TRLFS Study of U(VI) at Variable Temperatures

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1. Introduction

Uranium is one of the most important radionuclides in a nuclear waste repository. Transport phenomena for radioactive elements are of crucial importance for a safe geological disposal of nuclear waste. Chemical speciation and solubility are used for understanding and predicting radionuclides migration in aquifer system. Decay heat released from high level waste and geothermal temperature gradient cause higher temperature above room temperature in deep geologic formation. However, most chemical thermodynamic data are obtained at room temperature until recently. There are few studies at temperatures above 25 °C. Therefore, a better understanding of thermodynamic properties at high temperatures is necessary for reliable safety assessment of high level waste repositories.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) has been applied as a sensitive and selective method for chemical speciation [1]. The fluorescence spectrum is unique for each chemical species. The duration time of fluorescence emission is used as another indicator for decomposition of overlapped fluorescence spectrum [2].

The objective of this study is to investigate fluorescence properties of uranium hydrolysis species at elevated temperature using TRLFS.

2. Experimental

2.1 Sample Preparation

Standard solutions of U(VI) were prepared by dissolving an $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) in 10^{-2} M HNO_3 (Merck) under aerobic conditions. The concentration of U(VI) was kept at 1×10^{-4} M. Deionized water obtained from ultrapure water purification system (Millipore Milli-Q/RiOs) was used for sample preparation. $HClO_4$ and NaOH solutions were used for pH control. The ionic strength was kept at 0.5 M $NaClO_4$. Samples were prepared in a standard 1 cm sealable quartz cuvettes (Hellma GmbH & Co KG). A copper block held the sample cuvette and controls the temperature by a circulation of tempered water.

2.2 Instruments

For the excitation, a pulsed Nd-YAG laser beam of 266 nm after fourth harmonic generator was used (Continuum, Surelite II-20, 20Hz). The pulse power was 3.0 ± 0.2 mJ and the pulse duration was 6 ns. The laser output energy was measured by a laser energy meter (Gentec·eo, XLD 12-1s-H2-DO). The incident laser pulse energy was continuously monitored by reflecting ca. 5% of the laser beam into a photodiode detector (Gentec·eo, XLE4) during fluorescence measurements. The fluorescence emission was delivered to a spectrometer (ANDOR, SR-303i-A) by optical fiber and recorded by ICCD camera (ANDOR, DH734-18F-C3). The emission was measured in the wavelength range from 459.13 nm to 600.75 nm.

3. Results & Discussion

Uranium fluorescence spectra are shown in Fig. 1. TRLFS measurements were performed in the pH range of 1.2 to 7.3. Five different uranium hydrolysis species, UO_2^{2+}, UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$ was identified with TRLFS. Species peak positions are listed in comparison with literature data (see Table 1).

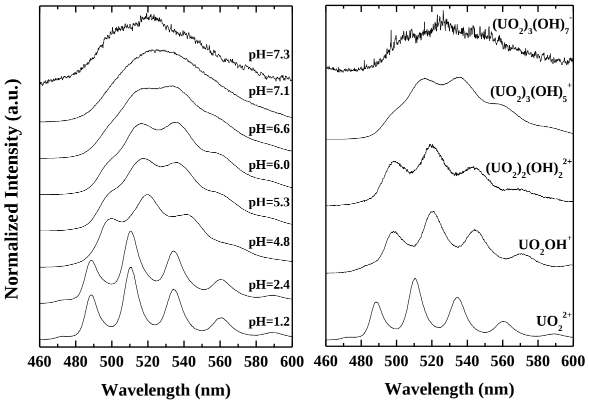

Fig. 1: Uranium fluorescence spectra (left) and pure uranium hydrolysis species spectra (right) in the pH range of 1.2 to 7.3 at 25°C. [U] : 1×10^{-4} M, I = 0.5 M $H/NaClO_4$.

Table 1: Fluorescence spectrum wavelengths of uranium hydrolysis species

Species	Fluorescence position (nm)	Ref.
UO_2^{2+}	473-490-511-534-560-589 470-488-509-533-559-588	p.w. [1]
UO_2OH^+	482-499-520-544-570-604 480-497-519-544-570-598	p.w. [1]
$(UO_2)_2(OH)_2^{2+}$	480-499-520-542-565 480-497-519-542-570-598 499-519-542-566	p.w. [1] [3]
$(UO_2)_3(OH)_5^+$	499-515-536-559-581 479-496-514-535-556-584 500-516-533-554	p.w. [1] [3]
$(UO_2)_3(OH)_7^-$	504-523-543-571-588 503-523-547-574	p.w. [1]

Fluorescence lifetimes of uranium species are presented in Table 2. Lifetimes of uranyl free ion was increased when the pH of uranium sample decreased. Many literatures [4,5] reported a similar phenomenon for UO_2^{2+}, but it was not yet explained clearly.

