Extraction of niobium and tantalum isotopes using organophosphorus compounds – Part II – Extraction of ‘carrier-free’ concentrations from HCl/LiCl solutions

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Niobium/Tantalum/Liquid-Liquid Extraction/HDEHP/BEHP/Kinetics

Summary

We have studied the extraction of niobium and tantalum from mixed hydrochloric acid/lithium chloride media by bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and bis(2-ethylhexyl) hydrogen phosphite (BEHP) as a function of hydrogen ion (H^+) concentration. The amount of niobium extracted by both HDEHP and BEHP decreased with increasing hydrogen ion concentration. Equilibrium with niobium occurred within 10 s at all hydrogen ion concentrations for both systems. For tantalum, the amount extracted increased until 6 – 9 M H^+ , before decreasing at higher H^+ concentrations when extracted by both HDEHP and BEHP. Equilibrium occurred within 10 s at two H^+

concentrations when extracted by HDEHP. The data obtained are used as the basis to discuss the speciation of Nb and Ta under the conditions studied and to evaluate possible extraction mechanisms.

1. Introduction

The aqueous chemistry of the group five elements [niobium (Nb), tantalum (Ta) and dubnium (Db, $Z=105$)] at very low concentrations is of interest due to the roles that hydrolysis and relativistic effects play in the complex formation of these elements. Niobium and tantalum hydrolyze in different ways in the presence of water [1, 2]. In addition, calculations taking into account relativistic effects [3, 4], which increase with Z^2 , predicted that the chemical properties of Db will deviate from those of its lighter homologues [4]. Systems that probe differences in chemical properties between the group 5 elements offer insights into the role of hydrolysis and relativistic effects in complex formation. However, because Db isotopes can only be produced one atom-at-a-time through nuclear reactions and having half-lives in the order of seconds, chemical systems are limited and must fulfill three requirements: First, the atoms must undergo the same reaction multiple times to ensure reproducible results. Second, to investigate differences in chemistry between the transactinide and its lighter homologues, a physical pre-separator must be used to separate the atom of interest from the unwanted reaction products. And third, equilibrium should preferentially be reached within a time (<10 s). For these reasons, we have chosen to investigate the liquid-liquid extraction of the lighter homologues of group 5.

Our previous studies [5] have shown that extraction by the organophosphorous compounds, bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and bis(2-ethylhexyl) hydrogen phosphite (BEHP) from HCl solutions, are promising systems for studying differences in complex formation and extraction behavior between the group five elements. In organic media, HDEHP predominantly acts as a cationic complex extractor. HDEHP also has a tendency to form dimers of the following type in organic media [6]:

In contrast, BEHP extracts neutral complexes and exists as a monomer in organic solutions.

Reactions with these systems are hindered by the relatively long equilibration times. The time necessary to reach equilibrium can reach up to several times the half-life of the long-lived ^{262}Db isotope. Equilibrium was reached faster at higher HCl concentration, indicating that either the hydrogen ion (H^+) or chloride ion (Cl^-) or both may influence the species formed and/or the extraction kinetics [5]. In this paper, we report on results of experiments designed to investigate the role of the hydrogen ion concentration in the equilibrium and complex formation of the extraction systems.

2. Experimental

Bis(2-ethylhexyl) hydrogen phosphate (97%) and bis(2-ethylhexyl) hydrogen phosphite (96%) were purchased from Aldrich Chemical Company and used as received. Chloroform (ACS reagent, $\geq 99.8\%$) was obtained from Sigma-Aldrich, Inc. The lithium chloride ($>99.0\%$) and the hydrochloric acid (puriss.) used for the preparation of solutions were obtained from Fluka Chemika.

Short-lived niobium, $^{88\text{g}}\text{Nb}$ ($T_{1/2} = 14.5$ m), and tantalum, ^{170}Ta ($T_{1/2} = 6.76$ m), were produced at the Lawrence Berkeley National Laboratory's 88-Inch Cyclotron using the $^{74}\text{Se}(^{18}\text{O}, p3n)$ and $^{124}\text{Sn}(^{51}\text{V}, 5n)$ reactions, respectively. The details of the targets, beams, experimental apparatus and procedure are the same as described in the previous paper [5]. The $^{88\text{g}}\text{Nb}$ and ^{170}Ta evaporation residues (EVRs) were formed with the momentum of the beam, recoiled out of the target and were separated from the beam and unwanted reaction products in the Berkeley Gas-filled Separator (BGS) [7, 8], based upon differing magnetic rigidities in 66-Pa helium (He) gas [9]. The EVRs then passed through a Mylar window at the back of the BGS and were thermalized in ~ 1.3 -bar He in the recoil transfer chamber (RTC) [10, 11]. The thermalized EVRs were captured on potassium chloride aerosols, transported to a chemistry site using a He-gas jet and collected. The organic phases were 0.01 M HDEHP or 0.01 M BEHP in chloroform. The aqueous phases consisted of mixtures of HCl and LiCl with the chloride ion concentration held constant at 12 M and the hydrogen ion concentration varied between 1 - 11 M. The concentration of niobium and tantalum present in the samples was calculated to be $\sim 10^{-16}$ M.

