TEMPERATURE EFFECTS ON THE ABSORPTION SPECTRA OF PLUTONIUM IN AQUEOUS SOLUTIONS

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I. INTRODUCTION

Thermodynamic data for actinides and long-lived fission products in aqueous solutions are important for the safety assessment of nuclear waste disposal. In the case of disposal of high-level radioactive waste, the disposal environment is expected to be a high temperature owing to the decay heat of the waste at an early stage of the repository operation. Therefore, it is necessary to understand the actinide chemistry at elevated temperatures and evaluate the available thermodynamic data, such as ΔH and ΔS. Plutonium chemistry in an aquatic system is very complex owing to its redox reaction, hydrolysis, polymerization, and formation of colloids. Experimental investigations on plutonium chemistry at the elevated temperatures and the available thermodynamic data for plutonium in a deep geological system (anaerobic, neutral pH, etc.) are scarce.[1-2] The aim of this work is to determine absorption characteristics for plutonium at elevated temperatures, which are necessary for chemical speciation to evaluate thermodynamic data. The absorption spectra of standard samples of Pu(III-VI) are measured at different temperatures of 10 to 90 °C, and the temperature effects on the absorption features of different plutonium oxidation states will be discussed.

II. EXPERIMENTAL

Chemically purified plutonium (> 99.9% ^{242}Pu) in $HClO_4$ solutions was prepared through the dissolution of PuO_2, in a concentrate HNO_3 + HF solution, separation using an anion-exchange resin in HCl media, and evaporation in concentrated $HClO_4$ solutions. Pu(III-VI) stock solutions are prepared through electrolysis based on the literature.[3] The electrolysis setup and process are described in detail elsewhere.[4] Aliquots of Pu(III-VI) stock solutions are appropriately diluted using an acidic solution (0.1 M $HClO_4$) and the concentrations of plutonium were determined using liquid scintillation counting (LSC, TriCarb 2500 TR/AB, Packard).

The absorption spectra of the plutonium standard samples are measured using a spectrophotometer (Cary5000, Agilent Technologies) with a Peltier-thermostatted 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.

III. RESULTS AND DISCUSSION

Figure 1 (a) shows the absorption spectra measured during the preparation of tetravalent plutonium (Pu(IV)) in 1.0 M $HClO_4$ using electrolysis. After chemical purification, the oxidation state of plutonium in a $HClO_4$ solution was hexavalent (Pu(IV)). In order to prepare Pu(IV), the Pu(VI) was fully reduced to Pu(III) by applying -0.2 V to the working electrode (vs. Ag/AgCl reference electrode). The absorption spectrum measured after a reduction (the black line, 0 min, before oxidation to Pu(IV)) indicates that the plutonium solution contained only Pu(III). The solution of Pu(III) was oxidized to Pu(IV) by applying over 1.0 V vs. SHE (standard hydrogen electrode). The blue (70 min) and red (470 min) lines represent the absorption spectra measured during the oxidation. The absorbance of Pu(III) at 561, 601 and 665 nm disappeared and the newly appeared absorption spectrum was consistent with the reported spectrum of Pu(IV) in 1 M $HClO_4$.[5] The absorbance of three samples at shorter than 500 nm slightly increases owing to the existence of colloidal contaminants. The concentration of plutonium was 0.17 mM, determined by the LSC. To investigate the absorption characteristic of hydrated Pu^{4+} ions depending on temperature, the absorption spectra were measured for several standard

solutions having concentrations of 10 to 200 μM at different temperatures. Figure 1 (b) shows the absorption spectra of Pu(IV) solutions in 1.0 M $HClO_4$ recorded using a standard quartz cell at room temperature. The experimentally determined molar absorption coefficient is 52.3 ± 1.4 $M^{-1}cm^{-1}$ at 470 nm, which agrees well with the reported value (50) of Pu(IV) in 1 M $HClO_4$.[5] The main absorption band of Pu(IV) at around 470 nm seems to be overlapped with other peaks. In order to determine accurate spectroscopic parameters for Pu^{4+} ions, such as the peak maximum and width, the spectra should be analyzed through deconvolution. The results of a spectroscopic analysis for the different oxidation states of plutonium measured at 10, 25, and 50 °C will be discussed in detail.

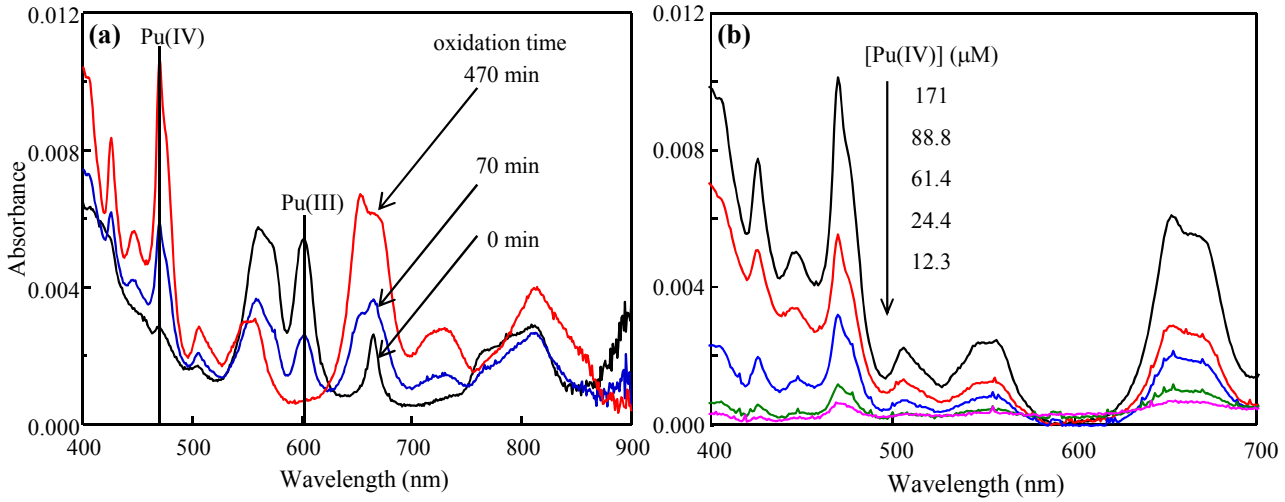

Fig. 1. (a) Absorption spectra measured during electrochemical oxidation from Pu(III) to Pu(IV) in 1 M $HClO_4$ ([Pu] = 0.17 mM). (b) Absorption spectra of Pu(IV) solutions with different concentrations in 1.0 M $HClO_4$.

IV. CONCLUSIONS

The standard solutions for different oxidation states of plutonium were successively prepared through electrolysis. 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 in Korea to extend research activities for understanding the plutonium chemistry in aquatic solutions at high temperature.

ACKNOWLEDGMENTS

The work was supported by a grant from the Nuclear Research and Development Programme of the National Research Foundation of Korea funded by the Korean Ministry of Science, the ICT, and Future Planning (Grant code: 2012M2A8A5025924).

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