Extraction Chromatographic Behavior of Rf, Zr, and Hf in HCl Solution with Styrene-divinylbenzene Copolymer Resin Modified by TOPO (trioctylphosphine oxide)


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The extraction behavior of rutherfordium (Rf) onto trioctylphosphine oxide (TOPO) resin from 2.0 – 7.0 M HCl solutions was studied together with that of the homologues Zr and Hf. The extraction yields of Rf, Zr, and Hf increased with an increase of HCl concentration, and the sequence of their extraction was Zr > Hf > Rf. It is suggested that the stability of the RfCl$_2$(TOPO) complex is lower than that of the corresponding species of the homologues.

1. Introduction

It is of great interest to study chemical properties of the transactinide elements with atomic numbers (Z) ≥ 104. One of the most important subjects is to establish the position of the elements at the extreme end of the periodic table. To this end we perform studies of chemical properties of these transactinides and compare them with those of their lighter homologues and with the ones expected from extrapolations in the periodic table. So far, chromatographic studies of the transactinides have provided experimental proof of placing rutherfordium (Rf, Z = 104) through hassium (Hs, Z = 118) in groups 4 to 8, respectively. Quite recently, copernicium (Cn, Z = 112) has been shown to be a member of group 12. To gain a better understanding, it is even more interesting to study chemical properties of the transactinide elements in greater detail and to compare those with the ones of their lighter homologues. Theoretical calculations predict that the ground state electronic structure of the heaviest elements varies due to strong relativistic effects. Accordingly, chemical properties of these elements may deviate from those expected from linear extrapolations based on lighter homologues. Systematically, detailed chemical investigations are, therefore, required to characterize properties of the transactinide elements influenced by relativistic effects.

In general, rutherfordium shows chemical properties typical for a member of the group 4 of the periodic table. Chemical studies of Rf in HCl solution have been extensively conducted together with its lighter homologues Zr and Hf to compare these group-4 elements. The formation of anionic chloride species of Rf was investigated by anion-exchange chromatography in 4.0 – 11.5 M HCl using the Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA). These results show that anionic complexes of the type [MCl$_6$]$^{2-}$ (M = Rf, Zr, and Hf) are formed and it suggests that the complexing strength decreases in the order of Rf ≥ Zr > Hf. The extraction behavior of Rf and its homologues into tri-n-butyl phosphate (TBP) from HCl has been also investigated. Czerwinski et al. first performed the extraction of Rf, Zr, and Hf from 8 – 12 M HCl into 0.25 M TBP benzene solution and reported that the extraction yields of these elements increase as a function of HCl concentration in the order of Zr > Rf > Hf. This order was afterwards revised by Kacher et al. to Zr > Hf > Rf > Ti by comparing the extraction yields of Rf with the reexamined extraction data of Ti, Zr, and Hf. Günther et al. then showed the extraction sequence into TBP from 8.0 M HCl to be Zr > Rf > Hf. Here reversed-phase chromatography experiments using the Automated Rapid Chemistry Apparatus (ARCA) were carried out, and the earlier results reported in References 17 and 18 were criticized because of their unsatisfactory experimental conditions. Recently, we performed TBP reversed-phase extraction chromatography of Rf and its homologues in 7.2 – 8.0 M HCl using AIDA. The extraction order Zr > Hf = Rf was found, which suggested that the stability of the extracted TBP complex of Rf (RfCl$_2$(2TBP) is lower than those of Zr and Hf. This interpretation was based on the different sequences in the TBP extraction and in the anion-exchange, assuming that the sequence of the formation of MCl$_n$ in HCl solution is the same as that of [MCl$_n$]$^{2-}$.

