

Spectroscopic Studies on Complex Formation of U(VI)-thiosalicylate

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1. Introduction

The dynamic interaction between radionuclides and organic ligands is largely dependent on the composition of functional groups in a ligand chemical structure. Therefore, the structural mimics of natural ligands possessing specific functional groups, such as hydroxy, phenol, carboxyl, thiol and amine groups, have been studied to understand their influence on the migration of radionuclides including actinide species under geological groundwater conditions [1]. In previous studies, we demonstrated that the fraction of hydrolyzed U(VI) species occurring in weak acidic solutions (pH ~4.5) is significantly influenced by the presence of salicylate (Sal) ligand due to the simultaneous participation of both phenol and carboxyl groups in the formation of U(VI)-complexes [2].

Thiosalicylic acid (TSalH₂) is a good model compound for studying the effects of both carboxyl and thiol (-SH) groups. The fraction of di-anionic ligand form (TSal²⁻) is higher at near neutral pH due to the lower pK_a (~ 8) of the thiol group than the case of salicylic acid (pK_a, ~13 for salicylic -OH), despite the structural similarity. In addition, the redox capability of the thiol group is expected to influence the reducible radionuclides and the chemical structures of natural ligands by creating cross-linkage (-S-S-) upon oxidation.

The goal of the present study is to investigate aqueous U(VI)-TSal complexation equilibrium via laser-based spectroscopic techniques including time-resolved laser-induced fluorescence spectroscopy (TRLFS). In this preliminary work, we report the results of spectroscopic studies using conventional UV-Vis absorbance and fluorescence (FL) measurement methods. The photo-stability of U(VI)-TSal complex or ligand itself upon exposure to a series of laser pulses is estimated by monitoring the change in their absorption bands. Additionally, TSal FL-quenching effect by U(VI) ions is discussed in comparison with that of Sal FL-quenching.

2. Experimental

Stock solution of uranium(VI) perchlorate was prepared from uranium dioxide as reported in [3]. Aqueous UO₂²⁺, TSal and Sal solutions were prepared in HClO₄-NaClO₄ (0.1 M) electrolyte solution by adjusting pH with CO₂ free NaOH at room temperature. The pH measurements had a precision of 0.02 units. In all experiments to maintain the O₂-free condition during the measurement a final sample solution was contained in a screw-capped 1-cm-pathlength quartz

cell for a tight seal. The UV-Vis absorption spectra were obtained using a spectrophotometer (Cary 3E, Varian) and the fluorescence spectra using a fluorometer (Series 2, SLM-Aminco Spectronic Inc.) at room temperature (26.0 ± 1.0 °C). The photo-stability of reagents was carried out by exposing the sample solutions (in quartz cells) continuously to 415-nm laser pulse using a tunable laser system (VIBRANTTM, OPOTEK Inc.) and intermittently taking the samples to measure their absorbance change. For the fluorescence experiments 310-nm excitation wavelength and 500-V PMT voltage were applied.

3. Results and Discussion

3.1. Characteristic UV-Vis Absorbance Spectrum of U(VI)-TSal Complex

As shown in Fig. 1, U(VI)-TSal complex shows a characteristic UV-Vis absorption spectrum that is different from that of U(VI) species and TSal itself. As inferred from our previous studies of U(VI)-Sal complex this is due to the electrostatic association between uranyl ion and TSal anion resulting in the formation of ligand-to-metal charge-transfer (LMCT) complex [2]. The non-linear curve fitting result of U(VI)-TSal absorption spectrum as demonstrated in Fig. 1 (inset) shows that the λ_{\max} of U(VI)-TSal LMCT band appears at both 392 nm and 501 nm. Although the UV-Vis absorption band of U(VI) species also appears in this region (λ_{\max} , 410 nm ~ 460 nm) the concentration-dependent absorbance change of the complex LMCT band is considered useful to study the complexation equilibrium since the molar absorptivity

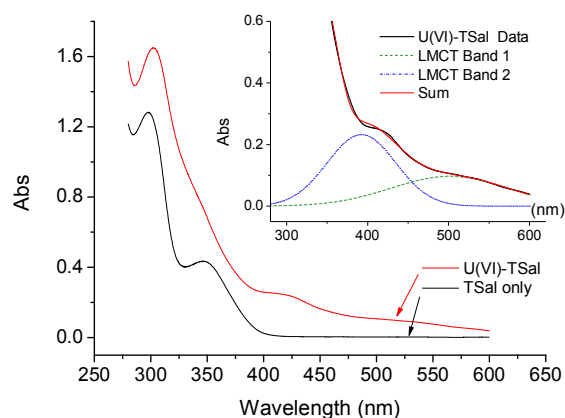


Figure 1. UV-Vis absorption spectra of TSal and U(VI)-TSal. Inset figure shows a non-linear fitting result of U(VI)-TSal spectrum; only the deconvoluted peaks of LMCT bands were shown. [TSal] = 1.0 mM, [U(VI)] = 0.2 mM at pH 4.6 in 0.1 M NaClO₄.

of the complex observed is much greater than those of U(VI) species around pH 4.6. Further discussion regarding the complex formation equilibrium will be available along with quantitative analysis of spectrophotometric data.

