

The Speciation of U(VI) Complexes in Solutions by TRLIF Spectroscopy

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1. Introduction

Speciation of actinide in natural aquatic system is of great interest for the safety assessment of a nuclear waste disposal in deep geological system [1]. Actinide ions form complicate complexes with various ligands such as OH⁻, CO₃²⁻, and humic substances in groundwater. These complexes can enhance or reduce the migration of actinide elements. The direct speciation of these complexes in groundwater requires a highly sensitive and selective method which is capable to determine trace amount of actinides (down to 10⁻⁹ M) and to identify the different complexes without separation. Time-resolved laser-induced fluorescence (TRLIF) spectroscopy is a very suitable method for trace analysis of some actinides such as uranium, curium and americium due to their fluorescence feature.

In our recent work [2, 3], a TRLIF system using a photomultiplier tube (PMT) coupled to a spectrometer was applied to investigate various U(VI) complexes. In this work, a modified TRLIF system using an intensified charge-coupled device (ICCD) camera is introduced and its performance is compared with the previous system for the speciation of uranium complexes. We have investigated the effect of background materials, such as HClO₄ and NaClO₄, on the lifetime of the UO₂²⁺ ions in liquid solutions. In addition, the speciation of U(VI)-OH complexes has been carried out in considering the lifetime of the free uranyl ions at a certain background material.

2. Experimental

U(VI) samples in the concentration range of 1×10⁻⁸-4×10⁻⁶ M at a pH range of 0-6.0 were prepared from a uranium stock solution in 0.1 M HClO₄. All the samples were prepared at constant ionic strength of 0.1 M except the samples for the investigation of the effect of the HClO₄ concentration on lifetime. The samples were appropriately diluted with a HClO₄ (analytical grade, Merck) solution, a NaClO₄ (Merck) solution and distilled water (Academic, Milli-Q system, Millipore). The pH measurement was carried out by a Ross-type combination glass electrode calibrated with pH buffer solutions. The uranium concentration of the stock solution was determined by using a kinetic phosphorescence analyzer (KPA-11, Chemchek).

An experimental setup is similar to the system described in the previous works [2, 3]. A pulsed Nd:YAG laser (5000 Series, B.M. Industries) operating at 266 nm (the forth harmonic) with a repetition rate of

20 Hz (8 mJ) or 10 Hz (10 mJ) was used as the excitation source. The laser beam was irradiated in a sample cell (10×10×45 mm³) and the emitted fluorescence light was collected by a specially designed bundle of optical fibers which was close to the cell surface. The other end of the bundle of fibers was connected to the entrance slit of a spectrometer (Shamrock, SR-303i system, Andor Tech.) coupled to a high-speed gated ICCD camera (iStar 734, Andor Tech.). The fluorescence spectra of UO₂²⁺ ion in acidic solutions were measured from 450 to 590 nm in wavelength at a gate delay time of 0.1 μs and a gate width of 5 μs. The lifetimes were obtained from the fluorescence intensities which decrease with a stepwise increasing of a gate delay time with a constant gate width. For the speciation of U(VI) complexes, the spectra were measured at appropriate gate conditions.

3. Results and Discussion

The fluorescence spectrum of the UO₂²⁺ ions in acidic solutions shows the same feature as the well known six peaks (the four main peaks at 488, 509, 533, 559 nm). The fluorescence lifetime for the UO₂²⁺ ion in 0.1 M HClO₄ is determined as 1.92±0.17 μs. To estimate the limit of detection (LOD) of the present TRLIF system for the UO₂²⁺ ions, several fluorescence spectra were measured in the concentration range from 10⁻⁸ to 10⁻⁶ M at pH 1. When the fluorescence intensities at 509 nm are plotted as a function of uranium concentration, then the calibration curve for the measurement of uranium concentration is obtained with a linear dependency (R²=0.981). The LOD for the UO₂²⁺ ions defined as a 3σ of the background signal is about 2×10⁻⁹ M. When the LOD is compared with the previous system using a PMT, it is similar in order of magnitude.

We investigated the lifetimes of the UO₂²⁺ ions (4.2×10⁻⁶ M) as a function of HClO₄ concentration at the increased ionic strength and the constant ionic strength. In order to maintain the ionic strength, an appropriate amount of a NaClO₄ solution was added. The results are shown in figure 1. As the concentration of HClO₄ increases, the lifetime of the UO₂²⁺ ions is dramatically increased. This results show a similar tendency with the previous data [4]. In the same literature, the decrease of the lifetime with increase of [Na⁺] was reported. When the concentration of Na⁺ ion is lower than 0.1 M, however, the measured lifetime is similar to that of the sample without Na⁺ ions at the same [HClO₄] as shown in figure 1.

