

Determination of U(VI)-Thiosalicylate Complex Formation Constants via Time-resolved Laser-induced Fluorescence Spectroscopy

Wansik Cha*, Hye-Ryun Cho, Euo Chang Jung

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
1045 Daedeok-daero, Yuseong, Daejeon 305-353, Korea

*Corresponding author: wscha@kaeri.re.kr

1. Introduction

Natural ligands like humic acid and fulvic acid are known to dynamically interact with radionuclides and influence their migration behaviors under groundwater conditions. Roles of functional groups and their composition in the macromolecular structures of natural ligands have been the subject of recent studies [1]. Hydroxy, phenol, carboxyl, thiol, and amine groups that constitute the major functional groups in natural ligands have been investigated to determine their binding affinity to radionuclide species [1].

In the previous study thiosalicylic acid (TSalH₂) was selected as a model ligand mimicking the functionality of humic acid possessing carboxyl and thiol (-SH) groups [2]. Based on the spectrophotometric analysis the stoichiometry and complex formation constants were reported. The 1:1 and 1:2 U(VI)-TSal complexes were identified to form chelate structures. The step-wise formation constants determined were 7.9 (log K_1) and 6.2 (log K_2).

In this study U(VI)-TSal complex equilibrium was further examined by using time-resolved laser-induced fluorescence spectroscopy (TRLFS). To prevent the photodecomposition of TSal by laser pulses as shown in the previous study, a flow-through setup was applied to provide fresh sample solution during the TRLFS measurement as illustrated in Fig. 1. Fluorescence (FL) intensity and lifetime of uranyl ions were monitored to investigate the FL quenching behavior by aqueous TSal anions. A new complex formation constant of $UO_2(TSalH)^+$ was determined via Stern-Volmer analysis of TRLFS data.

2. Experimental

The stock solution of uranium(VI) perchlorate was prepared from uranium dioxide as reported in [3]. Aqueous UO_2^{2+} and thiosalicylate (TSal, or L) solutions were prepared in a HClO₄-NaClO₄ (0.1 M) electrolyte solution by adjusting the pH with CO₂-free NaOH at room temperature. The pH measurements had a precision of 0.02 units. To maintain the O₂-free condition all sample solutions were prepared and stored in an Ar-filled globe box. Finally, each sample solution were transferred into a disposable syringe (no Si oil coated) and supplied to a flow-through quartz cuvette cell (Starna Scientific, Essex, UK) using a syringe pump (KM Scientific, Holliston, MA) at a flow rate of 120 mL/h. As shown in Fig. 1 a pulsed Nd:YAG laser (Surelite II, Continuum) operating at 355 nm (the third harmonic) with a repetition rate of 20 Hz (3.5 mJ) was

used as the excitation source. FL spectra were measured by using a gated ICCD (SR-303i-A, Andor) with a gate delay time of 500 ns and a gate width of 10 μ s. FL lifetime was measured by analyzing the FL decay profile obtained in a kinetic mode measurement with settings of delay/gate-width/step at 200/150/150 ns with total 35 steps.

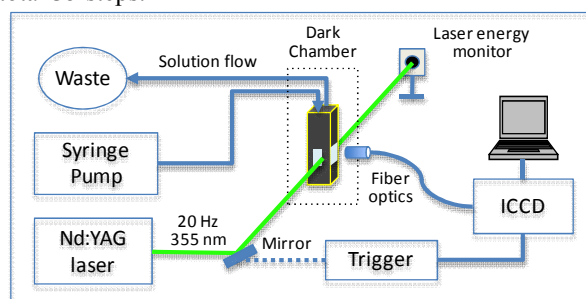


Figure 1. Scheme of TRLFS experimental setup.

3. Results and Discussion

3.1. UO_2^{2+} Fluorescence Quenching by TSal

As shown in Fig. 1 all the FL spectra measured exhibit the typical shape of UO_2^{2+} spectrum at pH 3.0 and ionic strength (0.1 M NaClO₄) indicating that UO_2^{2+} is the major fluorophore. At higher flow rate (> 120 mL/h) the measured FL intensity and lifetime do not differ significantly (the flow rate effect will be discussed in the presentation). In the absence of ligand the FL lifetime (τ_0) was measured at 1.53 μ s (see the inset of Fig. 1). As demonstrated in Fig. 1, the presence of TSal ligand induces a FL quenching effect; the reduction of FL intensity (I) and shortened FL lifetime (τ) with increasing ligand concentration. Such FL

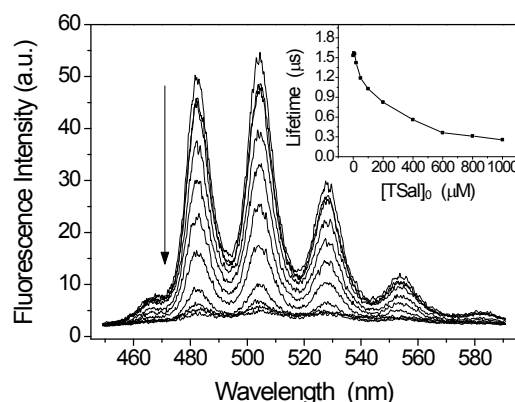


Figure 2. Fluorescence spectra and lifetime measured by TRLFS technique at different TSal concentrations. ($[U(VI)_{total}]$, 20 μ M at pH 3.02).