In the present work, the extraction behavior of Rf into trioctylphosphine oxide (TOPO) resin from 2.0 – 7.0 M HCl solutions was investigated together with Zr and Hf. Triclytylphosphine oxide has a chemical structure similar to that of TBP and has a higher basicity value as a donor than that of TBP. The effect of the basicity of organophosphorus compounds on the strength of the formation of a Rf complex was examined by comparing the extraction sequence of the group-4 elements into TOPO with that into TBP. Distribution coefficients (K$_D$ [mL g$^{-1}$]) of $^{88}$Zr and $^{176}$Hf from HCl onto TOPO resin were measured prior to the experiment with Rf applying a batch method. Reversed-phase chromatography of Rf was then investigated in 2.0 – 7.0 HCl together with Zr and Hf using...
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2. Experimental

2.1. Batch experiment. The radioisotopes $^{88}\text{Zr}$ ($T_{1/2} = 83.4$ d) and $^{175}\text{Hf}$ ($T_{1/2} = 70.2$ d) were produced in the $^{248}\text{Y}(p, 2n)$ and $^{176}\text{Lu}(p, n)$ reactions, respectively, at the JAEA tandem accelerator. The produced radioisotopes were chemically separated from the target materials by an anion-exchange method$^{32}$ and were then stored as 11.6 M HCl solution. The concentration of the HCl solution was determined by titration with a standardized Na$_2$CO$_3$ solution.

The TOPO resin was prepared by modifying a support material with TOPO dodecane solution. The support material was MCI GEL CHP20Y, a styrene-divinylbenzene copolymer with a particle size of about 30 µm and supplied by Mitsubishi Chemical Corporation. The weight amount of TOPO dodecane solution was mixed with the same amount of CHP20Y resin and stirred for 10 min. We precisely adjusted the weight ratio of resin to the dodecane solution to be 50%. The prepared TOPO resin was then stored in a desiccator.

The stability and uniformity of TOPO on CHP20Y was examined by measuring extraction yields of $^{88}\text{Zr}$ and $^{175}\text{Hf}$ on the TOPO resin against storage time for several days. No variation of extraction yields versus the storage time was observed for Zr and Hf, showing that the resin is satisfactorily prepared. In the batch experiment, individual portions of 10 to 100 mg of the resin and 2.0 mL of 1.0 to 11.6 M HCl solution containing 50 µL of the radiotracer solution were mixed in a polypropylene tube for 1 h at 22 ± 1 °C. After centrifuging, a 1 mL aliquot was transferred to a polyethylene tube and was then subjected to γ-ray spectrometry using a Ge detector. A standard sample solution prepared by diluting 50 µL of the radiotracer solution to 1 mL with water in a polyethylene tube was assayed by γ-ray spectrometry. Control experiments were also performed to exclude adsorption of the radiotracer on the walls of the tubes. The numbers of $^{88}\text{Zr}$ and $^{175}\text{Hf}$ atoms used for each batch experiment were about 10$^5$. The $K_o$ is defined as $K_o$(mL g$^{-1}$) = $A_V / A_W$ with solution volume $V_s$, weight of dry resin $W_s$, and the radioactivities $A_V$ and $A_W$ (Bq) in the resin and solution phases, respectively.

2.2. Production of short-lived radioisotopes. The isotope $^{261}\text{Rf}$ ($T_{1/2} = 78$ s)$^{33}$ was produced in the $^{248}\text{Cm}(^{18}\text{O}, 5n)$ reaction at the JAEA tandem accelerator. It is important to investigate the chemical behavior of Rf together with that of the homologues under identical conditions in order to make a reliable comparison among the group-4 elements. Thus, $^{175}\text{Hf}$ ($T_{1/2} = 3.24$ min) was simultaneously produced in the $^{248}\text{Cm}(^{18}\text{O}, n \gamma)$ reactions to monitor the chemical behavior and the yield of Hf during repetitive chromatographic experiments with Rf. The $^{248}\text{Cm}$ target of 540 µg cm$^{-2}$ thickness including Gd with a thickness of 32 µg cm$^{-2}$ (the isotopic composition was 39.3% $^{152}\text{Gd}$, 5.9% $^{154}\text{Gd}$, 16.7% $^{155}\text{Gd}$, 13.8% $^{156}\text{Gd}$, 7.7% $^{157}\text{Gd}$, 10.0% $^{158}\text{Gd}$, and 6.6% $^{160}\text{Gd}$) was prepared by electrodeposition of a Cd compound in 2-propyl alcohol onto a 1.80 mg cm$^{-2}$ thickness of a Cm compound in 2-propyl alcohol onto a 1.80 mg cm$^{-2}$ thickness. The Gd was sublimed from a Gd target of 660 µg cm$^{-2}$ Be backing foil. The resulting $^{154}\text{Gd}$ target was covered by vacuum-evaporated $^{60}\text{Ge}$ of 660 µg cm$^{-2}$ thickness.

