

Spectroscopic Study on the Ternary Complex Formation of U(VI) with Salicylic Acid

E. C. Jung*, H.-R. Cho, K. K. Park

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute

P.O. Box 105, Yuseong, Daejeon 305-353, Korea

*ecjung@kaeri.re.kr

1. Introduction

From the nuclear chemical point of view, ternary complex formation of actinide ions with ligands has attracted attention for understanding radionuclides' migration in the environment [1]. There are various ligands in natural aquatic systems which can form stable ternary actinide complexes. Humic substance in a near-neutral groundwater is one of them and carboxylic groups in a humic substance are considered as the most likely functional group which interacts with actinides.

In this work, the formation of the ternary complex of U(VI) with salicylic acid (SAH₂) was investigated by two different laser-based spectroscopic methods, i.e., laser-induced breakdown detection (LIBD) and time-resolved laser fluorescence spectroscopy (TRLFS). The notable features are as follows: (i) the breakdown probability increases slightly, (ii) the absorbance of U(VI) increases, whereas the fluorescence intensity decreases with increasing salicylic acid concentration. The increase of the breakdown probability indicates that insoluble species are formed due to the complexation of U(VI) with SAH₂. The decrease of the fluorescence intensity is due to the quenching effect of the SAH₂ in the complexes.

With regards to the instrumentation, the characteristics of a newly developed LIBD system adopting a probe beam deflection method are presented. We report also on the improved speciation sensitivity ($\sim 10^{-9}$ M for UO₂²⁺) of the TRLFS system.

2. Experimental

All solutions were prepared using deionized water from the Milli-Q system. A uranium stock solution was prepared with natural ²³⁸U purified by a H₂O₂ precipitation in 6 M HClO₄. U(VI) samples with a pH range of 1.0-7.0 were prepared from a stock solution at room temperature. All the samples were appropriately diluted with 0.1 M HClO₄ (analysis grade, Merck), 0.1 M NaOH (Titrisol, Merck) and 0.1 M NaClO₄ solutions to maintain a 0.1 M ionic strength. The pH measurement was carried out by a Ross-type combination glass electrode calibrated with several pH buffer solutions.

The hydrolysis of U(VI) and the complexation of U(VI) with SAH₂ were investigated at [U(VI)] < 0.1 mM and a pH < 7 in an Ar atmosphere. A colloid-free U(VI) stock solution of 1 mM at pH 4 was slowly diluted with a 0.1 M NaClO₄ solution with or without SAH₂. The concentration of U(VI) was determined by

using a kinetic phosphorescence analyzer (KPA-11, Chemchek instrument Inc.).

Experimental setups for LIBD and TRLFS have been described elsewhere [2,3].

The formation of U(VI) colloids was monitored by a LIBD technique, i.e., the onset of a breakdown probability. For the concentrations of [U(VI)] < 0.1 mM at a pH < 4, only binary complexes (UO₂)(SAH)_r^(2-r) can be formed, because more than 95% of the uranium is present as a UO₂²⁺ free ion. However, for the same concentration of [U(VI)] < 0.1 mM at pH levels larger than 4, ternary complexes (UO₂)_p(OH)_q(SAH)_r^(2p-q-r) should also be considered due to the dominant fraction of the uranium hydrolysis species.

3. Results and Discussion

Figure 1 shows the breakdown probability as a function of the pH of the samples with different uranium concentrations. The breakdown probabilities are almost zero for a solution below a certain pH where the given uranium concentration exceeds the solubility limit of the U(VI) hydrolysis compounds. At a pH where an increase in the breakdown probability is observed, uranium colloids are formed. In the case of the sample with uranium concentrations of 2.0×10^{-4} M, the onset of a uranium colloid formation is observed at a pH of 4.54, designated as arrows in Fig. 1. In the presence of SAH₂, as shown in the inset in Fig. 1, the uranium colloid formation begins at about a pH of 4.4. The slightly lower pH value for the colloid formation indicates that the ternary hydroxo complex of U(VI)-OH-SAH₂ could be formed as a colloid.

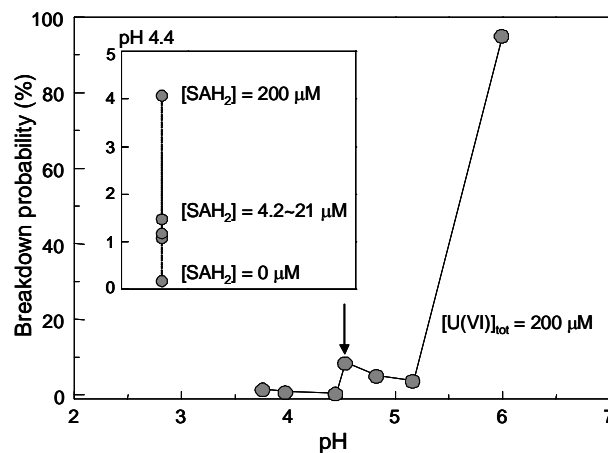


Fig. 1. Breakdown probability as a function of pH shows the formation of uranium colloidal particles.

