

Studies on U(VI)-salicylate Charge Transfer Complex Formation by Using Time-resolved Laser Fluorescence Spectroscopy

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1. Introduction

Organic ligands, such as humic and fulvic acids, play important roles in dissolution and migration of actinide radionuclide species. They can form stable actinide complexes in the presence of inorganic ions like hydroxides and carbonates. Therefore, the structural mimics of such ligands containing carboxylic and phenolic functional groups have been targets of studies to understand their chemical behaviors migrating actinides under geological groundwater conditions [1-3]. Among many carboxylic ligands salicylate (SA) is useful to examine the role of phenolic groups on humic substances.

Salicylate ion can form ligand-to-metal charge-transfer (LMCT) complexes with various metal ions. It has been shown that the fluorescence of SA is suppressed in the presence of Cu(II) or Eu(III) at pH 4 by forming ground state complexes [1,4]. While uranyl ions also can form complex with SA, the dominant species at pH 4-7 region is known to be an 1:1 complex [5]. However, the chemical structures reported on this 1:1 species are different among $[\text{UO}_2\text{SA}]^0$, $[\text{UO}_2(\text{OH})\text{SAH}]^0$ and $[\text{UO}_2(\text{OH})\text{SA}]^-$. For α -hydroxycarboxylates cyclic chelate structures were suggested where both carboxylate and phenolate groups simultaneously bind to uranyl ion [2,6].

In the present study we investigate aqueous U(VI)-SA complex systems by using UV-Vis absorbance measurement and highly sensitive time-resolved laser-induced fluorescence spectroscopic (TRLFS) technique. The U(VI)-SA complex shows two characteristic charge-transfer (CT) bands at higher pH (> 4), which we found useful to examine the complexation equilibrium. Further, the TRLFS method is used to study the fluorescence (FL) quenching of U(VI) species, particularly for hydroxouranyl species at pH 4.5 of which FL is significantly suppressed as SA concentration elevates in aqueous solution. Fluorescence quenching mechanism in conjunction with the formation of U(VI)-SA CT complex is discussed.

2. Experimental

Stock solution of uranium(VI) perchlorate was prepared from sodium diuranate as described in [7]. Aqueous UO_2^{2+} and SA solutions were prepared in HClO_4 - NaClO_4 (10 mM) electrolyte solution by adjusting pH with CO_2 free NaOH at room temperature. The pH measurements had a precision of 0.02 units. In all experiments the sodium concentration was kept constant by adjusting the amount of NaClO_4 . The

absorption and emission spectra and lifetime were measured by using the setup constructed in our laboratory. The experimental setup is described elsewhere (see details of instrumentation in our previous work [7]). 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 the 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 are measured by using a gated ICCD (SR-303i-A, Andor) with a gate delay time of 1.5 μs and a gate width of 2 μs .

3. Results and Discussion

3.1. Formation of U(VI)-SA Charge-transfer Complex

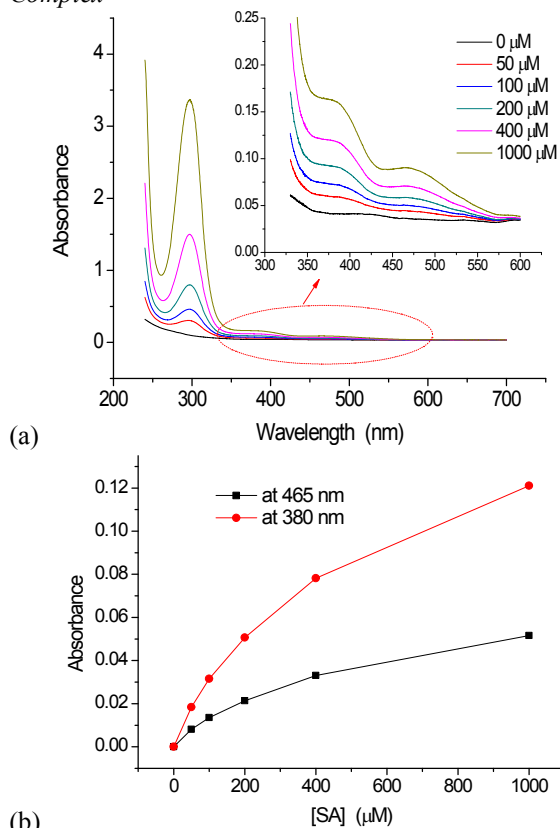


Figure 1. Growth of two charge-transfer bands absorption upon addition of SA into the aqueous solution containing U(VI) (0.2 mM, pH 4.5, in 0.1 M NaClO_4). (a) absorption spectrum; (b) absorbance change upon addition of SA at the two CT bands.

