

## Studies on Ternary Complex Formation of U(VI)-salicylate by Using Time-resolved Fluorescence Spectroscopy

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### 1. Introduction

Organic ligands containing carboxylic and phenolic functional groups naturally occur in groundwater environment, particularly in forms of polyelectrolytes such as humic and fulvic acids, from microbial degradation of biomass, e.g., plant and animal tissues. These ligands play important roles in dissolution and migration of actinide radionuclide species since they can form stable ternary actinide complexes with common inorganic ions like hydroxides and carbonates. Therefore, model ternary complexes of lanthanides and actinides have been targets of studies to understand their chemical behaviors under near-neutral pH groundwater conditions. Previous model carboxylic ligands include phthalates, maleic acids, or  $\alpha$ -substituted carboxylic acids [1-4]. However, majority of previous studies investigated binary systems or used potentiometric titration method that requires high ligand concentration in mM levels.

Recently, highly sensitive time-resolved laser-induced fluorescence spectroscopy (TRLFS) has been used to investigate lower concentration (e.g., a few  $\mu\text{M}$  levels) reactions of binary complexes between of ligands and metal ions. This technique provides information regarding electronic structures and complexation constants as well as fluorescence quenching mechanism. In the present study, we studied the U(VI)-OH-salicylate (SA) ternary complex formation at higher pH ( $> 4$ ) via TRLF spectrum and UV-Vis absorbance measurement. Preliminary studies show that the fluorescence (FL) intensity of hydroxouranyl species at pH 4.5 decreases as SA concentration elevates in aqueous solution. Fluorescence quenching mechanism by SA is suggested based on FL intensity ( $I$ ) and lifetime ( $\tau$ ) measurement via TRLF.

### 2. Experimental

Stock solution of uranium(VI) perchlorate was prepared from sodium diuranate as described in [5]. Aqueous  $\text{UO}_2^{2+}$  and SA solutions were prepared in  $\text{HClO}_4$ - $\text{NaClO}_4$  (10 mM) electrolyte solution by adjusting pH with  $\text{CO}_2$  free  $\text{NaOH}$  at room temperature. The pH measurements had a precision of 0.05 units. In all experiments the sodium concentration was kept constant by adjusting the amount of  $\text{NaClO}_4$ . The emission spectra and lifetime were measured by using TRLF setup constructed in our laboratory. The experimental setup is described elsewhere (see details of instrumentation in our previous work [6]). A pulsed

Nd:YAG laser (Surelite II, Continuum) operating at 355 nm (the third harmonic) with a repetition rate of 20 Hz (8 mJ) was used as an excitation source. The FL emission was passed through a monochromator (HR-250, Jobin Yvon) coupled to a PMT (R928, Hamamatsu) for monitoring FL lifetime at a certain wavelength by using a digital oscilloscope (DPO7104, Tektronix). Fluorescence spectra were measured by using a gated ICCD (SR-303i-A, Andor) with a gate delay time of 1.5  $\mu\text{s}$  and a gate width of 2  $\mu\text{s}$ .

### 3. Results and Discussion

#### 3.1. Influence of SA for U(VI) fluorescence intensity

At pH 4.5 free uranyl ion co-exists with its hydrolysis products such as  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ . These hydroxo-U(VI) species have longer FL lifetime and exhibit larger emission intensity than those of free uranyl ions (at pH 3.8, data not shown). However, in the presence of SA ligand the overall FL intensity decreases as shown in Fig. 2. This implies that the presence of SA anion contributes to the quenching of U(VI) species fluorescence. In addition, the reduction of FL intensity is inversely proportional to the concentration of SA (see below, Fig. 3).

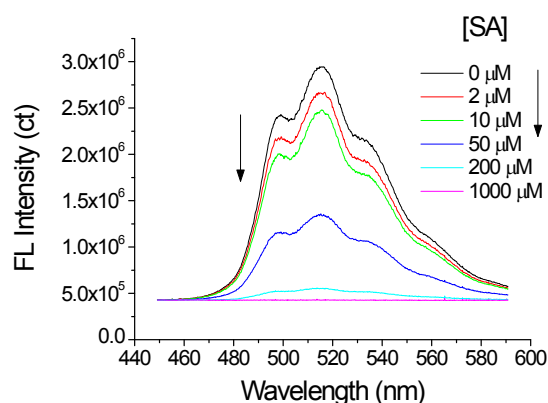


Figure 1. Fluorescence spectrum obtained from a gated ICCD spectrometer. FL intensity decreases upon as SA level increases in the solution containing U(VI), 50  $\mu\text{M}$  at pH 4.5.

