

Cation- and anion-exchange behavior and UV-vis spectroscopy of Zr in HBr for chemical characterization of bromide complexes of Rf

T. Yokokita*¹ and H. Haba*¹

The chemical properties of superheavy elements (SHEs) with atomic number $Z \geq 104$ deviate from the periodicity of their lighter homologues in the periodic table because of the strong relativistic effects on valence electron shells in these heavy atoms. Therefore, chemical research studies on these elements are intriguing and of great importance. However, the chemical study of these elements is very difficult because the half-lives of these elements are short and the production rates of these elements are low.¹⁾

Anion-exchange studies in HF and HCl have been reported for element 104, Rf.^{2,3)} The observed adsorption strength on the anion-exchange resin is $Zr \approx Hf > Rf$ in 1.9–13.9 M HF²⁾ and $Rf > Zr > Hf$ in 7.0–9.0 M HCl.³⁾ We are interested in the anion-exchange result of Rf in HBr because the adsorption sequence is different between HF and HCl media. There is one report on the bromide complex of Rf.⁴⁾ In this report, the solvent extraction of Rf and its homologous elements were performed. Rf was not extracted from 7.75–9.0 M HBr, while Zr and Hf were extracted. Further study on the bromide complexation of Rf is required to understand the halide complexation of Rf in detail. In this work, cation and anion exchanges of Zr were performed to obtain the comparison data for Rf. The UV-vis spectra of Zr in HBr solution was measured to discuss the ion-exchange behavior of Zr.

The ⁸⁸Zr was produced in the ⁸⁹Y(*d*, 3*n*) reaction using the RIKEN AVF cyclotron; further, ⁸⁸Zr was purified by an anion-exchange method. The cation- and anion-exchange of Zr were performed by employing the batch method in 1.1–8.8 M HBr, which is the same procedure as in Ref. 5). Further, control experiments without the resin were performed to determine the standard radioactivity of the solution sample. The distribution coefficient (K_d) was obtained according to $K_d = (A_c - A_s)V/A_s w$; here, A_c and A_s denote the radioactivities in the control and exchanged solutions, respectively. V denotes the volume of the solution, and w denotes the weight of the ion-exchange resin.

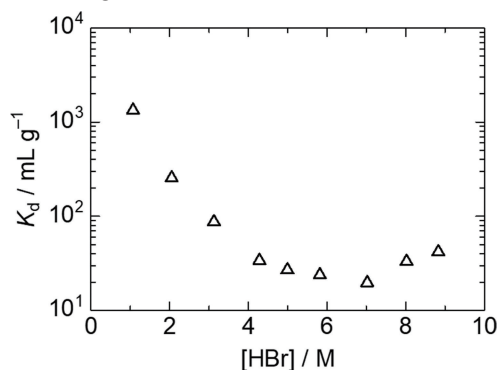


Fig. 1. Variation of the K_d values of Zr on the cation exchange resin as a function of [HBr].

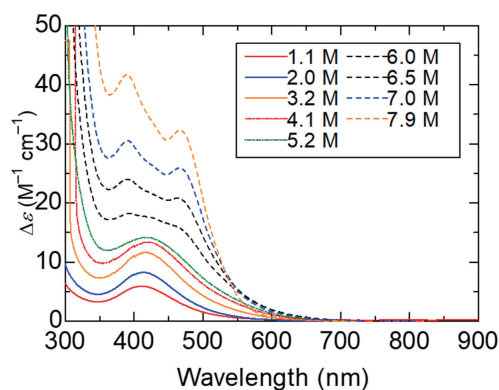


Fig. 2. UV-vis spectra of Zr in 1.1–7.9 M HBr.

The UV-vis spectra of 0.016–0.33 M Zr in the 1.1–7.9 M HBr solution were measured with UV-vis spectrophotometer (JASCO Co., V-730) to obtain the structural information on the Zr species in HBr.

In the anion exchange, the K_d values of Zr are low (< 10 mL g⁻¹) for all [HBr] studied in this work, indicating which implies Zr does not form anionic species at 1.1–8.8 M. This anion-exchange behavior is consistent with that using macro amounts of Zr.⁶⁾ The variation of the K_d values of Zr on the cation exchange resin are shown in Fig. 1. The K_d values decrease with an increase in [HBr] in the range 1.1–7.0 M, and they increase above 7.0 M.

The UV-vis spectra of Zr in HBr solution are shown in Fig. 2. At 1.1–5.2 M, one adsorption band is seen at $\lambda_{\max} = 410$ –421 nm, and its molar adsorption coefficient ($\Delta\varepsilon$) increases with an increase of [HBr]. Above 6.0 M, the UV-vis spectra shows two adsorption bands at $\lambda_{\max} = 390$ –391 and 463–467 nm, and both increase with an increase in [HBr], which indicates that the dominant Zr species is changed. This spectral change at 6.0 M is reasonably reflected on the variation of the K_d values in Fig. 1: bromide complexes are increasingly formed with an increase in [HBr], and above 7.0 M, a different bromide complex is adsorbed on the cation-exchange resin. It is possibility that the oxybromide complex of Zr is protonated and the cationic species of Zr increases.

In the future, we plan to measure the Raman spectra of $ZrBr_4$ in the HBr solution and the mass spectra of the solvent extracted Zr species to determine the Zr species in the HBr solution.

References

- 1) A. Türlér, V. Pershina., *Chem. Rev.* **113**, 1273 (2013).
- 2) H. Haba *et al.*, *J. Am. Chem. Soc.* **126**, 5219 (2004).
- 3) H. Haba *et al.*, *J. Nucl. Radiochem. Sci.* **3**, 143 (2002).
- 4) D. C. Kacher *et al.*, *Radiochim. Acta* **75**, 127 (1996).
- 5) T. Yokokita *et al.*, *RIKEN Accel. Prog. Rep.* **53**, 164 (2020).
- 6) *Gmelin Handbuch der Anorganischen Chemie Uranium Suppl.* Vol. D3, edited by R. Warncke (Springer-Verlag, Berlin, Heidelberg, New York, 1982).

*¹ RIKEN Nishina Center