

Spectroscopic Study on the Hydrolysis Species of Hexavalent Plutonium

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1. Introduction

The hydrolysis of hexavalent plutonium has been investigated by using various techniques such as potentiometry, spectrophotometry and solubility measurement. In most cases, it was assumed that a hydrolysis is a fast reaction and its thermodynamic data can be determined in a few hours before the other oxidation states of plutonium are released. However, reactions being relative slow, such as reduction of Pu(VI) induced by radiolysis, agglomeration of Pu(VI) hydrolysis species and precipitation, were reported possible hindrances to determine accurate formation constants of the Pu(VI) hydrolysis [1].

In our recent work [2], the reduction of Pu(VI) was observed with an aid of a higher detection sensitivity of a 1.0-meter liquid waveguide capillary cell (LWCC, WPI). Direct after sample preparation from a stock solution which contains only Pu(VI), the considerable Pu(V) was released in every sample at weak acidic or near neutral condition. In the present work, the formation constants of Pu(VI)-OH complexes are investigated with the consideration for the effect of the reduction of Pu(VI) in a long time-period. In addition, the absorption features for the hydrolysis species of Pu(VI) are reported in visible range measured by using a 1.0-meter LWCC compared with absorption spectra in near IR ranges measured by using a 1 cm quartz cell.

2. Experimental

The preparation of a Pu(VI) stock solution was detailed in the previous report [2]. In order to minimize the effect of a radiolysis, $^{242}\text{PuO}_2$ (Pu-242 isotope 99.932%, ORNL) were dissolved with concentrated HNO_3 and HF, and oxidized to Pu(VI) by fuming several times with concentrated HClO_4 . At the last step, the Pu solution was totally dried and then dissolved in 0.5 M HClO_4 and softly heated to minimize the insoluble Pu. The concentrations of the other oxidation states (Pu(III), Pu(IV), Pu(V)) are lower than the detection limit of a LWCC coupled with a spectrophotometer (Cary 5, Varian) being 0.2 μM for Pu(III), 0.1 μM for Pu(IV) and 0.4 μM for Pu(V).

In order to obtain the calibration curve for the measurement of a PuO_2^{2+} ion concentration, Pu(V) samples were prepared in 0.001 M HClO_4 . For the investigation of the Pu(VI) hydrolysis species, samples with concentrations less than 0.1 mM at a pH range of 2.0-12.0 were prepared in an Ar atmosphere. An aliquot of a stock solution was appropriately diluted with

distilled water (Milli-Q system, Millipore) or 0.01 M NaClO_4 solution added NaOH (99.99%, semiconductor grade, Aldrich) solutions to adjust the pH. The ionic strength of sample is maintained at 0.01 M NaClO_4 . For a purification, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (analysis grade, Merck) was carefully recrystallized and then dissolved in distilled water. The pH measurement was carried out by a Ross-type combination glass electrode calibrated with 4 pH buffer solutions (pH 2.00, pH 4.01, pH 7.00 and pH 9.21, Mettler Toledo). When a sample contains plutonium precipitate, it was separated by using a cellulose filter (10 kD, Centricon YM-10, Millipore) and the concentration of plutonium in filtrate was determined by LSC. The absorption spectra of aqueous plutonium species were measured as a function of the time by using a 1.0-m LWCC in visible wavelength range and also using a sealable 1.0-cm cell (Hellma) in NIR range.

3. Results and Discussion

Figure 1. (bottom) shows the absorption spectra of the Pu(VI) and Pu(V) standard solutions measured by using a 1.0-meter LWCC. The absorption spectrum of the Pu(V) standard solution ($[\text{Pu}] = 0.12 \text{ mM}$, pH 4, $I = 0.01 \text{ M NaClO}_4$) is characterized by a weak transition with a maximum peak at 569 nm. The measured molar absorption coefficient is $17 \text{ M}^{-1}\text{cm}^{-1}$ which agrees with a previously reported value ($\epsilon = 17.1 \text{ M}^{-1}\text{cm}^{-1}$ [3]). The absorption feature of PuO_2^{2+} ion in a visible range designated as a black line in Fig. 1 (bottom). The Pu(VI) standard solution (0.099 mM, 1 M HClO_4) contains only small Pu(V) being about 3 μM and no Pu(IV) and Pu(III).