Samples were mixed for 10 - 60 s using a vortex mixer and then centrifuged for 20 s. 3 mL aliquots of each phase were then assayed on a high purity germanium γ -ray detector. Five parallel experiments were performed for each acid concentration and mixing time and extraction yields were determined using:

$$E(\%) = \frac{[\text{Me}]_{\text{org}}}{[\text{Me}]_{\text{org}} + [\text{Me}]_{\text{aq}}} \times 100 \quad (2)$$

where $E(\%)$ is the percentage of the metal ions in the organic phase. γ -ray radioactivity was used to determine the relative metal concentrations in each phase. A weighted mean of the values for the five samples were used to determine final values for the extraction

yield at each set of conditions. Statistical counting uncertainty and standard error propagation techniques were used to determine the error on the results at the one sigma level.

3. Results and Discussion

3.1. Extraction Kinetics

For each aqueous phase, the samples were mixed for 10 - 60 s to obtain information regarding the amount of time the system needed to reach equilibrium. Results of these experiments are contained in Figs. 1 - 4. Niobium extraction equilibrium was reached within 10 s at all H^+ concentrations studied for both of the extraction systems (See Figs. 1 and 3). Tantalum showed a different equilibrium behavior as equilibrium was reached within 10 s only when HDEHP was used as an extractant and the aqueous phase consisted of 1 or 3 M H^+ . Equilibrium was not reached within 60 s at the other three H^+ concentrations when HDEHP was used as an extractant (See Fig. 2). In contrast, equilibrium was reached within 30 s when tantalum was extracted by BEHP from 11 M H^+ and not reached within 60 s when the H^+ concentration was decreased (See Fig. 4). Based on these results and the short half-lives of the isotopes studied, mixing times of 60 s were chosen for both the Nb and Ta experiments.

3.2. Niobium

The extraction of niobium in mixed HCl/LiCl solutions by 0.01 M HDEHP and 0.01 M BEHP in chloroform was studied at Cl^- concentrations of 12 M and over a H^+ concentration of 1 – 11 M, as shown in Figure 5. When HDEHP is used, the extraction of niobium decreases from $90 \pm 10\%$ to $17.4 \pm 1.4\%$ as the H^+ is increased from 1 to 11 M. The extraction of Nb by BEHP followed a similar pattern. The maximum amount

(69±5%) of niobium was extracted at 1 M H⁺ and the extraction yield decreased with increasing H⁺ concentration to a minimum of 12.7±0.4% at 11 M H⁺. The low extraction yields at increased H⁺ concentrations are consistent with the observations made in our previous work [5].

Kanzelmeyer *et. al* [12, 13] performed a series of spectroscopic studies on niobium in mixed HCl/LiCl solutions, in which Cl⁻ concentration held constant at 10.5 M, and the H⁺ concentration was varied from 0.02 to 9.86 M. From their data, they determined that the predominant species in solution at high H⁺ and Cl⁻ concentration is Nb(OH)₂Cl₄⁻. As the H⁺ concentration is lowered, insoluble colloids based upon Nb(OH)₃Cl₂ are formed via the reaction:

Colloidal Nb(OH)₃Cl₂ then becomes the predominant specie <2 M H⁺. Due to the low Nb concentrations used in this work, the formation of colloidal species is significantly reduced. Instead, the dominant species at low H⁺ concentrations is expected to be the monomer Nb(OH)₃Cl₂. Experiments with macroscopic amounts of Nb have also determined that cationic Nb species such as Nb(OH)₂Cl₂⁺ and NbOCl₂⁺ exist at low HCl concentrations [14]. Based upon this information we tentatively propose the following extraction mechanisms at low H⁺ concentrations:

1. Adduct formation of the neutral complexes and HDEHP dimers or BEHP at low H⁺ concentrations:

2. Ionic association of HDEHP dimers with cationic complexes at low H^+ concentrations:

With increasing H^+ concentration, the formation of the anionic $Nb(OH)_2 Cl_4^-$ complex begins to dominate, resulting in decreased extraction yields.

3.3. Tantalum

Figure 5 contains the results of the extraction of Ta by 0.01 M HDEHP or 0.01 M BEHP in chloroform from solutions of 12 M Cl^- and 1 – 11 M H^+ . Over the H^+ concentration range, the amount of tantalum extracted by HDEHP increased from $26 \pm 1\%$ to $87 \pm 1\%$ as the H^+ concentration was raised from 1 to 9 M and then decreased slightly to $84 \pm 1\%$ at 11 M H^+ . The extraction with BEHP showed a similar pattern as amount of Ta that was extracted increased as the H^+ concentration was raised from 1 M ($25 \pm 2\%$) to 6 M ($79 \pm 1\%$). A decrease in extraction yield, to $44 \pm 2\%$, was then observed at 11 M H^+ . The extraction yields observed at 11 M H^+ are consistent with the observations made in our previous work [5].

