Solvent extraction of ^{181}W with tri-n-octylamine in HF/HNO_3 system towards the chemistry of Sg

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Seaborgium (Sg) is the group 6 member of the Periodic Table, sharing its group with Mo and W. The pioneering aqueous chemistry of Sg was to study the fluoride complexation and hydrolysis in 5×10^{-4} M HF/0.1 M HNO_3 and in 0.1 M HNO_3 by cation exchange chromatography.[1,2] The decay events of the short-lived ^{265}Sg ($T_{1/2} = 7.1$ s),[1,2] however, could not be observed because of time consuming sample preparation and the chemical properties of Sg was discussed based on only three[1] and one[2] time-correlated α-α events of the decay products of ^{265}Sg, *i.e.*, ^{261}Rf and ^{257}No. After those pioneering studies, there have been no reports on the aqueous chemistry of Sg for more than 20 years. The decay data of ^{265}Sg and ^{261}Rf used in the experiments at the time were significantly revised by our group and the long-lived ^{265}Sg^{a,b} ($T_{1/2}$ = 8.5 s, 14.4 s)[3] opened up the possibility of next-generation Sg chemistry by directly observing Sg isotopes with the GARIS gas-jet system and the continuous flow extraction apparatus coupled to liquid scintillation counters.[4] The first step towards such exploration is to choose a chemical system for Sg by studying chemical properties of its lighter homologues Mo and W. Complex formations of Mo and W with chloride, fluoride and sulphate have been studied by ion exchange chromatography and solvent extraction.[5–7] In this work, we studied the fluoride complexation of W using tri-n-octylamine (TOA) as an extractant.

The radiotracer ^{181}W ($T_{1/2} = 121.2$ d) was produced by bombardment of ^{nat}Ta metal foils (100 μm$\times$4) with a 24-MeV d beam extracted from the RIKEN AVF cyclotron. After irradiation, ^{181}W was chemically separated from Ta by a liquid-liquid extraction method using methylisobutyl ketone as the extractant. The purified ^{181}W was stored in 0.01 M HNO_3. The solvent extraction of ^{181}W was carried out with 0.01 M TOA in toluene from $10^{-4} - 1$ M HF/0.01 M HNO_3 solutions. To 1.9 mL of the acid solutions, 100 μL of ^{181}W stock solution was added followed by the addition of 2 mL 0.01 M TOA in polypropylene (PP) tubes. The number of ^{181}W atoms used for each batch extraction was 9×10^{10}. The PP tubes were shaken for 10 min at 20°C and centrifuged for 5 min to achieve complete phase separation; we confirmed the extraction equilibrium was reached within 5 s in 0.5 M HF/0.01 M HNO_3 in a separate experiment. After that, 1 mL aliquots of both phases were subjected to γ-ray spectrometry employing a Ge detector. The concentration of TOA was also varied to deduce chemical species of W. Distribution ratio was calculated by $D = A_{org}/A_{aq}$, where A_{org} and A_{aq} are the radioactivity in the organic and aqueous phases, respectively.

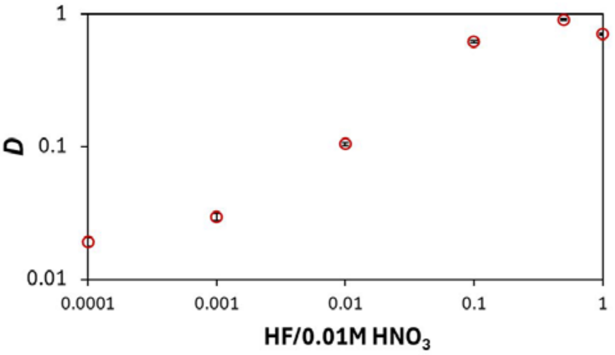

Fig. 1. Variation of D value with increasing [HF] ([HNO_3 = 0.01 M; [TOA] = 0.01 M).

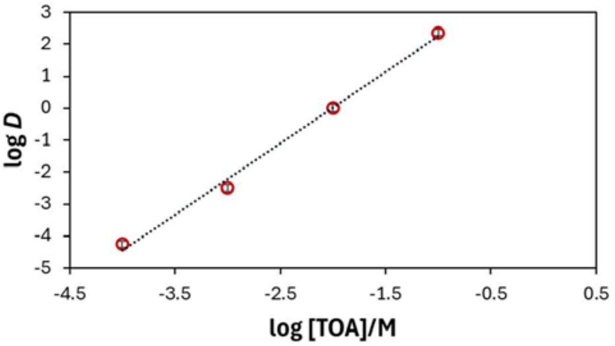

Fig. 2. Variation of D values as a function of [TOA].

Figure 1 represents the variation of D values with increasing [HF]. The D value of W increases with increasing [HF] suggesting the formation of anionic oxo-fluoro-complexes like $[WO_3F]^-$, $WO_2F_2(H_2O)_2$, $WO_2F_3(H_2O)^-$, $[WO_2F_4]^{2-}$, and $[WOF_5]^-$.[6,8,9]

In Fig. 2, a slope of the D value in 0.5 M HF/0.01 M HNO_3 vs. [TOA] plot in logarithmic scale is estimated to be 2.2 ± 0.1 indicating that two molecules of TOA are associated with the extracted complex of W. The extracted species is possibly $[WO_2F_4]^{2-}$ as deduced in Refs. 8) and 9) Next, we plan to study the variation of D values of W along with Mo by changing [HF] and [TOA] to understand the speciation mechanism in more detail.

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