Extraction behavior of carrier-free and macro amounts of molybdenum and tungsten from HCl solution

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Summary. Solvent extraction behavior of carrier-free Mo and W from 0.1–11 M HCl into 0.05 M Aliquat 336-chloroform solution was investigated and compared with that of macro amounts of Mo and W. The distribution ratios of carrier-free Mo and W were in good agreement with those of macro amounts of Mo and W in 6–11 M HCl, while the extraction efficiencies of carrier-free Mo and W were different from those of macro amounts of Mo and W in < 6 M HCl. Therefore, it appears that the carrier-free as well as macro amounts of Mo and W form mononuclear species in 6–11 M HCl. The disagreement in < 6 M HCl is probably due to the formation of polynuclear species of the macro amounts of Mo and W.

1. Introduction

The aqueous chemistry of molybdenum (Mo) and tungsten (W) is complicated because these elements form polynuclear species such as $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $[\text{W}_{12}\text{O}_{39}]^{6-}$ in neutral to acidic solution [1]. These elements are lighter homologues of element 106, seaborgium (Sg) and, therefore, the chemical behavior of these elements is important for investigation of chemical properties of Sg. Because Sg cannot form polynuclear species due to an extremely low production rate in the order of one atom per hour, an investigation of the chemical behavior of mononuclear Mo and W species is required for a comparison with that of Sg. It was reported that macro amounts of Mo and W exist as monomeric oxochloride complexes in concentrated hydrochloric acid (HCl) (> 6–7 M HCl) [2–6]. There is a possibility of existence of polymeric Mo and W complexes in diluted HCl. In this study, solvent extraction behavior of Mo and W under the carrier-free condition was investigated by ion-pair extraction from HCl with Aliquat 336 that extracts anionic species from aqueous solution. Moreover, the results under carrier-free condition were compared with those measured

with macro amounts. Solvent extraction coefficients of Mo and W obtained under carrier-free condition are much different from those determined with macroscopic amounts in diluted HCl concentration, while almost the same solvent extraction coefficients for both Mo and W were obtained in concentrated HCl solution (6–11 M HCl). It is found that 6–11 M HCl solution is the best condition for the ion-pair solvent extraction experiment of Sg in HCl.

2. Experimental

In the experiments with carrier-free Mo and W, HCl (Wako Pure Chemical Industries, for ultratrace analysis) was diluted to desired concentration with ultrapure water (resistivity of 18.2 MΩ cm). Aliquat 336 was purchased from Sigma Aldrich and was dissolved in chloroform (Kishida Reagents Chemicals, super special grade) to become 0.05 M Aliquat 336 in chloroform. Short-lived isotopes, ^{90}Mo ($T_{1/2} = 5.7$ h) and ^{173}W ($T_{1/2} = 7.6$ min), were produced in the $^{nat}\text{Ge}(^{22}\text{Ne}, xn)$ and $^{nat}\text{Gd}(^{22}\text{Ne}, xn)$ reactions, respectively, using the RIKEN K70 AVF cyclotron. The $300\text{ }\mu\text{g}/\text{cm}^2$ ^{nat}Ge and $570\text{ }\mu\text{g}/\text{cm}^2$ ^{nat}Gd targets were separately prepared by vacuum deposition and electrodeposition, respectively, on beryllium backing foils. The bombarding energies of ^{22}Ne were 120 MeV in the Mo experiment and 118 MeV in the W experiment. These beam energies were selected to be at about the top of the excitation function in the $^{248}\text{Cm}(^{22}\text{Ne}, 5n)^{265}\text{Sg}$ reaction [7]. Average beam intensities were approximately 100 particle nA in the Mo experiment and 300 particle nA in the W experiment, respectively. Reaction products recoiling out of the target were thermalized in a helium gas flow (1.8 L/min), attached to KCl aerosols generated by sublimation of KCl powder at 620 °C, and were then transported to a chemistry laboratory. Transported products were deposited on a polyester or Naflon sheet for 5 min and were then dissolved in 200 μL of 0.1–11 M HCl for Mo or 4–11 M HCl for W. The concentrations of Mo and W isotopes calculated from their radioactivities were *ca.* 10^{-13} M. The aqueous solution was mixed with an equal volume of the 0.05 M Aliquat 336-chloroform solution, and was then shaken for 3 min at 25 °C. It was showed that the shaking time of 1 min was sufficient to attain extraction

