison with Zr and Hf.

4. Conclusion

The extraction behavior of Zr and Hf (as homologues of Rf) into TIOA-benzene solutions from HCl solutions was studied by batch method. From the dependences of the $D$ values of Zr and Hf on the shaking time, we found that the chemical reactions taking place in the extraction reached equilibrium within about 20 min regardless of the TIOA and HCl concentrations. The dependences of the $D$ values on the TIOA and HCl concentrations indicate that the abundance of the anionic chloride complexes of Zr and Hf increases with increasing HCl concentration in the range 7–11 M, and that these complexes assemble with protonated TIOA ions, (R$_3$NH)$_2$[MCls] (M = Zr or Hf) and are extracted into the organic phase. We found that the formation of the anionic chloride complexes can be studied for the group 4 elements through solvent extraction experiments with TIOA and HCl. Based on these results, we determined the experimental conditions for the extraction of Rf to be 0.1–1.0 M TIOA (at 7.4 M HCl) for the organic phase and 7–11 M HCl (at 0.1 M TIOA) for the aqueous phase.

Acknowledgement

We express our gratitude to the staff of the Accelerator Facility in RCNP for the production of $^{88}$Zr and $^{175}$Hf. This work was supported by JSPS KAKENHI Grant Number 23750082.

References

7) H. Haba, K. Tsukada, M. Asai, S. Goto, A. Toyoshima, I. Nishinaka, K. Akiyama, M. Hirata, S.


