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ATR-FTIR and UV-Vis Spectroscopic Studies of Aqueous U(IV)-oxalate Complexes under Mild Acidic Conditions

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1. Introduction

Tetravalent uranium (U(IV)) is the major reduced form of uranium under anoxic and reducing conditions of deep groundwater systems. It is generally known that U(IV) exists mostly in solid forms in near neutral aqueous solutions, such as U(IV) hydrous oxide ($UO_2 \cdot xH_2O(am)$) and crystalline U(IV) ($UO_2(cr)$) precipitates due to its low solubility. Thus, the transformation processes between U(VI) and U(IV) either by microbes or by abiotic geochemical reactions have been extensively studied for the sequestration or immobilization of uranium in contaminated sites [1]. The redox transformation process between U(VI) and U(IV) likely involves the participation of soluble or dissolved U(IV) species, such as U(IV)-hydroxo compounds and organic/inorganic ligand complexes. However, their role in the redox process has not been well documented, partly due to the ready oxidation of soluble U(IV) species, and partly due to the assumption that soluble or dissolved forms of U(IV) account for only a minor fraction of uranium in groundwater systems.

In this study, a bidentate chelate ligand, oxalate (Ox) was selected to examine the complexation behaviors of U(IV) and ultimately its impact on the U(IV) solubility in mildly acidic solutions. Although some early studies reported that oxalate and pyrophosphate, i.e., multivalent anions, can form soluble U(IV) complexes, the related thermodynamic data and evidences for chemical speciation are very scarce. In our previous work, the U(IV)-Ox 1:1 complex was identified by monitoring the gradual transition of the characteristic absorption spectrum of $U(OH)^{3+}$ to that of UOx^{2+} upon the addition of oxalate at pH 1.6–2.0 [2]. This work aims to further provide spectroscopic evidence for the formation of multi-ligand complexes, i.e., $U(Ox)_n^{4-2n}$ ($n \geq 2$) at pH 2-5 using attenuated total reflectance (ATR)-FTIR spectroscopy and UV-Vis absorption spectroscopy. In addition, a U(IV)-Ox complex system exhibits a distinct solid phase formation, i.e., $U(Ox)_2 \cdot 6H_2O(s)$. Thus, the thermodynamic data estimated in this work for the U(IV)-Ox complexation system will be discussed in conjunction with the solubility of $U(Ox)_2 \cdot 6H_2O(s)$.

2. Experimental

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 [3]. Oxalic acid and sodium oxalate (Na_2Ox) were of reagent grade and used as received (Sigma-Aldrich, St. Louis, MO). The aqueous sample solutions prepared were equilibrated for at least three days before use. All solutions were handled in an Ar-filled glove box. Solid precipitates obtained from aqueous U(IV)/Ox samples were confirmed as $U(Ox)_2 \cdot 6H_2O(s)$ through an XRD analysis.

UV-Vis absorption spectra of U(IV)-Ox complexes were measured using a dual-beam UV-Vis spectrophotometer (CARY 3E, Varian, Palo Alto, CA) and a liquid-waveguide capillary cell (LWCC) system having an 1-m optical pathlength. All spectra were measured at room temperature and finally baseline-corrected.

The FTIR spectra of oxalate and its U(IV) complexes were measured using a spectrometer (Nicolet iS-50, Thermo Fisher Scientific Inc.) equipped with a CsI beam splitter, a DLaTGS detector (6400-200 cm^{-1}) and a single bounce ATR module containing a diamond crystal (30 cm^{-1} cutoff range, GladiATR, PIKE Technologies). A home-made flow cell was constructed on the top surface of the ATR module to continuously introduce fresh Ar-purged solution samples onto the surface of the diamond crystal and to avoid ambient oxygen contact. The flow cell chamber has a dimension of 13-mm in diameter and 150-μm in height and a nominal cell volume of ~18 μL. The FTIR spectra were measured at room temperature.

3. Results and Discussion

3.1 UV-Vis absorption spectra of $U(Ox)_n^{4-2n}$ ($n \geq 2$)

In a previous study, it was confirmed that UOx^{2+} is a dominant complex form at a concentration of 0.1 mM U(IV) and pH 1.6 – 2.0 [2]. The spectrum of the UOx^{2+} appears to have its absorption maximum at near 652 nm, as shown in Fig. 1 (one at the left end). With additional amounts of oxalate the complex absorption band further changes to exhibit a gradual red shift. The addition of an excess amount of oxalate (e.g., 100 mM) results in the absorption maximum at near 663 nm (see the spectrum at the right end in Fig. 1). This result strongly indicates the presence of multiple equilibria forming $U(Ox)_n^{4-2n}$ ($n \geq 2$). However, further spectroscopic analysis requiring higher U(IV) concentrations to determine the complexation stoichiometry and stability constants is hampered by the slow formation of solid precipitates in wide pH and U(IV)/oxalate concentration ranges. As shown in Fig. 2 the solid precipitates are in fact fine crystals, which are identified as $U(Ox)_2{\cdot}6H_2O(s)$ through an XRD pattern analysis (data not shown) and gradually converted into $U(Ox)_2{\cdot}2H_2O$ upon drying. Thus, to derive reliable thermodynamic data the complexation equilibria should be examined carefully by considering the solubility of $U(Ox)_2{\cdot}6H_2O(s)$. The solubility measured in this study will be compared to those reported in the literature and used to estimate the solubility product ($K_S = [U^{4+}][Ox^{2-}]^2$) based on spectrophotometric analysis results for U^{4+}, $U(OH)^{3+}$ and $U(Ox)_n^{4-2n}$ ($n \geq 1$).