Nuclear reaction products recoiling out of the target were stopped in He gas (~10$^3$ Pa), attached to KCl aerosols generated by sublimation of KCl powder at 640 °C, and were continuously transported to AIDA through a Teflon capillary of 2.0 mm i.d. and 25 m length at a flow rate of 2.0 L min$^{-1}$. The transport efficiency of the He/KCl gas-jet system was estimated to be 35%.$^{27}$

2.3. On-line reversed-phase chromatography of $^{261}\text{Rf}$, $^{88}\text{Zr}$, and $^{175}\text{Hf}$. The reaction products transported by the gas-jet were collected on the deposition site of AIDA for 125 s. After collection, all deposited products were dissolved with 190 µL of 11.6 M HCl solution heated in a water bath at 95 °C and were subsequently fed onto the 1.6 mm i.d. and 7.0 mm long TOPO column at a flow rate of 700 µL min$^{-1}$. The TOPO resin used was a mixture of the same amount of CHP20Y and 0.04 M TOPO in dodecane and it was preconditioned with 190 µL of 11.6 M HCl solution. The effluent from the column was discarded. Then, 210 µL HCl with a concentration of 2.0, 3.5, 5.0, or 7.0 M, respectively, was fed into the column at a flow rate of 700 µL min$^{-1}$. The effluent was collected on a Ta disc as fraction 1. Then it was evaporated to dryness with hot He gas and a halogen heat lamp to prepare a sample for α-spectrometry. Reaction products remaining on the TOPO resin were stripped from the column with 350 µL of 2.0 M HCl at a flow rate of 1000 µL min$^{-1}$. This effluent was collected on another Ta disc and was prepared as fraction 2 by evaporation to dryness. Each Ta disc was transferred to the α-spectrometry station of AIDA equipped with eight 600 mm$^2$ passivated implanted planar silicon (PIPS) detectors. Counting efficiency and energy resolution of the detectors were 35% and about 90 keV FWHM, respectively. All events were registered event by event. After the α-particle measurement, the 493 keV γ-ray of $^{89}\text{Hg}$ was monitored using Ge detectors for every third pair of Ta discs to determine the extraction probability and the chemical yield. The percent extraction (% ext) on the resin is defined as % ext = $100 \frac{A_{s}}{A_{t} + A_{s}}$ with the radioactivities $A_s$ and $A_t$ (Bq) in fractions 1 and 2, respectively.

In experiments with $^{88}\text{Zr}$ and $^{175}\text{Hf}$, reaction products transported by the He/KCl gas-jet were collected on the deposition site of AIDA for 180 s. The same procedure as used in the Rf experiments was applied to Zr and Hf. The effluent was fractionated in seven aliquots which were separately collected in seven polyethylene tubes. Remaining products on the column were stripped with 350 µL of 2.0 M HCl and were collected in a separate tube. For each tube the 416 keV and 370 keV γ-rays of $^{28}\text{Zr}$ and $^{89}\text{Hg}$, respectively, were measured to obtain their elution curves. The number of $^{88}\text{Zr}$ and $^{175}\text{Hf}$ atoms used in the extraction chromatography was approximately 10$^6$.

