Extraction behavior of Mo and W from H_2SO_4 using amine-extractant (Aliquat336) as homologs of seaborgium

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Recently, we began to study the aqueous chemistry of a group-6 transactinide element, Sg. At present, we focus on the formation of anionic sulfate complexes of Mo and W, which are lighter homologs of Sg, by means of amine-extraction in H_2SO_4 as a preparatory experiment for Sg. Previously, we have found that the group-4 transactinide, Rf, has a weaker preference to form a sulfate complex than its lighter homologs, Zr and Hf.[1] This is consistent with its predicted, larger ionic radius compared to the measured radii of Zr and Hf; moreover, this is in good agreement with a theoretical prediction[2] that the stability of Rf complexes is lower because of the smaller ionic contribution to the chemical bond. The investigation of sulfate complex formation of Sg is, therefore, expected to provide valuable information on its ionic radius and chemical bonding.

This paper reports on the extraction behavior of the carrier-free radioisotopes ^{93m}Mo and ^{181}W from aqueous H_2SO_4 solution using an amine extractant, Aliquat336, by a batch method to ensure that the chemical behavior of mononuclear complexes of these homologs is retained. First, the extraction kinetics of these radioisotopes in 0.1, 4.3 and 8.6 M H_2SO_4 with 0.2 M Aliquat336 were studied. Then, extraction probabilities were investigated as a function of H_2SO_4 concentration, $[H_2SO_4]$.

In the experiments of Mo, ^{93m}Mo was produced in the $^{nat}Zr(\alpha, xn)$ reaction at the RIKEN K70 AVF cyclotron. Nuclear reaction products transported by a KCl/He gas-jet at a flow rate of 2.5 L/min were deposited on a small piece of plastic (Naflon®, ~2 cm × 1.5 cm) for 3 min. KCl aerosols were produced by sublimation at 640°C. Then, the deposited products were dissolved win 100 μL of 0.1 – 8.6 M H_2SO_4 solution. The solution was then added to 600 μL of H_2SO_4 solution with the same concentration in a plastic vial. Subsequently, 700 μL of the toluene solution of Aliquat336 was added. After shaking with a Vortex mixer for 360 s, the mixed sample was centrifuged for 30 s. From both the phases, 500 μL solutions were collected separately in 2 vials. These 2 samples were then subjected to γ-ray spectrometry with a Ge detector. The distribution ratio, D, was evaluated with the equation, $D = (A_{org} / V_{org}) / (A_{aq} / V_{aq})$, where A_{org} and A_{aq} are the radioactivities in organic and aqueous phases, respectively, and V_{org} and V_{aq} are the

volumes of the organic and aqueous phases, respectively.

In the experiments of W, ^{181}W was produced in the $^{181}Ta(d, xn)^{181}W$ reaction at the RIKEN K70 AVF cyclotron. After the chemical separation of ^{181}W from a Ta target material through an ion-exchange, carrier-free ^{181}W was stocked in H_2SO_4 solutions. The procedure of the subsequent batch experiment was the same as that for ^{93m}Mo described above.

Results of kinetics experiments showed that the extraction equilibrium of ^{93m}Mo was reached within 5 s in the range of 0.1 M < $[H_2SO_4]$ < 8.6 M, while that of W was dependent on $[H_2SO_4]$; the equilibrium was attained within 40 s at $[H_2SO_4]$ < 1 M and within 2 min at 1 M < $[H_2SO_4]$ < 8.6 M. In Fig. 1, the D values of Mo and W under equilibrated conditions are shown as a function of $[H_2SO_4]$. The D values of Mo and W decrease up to 3 M and 2 M, respectively, with increasing $[H_2SO_4]$. This is probably due to protonation reactions of hydrolyzed Mo and W species. On the other hand, when $[H_2SO_4]$ > 3 M and > 4 M, the D values of W and Mo, respectively, show a sharp increase. This clearly indicates the formation of anionic sulfate complexes of Mo and W. Sulfate complexation of Sg under the present experimental conditions will be clarified in our future experiments.
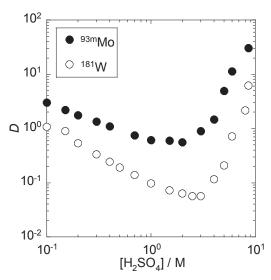

Fig. 1. Variation of D value of Mo and W as a function of H_2SO_4 concentration, $[H_2SO_4]$.

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