

Extraction behavior of rutherfordium as a cationic fluoride complex with a TTA chelate extractant from HF/HNO₃ acidic solutions[†]

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Rutherfordium (Rf) has atomic number 104 and is the lightest among the transactinide, or superheavy, elements. The element is positioned as a homologue in group 4 of the Periodic Table of elements, which is predicted to be in the 6d transition series. The chemical properties of such elements have attracted much attention because of possible deviations from those of their homologs as a result of enhancement of the relativistic effect for heavy elements. It was found difficult that the characterization is performed based on one-atom-at-a-time chemistry for their low production rates and short half-lives.

In the present study, we used reversed-phase chromatography with 2-thenoyltrifluoroacetone (TTA) as a chelating extractant to clarify the chemical properties of the cationic fluoride complexes of the superheavy element Rf. Unlike previous studies with cation-exchange resins, the use of TTA enables preferential extraction of metal ions in group 4, therefore the specific complex formation constant of Rf can be determined. The experiments were performed at various HF/0.01 M HNO₃ concentrations, with a newly developed resin containing a solution of TTA in n-octanol. Fluoride complexation with Rf was investigated by extraction with TTA, which is sensitive to the valence of the metal complex. The Rf behavior was compared with those of Zr and Hf.

In the chromatography experiments with TTA, 222 α -events, including formation of 29 time-correlated α -particle pairs (8.00–8.40 MeV) from ²⁶¹Rf and its daughter nuclide ²⁵⁷No, were observed in 1771 cycles. The %ads values for Rf were constant at around 60% in the [F⁻]_{eq} range up to 5 × 10⁻⁴ M and then steeply decreased at [F⁻]_{eq} = 9 × 10⁻⁴ M. In contrast, the value for Hf decreased significantly from 100% to a few percent at around [F⁻]_{eq} = 1 × 10⁻⁴ M. This is in good agreement with the results of the Zr and Hf experiments. This suggests that the cationic fluoride complexes of Rf are more stable than those of Hf at [F⁻]_{eq} > 1 × 10⁻⁴ M. Differences among fluoride species formation with Rf and its homologs are

therefore clearly observed in these [F⁻]_{eq} ranges.

Decay of No was taken into account in correction of the %ads values. The %ads values for ²⁵⁵No as a function of [F⁻]_{eq} in the range 1.93 × 10⁻⁵ to 1.66 × 10⁻³ M were obtained in the study. In the Rf experiments, the %ads values for ²⁶¹Rf were constant, at around 60%, in the [F⁻]_{eq} range up to 5 × 10⁻⁴ M and then steeply decreased at [F⁻]_{eq} = 9 × 10⁻⁴ M. In contrast, in the No experiments, the %ads values for ²⁵⁵No were less than 10% across the entire range of [F⁻]_{eq}. The results of the present work confirm that No is adsorbed on TTA to a small extent and the effect on the %ads values of ²⁶¹Rf is negligible.

The obtained *K_d* values for Rf are compared with those for Zr and Hf from the independent experiments in the present study. The result shows significant differences between the behavior of Rf and those of its homologs. The *K_d* values for Rf appear at higher F⁻ concentrations than those for Zr and Hf. Assuming that during extraction Rf forms species with TTA, similarly to the other elements in group 4, the decrease in extraction may be caused by additional cationic fluoride complexation. The *K_d* results show that the cationic complex of Rf, [RfF]³⁺, is more stable than those of the other elements at high fluoride concentrations. This stability means that fluoride complexation with the extracted Rf species is weaker than in the cases of the other elements. This conclusion is consistent with the experimental results obtained with a cation-exchange resin.

In conclusion, the adsorption behaviors of Rf, Zr, and Hf with a TTA extractant were observed in dilute solutions of HF and HNO₃. The behaviors of the No atoms produced in the decay of Rf were determined with ²⁵⁵No nuclides produced in runs other than the Rf experiments to assess the precise behavior of Rf, without the effects of its daughters. The results of the present study suggest that the chemical species involved in TTA extraction may be [RfF]³⁺, based on comparisons with the results for Zr and Hf. It was concluded that fluoride complexation with Rf cations is weaker than that with either Zr or Hf, which are group 4 homologs. The observed behavior of Rf is supported by theoretical calculations and agrees with the results of previous experiment on cation exchange. This study is the first comparison of complexation data for Rf cations with those for Zr and Hf, other than those based on cation-exchange experiments.

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