The difference between Ta and Nb extractions as the H^+ concentration is increased indicates that Nb and Ta are not forming similar complexes. The increase in the extraction yield of Ta over the same concentration range for which the extraction of Nb decreases suggests that the formation of the anionic species, such as $Ta(OH)_2 Cl_4^-$, is not favorable. It is also notable that the extraction of Ta by HDEHP is below 50% at ≤ 3 M HCl. The extraction of Ta by BEHP begins at lower H^+ concentrations than it does for HDEHP, while high extraction of Ta by HDEHP occurs through 11 M H^+ . These

observations may suggest the formation of neutral complexes, e.g. $\text{Ta}(\text{OH})_3\text{Cl}_2$, at H^+ concentrations of 3 – 9 M and cationic species, e.g. HTaOCl_3^+ , as the H^+ concentration is increased. From these assumptions, the following extraction mechanisms *may be* examples of the types of reactions between Ta and HDEHP or BEHP:

1. Adduct formation of neutral complexes with HDEHP dimers or BEHP at 3 - 6 M H^+ :

2. Ionic association of HDEHP dimers with cationic complexes at high H^+ concentrations:

3. Adduct formation of HDEHP dimers with cationic complexes at high H^+ concentrations:

Eqn. (10) requires the existence of a deprotonated HDEHP complex in the same solutions that form a protonated TaOCl_3 . As such, mechanisms similar to those proposed in eqn. (11) may more realistically represent extraction at high H^+ and Cl^- ion concentrations than eqn. (10).

4. Conclusion

In this work, the extraction of niobium and tantalum by 0.01 M HDEHP and 0.01 M BEHP as a function of H^+ concentration and mixing time was studied. Niobium and tantalum show different extraction behavior at both low (1 M) and high (6 - 9 M) H^+ concentrations. The amount of time needed for each system to reach equilibrium is also

significantly different between the two elements. However, both niobium and tantalum reach equilibrium within 10 s when the extractant was HDEHP and the aqueous phase consisted of 1 or 3 M H^+ . Under these conditions, niobium and tantalum also show large differences in extraction behavior: as the H^+ concentration was increased, a decrease was observed in the amount of niobium that was extracted, while the amount of tantalum extracted increased over the same acid range. This data, when compared to that obtained previously in [5] indicates that an increase in the H^+ concentration results in increase in the formation of anionic Nb complexes and either neutral or cationic Ta complexes. However, .The fast kinetics and drastically different chemical behavior make this region of the system suitable for the study of the chemical properties of dubnium.

5. Acknowledgements

The authors gratefully acknowledge the staff of the 88-inch cyclotron at Lawrence Berkeley National Laboratory for providing the ^{51}V and ^{18}O beams. This work was supported by the Director, Office of Science, Office of High Energy and Nuclear Physics, Division of Nuclear Physics, US Department of Energy under Contract No. DE-AC02-05CH11231.

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Figure 1: Extraction of niobium from solutions of 12 M Cl⁻ and 1 (●), 3 (▲), 6 (▼), 9 (◆) and 11 (■) M H⁺ by 0.01 M HDEHP in CHCl₃ as a function of mixing time. Error bars are shown when larger than the symbol.

Figure 2: Extraction of tantalum from solutions of 12 M Cl⁻ and 1 (○), 3 (△), 6 (▽), 9 (◇) and 11 (□) M H⁺ by 0.01 M HDEHP in CHCl₃ as a function of mixing time. Error bars are smaller than the symbols.

Figure 3: Extraction of niobium from solutions of 12 M Cl^- and 1 (●), 3 (▲), 6 (▼), 9 (◆) and 11 (■) M H^+ by 0.01 M BEHP in CHCl_3 as a function of mixing. Error bars are shown when larger than the symbol.

Figure 4: Extraction of tantalum from solutions of 12 M Cl⁻ and 1 (○), 3 (△), 6 (▽), 9 (◇) and 11 (□) M H⁺ by 0.01 M BEHP in CHCl₃ as a function of mixing time. Error bars are smaller than the symbols.

Figure 5: Comparison of extraction yields for niobium (■,●) and tantalum (□,○) after 60 seconds of mixing. The organic phase was 0.01 M HDEHP (■,□) and 0.01 M BEHP (●,○) in CHCl₃. The aqueous phase consisted of 12 M Cl⁻ and 1 - 11 M H⁺. Error bars are shown when larger than the symbols.