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equilibrium of Mo and W in separate experiments where the shaking times were varied from 1 to 10 min for Mo and 1 to 5 min for W. After centrifuging, 160 μL aliquots of the aqueous and the organic phase were separated into polypropylene tubes, and then each tubes was subjected to γ -ray spectrometry using Ge detectors. In the Mo experiments, γ -ray measurements were carried out after the decay of the by-product activities (after about 1 h after the end of deposition of reaction products) because the 259.1 keV γ -ray from the decay of $^{83\text{m}}\text{Y}$ ($T_{1/2} = 2.85$ min)- $^{83\text{m}}\text{Sr}$ ($T_{1/2} = 4.95$ s) interfered with the detection of ^{90}Mo ($E_\gamma = 257.34$ keV). Distribution ratios (D) for Mo and W were calculated with the following equation:

$$D = \frac{C_{\text{M,o}}}{C_{\text{M,a}}} = \frac{A_{\text{o}}V_{\text{a}}}{A_{\text{a}}V_{\text{o}}}, \quad (1)$$

where C_{M} is the concentration of Mo or W, A the radioactivity of the metal, and V the volume of aqueous or organic phase. The subscripts a and o denote the aqueous and organic phases, respectively. Each experiment was repeated three times.

In the experiments with macro amounts of Mo and W, HCl (Kishida Reagents Chemicals, special grade) was diluted to the desired concentration with distilled water. For the preparation of the organic phase, the same reagents as in the carrier-free experiment were used. $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ (Wako Pure Chemical Industries, special grade) and $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$ (Kishida Reagents Chemicals, special grade) were dissolved in 2–11 M HCl. The concentrations of Mo and W were approximately 10^{-3} M for Mo and 7×10^{-5} to 8×10^{-3} M for W. After the dissolution, the solutions were allowed to stand for some time for polymerization of Mo and W (experimental conditions are summarized in Table 1). 2 ml of the aqueous solution containing Mo or W were mixed with an equal volume of the 0.05 M Aliquat 336-chloroform solution. These mixtures were then shaken for 3 min at 25 $^\circ\text{C}$. After centrifuging, the two phases in each sample were separated to determine the metal concentrations in each phase. The aqueous phase was evaporated to dryness, and the residue was dissolved in 1 mL of 2 M NaOH solution. The organic phase was mixed with 2 mL of 2 M NaOH solution and the mixture was shaken for 10 min

to back-extract Mo or W. Metal concentrations in the NaOH solutions were determined spectrophotometrically by a thiocyanate method [8]. The sample solution was prepared by adding 200 μL of 3.2 M NH_4SCN (for Mo) or 5 M NH_4SCN (for W) solution to 1 mL of 2 M NaOH solutions, and then it was diluted to 5 mL with 0.2 M SnCl_2 in 2 M HCl (for Mo) or 0.2 M SnCl_2 in 8 M HCl (for W) solution. Each solution was allowed to stand for 30 min (Mo) or 1 h (W) to let the color develop. Absorbances of these solutions were measured at 465 nm and 402.5 nm for Mo and W, respectively. Each experiment was repeated at least three times.

3. Results and discussion

The results of our extraction experiments of carrier-free and macro amounts of Mo and W are shown in Figs. 1 and 2, respectively. D values for carrier-free Mo and W increase with an increase of HCl concentration, indicating that anionic chloride complexes of Mo and W such as $[\text{MO}_2\text{Cl}_3]^-$ ($\text{M} = \text{Mo}$ and W) [2, 4, 9] are formed. The extraction efficiency of Mo is higher than that of W under the studied conditions. These results are in good agreement with previously reported results of anion exchange experiments [10, 11]. Tungsten in carrier-free condition is almost not extracted in 4 M HCl, suggesting that W exists as cationic and/or neutral species under these conditions in the HCl.

