Extraction behavior of Nb and Ta with Aliquat 336 in HF solutions

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Studies on the chemical properties of transactinide elements with atomic numbers $Z \ge 104$ are extremely interesting. It is suggested that the chemical properties of these elements are different from those of their lighter homologs because of the strong relativistic effects on the valence electrons¹). Therefore, comparative studies on the chemical behaviors of transactinide elements and their lighter homologs are very important.

We are planning to investigate the chemical properties of Db, which is the 105^{th} element in the periodic table. Because a fluoride ion is known as a strong complexing reagent for group 5 elements²⁾, ion-pair extractions of Nb and Ta, which are the lighter homologs of Db, with quaternary ammonium (Aliquat 336) in HF solutions were carried out to study complex formations of these elements with fluoride ions.

Long-lived radiotracers, ^{95g}Nb ($T_{1/2} = 34.97$ d) and ¹⁷⁹Ta ($T_{1/2} = 665$ d), were produced during proton bombardments of Zr and Hf metallic foil targets with natural isotopic abundances, respectively, using the RIKEN AVF Cyclotron. These radiotracers in the targets were chemically isolated by ion-exchange separation. The tracers were dissolved in 600 µL of 1 M HF and then mixed with the same volume of 10^{-8} - 10^{-3} M Aliquat 336-1,2-dichloroethane solutions in a polypropylene tube. After shaking the solutions for 5 min, followed by centrifugation, the two phases were separately pipetted into sample tubes. The radioactivities of the two samples were assessed with a Ge detector. Distribution ratios (*D*) of Nb and Ta were obtained from the ratio of the radioactivities of the two phases.

The dependence of the distribution ratios of 95g Nb and 179 Ta in 1 M HF on the concentrations of Aliquat 336 are shown in Fig. 1. The results show a linear relation with a slope of ≈ 1 for both Nb and Ta, which indicates that univalent anionic fluoride complexes are extracted by Aliquat 336.

The dependences of D values of 95g Nb and 179 Ta on the HF concentration were also investigated for varying HF concentrations (10^{-2} -10 M) with 10^{-4} M Aliquat 336-1,2-dichloroethane solution (Fig. 2). The maximum D value of Ta is obtained in 0.27 M HF. On the other hand, the D value of Nb decreases gradually with HF concentration from 10^{-2} M to 10 M, thus, there was a clear differences in the extraction behaviors of Nb and Ta. The large difference in the D values of Nb and Ta is probably due to the fact that Ta forms fluoro-complexes TaF_n⁵⁻ⁿ, while Nb is predominantly present as oxo-fluoro complexes NbOF_n^{3-n 3}.

As mentioned above, the results obtained from Fig.1 show that the extracted species of Nb and Ta are both univalent anionic complexes. Therefore, Nb and Ta exist as TaF_6^- and $NbOF_4^-$ under these experimental conditions.

The fluoro-complex formation of Db needs to be investigated from the experimental result to dtermine whether the extraction behavior of Db from HF solutions into Aliquat 336-1,2-dichloroethane solution is closer to that of Nb or Ta.



Fig. 1: Variation of the distribution ratio D of ^{95g}Nb and ¹⁷⁹Ta vs. concentration of Aliquat 336 in 1 M HF



Fig. 2: Variation of the distribution ratio D of 95g Nb and 179 Ta vs. initial concentration of HF

References

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