3. Results and Discussion

3.1. Batch experiment of $^{88}\text{Zr}$ and $^{175}\text{Hf}$. Figure 1 shows $K_o$ values of $^{88}\text{Zr}$ and $^{175}\text{Hf}$ extracted onto the 0.1 M TOPO resin as a function of HCl concentration [HCl]. Extraction yields of $^{88}\text{Zr}$ are higher than those of $^{175}\text{Hf}$. The $K_o$ values of $^{88}\text{Zr}$ and $^{175}\text{Hf}$ increase with increasing of HCl concentration. This indicates that the formation of the extractable neutral species increases through successive chloride complex formation. Figure 2 shows the variation of $K_o$ values for Zr and Hf extraction from 4.0 and 6.0 M HCl as a function of the TOPO concentration [TOPO] on the resin which represents the concentration of TOPO in dodecane used to modify CHP20Y resin. Extraction yields of both $^{88}\text{Zr}$ and $^{175}\text{Hf}$ increase with increasing TOPO concentration; the log$K_o$ values increase linearly with log[TOPO] with average slopes of $2.2 ± 0.2$ and $2.0 ± 0.2$ for $^{88}\text{Zr}$ and $^{175}\text{Hf}$, respectively.

Based on molar ratio measurements of Zr to Cl in 3 – 6 M


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HCl, White and Ross found that Zr is extracted as ZrCl₄·2(TOPO). Therefore, the extraction reaction of the neutral species can be written as

\[ MCl₄ + 2TOPO \rightleftharpoons MCl₄·2(TOPO) \]  

with the equilibrium constant \( D \), where \( M \) symbols Zr and Hf.

From equation 1, the relation of \( K_d \) with the concentration of TOPO is expressed as

\[ \log K_d = \log D + 2 \log [TOPO]. \]  

Thus, the slopes of +2 observed for ⁸⁸Zr and ¹⁷⁵Hf in our experiment confirm that the MCl₄·2(TOPO) compound is extracted into the TOPO resin according to equation (2).

### 3.2. On-line experiment of ²⁶ⁱRf, ⁸⁵Zr, and ¹⁶⁹Hf.

Figure 3 shows cumulative elution curves of ⁸⁵Zr and ¹⁶⁹Hf in 2.0, 3.5, and 5.0 M HCl. It is found that the extraction of ⁸⁵Zr and ¹⁶⁹Hf onto the TOPO resin increases with increasing HCl concentration. This is consistent with previous batch experiment.

Results of the reversed-phase chromatography of ²⁶¹Rf and ¹⁶⁹Hf are summarized in Table 1. In a total of 936 separation cycles, 110 \( \alpha \)-singles from ²⁶¹Rf and ²⁵⁷No including 18 \( \alpha-\alpha \) pairs of ²⁶¹Rf and ²⁵⁷No were detected. Before determining the \( %_{\text{ext}} \) values of ²⁶¹Rf firstly we evaluated contributions from background \( \alpha \)-singles and from ²⁵⁷No which can be formed as the \( \alpha \)-decay product of ²⁶¹Rf already during the collection and the chromatographic experiment. An average background measured in a long time interval before the Rf experiment was 3.2 × 10⁻⁶ counts/s for each detector in the energy range of 8.00 - 8.36 MeV. The contribution of ²⁵⁷No (\( T_{1/2} = 25 \) s) was evaluated based on calculated growth and decay of ²⁶¹Rf and ²⁵⁷No as well as on the extraction of nobelium. Because the distribution ratios of Sr²⁺ and Ca²⁺ into TOPO from 1 to 12 M HCl are 10⁻³ - 10⁻⁴, the extraction of No²⁺ ions is negligible under our experimental conditions. Within counting statistics the measured ratio of 110 : 18 (= 6.1 : 1) between \( \alpha \)-singles and \( \alpha-\alpha \) correlation pairs agrees well with the estimated value of 7 : 1. Observed decay rates of ²⁶¹Rf divided by the \( \alpha \)-beam doses and normalized with the chemical yields obtained from Hf are, within counting statistics, almost the same under all conditions, showing a good reproducibility of the chromatographic experiments. The asymmetric error limits of the \( %_{\text{ext}} \) values of ²⁶¹Rf were evaluated from the counting statistics of the observed \( \alpha \)-events based on a 68% confidence level (1\( \sigma \)) for Poisson distributed variables. The \( %_{\text{ext}} \) values for ⁸⁵Zr and ¹⁶⁹Hf were evaluated from their chromatogram. Errors are standard deviations from the weighted average of the \( %_{\text{ext}} \) values.

