Extraction behavior of Nb and Ta in HF solution with F-form TOMA resin

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Elements with atomic numbers ≥104 are called superheavy elements. The purpose of Db chemistry research is to investigate the relativistic effects of orbital electrons, which are more pronounced in heavier elements. Furthermore, in the search for new elements, if the anchor nucleus (last nucleus in the observed decay chain) is a neutron-rich Db isotope, the chemical identity of the Db can determine the formation of the new element, because such isotopes have a relatively long half-life.

Group 5 elements, including Db in hydrofluoric acid, form fluorine-containing complexes very quickly, making this reaction system suitable for on-line chemical experiments with short-lived Db isotopes. However, group 5 elements may also form oxyfluoride complexes, thus a method to identify the chemical species is desired.[1] We have studied solid-phase extraction of Nb and Ta anion complexes from hydrofluoric acid using Aliquat 336-supported resin.[2] This extraction system differs from anion exchange in that the distribution coefficients of Nb is very different from Ta; however, the extracted chemical species are not yet clearly known. The resin used in this study was trioctyl methyl ammonium chloride (TOMA-Cl), one of the main components of Aliquat 336. The counter ions in Aliquat 336 and TOMA are generally chloride ions. In order to clarify the effect of chloride ions in solid-phase extraction with hydrofluoric acid, we prepared resins in which the chloride ion was replaced with an anion originating from the hydrofluoric acid, and investigated the extraction behavior of Nb and Ta.

Radiotracers, ^{95g}Nb ($T_{1/2}$ = 34.991 d) and ^{179}Ta ($T_{1/2}$ = 1.82 y), were produced with deuteron irradiation on Zr and Hf metallic foil targets with natural isotopic abundance, respectively, using the RIKEN K70 AVF cyclotron. The radiotracers in the targets were chemically isolated by anion exchange. The 40-wt% TOMA-Cl resin was prepared by mixing TOMA-Cl dissolved in methanol with MCI GEL CHP20/P30 for approximately 1 day.[3] To obtain Cl^- free F-type resin the TOMA-Cl resin was shaken well with 10 M HF, and then dried. A 400 μL of 1–27 M HF solution containing ^{95g}Nb and ^{179}Ta tracers was shaken with approximately 11 mg of TOMA resin for 1 h using a syringeless filter. After filtering the resin, the 250 μL solution was aliquoted and the radioactivity was measured with an HPGe detector. Aqueous solution control samples without resin were also measured to determine the radioactivity of the resin. The distribution coefficients K_d for ^{95g}Nb and ^{179}Ta were obtained from the following equation:

$$K_d = \frac{(A_{ini} - A_a)/m_r}{A_a/V_a}, \quad (1)$$

where the subscripts a and r represent the aqueous phase and the resin, respectively, for the radioactivity A, mass m, and volume V. A_{ini} is the radioactivity relative to the control sample.

According to the reported dissociation constant for hydrofluoric acid,[4] the anions originating from HF are mostly HF_2^- at the concentrationns of HF in this study. The dependence of K_d on the HF_2^- concentration is shown in Fig. 1. For both Nb and Ta, K_d was smaller in pure hydrofluoric acid than in the aqueous phase containing Cl^-. This may indicate a difference in the adsorption of Cl^- and HF_2^- on the resin. However, further investigation is needed because the formation of complexes containing Cl is also possible when Cl-form resins were used.

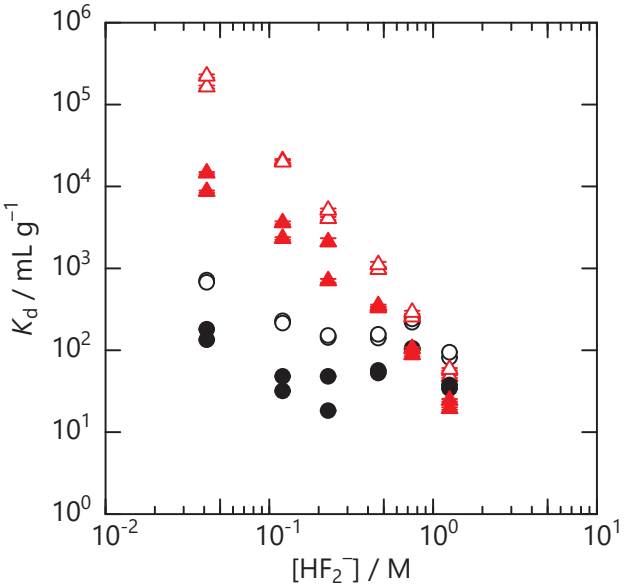

Fig. 1. Dependence of the distribution coefficients K_d for Nb (black) and Ta (red) on [HF_2^-] with F-type (solid symbols) and Cl-type (hollow symbols) TOMA resins.

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References
1) O. L. Keller, Jr., Inorg. Chem. **2**, 783 (1963).
2) D. Sato *et al.*, RIKEN Accel. Prog. Rep. **50**, 246 (2017).
3) H. Haba *et al.*, Radiochim. Acta **95**, 1 (2007).
4) H. H. Broene *et al.*, J. Am. Chem. Soc. **69**, 1644 (1947).