As shown in Fig. 1(a) SA can form CT complex with U(VI) species. Two new bands (λ_{\max} at 380 nm and 465 nm) grow as SA is added into the solution containing U(VI) species, i.e., UO_2^{2+} , UO_2OH^+ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$ at the given pH. The absorbance shows a steady growth initially and it becomes saturated as SA concentration increases as shown in Fig. 1(b). This implies that the formation of U(VI)-SA CT complex is in equilibrium. At the given pH we can estimate the complex formation constant and the molar extinction coefficients of two CT bands by interpreting Scatchard plots with the experimental results shown in Fig. 1. The approximate values are given below.

$$K = 4 \times 10^3 \text{ M}^{-1}; \log K = 3.6$$

$$\epsilon_{380\text{nm}} = 730 \text{ M}^{-1}\text{cm}^{-1}, \epsilon_{465\text{nm}} = 320 \text{ M}^{-1}\text{cm}^{-1}$$

Also we have evidence that the stoichiometry of the U(VI)-SA varies from 1:1 to 1:2 (U(VI):SA) depending on the SA concentration and solution pH. Supporting results and details will be presented.

3.2. Stern-Volmer plots from fluorescence intensity and lifetime.

In aqueous solutions (pH >4) free uranyl ions co-exist with its hydrolyzed forms including UO_2OH^+ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$. All these are fluorescent species having their own lifetime. By using TRLFS technique we monitored the fluorescence (FL) spectrum and decay over time. The presence of SA in U(VI) solutions typically results in FL quenching, which exhibits both dynamic and static modes of FL quenching. However, at low pH (e.g., <3) where free uranyl (UO_2^{2+}) is the only dominant species no significant static quenching is observed (data not shown). Thus, we can conclude that free uranyl-SA complexes are still fluorescent and only collisional deactivation of excited uranyl ions is important in the FL quenching process. In contrast, at higher pH (>4) the static process is dominant as shown in Fig. 2. As the FL lifetime ratio, τ_0/τ , represents the dynamic portion of the observed quenching, the difference between the two traces (i.e., I_0/I and τ_0/τ) in Fig. 2 is due to the presence of static quenching mode and the formation of FL inactive ground state complexes. The association constant (K_S) of such complex can be calculated based on the results in Fig. 2 as described elsewhere. The K_S calculated is approximately $2 \times 10^3 \text{ M}^{-1}$, ($\log K_S = 3.3$), which is close to K obtained from the absorbance measurement as mentioned in Section 3.1. Therefore, we believe that the U(VI)-SA CT complex is the ground state complex inducing the observed static quenching process. Further the competitive equilibrium reactions between the U(VI)-SA CT complex and hydroxouranyl species are suggested.

4. Conclusion

The formation of U(VI)-SA CT complex is

spectroscopically investigated. Two CT bands are used to determine the stoichiometry of U(VI)-SA complex, molar extinction coefficients and formation constants. The TRLFS study shows that SA serves as a static quencher for FL of hydroxouranyl species at higher pH (> 4). With the K_S values obtained from Stern-Volmer plots of TRLFS results, we conclude that the formation of U(VI)-SA CT complex is responsible for such static quenching. We will provide more details with further study regarding the equilibrium reactions between the CT complex and hydroxouranyl species.

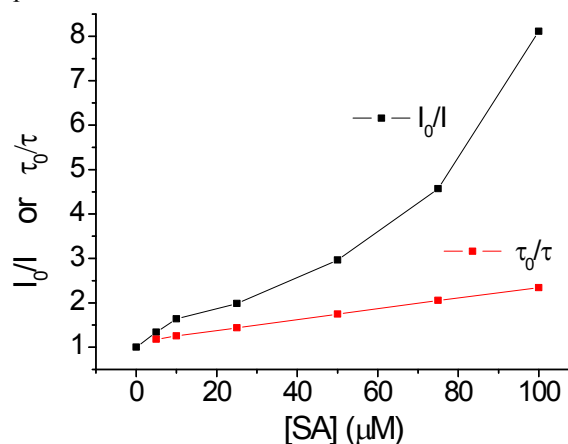


Figure 2. Stern-Volmer plot of FL intensity (I_0/I) and lifetime τ_0/τ . (pH 4.5, $[\text{UO}_2^{2+}] = 50 \mu\text{M}$ in 10 mM NaClO_4)

Acknowledgements

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