

Solvent extraction of tungsten from oxalic acid solution with Aliquat 336 toward chemical studies of seaborgium

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The aqueous chemical experiments of element 106, seaborgium (Sg), have been reported by Schädel et al. in 1997¹⁾ and 1998²⁾. In these experiments, the cation exchange chromatography of Sg was conducted in HF/HNO₃¹⁾ and HNO₃²⁾ solutions. However, no chemical experiments for Sg have been reported since these experiments. Therefore, further experimental results are required for detailed discussion of chemical properties of Sg in aqueous solutions. We are planning to investigate solvent extraction behavior of Sg. Oxalic acid is a typical organic acid used as ligand for transition metals. It is reported that molybdenum (Mo) and tungsten (W), which are lighter homologs of Sg, form anionic oxalate complexes and are extracted into an organic phase with ion-pair extractant. In this work, we investigated the extraction behavior and extracted species of W from oxalic acid solution into toluene with Aliquat 336 toward the chemical studies of Sg. The experiments were performed using ¹⁸¹W in tracer scale to prevent the formation of polyoxometalate complexes of W.

The radiotracer ¹⁸¹W ($T_{1/2} = 121.2$ d) was produced in the bombardments of 24-MeV deuteron beam supplied by the RIKEN AVF cyclotron on ^{nat}Ta target foils. The ¹⁸¹W tracer was chemically separated from the target material by an anion exchange method and stored in 1 M HCl solution.

The solvent extraction of ¹⁸¹W was carried out as following procedure. One μ L of the tracer solution was pipetted to a 1.5 mL polypropylene tube. Then, 700 μ L of the oxalic acid solution containing 0.1 M HCl/0.9 M LiCl for keeping ionic strength constant was added. The same volume of Aliquat 336/toluene solution was mixed to the aqueous solution, and the mixture was shaken by a mechanical shaker for 5 min. After centrifuging for 30 s, 500 μ L aliquot of each phase was separately taken into vials, and radioactivities of both phases were measured with a Ge detector. The distribution ratio (D) of ¹⁸¹W was calculated using the following equation:

$$D = (A_{\text{org}} / V_{\text{org}}) / (A_{\text{aq}} / V_{\text{aq}}),$$

where A_{org} and A_{aq} are the radioactivities of organic and aqueous phases, respectively, and V_{org} and V_{aq} are the volumes of organic and aqueous phases, respectively. The extraction kinetics was also investigated from 1.0×10^{-2} M oxalic acid with 0.1 M HCl/0.9 M LiCl into 2.0×10^{-3} M Aliquat 336/toluene solution by changing the shaking time from 3 to 3600 s.

In the experiment of the investigation of extraction kinetics, the D value of ¹⁸¹W became constant in shaking time longer than 30 s. This result shows that the extraction of W from oxalic acid solution with Aliquat 336 is fast. The dependence of the D values of ¹⁸¹W on the Aliquat 336 concentration from 1.0×10^{-2} M oxalic acid with 0.1 M HCl/0.9 M LiCl is shown in Fig. 1. The D value of W increases with increasing [Aliquat 336]. The slope of the D value of W vs. [Aliquat 336] plot in logarithmic scale is estimated to be 0.95 ± 0.08 with a weighted least-squares fitting. This indicates that extracted anionic oxalate complex of W is associated with one molecule of Aliquat 336. However, in macro scale, it was reported that W is extracted as $(R_3NH)_2WO_2(C_2O_4)_2$, where R_3N shows a trioctylamine (TOA) molecule, when the mole ratio (Oxalate / WO_4^{2-}) in the aqueous phase was higher than 4.5⁴⁾. This discrepancy might be caused by the protonation to the W complex in the present experimental condition. Further experiments such as an investigation of dependence of D value on H^+ concentration would be performed for the speciation of the extracted species.

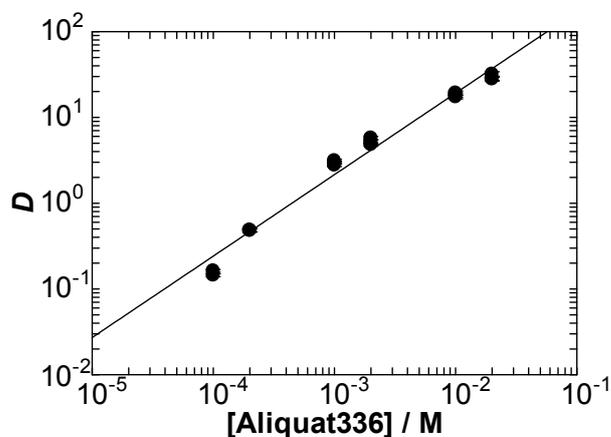


Fig. 1. Variation of the distribution ratio of ¹⁸¹W from 1.0×10^{-2} M oxalic acid with 0.1 M HCl/0.9 M LiCl as a function of the concentration of Aliquat 336.

References

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