

Study of a ternary system of U(VI)-OH-acetate under neutral to alkaline conditions

Hee-Kyung Kim,^{1*} Euo Chang Jung,¹ Minji Kim,¹ Jang-Soon Kwon²

¹Nuclear Chemistry Technology Division, ²Disposal Performance Demonstration R&D Division,
Korea Atomic Energy Research Institute, Daejeon, Korea

*Corresponding author: hkim11@kaeri.re.kr

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1. Introduction

The acetate ion (CH_3COO^- , Ac) is known to play a role as an electron donor in the microbiological reduction of hexavalent U(VI) to tetravalent U(IV) [1]. This reduction process can retard the migration of uranium. However, the details of the reduction pathways are not fully elucidated. Complex formation of $\text{UO}_2(\text{Ac})^+$ and $\text{UO}_2(\text{Ac})_2(\text{aq})$ have been reported in acidic conditions, showing their characteristic absorption and luminescence properties [2]. Nonetheless, the U(VI)-Ac system has not been studied under circumneutral pH conditions, which are more relevant to effective microbial activities. In neutral to alkaline pH conditions, uranyl ions hydrolyze to form a series of species such as $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_3(\text{OH})_7^-$ and $\text{UO}_2(\text{OH})_3^-$. The addition of Ac to these hydrolyzed uranyl species can induce the formation of ternary U(IV)-OH-Ac complexes. This study presents preliminary results on the investigation of the ternary system, U(VI)-OH-Ac under the neutral to alkaline conditions. The research employs spectroscopic techniques for luminescence, absorption, and excitation spectroscopies. The effect of Ac on U solubility was investigated after phase separation by using ultrafiltration.

2. Methods

2.1 Sample preparation

A series U(VI) samples ranging from 10 to 50 μM were prepared in the absence and presence of 20-30 mM sodium acetate (NaAc), with variations in pH values. The background electrolyte was 0.1 M NaClO_4 . The pH of the samples was adjusted to the range of pH 1-9.5 adding HClO_4 or NaOH, while the pH measurements were conducted using a combined pH glass electrode (Orion RossTM). All sample preparation procedures were carried out in an Ar-filled glovebox to prevent CO_2 interference.

2.2 Time-resolved luminescence spectroscopy

Time-resolved laser induced fluorescence spectroscopy (TRLFS) was employed to investigate the luminescence properties of the U-Ac samples. Three-different excitation wavelengths of 266, 355, and 430 nm were used for luminescence measurements. In

particular, 266 nm was used with low pulse energy (0.1 mJ) to avoid photophysical effects on the Ac and U. Time-resolved luminescence spectra were collected through a spectrograph (Andor Technology) and a gated intensified CCD.

2.3 Absorption and excitation spectroscopy

UV-Vis absorption spectra were collected using Cary 5 (Agilent) with a 0.2 nm resolution, 0.5 nm spectral bandwidth, 0.5 s averaging time. Excitation-Emission Matrix (EEM) spectra were collected by using Aqualog (Horiba Sci.). Excitation spectra in the range of 260-450 nm were monitored by collecting emission in between 470-650 nm.

3. Results and discussion

3.1 Species distributions of U and U-Ac

Fig. 1 illustrates the species distributions of U(VI) in the presence of Ac as a function of pH. Solid phases were excluded from the calculations to evaluate only aqueous species. In weakly acidic conditions (pH 3-6), dominant species include U-Ac complexes with ratios of 1:1 to 1:3. Above pH 6, uranyl ions undergo hydrolysis, resulting in the dominance of U-OH complexes with ratios of 3:5, 3:7 and 1:3. Due to the absence of thermodynamic data on ternary U-OH-Ac complexes, only U-OH complexes appear in the near-neutral to alkaline pH range.

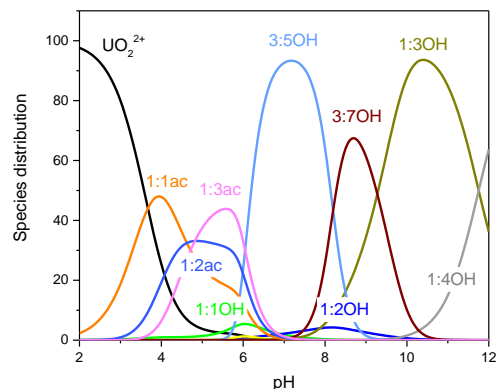


Fig. 1. Species distribution of 10 μM U(VI) in the presence of 20 mM NaAc in 0.1 M NaClO_4 .