Fig. 1. Extractions of carrier-free and macro amounts of Mo from hydrochloric acid with 0.05 M Aliquat 336-chloroform solution.

Fig. 2. Extractions of carrier-free and macro amounts of W from hydrochloric acid with 0.05 M Aliquat 336-chloroform solution.

Table 1. Summary of experimental conditions with macro amounts of Mo and W.

HCl concentration	Time of standing from dissolution of the metal	Metal concentration
	Mo	
11.00 M	< 1 d	9×10^{-4} M
7.93 M	7 d	9×10^{-4} M
5.95 M	11 d	9×10^{-4} M
3.98 M	4 d	8×10^{-4} M
3.03 M	< 1 d	8×10^{-4} M
2.02 M	10 d	8×10^{-4} M
	W	
11.14 M	30 d	8×10^{-3} M
7.77 M	4 d	1×10^{-3} M
5.74 M	4 d	1×10^{-4} M
3.78 M	4 d	7×10^{-5} M

D values of carrier-free Mo are higher than the ones with macro amounts of Mo in < 6 M HCl. It was reported that cationic dimer species of Mo, such as $[\text{Mo}_2\text{O}_5(\text{H}_2\text{O})_6]^{2+}$, which are not extracted with Aliquat 336, is formed in < 6 M HCl [12, 13] in addition to other cationic monomers and neutral species such as MoO_2^{2+} and MoO_2Cl_2 [14, 15]. Therefore, the steeper decrease in D value of macro amounts of Mo compared to carrier-free condition when going to lower HCl concentrations is probably attributed to the formation of cationic dimer species of Mo in < 6 M HCl. Macro amounts of W are extracted with a much higher distribution ratio as compared with carrier-free W in 4 M HCl. Presumably, macro amounts of W form anionic polynuclear species in 4 M HCl while carrier-free W forms cationic and/or neutral species in 4 M HCl. These results strongly suggest that the chemical species of macro amounts of Mo and W in < 6 M HCl are different from those of carrier-free Mo and W.

On the other hand, the D values of carrier-free Mo and W are in good agreement with those of macro amounts of Mo and W, respectively, in 6–11 M HCl. As described above, it was reported that macro amounts of Mo and W exist as monomeric oxochloride complexes in concentrated HCl. The fact that the D values are almost the same in both macroscopic and carrier-free conditions suggests that the carrier-free as well as macro amounts of Mo and W would form the mononuclear species in 6–11 M HCl. Therefore, we conclude that the ion-pair extraction of Mo and W from 6–11 M HCl with Aliquat 336 is available for the comparison with that of Sg, and information on the formation of anionic chloride complexes of Sg can be obtained from this extraction condition. It is reported that the nuclear reaction products such as Po produced from Pb impurities in the Cm target disturb the detection of α -lines of ^{265}Sg [16], however, these reaction products are observed at least in either aqueous or organic phase in the solvent extraction experiments. Therefore, the chemical studies of Sg should be performed with a physical separator such as GARIS [17].

4. Conclusion

Solvent extraction experiments with carrier-free and macro amounts of Mo and W from 0.1–11 M HCl into 0.05 M Aliquat 336-chloroform solution were carried out, and these results were utilized for the discussion of experimental conditions under which the extraction behavior of Mo and W can be compared to that of Sg. The extraction behavior of carrier-free Mo and W corresponded to that of macro amounts of Mo and W in 6–11 M HCl. This result shows that Mo and W exist as mononuclear species in both macro amount and carrier-free conditions in 6–11 M HCl. In conclusion, the present extraction system in 6–11 M HCl is applicable to study mononuclear species of Sg. Extraction efficiencies of carrier-free Mo and W are different from those of macro amounts of Mo and W below 6 M HCl, indicating the formation of polynuclear species in experiments

with macro amounts of Mo and W. We will further investigate the chemical species of carrier-free Mo and W in < 6 M HCl for more detailed chemical studies of Sg in 4 M HCl, where the extraction behavior of Mo is quite different from that of W.

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