### Table 1: Summary of the chromatography experiment for ²⁶ⁱRf and ¹⁶⁹Hf

<table>
<thead>
<tr>
<th>HCl / M</th>
<th>Beam dose ( \times 10^{17} )</th>
<th>Number of Cycles</th>
<th>( \alpha )-count in frac. 1</th>
<th>( \alpha-\alpha )-count</th>
<th>( \alpha )-count in frac. 2</th>
<th>( \alpha-\alpha )-count</th>
<th>Chemical Yield / %</th>
<th>( %_{\text{ext}} / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.54</td>
<td>144</td>
<td>24</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>28 ± 7</td>
<td>10.2 ( ^{+0.0}_{-0.7} )</td>
</tr>
<tr>
<td>3.5</td>
<td>1.09</td>
<td>252</td>
<td>24</td>
<td>2</td>
<td>12</td>
<td>3</td>
<td>28 ± 11</td>
<td>41.8 ( ^{+8.3}_{-8.7} )</td>
</tr>
<tr>
<td>5.0</td>
<td>1.27</td>
<td>360</td>
<td>6</td>
<td>1</td>
<td>22</td>
<td>4</td>
<td>26 ± 4</td>
<td>86.3 ( ^{+4.2}_{-5.8} )</td>
</tr>
<tr>
<td>7.0</td>
<td>0.57</td>
<td>180</td>
<td>2</td>
<td>0</td>
<td>18</td>
<td>2</td>
<td>34 ± 2</td>
<td>95.3 ( ^{+9.0}_{-6.5} )</td>
</tr>
</tbody>
</table>

FIGURE 1. Variations of the \( K_d \) values for ⁸⁸Zr and ¹⁷⁵Hf on the 0.1 M TOPO resin as a function of HCl concentration.

FIGURE 2. Variations of the \( K_d \) values for ⁸⁸Zr and ¹⁷⁵Hf in 4.0 M and 6.0 M HCl solutions as a function of the TOPO concentration.

FIGURE 3. Cumulative elution curves of ⁸⁵Zr and ¹⁶⁹Hf in 2.0, 3.5, and 5.0 M HCl (see text).
same as that of the hexachlorides (Rf > Zr > Hf) previously reported. The chloride complexes of Rf, Zr, and Hf in HCl solution is the most preferable among the three elements. Rf is also extracted as RfCl4·2(TOPO) through the same extraction reaction as those of Zr and Hf. A basicity effect in the formation of TOPO and TBP complexes was not observed between Rf, Zr, and Hf in HCl. The extraction order of the group-4 elements Rf, Zr, and Hf into TOPO was Zr > Hf ≥ Rf. This suggests that the stability of the TOPO complex of Rf (RfCl4·2TOPO) is lower than those of Zr and Hf, which is the same trend as the one observed previously in TBP.

4. Conclusion

The extraction probabilities of Rf into TOPO from 2.0 to 7.0 M HCl solution increased with an increase of HCl concentration and the extraction order of the group-4 elements Rf, Zr, and Hf into TOPO was Zr > Hf ≥ Rf. This suggests that the stability of the RfCl4·2(TOPO) complex is lower than that of the corresponding species of Zr and Hf. A basicity effect in the formation of TOPO and TBP complexes was not observed in the extraction sequence among Rf, Zr, and Hf in HCl.

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References