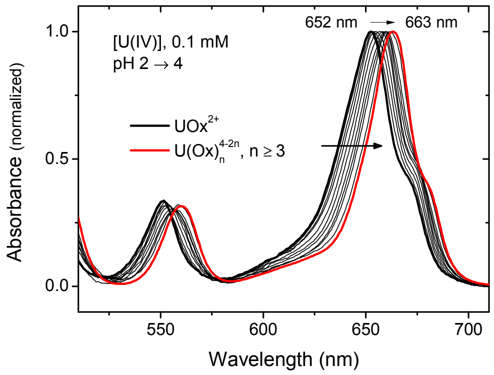

Fig. 1. Normalized UV-Vis absorption spectra of U(IV)-Ox complexes at various oxalate concentrations and pHs. The oxalate concentration and solution pH increased from 0.2 mM to 100 mM and from 2 to 4, respectively, as indicated by arrows (I = 0.1 M).

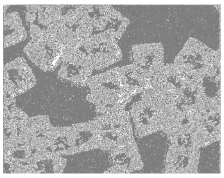

Fig. 2. Microscope image of $U(Ox)_2{\cdot}6H_2O$ crystals formed in an aqueous solution containing 1 mM U(IV) and an excess amount of oxalate at pH ~0.7 (the crystal size, ~50 μm).

3.2 ATR-FTIR Spectroscopy

FTIR spectroscopy is often used to identify molecular structures because functional groups give rise to characteristic bands in terms of both intensity and vibrational frequency. ATR-FTIR spectroscopy is particularly useful for samples with highly absorbing media such as aqueous solutions due to the short pathlength of the evanescent wave penetrating into the sample media (typically a few-μm for a single bounce ATR). In addition, it requires a minimal sample preparation for those samples.

In this study, ATR-FTIR spectroscopy was applied to examine the complex structure and stoichiometry of the multi-ligand complexes for the U(IV)-Ox system, particularly for $U(Ox)_n^{4-2n}$ ($n \geq 3$). In Fig. 3 the FTIR spectrum of oxalate was obtained at pH 4.1, where it exists in both di-anion (Ox^{2-}) and mono-anion (HOx^-) species at a ratio of approximately 1:1 owing to its pK_a values (1.1 and 4.2). The ν_1 and ν_5 peaks correspond to the frequency of C-O-H bending and C=O stretch modes, respectively, for the carboxylic acid of HOx^-. The ν_{as} peaks (C-O, asymmetric stretch) of Ox^{2-} and HOx^- are well separated at 1569 cm^{-1} (ν_3) and 1626 cm^{-1} (ν_4), respectively. In contrast, the ν_s (C-O, symmetric stretch) peaks of the two species are nearly identical (1306 cm^{-1}, ν_2) [4]. Upon complexation, the absorbance of these bands for the free oxalate decreases quantitatively (see ν_2 and ν_3 in Fig. 3), and new bands originating from the ligand bound to U(IV) emerge, i.e., ν_{C1} and ν_{C2}., which are reported for the first time in this study. By applying the spectral deconvolution method described in our previous study [5], it was concluded that the dominant complex species at pH 4.1 are $U(Ox)_n^{4-2n}$, n = 3 and 4. Moreover, previous ATR-FTIR studies regarding metal-complexed or surface-adsorbed oxalate ions correlate with the appearance of bands near ν_{C1} to the formation of inner-sphere chelate complexes [6]. Thus, we speculate that in the predominating U(IV) complexes, oxalate forms five-membered ring chelate structures by bonding to the metal ion through one oxygen atom from each carboxylate group.

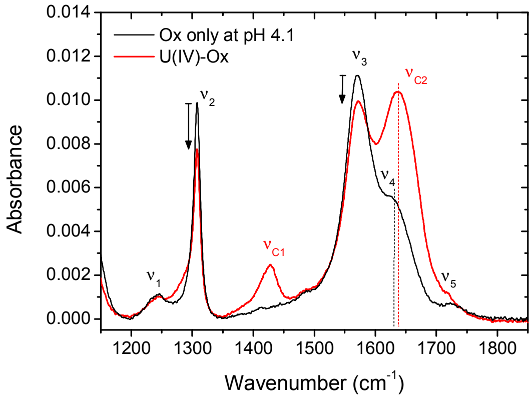

Fig. 3. ATR-FTIR spectra of oxalate and U(IV)-Ox at pH 4.1. ($[U(IV)]$ = 6.3 mM and $[Ox]_{total}$ = 100 mM, I = 0.1 M)

4. Conclusions

Both UV-Vis and ATR-FTIR spectroscopy were used to identify the soluble U(IV)-Ox complexes under mildly acidic conditions. The solid phase of U(IV)-Ox complex system was also characterized through an XRD analysis. Analysis of the FTIR spectra is found to be useful to determine the complexation stoichiometry and to obtain the structural information of the complexes. The outcome of the spectroscopic analysis for the multi-ligand complexation equilibria will be discussed in detail.

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