3.2. Photo-stability Test of TSal and U(VI)-TSal

As shown in Fig. 2 the degradation of TSal ligand itself or U(VI)-TSal complex is evident after the exposure to the laser pulses. The reduction of the complex absorption band is more prominent than that of TSal ligand band. More rapid absorbance decrease was observed when high energy and short wavelength laser pulses were applied (data not shown). Therefore, in order to implement TRFLS or other laser-based spectroscopic methods in future studies the use of flow-through cell system is required to maintain the initial metal-ligand equilibrium condition by providing fresh solution into a quartz cell. While it seems that such photo-instability results from the loss of TSal ligand in each system, the detailed photo-induced decomposition mechanism remains to be elucidated with further studies.

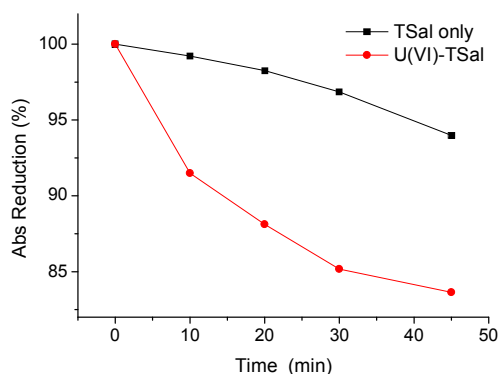


Figure 2. Absorbance reduction of TSal and U(VI)-TSal monitored at 350 nm and 430 nm, respectively, upon exposure to laser pulses at 415 nm.

3.3. Ligand Fluorescence Quenching by U(VI)-ions

Both ligands, i.e., Sal and TSal, exhibit FL emission under the same excitation condition as shown in Fig. 3. Salicylate ligand shows approximately 25-fold greater FL intensity than that of TSal. In the presence of U(VI) species, such as uranyl ion and $(\text{UO}_2)_2(\text{OH})_2^{2+}$ at the given pH, FL quenching effects are evident in both cases. As reported elsewhere for Eu(III)-Sal system [4], these quenching effects are thought to result from the formation of ground-state complex formation, which induces a static quenching of FL emission. Thus, we speculated that a quantitative analysis of U(VI) FL quenching behaviors also can provide insight on U(VI)-TSal complexation equilibrium with a particular interest in the involvement of hydrolyzed U(VI) species.

4. Conclusion

In the present study the U(VI)-TSal complex

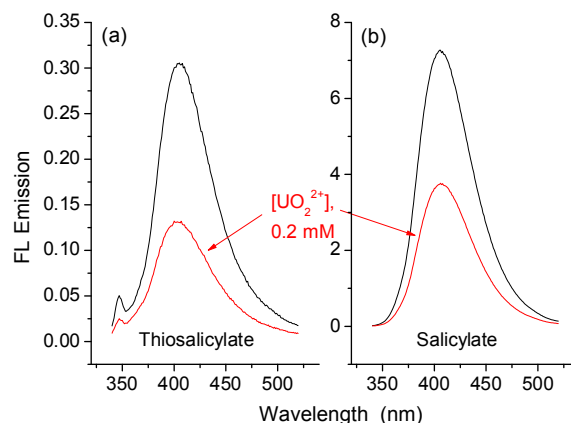


Figure 3. Ligand FL quenching effects by uranium (VI) at pH 4.6. Ligand concentration was 1 mM in each solution containing 0.1 M NaClO_4 .

formation is investigated via UV-Vis spectrophotometric methods and ligand FL measurement. At pH 4.6 the formation of U(VI)-TSal LMCT complex is observed with two maxima of absorbance near 392 nm and 501 nm. Additionally, the ligand FL quenching behavior also supports the formation of non-FL complex formation. However, it is found that degradation of TSal ligand and U(VI)-TSal complex is unavoidable upon exposure to a series of laser pulses (415 nm) that are necessary for applying laser-based spectroscopic approach such as TRFLS. Thus, it is required to use a flow cell setup for further spectroscopic study. Detailed information about the complexation stoichiometry and equilibrium constants as well as the FL quenching mechanism will be provided in detail.

Acknowledgements

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