3.2 Luminescence spectra of U-Ac in acidic conditions

Fig. 2 displays the pH-dependent luminescence properties of U-Ac in acidic pH conditions. At pH < 3, a significant decrease in luminescence intensity is observed while the spectral shape remains unchanged. This observation is consistent with the properties of the 1:1 $\text{UO}_2(\text{Ac})^+$ complex reported previously, which is non-luminescent [2]. In the pH range of 3-5, luminescence peak positions shift and overall spectral shapes progressively change while intensifying. Absorption spectra are also red-shifted with enhanced absorbance (Fig. 2, bottom). These observations indicate the formation of 1:2 $\text{UO}_2(\text{Ac})_2(\text{aq})$ complex [2].

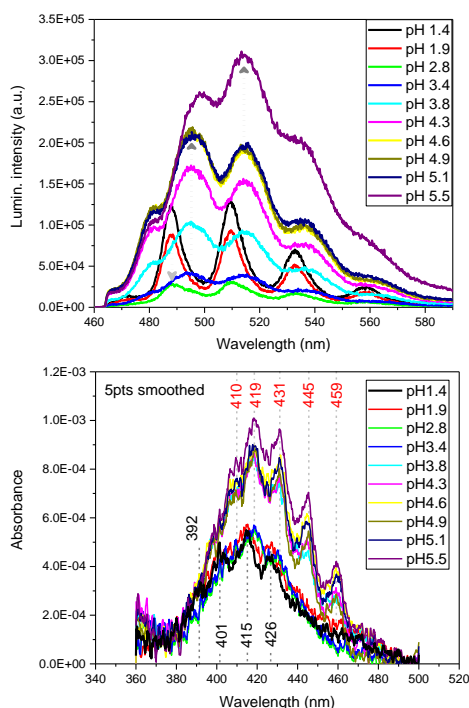


Fig. 2. Luminescence (upper) and absorption (bottom) spectra of 50 μM U(VI) + 30 mM NaAc in 0.1 M NaClO_4 under acidic pH conditions.

3.3 Luminescence properties of U-OH-Ac in near neutral to alkaline conditions

In the pH range of 5.5-9.5, luminescence spectra of U itself are depicted in the upper plots of Fig. 3. As pH increases, luminescence spectra and lifetimes of the samples indicate formation of 3:5 and 3:7 U-OH complexes [3]. In comparison, U-Ac samples exhibit different properties including spectral shapes (valley to peak ratio), peak positions, and lifetimes, all of which deviate from U-alone samples. These results suggest the formation of new species, likely aqueous U-OH-Ac ternary complex, though the formation of particulate matters is another possibility. Further analysis after phase separation are currently on going. Additionally, plans include conducting factor analysis and spectral

deconvolution of time-dependent luminescence spectra by using PARAFAC.

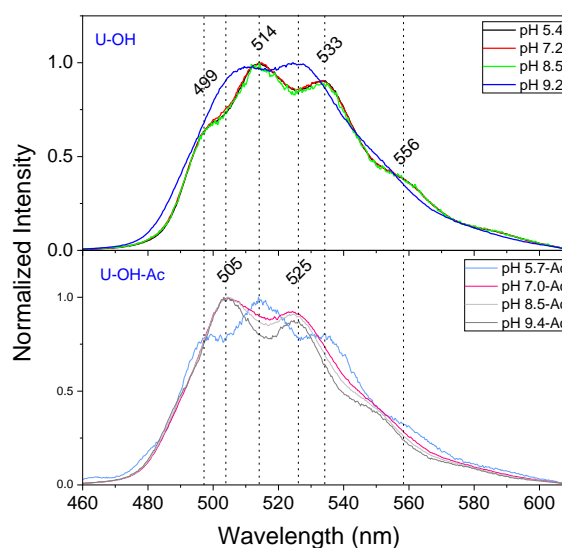


Fig. 3. Luminescence spectra of 10 μM U(VI) in the absence (upper) and presence (bottom) of 20 mM NaAc in the pH range of 5.5-9.5.

3.4 EEM spectra

Excitation spectra of U-Ac samples exhibit varying features depending on pH conditions. These results align with the observed differences in luminescence signal intensities depending on the excitation wavelength. However, emission spectral shapes remain independent of the excitation wavelength. Further investigation will explore these observations in terms of the symmetry changes in the ground and excited states of each complex.

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