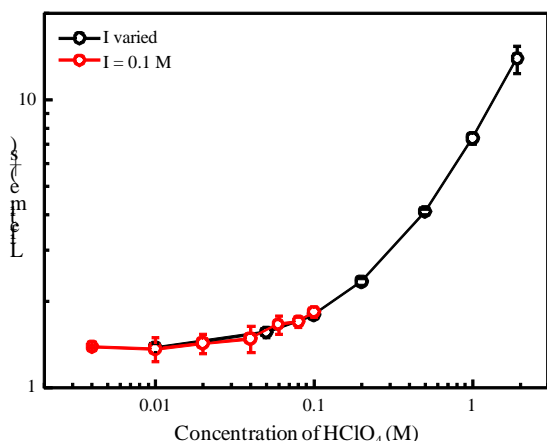


Figure 1. Lifetime variation of the UO_2^{2+} ion as a function of HClO_4 concentration at the varied or the constant (0.1 M) ionic strength.

For the investigation of the U(VI) complexes, it is important that the lifetime of UO_2^{2+} ion at a given condition is precisely determined. As an application, the spectra and lifetimes of the hydrolyzed U(VI) species have been measured and the results are shown in figure 2. At pH 2.4, the peak position of the fluorescence spectrum is not changed compared to the spectrum of the UO_2^{2+} ions but the fluorescence intensity is decreased due to the shorter lifetime of $1.39 \pm 0.01 \mu\text{s}$. At pH 5.8, $(\text{UO}_2)_3(\text{OH})_5^+$ is the dominant species according to the reported thermodynamic constants and the measured spectrum is similar to the reported spectrum of $(\text{UO}_2)_3(\text{OH})_5^+$ [5]. At this condition, the fluorescence intensity shows a single-component exponential decay ($t_1 = 11.72 \pm 0.12 \mu\text{s}$). At a relatively high concentration, we could observed a two-component exponential decay with $t_1 = 1.20 \pm 0.02 \mu\text{s}$ being a shorter lifetime of the UO_2^{2+} ions and $t_2 = 11.33 \pm 0.30 \mu\text{s}$ of the $(\text{UO}_2)_3(\text{OH})_5^+$ species.

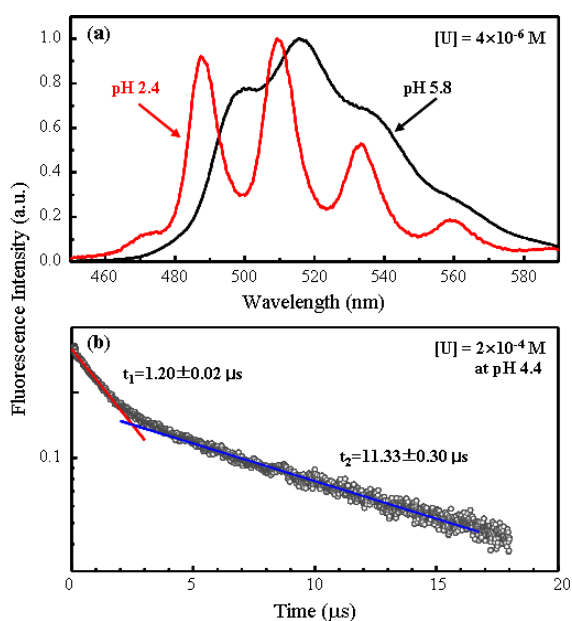


Figure 2. The speciation of UO_2^{2+} and $(\text{UO}_2)_3(\text{OH})_5^+$ species by spectra (a) and lifetime (b) measurement.

The shorter lifetime of the UO_2^{2+} ions at a high pH (low HClO_4 concentration) has to be considered for the speciation of the $(\text{UO}_2)_m(\text{OH})_n^{+2m-n}$ complexes. The measurement of the lifetimes and spectra of the other hydrolysis species is in progress.

4. Conclusions

A TRLIF system with an ICCD has been applied for the analysis of the UO_2^{2+} ions at several different conditions. The speciation sensitivity for the UO_2^{2+} ions at pH 1 is down to about 10^{-9} M and it is comparable to the result of a previous system. The lifetime of the free uranyl ions is varied with the background materials. Therefore, when the hydrolyzed species coexist with the UO_2^{2+} ions in a weak acidic solution, the fluorescence characteristics, such as the spectrum and lifetime, for the hydrolyzed uranium species should be considered with a shorter lifetime of the UO_2^{2+} ions. The speciation of U(VI)-OH complexes is discussed in this manner.

Acknowledgement

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