

## Studies of Aqueous U(IV) Complexation under Thiol-rich Conditions

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### 1. Introduction

Understanding aqueous chemistry of U(IV) species is important to predict long-term migration behaviors of uranium in groundwater environments. In deep geological repositories under anoxic and reducing aqueous conditions, U(IV) is a major reduced form of uranium. It exists mostly in a solid form of U(IV) hydrous oxide ( $\text{UO}_2 \cdot x\text{H}_2\text{O}$ )(am), which is known to be much less soluble than U(VI). However, U(IV) may become mobile in the presence of inorganic or organic ligands due to the formation of soluble complexes or nanoparticles [1].

Organic thiol compounds and hydrogen sulfide ( $\text{H}_2\text{S}$ ) are electron donors and metabolic products of sulfate reducing bacteria. In addition, they are among redox potential ( $E_h$ ) determinants of groundwater systems due to their redox characteristics. The low values of acid dissociation constants for  $-\text{SH}$  ( $\text{p}K_a$ , 7-9) compared to those of aliphatic or phenolic  $-\text{OH}$ , impart greater anionic and metal-binding properties to the molecules. Recently, we demonstrated that a thiol compound (*i.e.*, thiosalicylate) enhances the solubility of U(VI) at higher pH levels ( $< \sim 9$ ) [2].

In this study, to have a better knowledge of the behaviors of U(IV) species under anaerobic conditions, the U(IV)-OH complex formation in the presence of thiol was examined using UV-Vis spectrophotometry and TRLFS (time-resolved laser-induced fluorescence spectroscopy). A TRLFS-based U(IV) quantification methodology developed earlier [3] was applied to examine the effects of thiol species on the dissolution behaviors.

### 2. Experimental Methods

The acidified U(VI) stock solution (pH 0) was electrochemically reduced using Hg/Pt electrodes to prepare a stock solution of U(IV), as described in [4]. All chemicals including cysteamine (CTA), cysteine (Cys) and thiosalicylate (TSal) were of reagent grade and used as received (Sigma-Aldrich, St. Louis, MO). Aqueous stock solutions of these compounds were prepared fresh for each test. All solutions were handled in an Ar-filled glove box.

Absorbance measurements were carried out using a dual-beam UV-Vis spectrophotometer (CARY 3E, Varian, Palo Alto, CA) and all spectra were baseline-corrected. The UV-Vis absorption spectra were collected at room temperature using a liquid-waveguide

capillary cell (LWCC) system having an 1-m optical pathlength.

The concentrations of dissolved U(IV) in samples were determined after filtration of samples using 0.2- $\mu\text{m}$  membrane filters. The filtrate solutions were mixed with a phosphate-based luminescence enhancing agent and an oxidant, monopersulfate [5]. Then, the uranium concentrations were measured using TRLFS and a standard addition method [3]. To collect LM spectra of U(VI) a gated ICCD-based TRLFS system was used as described elsewhere [5], with a gate delay time of 4  $\mu\text{s}$  and a width of 500  $\mu\text{s}$ . The LM intensity was calculated by area-integration of each spectrum.

### 3. Results and Discussion

#### 3.1 Formation of U(IV)-OH complexes at low pHs

Although U(IV) is sparingly soluble, it exists in soluble U(IV)-OH complex forms at low pH (*e.g.*, pH  $< 1$ ). As pH or U(IV) concentration increases the complexation equilibria move to form more hydrolyzed complexes, *i.e.*, from  $\text{U}(\text{OH})^{3+}$  to  $\text{U}(\text{OH})_2^{2+}$  and  $\text{U}(\text{OH})_3^+$ , and eventually  $\text{U}(\text{OH})_4(\text{aq})$  and  $\text{UO}_2(\text{am})$ . To examine the effect of thiol on the U(IV)-OH complex formation the UV-Vis absorption spectra of U(IV) was monitored in the presence of excess of CTA (100 mM) as shown in Fig. 1. The spectra were obtained using a LWCC setup of 1-m optical pathlength. It is found that the presence of an excess amount CTA does not significantly influence the U(IV)-OH complexation at low pH levels.

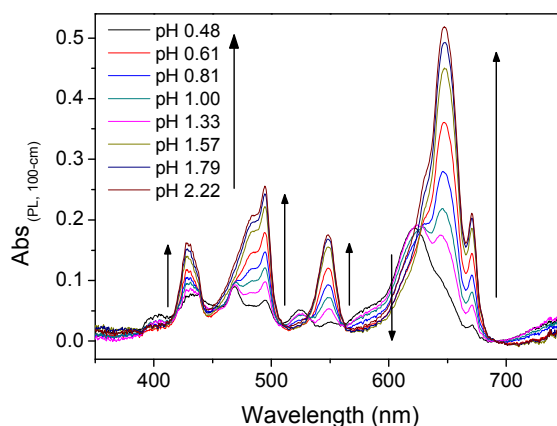


Fig. 1. U(IV) absorption spectra obtained using a LWCC system by varying the solution pH in the presence of 100 mM CTA and 100  $\mu\text{M}$  U(IV) ( $I = 1.0 \text{ M}$ ).