#### 3.2. Influence of SA for U(VI) fluorescence lifetime

The FL lifetime was monitored by using the waveforms obtained from an oscilloscope that was connected to a monochromator-coupled PMT. The overall fluorescence lifetime measured shortens upon addition of SA in the aqueous solution. Interestingly,

at higher SA concentrations bi-exponential FL decay patterns become evident as indicated in Fig.2 as 'S' and 'L' for short and long lifetime components, respectively. Both components shows decrease in lifetime as SA concentration increases in the system. Such results also indicate the role of SA as FL quenching species.

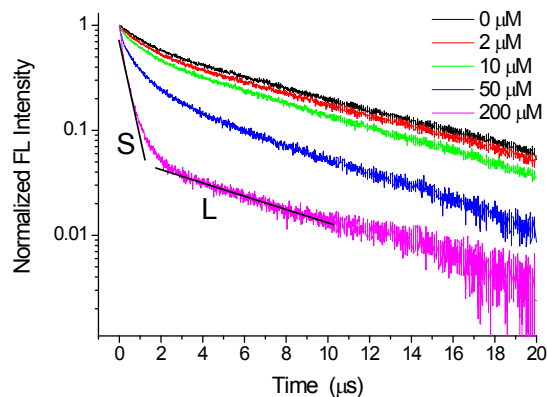


Figure 2. Logarithmic plot of TRLF lifetime of U(VI) at different salicylate concentrations (pH 4.5, from 515 nm (the highest peak position)). Initial concentration of U(VI) is 50  $\mu\text{M}$ . Note that the distinction of short and long lifetime components (denoted as 'S' and 'L', respectively) at higher salicylate concentration; at [SA]=0, the lifetimes obtained are 1.3  $\mu\text{s}$  and 8.3  $\mu\text{s}$ .

### 3.3. Stern-Volmer plots from fluorescence intensity and lifetime.

Fig. 3 shows Stern-Volmer plots based on the results from Figs. 1 and 2. Two different lifetimes were obtained from the least-square fitting of the results in Fig. 2 as second order exponential decay. The trace in Fig. 3a and the plot of short lifetime component in Fig. 3b display nearly linear increase of quenching ratios, i.e.,  $I_0/I$  and  $\tau_0/\tau$ , respectively, with ligand concentration. This is an evidence of collisional quenching mechanism by the ligand. However, in Fig. 3b the plot of the longer lifetime component shows large deviation from linearity. Therefore, we hypothesize that SA may play dual roles in quenching of FL in this case, i.e., via dynamic (collisional) and static (forming non-fluorescent complex) mechanisms, likely involving the long lifetime species in the system, such as  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ . Additionally, we have separate UV-VIS absorbance results that evidence the formation of new U(VI)-SA complex (with a broad peak near 460 ~ 480 nm) at pH 4.4. For the short lifetime species, i.e., free uranyl ions, in contrast, we concluded that SA only serves as dynamic quencher for fluorescence emission.

## 4. Conclusion

In this study we examined the formation of ternary complex of uranyl ions at pH 4.5 by using SA as a model ligand containing carboxylic and phenolic functional groups. With the highly sensitive TRLFS

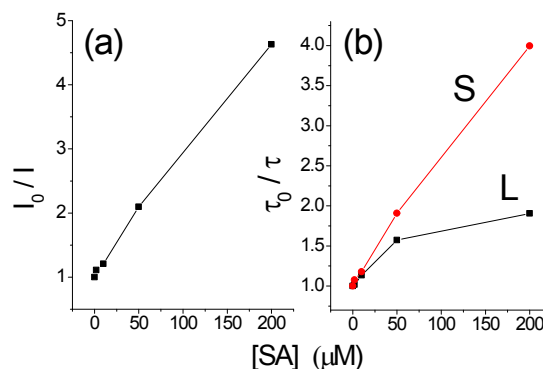


Figure 3. Stern-Volmer plot of FL intensity (a) and lifetime (b) of U(VI) species with salicylate concentration. Note that 'S' and 'L' represent the calculated short and long lifetime components obtained from the second order exponential fitting of data in Fig. 2. on silica surface with Eu(III) at pH 7.

and absorbance spectroscopy we were able to assess the influence of SA to the U(VI) FL emission intensity and lifetime. The fluorescence intensity and lifetime decrease as SA levels in solution increases. Based on Stern- Volmer plots of  $I_0/I$  and  $\tau_0/\tau$  SA is found to serve as a dynamic quencher for FL of short lifetime U(VI) species at pH 4.5. On the other hand, long lifetime U(VI) species seems to exhibit mixed (dynamic and static) quenching modes by formation of non-fluorescent complex with SA. We will provide detailed information with further study regarding the quenching mechanism and speciation involved in complexation reactions.

## Acknowledgements

This work was supported by the Nuclear Research and Development program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

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