Solvent extraction of short-lived radioisotopes of Mo and W from oxalic acid solution with Aliquat 336 for chemical studies of seaborgium (Sg)

N. Goto, *1 K. Ooe, *1 A. Toyoshima, *2 M. Murakami, *1,*3 Y. Komori, *3 H. Haba, *3 S. Goto, *1 and H. Kudo*4

Thus far, few studies of seaborgium (Sg) in an aqueous phase have been reported, where only a few events of Sg detected after batch-wise cation-exchange chromatography. 1,2) There have been few chemical studies of Sg owing to the experimental difficulties caused by its extremely low production yield and short half-life. To overcome the difficulties, we are developing a new rapid continuous chemistry apparatus based on the solvent extraction technique. We have been also studying solvent extraction behavior and extracted species of molybdenum (Mo) and tungsten (W), which are lighter homologs of Sg, to apply obtained results to development of the new apparatus and to compare extraction behavior among the homologs including Sg. Because it is well-known that Mo and W form polyoxometalate complexes, Mo and W should be extracted on a tracer scale for comparison of extraction behavior of their mononuclear complexes with that of Sg. which can exist only as single atoms. In a previous report, the solvent extraction of W from oxalic acid solution into toluene with Aliquat 336 was carried out with long-lived radiotracer, 181 W ($T_{1/2} = 121.2$ d). In this paper, we report on the extraction behavior of Mo using short-lived radioisotope along with W. The extracted species of these two elements will be discussed.

Short-lived radiotracers $^{93\text{m}}\text{Mo}$ ($T_{1/2} = 6.85 \text{ h}$) and ^{177}W $(T_{1/2} = 2.25 \text{ h})$ were produced in the irradiation with a 50-MeV α beam supplied from the RIKEN K70 AVF cyclotron on a metallic natZr and natHf target foils. Nuclear reaction products recoiling out of the targets were transported by a KCl/He gas-jet method at a He gas flow rate of 2.0 L/min. The transported products were deposited on a small plastic piece (Naflon®) for 1min. Then, the deposited products were dissolved with 100 µL of 0.01 M H₂C₂O₄ (oxalic acid)/0.1 M HCl/0.9 M LiCl solution. The solution was then pipetted to a plastic tube in which 600 µL of aqueous solution and 700 µL of Aliquat 336 in toluene had been added. After shaking with a Vortex mixer for 5 min, the mixed sample was centrifuged for 30 s. From both the phases, 500 µL of aliquots were separately taken into two vials. These two samples were then subjected to γ -ray spectrometry with a Ge detector. The distribution ratio (D) of $^{93\text{m}}$ Mo and 177 W was calculated using the equation of D = $(A_{\rm org} \ / \ V_{\rm org}) \ / \ (A_{\rm aq} \ / \ V_{\rm aq})$, where $A_{\rm org}$ and $A_{\rm aq}$ are the radioactivities in organic and aqueous phases, respectively, and V_{org} and V_{aq} are the volumes of organic and aqueous phases, respectively.

Dependence of the D values of 93 mMo and 177 W on the Aliquat 336 concentration with a 0.01 M oxalic acid/ 0.1 M HCl/0.9 M LiCl solution is shown in Fig. 1. Results previously obtained with ¹⁸¹W are also plotted in the same figure. The D values of Mo and W increase with increasing concentration of Aliquat 336. The slopes of the D value vs. [Aliquat 336] plot on logarithmic scales are evaluated to be 2.08 ± 0.03 for Mo and 1.33 ± 0.02 for W with a weighted least-squares fitting. This indicates that extracted anionic oxalate complex of Mo is associated with two molecules of Aliquat 336, while that of W is with one molecule. On a macro scale, it was reported that Mo and W are extracted as (R₃NH)₂MO₂(C₂O₄)₂ from oxalic acid solution, where R₃N shows a trioctylamine (TOA) molecule and M shows Mo or W.^{4,5)} The present result for Mo corresponds to the reported Mo oxalate complex. On the other hand, it seems that W forms a different complex from the Mo one. Under the present experimental condition, chloride ions of 1 M are present contrary to the experiment in the reference.⁵⁾ Therefore, the extracted W complex might contain one oxalate ion and one chloride ion. To obtain further information on the extracted species of W, we need to investigate the variation in the distribution ratio as a function of the concentration of chloride ions. Based on the extraction behavior of Mo and W obtained in these studies, oxalate complex formation of Sg will be investigated.

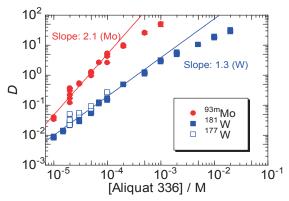


Fig. 1. Variation in the distribution ratio of $^{93\text{m}}$ Mo, 177 W and 181 W from 1.0×10^{-2} M oxalic acid with 0.1 M HCl/0.9 M LiCl as a function of the concentration of Aliquat 336.

References

- 1) M. Schädel et al.: Radiochim. Acta 77, 149 (1997).
- 2) M. Schädel et al.: Radiochim. Acta 83, 163 (1998).
- 3) N. Goto et al.: RIKEN Accel. Prog Rep. 47, 269 (2014).
- 4) K. Yakabe and S. Minami: Nippon Kagaku Kaishi 1045 (1983).
- 5) K. Yakabe, K. Iwamoto and S. Minami: Nippon Kagaku Kaishi 714 (1985).

^{*1} Graduate School of Science and Technology, Niigata University

^{*2} Advanced Science Research Center, Japan Atomic Energy Agency

^{*3} RIKEN Nishina Center

^{*4} Department of Chemistry, Faculty of Science, Niigata University