The absorption spectra shown in Fig. 1 are nearly identical to those of pure U(IV) spectra depending on the pH. The characteristic absorbance changes in a range of wavelength, 600-700 nm, were used to calculate the stability constants of the two U(IV)-OH species as noted in Table 1. The preliminary assessment shows that the measured stability constants are in well agreement with those from the literature values as shown in Table 1.

Table I: Stability constants of U(IV)-OH species [6]

Species	Stability constants	
$U(OH)^{3+}$	$\log \beta_{1:1}^{\circ}$	$13.6 \pm 0.2$ ( $13.9 \pm 0.5$ ) <sup>*</sup>
$U(OH)_2^{2+}$	$\log \beta_{1:2}^{\circ}$	$26.9 \pm 1$ ( $27.9 \pm 1$ ) <sup>*</sup>
$U(OH)_3^{+}$	$\log \beta_{1:3}^{\circ}$	$37.3 \pm 1$
$U(OH)_4(aq)$	$\log \beta_{1:4}^{\circ}$	$46.0 \pm 1$

<sup>\*</sup> Stability constants obtained in this study

### 3.2 Influence of thiols on the concentration of dissolved U(IV)

To examine the effects of thiol compounds on the U(IV) solubility the concentrations of U(IV) in filtrate solutions were measured after 2-day equilibration at pH  $8.05 \pm 0.05$ . Fig. 2 shows preliminary results that the dissolved U(IV) concentration increases as the thiol concentration is elevated in the mixture. The dissolved U(IV) can exist in forms of complex species including  $U(OH)_4(aq)$  and thiol-complexes, or as nanoparticles that pass through 0.2-  $\mu m$  filter pores. Therefore, it is not clear yet whether the formation of dissolved thiol-complexes or the stabilization of  $UO_2$  nanoparticles is the dominant process inducing the apparent solubility increase. In addition, the results of Fig. 2 indicate that the U(IV) solubility change is dependent on the structural difference of thiols. Although, the overall effect is far smaller than that for U(VI) as shown in a previous study [2], it should be noted that the increase of the dissolved U(IV) concentration is quite significant if compared with that of the thiol-free solution. Dissolution behaviors of U(IV) at lower pH levels and in the presence of oxalate ligand and U(VI) are examined in detail to identify the factors capable of affecting the U(IV) solubility under anoxic conditions.

### 3. Conclusions

Based on UV-Vis absorption monitoring, the presence of thiol does not result in a significant changes in the low-pH hydrolysis behaviors of U(IV). However, the concentration of U(IV) dissolved in bulk phase of aqueous solutions increased with the increase of thiol concentration. The formation of soluble thiol-complexes or the stabilization of  $UO_2$  nanoparticles may explain the observed solubility increase.

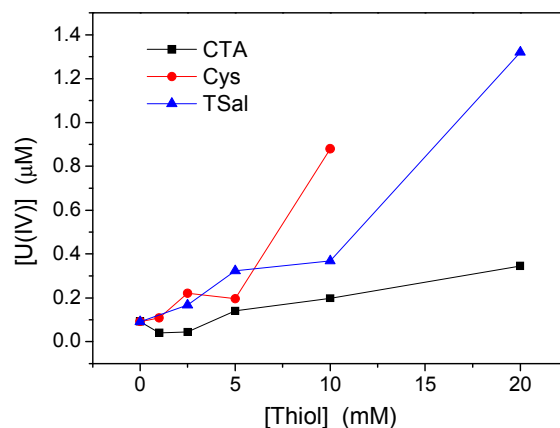


Fig. 2. The effect of thiol concentration on the concentration of U(IV) dissolved in filtrate solutions. Solutions containing U(IV) (0.5 mM) and each thiol were equilibrated for 2 days at pH  $8.05 \pm 0.05$  prior to the filtration and U(IV) quantification.

### REFERENCES

- [1] Y. Suzuki, S. D. Kelly, K. M. Kemner, J. F. Banfield, Nanometer-size products of uranium bioreduction, *Nature*, Vol.419, p.134, 2002
- [2] W. Cha, H.-R. Cho, E. C. Jung, Studies of aqueous U(VI)-thiosalicylate complex formation via UV-Vis absorption spectrophotometry, TRLFS, and potentiometry, *Polyhedron*, <http://dx.doi.org/10.1016/j.poly.2013.02.080>, 2013
- [3] W. Cha, S. Y. Lee, E. C. Jung, H.-R. Cho, M. H. Baik, Determination of U(VI) and U(IV) concentrations in aqueous samples containing strong luminescence quenchers using TRLFS and quencher oxidation reactions, *Talanta*, submitted 2013.
- [4] D. Cohen, W.T. Carnall, Absorption spectra of uranium (III) and uranium(IV) in  $DClO_4$  solution, *J. Phys. Chem.*, Vol.64, p.1933, 1960.
- [5] W. Cha, E. C. Jung, H.-R. Cho, *Transact. Kor. Nucl. Soc. Autumn Meeting, Oct.25-26, 2012, Jeju, Korea*
- [6] V. Neck, J. I. Kim, Solubility and hydrolysis of tetravalent actinides, *Radiochim. Acta*, Vol.89, p.1, 2001