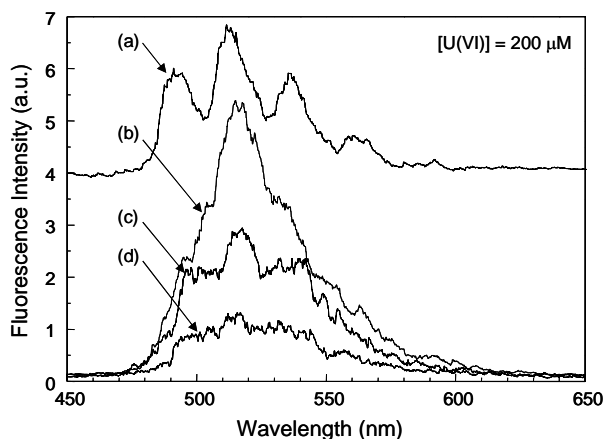


Fig. 2. Laser-induced fluorescence spectra with an excitation wavelength of 355 nm. (a) UO_2^{2+} spectrum at the gate delay of 1 μs and pH 1, (b) U(VI) spectrum at the gate delay of 8 μs and pH 4.4 (c) U(VI) spectrum with $[\text{SAH}_2]$ of 10 μM at the gate delay of 8 μs and pH 4.4, (d) U(VI) spectrum with $[\text{SAH}_2]$ of 40 μM at the gate delay of 8 μs and pH 4.4.

To confirm the formation of the ternary complex, absorption and fluorescence spectra were measured at various pH values for solutions of U(VI)-SAH₂. Laser fluorescence spectra with an excitation wavelength of 355 nm are shown in Fig. 2. For a comparison purpose, we present the typical fluorescence spectrum of UO_2^{2+} , designated as trace (a) in Fig. 2, measured at a pH of 1 with a concentration of 2×10^{-4} M. This spectrum was measured at the gate delay time of 1 μs after an incident laser pulse. Very well-known distinctive peaks in the spectrum appear at around 488, 509, 533, 559 nm. The spectrum for the same concentration of U(VI) measured at pH of 4.4 changes its shape as shown trace (b) in Fig. 2. As pH increases, U(VI) hydrolysis compounds are formed. Since these hydrolysis compounds have longer lifetimes than UO_2^{2+} ($\sim 1.9 \mu\text{s}$) with red-shifted peak wavelengths [4], the trace (b) was measured at a gate delay of 8 μs to remove the effect of UO_2^{2+} on the spectrum of the hydrolysis compounds. Traces (c) and (d) show the spectra of the hydrolysis compounds having the same U(VI) concentration with different SAH₂ concentrations. As the SAH₂ concentrations increase the fluorescence intensities decrease severely due to the quenching effect of SAH₂ on the fluorescence intensity for the ternary complexes.

4. Conclusions

We report on the characteristic features of a ternary complex formation for the U(VI)-OH-SAH₂ system. The formation of a ternary complex has been qualitatively measured by LIBD, and the colloid formation occurs at a lower pH for U(VI)-SAH₂ than for U(VI). We demonstrate a decrease of the U(VI) fluorescence intensity by the addition of SAH₂ as other evidence of a ternary complex formation. The reason for this quenching effect on the fluorescence intensity is unclear now. More quantitative works should be performed to understand the chemical properties of

these complexes. In addition, we report on the characteristics of a newly developed LIBD system and an improved speciation sensitivity ($\sim 10^{-9}$ M for UO_2^{2+}) of TRLFS system built in our laboratory.

Acknowledgement

This work is supported by the long-term nuclear R&D project of MEST of Korea.

REFERENCES

- [1] J.I. Kim, Significance of actinide chemistry for the long-term safety of waste disposal, Nuclear Engineering and Technology, Vol. 38, p. 459, 2006.
- [2] H.-R. Cho, E.C. Jung, K.Y. Jee, Probe beam detection of laser-induced breakdown for measuring solubility of actinide compounds, Jpn. J. Appl. Phys. Vol. 47, p. 3530, 2008.
- [3] E.C. Jung, H.-R. Cho, K. Song, K.K. Park, Y.J. Park, W.H. Kim, K.Y. Jee, Laser-based spectroscopic study on the speciation of U(VI)-OH complexes in aqueous media, Transaction of the Korean Nuclear Society Spring Meeting, Jeju, Korea, May 10-11, 2007.
- [4] C. Moulin, I. Laszak, V. Moulin, C. Tondre, Time-resolved laser-induced fluorescence as a unique tool for low-level uranium speciation, Appl. Spectrosc. Vol. 52, p. 528, 1998.