The activation energy was determined according to the Arrhenius equation:

$$E_a = -R \cdot \left(\frac{\partial \ln k_{obs}}{\partial (1/T)} \right)$$

where R is the gas constant, T is the absolute temperature and k_{obs} is the transition probability (inversed observed lifetime). The lifetimes of uranium species are temperature-dependent for uranyl free ion with activation energy of 23.9 kJ/mol. The solution temperature used in this work ranges from 15 ^{o}C to 75 ^{o}C. Activation energies of UO_2OH^+ and $(UO_2)_3(OH)_5^+$ correspond with other literature data.

Table 2: Fluorescence lifetimes and activation energies of uranium hydrolysis species.

Species	τ_{obs} (μs)	Ref.	E_a (kJ/mol)	Ref.
UO_2^{2+}	0.8 ± 0.1[a] 0.35 ± 0.1[b] 2 ± 0.1[e] 0.9 ± 0.3[f]	p.w. p.w. [1] [3]	23.9 ± 1.6 43.5 ± 1.8 41.5 ± 1.7 45.1 ± 0.3	p.w. [2] [6] [7]
UO_2OH^+	10.2 ± 1.1[b] 80 ± 5[g] 10.5 ± 1.1[h]	p.w. [1] [6]	25.0 ± 1.3 24.6 ± 1.6 34.2 ± 0.7	p.w. [6] [7]
$(UO_2)_2(OH)_2^{2+}$	5.1 ± 0.5[c] 9 ± 1[i] 2.9 ± 0.4[f]	p.w. [1] [3]	22.8 ± 2.6 35.1 ± 2.7 32.3 ± 0.3	p.w [6] [7]
$(UO_2)_3(OH)_5^+$	7.2 ± 0.5[c] 23 ± 3[j] 7 ± 1[k]	p.w. [1] [3]	23.8 ± 1.9 22.9 ± 2.1 36.6 ± 0.3	p.w [6] [7]
$(UO_2)_3(OH)_7^-$	121.4 ± 15[d] 230 ± 20[l]	p.w. [1]	14.9 ± 2.8	p.w

[a] pH = 1.2; [b] pH = 2.4; [c] pH = 4.8; [d] pH = 7.1
[e] pH = 2, I = 0.1 M [f] pH = 3.87, I = 0.1 M
[g] pH = 4, I = 0.1 M [h] pH = 5.1, I = 0.1 M
[i] pH = 4, I = 0.1 M [j] pH = 6.6, I = 0.1 M
[k] pH = 4.98, I = 0.1 M [l] pH = 8.9, I = 0.1 M

Relative fluorescence intensities of uranium species as a function of pH are shown in Fig. 2. Uranyl free ion appears predominantly at low pH, and other dimeric and trimeric hydrolysis species of U(VI) at higher pH.

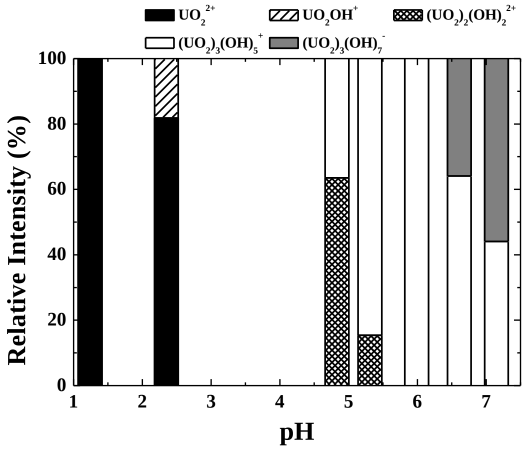

Fig. 2: Relative fluorescence intensity of uranium species in the pH range of 1.2 to 7.1 at 25 ^{o}C. [U] : 1×10^{-4} M, I=0.5 M.

A temperature-dependent tendency of uranium hydrolysis reactions is shown in Fig. 3. Further hydrolytic reactions did not proceed above 55^{o}C temperature at pH 4.8.

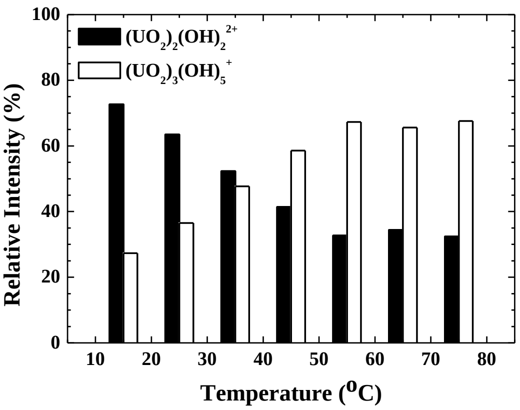

Fig. 3. Relative fluorescence intensity of uranium species at pH 4.8. [U] : 1×10^{-4} M, I = 0.5 M.

4. Conclusions

TRLFS has been used for the analysis of uranyl free ion and its hydrolysis species at different temperatures. Fluorescence peak positions of uranium species relatively well agree with other literatures. However, lifetimes and activation energies show discrepancies comparing with literature data. Additional experiments will be performed to identify the formation of the $(UO_2)_3(OH)_7^-$ species. The formation constants of the hydrolysis species of U(VI) as a function of temperature will be achieved after quantitative analysis by ICP-MS.

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