quenching effects occur due to the interaction between fluorophore molecules and quenchers. This can be quantitatively described using the Stern-Volmer equations (Eqs. (1) - (2)), where I_0 and τ_0 denotes FL intensity and lifetime, respectively, in the absence of TSaI; K_{SV} , Stern-Volmer coefficient; K_D , dynamic quenching coefficient; K_S , static quenching coefficient; $[L]$, unbound ligand (quencher) concentration. Fig. 2 displays the Stern-Volmer plots obtained from the results of Fig. 1.

$$\frac{I_0}{I} = 1 + K_{SV}[L] = (1 + K_D[L])(1 + K_S[L]) \quad \text{Eq. (1)}$$

$$\frac{\tau_0}{\tau} = 1 + K_D[L] \quad \text{Eq. (2)}$$

3.2. Analysis of Mixed Quenching Effect and Derivation of Complex Formation Constant

As shown in Fig. 2 the quenching of FL intensity is larger than that of FL lifetime. In addition, the plot of I_0/I vs. $[L]$ exhibits an upward curvature. These are the clear indication of mixed quenching, which can be expressed in a modified form of Stern-Volmer equation (see the term in bracket in Eq. (1)). Since the K_D can be directly obtained from the lifetime measurement (Eq. (2)), K_S also can be calculated. It should be noted that non-radiative ground-state complex formation is one of the major processes inducing static quenching. Under the given condition (oxygen free), it is reasonable to assume that the monodentate and bidentate U(VI)-TSaI complexes are the ground-state complexes inducing the static quenching effect (see Rxn. (1) and Eq. (3)). In Eq. (3) the term $\beta_1 \cdot K_A$ is equivalent to $K_1 \cdot K_{a2}$, where K_1 and K_{a2} denote formation constant for 1:1 chelate complex and -SH acid dissociation constant of TSaI, respectively. Since both K_1 and K_{a2} were estimated previously ($\log K_1 = 7.9$, $\text{p}K_{a2} = 8.5$), β_1 and K_A were determined in this study; $\log \beta_1$, 3.24 and $\log K_A$, 3.8. The validity of the assumption of two complexes in Rxn. (1) as ground-state complexes and the relationship between the complex formation and TSaI-induced quenching behaviors will be discussed in detail.

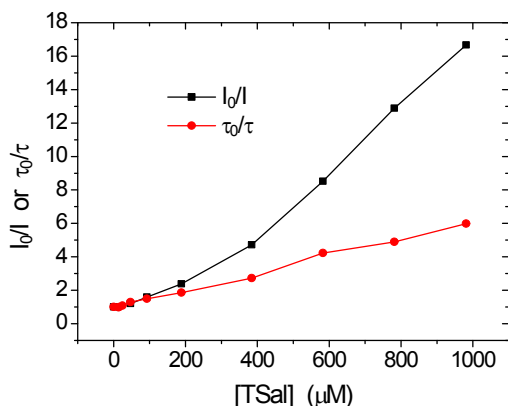
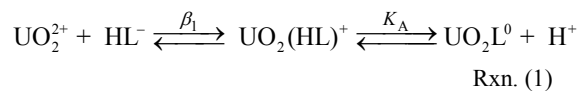


Figure 3. Stern-Volmer plots indicating mixed (dynamic and static) quenching process of UO_2^{2+} fluorescence by TSaI ligand.



$$K_S = \beta_1 + \beta_1 K_A \quad \text{Eq. (3)}$$

4. Conclusion

In the present study, the U(VI)-TSaI complex formation was investigated via TRLFS technique. A flow-through setup was successfully employed to minimize the photodegradation effect of TSaI. At pH 3.0 a mixed quenching effect of UO_2^{2+} FL by TSaI was observed and analyzed based on Stern-Volmer equation. The Stern-Volmer analysis yielded the formation constant ($\log \beta_1 = 3.24$) of monodentate complex, i.e., $\text{UO}_2(\text{TSaI}\text{H})^+$. This study provides a good example of determining a complex formation constant from the analysis of FL quenching process. using TRLFS technique work is clearly demonstrated The FL quenching mechanism and proposed complex structures will be discussed in detail.

Acknowledgements

This study is supported by the nuclear R&D program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

REFERENCE

- [1] A. Brachmann, G. Geipel, G. Bernhard, H. Nitsche, Radiochim. Acta 90 (2002) 147-153; H. Moll, G. Geipel, T. Reich, G. Bernhard, T. Fanghänel, I. Grenthe, Radiochim. Acta 91 (2003) 11-20; S. Sachs, T. Reich, G. Bernhard, Radiochim. Acta 98 (2010) 467-477; W. Cha, H.-R. Cho, K. Park, E.C. Jung, W. Kim, K. Song, Radiochim. Acta In review (2011)
- [2] W. Cha, H.-R. Cho, K.K. Park, E.C. Jung, Spectroscopic Studies on Complex Formation of U(VI)-Thiosalicylate. Transactions of the Korean Nuclear Society, Taebaek, Korea, May 25-27, 2011.
- [3] E.C. Jung, H.-R. Cho, K.K. Park, J.-W. Yeon, K. Song, Appl. Phys. B 97 (2009) 867-875.