

# UV-Vis Absorption Properties of Uranyl-Nicotinic Acid Complexes in Aqueous Medium

Seonggyu Choi and Jong-Il Yun\*

Department of Nuclear and Quantum Engineering, KAIST, 291, Daehak-ro, Yuseong-gu, Daejeon, Korea

\*jiyun@kaist.ac.kr

## 1. Introduction

The safety of a disposal facility for high level radioactive waste (HLW) is strongly dependent on the migration of released actinides through the natural water, such as groundwater and seawater. Therefore, a detailed understanding of the complexation reaction between actinides and natural organic matters (NOM) is required for the reliable safety assessment of the disposal facility since additional complexation leads to an increase in the solubility of actinides. Humic acids and fulvic acids are principal components of NOM, and those organic acids have carboxylic functionalities in their chemical structure. In addition, it was found that the organic acids also contain a small amount of nitrogen as amine functionalities or heterocyclic compounds arisen from humification [1]. In this study, nicotinic acid was selected as a representative simple N-modified model ligand of NOM, and its complexation with uranyl ( $\text{UO}_2^{2+}$ ) was observed by means of UV-Vis absorption spectrophotometry.

## 2. Experimental

### 2.1 Chemical reagents

All sample preparations and experiments were conducted under ambient aerobic condition at a temperature of  $23 \pm 2^\circ\text{C}$ . Aqueous solutions were prepared using deionized water (Millipore, Milli-Q/RiOs). Perchloric acid solutions were prepared by diluting 70wt% perchloric acid (Sigma-Aldrich, ACS reagent grade) with deionized water. Uranyl stock solutions were prepared by dissolving  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka, 98.0~102.0%) in perchloric acid solution, and nicotinic acid stock solutions were prepared by dissolving powdered nicotinic acid (Sigma-Aldrich,  $\geq 99.5\%$ ) in deionized water. The pH and ionic strength of samples were adjusted using perchloric acid solution, dissolved

sodium hydroxide solution (Sigma-Aldrich, 99.99%), and dissolved sodium perchlorate solution (Sigma-Aldrich, ACS reagent grade).

### 2.2 UV-Vis absorption measurement

The UV-Vis absorption measurements were performed using a ZEISS MCS601 UV-NIR C spectrometer, a ZEISS CLH600 light source, and Hellma QS quartz cuvettes with 1.00 cm pathlength.

## 3. Results and discussion

### 3.1 Hydrolysis behavior of U(VI)

The hydrolysis behavior of U(VI) was assessed as a function of pH in order to exclude hydrolyzed uranyl species in uranyl-nicotinic acid complexation experiments. The species distribution of U(VI) was calculated using the OECD NEA-TDB and the specific ion interaction theory (SIT), and the corresponding result is given in Fig. 1.

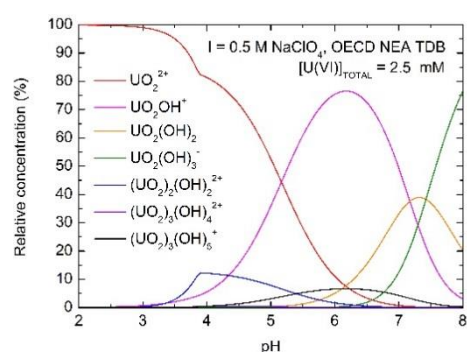


Fig. 1. Species distribution of U(VI) as a function of pH.

The species distribution shows that the hydrolyzed species are occupied less than 1% of 2.5 mM total concentration of U(VI) at pH less than 3.0, and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  is the most predominant hydrolyzed species in mild acidic condition.

This U(VI) hydrolysis behavior was also verified by means of UV-Vis absorption spectrophotometry.

Fig. 2 shows the UV-Vis absorption spectra of U(VI) at different pH values. The molar absorptivity and absorption bands of U(VI) did not change at pH up to 2.9. However, the molar absorptivity was increased and the UV-Vis absorption bands showed a red-shift tendency from pH 3.5. The change in the UV-Vis absorption properties is well adapted to the UV-Vis absorption properties of  $\text{UO}_2^{2+}$  and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  species reported in [2].

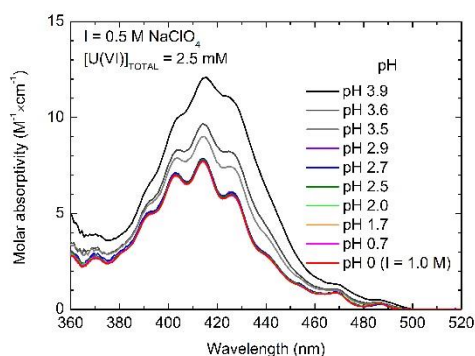


Fig. 2. UV-Vis absorption of U(VI) at different pH.

### 3.2 UV-Vis absorption properties of uranyl-nicotinic acid complexes

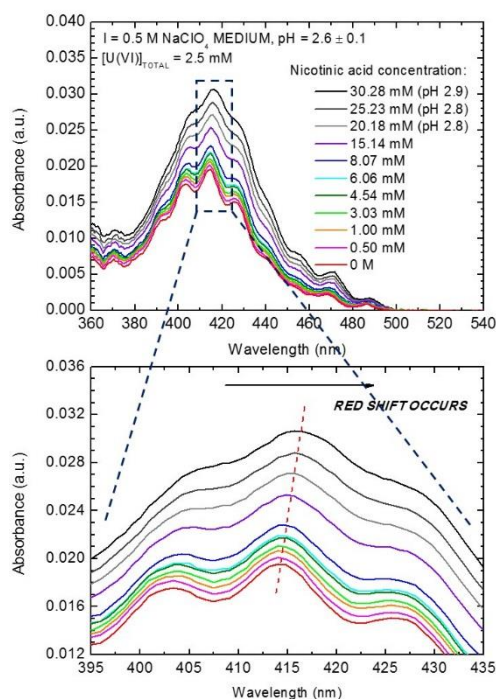


Fig. 3. UV-Vis absorption of uranyl-nicotinic acid complexes.

The uranyl-nicotinic acid complexation experiments were conducted with a constant total concentration of U(VI) at 2.5 mmol/L and various concentrations of

nicotinic acid. Fig. 3 shows the measured UV-Vis absorption of U(VI) as the concentration of nicotinic acid increases. The pH was controlled not to exceed 3.0, so the hydrolyzed species were surely excluded. The UV-Vis absorbance of U(VI) was gradually enhanced and the absorption bands exhibited the red-shift tendency by 2 nm when the concentration of nicotinic acid increases from 0 to 30.28 mmol/L. Since there was no significant UV-Vis absorption of nicotinic acid observed in the wavelength range 360~520 nm, these UV-Vis absorption changes indicate the complexation between uranyl and nicotinic acid.

## 4. Conclusion

The hydrolysis of U(VI) was evaluated by calculation using both reported thermochemical data and experimental method, and the complexation between uranyl and nicotinic acid, which is one of the major simple N-modified model ligands of NOM, was observed by means of UV-Vis absorption spectrophotometry.

## ACKNOWLEDGEMENT

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