

Spectroscopic Studies on Pu(III) Hydrolysis Under Reducing and Elevated Temperatures Conditions

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1. Introduction

Most countries operating nuclear power plants have planned development of deep geological facilities for the high-level radioactive waste disposal. Understanding the aquatic chemistry and determining thermodynamic data of actinides are important for the assurance of long-term safety for such permanent isolation of the high-level radioactive materials. The near-field environments of the repositories in an early stage of the operation are expected to be high temperatures due to the decay heat of the high-level radioactive waste. In addition, reducing conditions in groundwater surrounding the planned underground repositories are expected because there are many kinds of reducing materials such as Fe(II) compounds, sulfides, humic substances, and microorganisms living in anaerobic environments.

Plutonium exists significant amounts in the spent nuclear fuel and contributes to the long-term risk due to the long half-life of ^{239}Pu ($t_{1/2} = 2.4 \cdot 10^4$ year). The plutonium chemistry in aqueous solutions (solubility, hydrolysis, complexation, redox-reaction, sorption, etc.) is related to the transport of plutonium in geological environments and thus has been widely investigated [1]. However, reliable thermodynamic data on Pu(III) hydrolysis and solubility of Pu(III) hydroxide are few [1-3] because it is difficult to control the oxidation state of Pu(III) in the laboratory. In the previous report [4], Pu(III) hydrolysis in a neutral pH region was investigated under well controlled reducing conditions for maintaining Pu(III) by electrolysis. In this work, the previous investigation is expanded to the elevated temperature condition in order to determine thermodynamic data, such as ΔH and ΔS .

2. Experimental

2.1 Sample preparation

Chemically purified plutonium (> 99.9% ^{242}Pu) in

a solution of 0.1 M HClO_4 was prepared. A Pu(III) stock solution in 0.1 M HClO_4 was prepared through electrolysis by applying -0.2 V to the platinum working electrode versus Ag/AgCl reference electrode. The electrolysis setup and process were described in detail elsewhere [4]. Standard samples for absorption measurements were prepared by dilution of the Pu(III) stock solution with an 0.1 M HClO_4 solution. The concentrations of plutonium were determined using liquid scintillation counting (LSC, TriCarb 2500 TR/AB, Packard). For the investigation of Pu(III) hydrolysis, aliquots of the Pu(III) stock solution were diluted using an 0.1 M NaClO_4 solution and then the concentration of hydrogen ions of the solution is controlled to slowly decrease by electrolytic reduction described in the previous report [4].

2.2 Spectrophotometry

The absorption spectra of the plutonium samples are measured using a spectrophotometer (Cary5000, Agilent Technologies) with a Peltier-thormostatted multicell (6×6 cells) holder, which can control the temperature of the samples from 10 to 100 °C. The actual temperature of the sample solutions was monitored by dipping a built-in temperature probe in a blank solution during the measurements.

3. Results and discussions

Fig. 1 shows representative absorption spectra of Pu(III) measured at different temperatures. Absorption feature of trivalent plutonium in 0.1 M HClO_4 is well known, which shows absorption peaks centered at 556, 601 and 665 nm. Molar absorption coefficient at 601 nm is $37.5 \text{ M}^{-1}\text{cm}^{-1}$ at room temperature [4]. As increasing the temperature, decrease of molar absorption coefficient at 601 nm and increase of the full width at a half maximum (FWHM) were observed. The absorbance at 601 nm of the Pu(III) solution measured at 80°C was only 85 %

compared to that measured at 25°C, while peak areas, which are the summation of absorbance from 520 to 640 nm, remained constant.

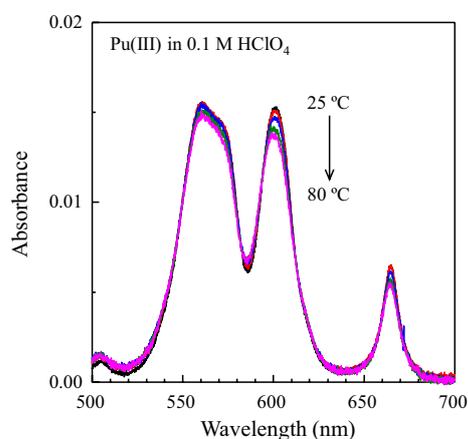


Fig. 1. Absorption spectra of Pu(III) in 0.1 M HClO₄ measured at different temperatures. The concentration of Pu(III) is 0.4 mM determined by LSC.

Fig. 2 shows absorption spectra of Pu(III) samples measured at 60°C. The total concentration of plutonium is constant throughout the coulometric titration ([Pu] = 0.5 mM). Absorbance of Pu(III) decreases with increasing pH. Based on the spectroscopic measurement, the formation of Pu(III)-OH species is determined and the results will be discussed.

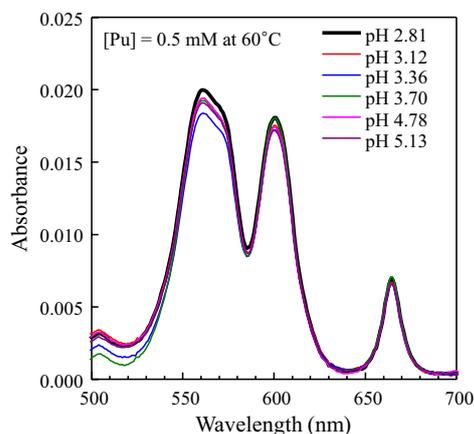


Fig. 2. Absorption spectra of Pu(III) at 60°C were measured at various pHs.

4. Summary

The spectroscopic reference data for plutonium at different temperatures are necessary information for the chemical speciation and evaluation of thermodynamic data at elevated temperature. This work is the initial step

to extend research activities for understanding the plutonium chemistry in aquatic solutions at high temperature. The hydrolysis of Pu(III) and the solubility of Pu(III) hydroxide at the elevated temperature will be discussed.

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