Laser-Based Spectroscopic Studies of Actinide Complexes: Plutonium

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1. Introduction

In the last year, a new book titled "The Heaviest Metals: Science and Technology of the Actinides and Beyond" was designed by John Wiley & Sons to cover both the fundamentals and recent advances in the science and technology of the "heaviest metals," i.e., the actinide and transactinide elements, starting with actinium, up to the current end of the periodic table [1]. This book will also be published online as part of the Encyclopedia of Inorganic & Bioinorganic Chemistry. We contribute one chapter entitled "Laser-Based Spectroscopic Studies of Actinide Complexes" and we would like to present description of the techniques and several representative application studies introduced in the chapter in a series of three poster presentations. Each poster presentation is specific to uranium, plutonium and americium.

The chemical speciation of actinide complexes is considered to be a key concept for the safe management of spent nuclear fuels in the back-end of a nuclear fuel cycle. Methodological approaches for chemical speciation have been reported in detail in several studies [2, 3]. However, it appears that most nuclear and chemical engineers who work in nuclear industries are not familiar with laser-based spectroscopic techniques. In this presentation, applications of the laser-based spectroscopic techniques to the chemical speciation of actinide complexes are introduced for those who are interested in the highly sensitive analytical techniques applicable in the nuclear industry.

The spectroscopic properties of hydroxo complexes of Pu(VI) are demonstrated as representative examples. The absorption characteristics of Pu(VI) species are measured by using laser-induced photoacoustic spectroscopy (LPAS) and spectrophotometry coupled with a liquid waveguide capillary cell(LWCC). We demonstrate here that LPAS and LWCC is a sensitive and specific technique, enabling the speciation of trace amounts of plutonium being different oxidation states. As a representative example, a few μM of Pu(VI)-OH complexes are identified and thermodynamic data of Pu(III)-OH are determined.

2. Experimentals

The Pu(VI) and Pu(III) samples preparation procedure and the experimental set-up of LPAS and spectrophotometry coupled with LWCC (LWCC-3100, WPI Inc.) were described in detail in the previous literatures [1, 4, 5].

3. Results and Discussion

Fig. 1 shows absorption spectra of plutonium samples (concentration of 0.05 mM) at different pH values from 5.9 to 6.8 measured by spectrophotometry coupled with LWCC (optical pathlength of 100 cm). The absorbance of Pu^{3+} ions decrease with the formation of Pu(III) hydroxo complexes as increase of pH. The formation constant of $PuOH^{2+}$ species and solubility data of $Pu(OH)_3$ (am) were revaluated by chemical speciation using this sensitive absorption measurement system [5]. Spectrophotometry coupled with an LWCC in the visible wavelength region is considered as a comparable technique with LPAS especially for Pu(III-V), U(IV), U(VI) and Np(IV) species [1].

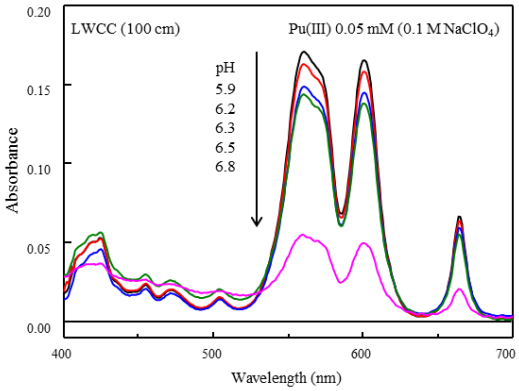

Fig. 1. Absorption spectra of Pu(III) measured by spectrophotometry coupled with LWCC (optical pathlength of 100 cm).

However, absorption spectrum in a near-IR wavelength region cannot be measured using LWCC. Thus, LPAS is a useful technique for the chemical speciation of aqueous actinide ions such as Pu(VI) and Np(V). Fig. 2 shows the LPAS spectra of plutonium samples (Pu concentration of 0.05 mM) at different pH values of 5.8, 8.0 and 10.4. Four peaks are observed at 830, 842, 850 and 861 nm. The peak at 830 nm represents the PuO_2^{2+} ions and the red-shifted peaks indicate the sequential formation of $PuO_2(OH)^+$, $PuO_2(OH)_2$ (aq) and $PuO_2(OH)_3^-$ species

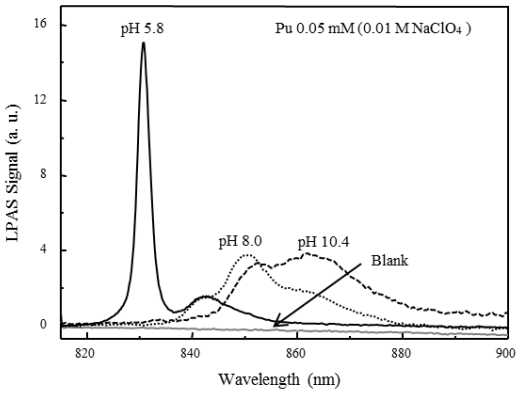

Fig. 2. Absorption spectra of Pu(VI)-OH complexes measured by LPAS.

4. Conclusion

The chemical speciation of actinides in aqueous solutions is important for the long-term isolation of high-level radioactive wastes. The laser-based spectroscopic technique, LPAS and spectrophotometry coupled with LWCC are very useful for speciation studies of these elements in dilute concentrations. Speciation studies related to the identification of Pu(VI)- and Pu(III)-hydroxo complexes in groundwater can be performed using LPAS or spectrophotometry coupled with LWCC.

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