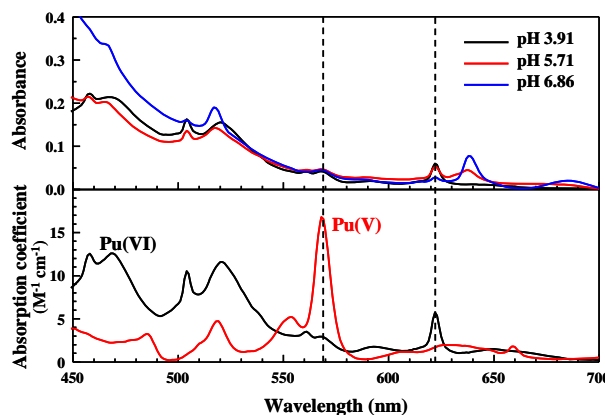


Fig. 1. Absorption spectra of Pu(VI) and Pu(V) standard solutions (bottom) and of Pu(VI) hydrolysis species at various pHs measured by using a 1.0-meter LWCC.

The absorption spectra of plutonium at the concentration of 0.1 mM and various values of pH are shown in Fig. 1. (top). Since no effort was made to stabilize the oxidation state of Pu(VI), the detectable amounts of Pu(V) by a 1.0-meter LWCC were emerged in samples directly after a sample preparation. In addition, the spectra measured by using a 1.0-meter LWCC also give information of the Pu(VI) hydrolysis species. The absorption peak at 622 nm ($\epsilon = 7.5 \text{ M}^{-1}\text{cm}^{-1}$ [4]) of PuO_2^{2+} ion decreases with an increase of the pH and the red-shifted absorption peaks are emerged. It is comparable with the absorption feature in the NIR range where the peak at 830.7 nm ($\epsilon = 550 \text{ M}^{-1}\text{cm}^{-1}$ [3]) of PuO_2^{2+} is shifted with the formation of hydrolysis species.

In Fig. 2. the absorption spectra of the Pu(VI)-OH complexes measured in a visible range by using a 1.0-meter LWCC (left) are compared with the absorption spectra measured in the NIR range by using a 1 cm cell (right). In both cases, the absorption peaks for the PuO_2^{2+} ion at 622 nm and 830.7 nm decrease due to the formation of Pu(VI) hydrolysis species with an increase of the pH. At pH 5.71 the absorption peaks of the two hydrolysis species at 632 nm and 638 nm are observed, whereas the absorption peak in the NIR range is not resolved. When the spectra measured by a 1.0-meter LWCC are compared with the previous reported work by LPAS [4], results indicate that the dimer hydrolysis species, $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, is formed as the first hydrolysis species at the present condition though it is not distinguished in the NIR range ($(\text{PuO}_2)_2(\text{OH})_2^{2+}$, $\epsilon = 270 \pm 10 \text{ M}^{-1}\text{cm}^{-1}$ at 845 nm [5]). The second hydrolysis species, $\text{PuO}_2(\text{OH})$ absorbing at 638 nm and 850 nm is formed at a neutral pH and the third hydrolysis species $\text{PuO}_2(\text{OH})_3^-$ absorbing at 650 nm at 860 nm is formed at a basic condition.

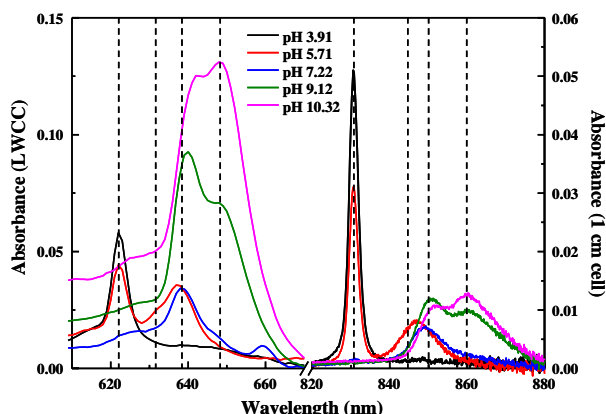


Fig. 2. Comparison with absorption features of Pu(VI) hydrolysis species measured in visible range using a 1.0-meter LWCC and in NIR range using a 1.0 cm quartz cell. Pu concentration and ionic strength are maintained constant at 0.1 mM and 0.01 M NaClO_4 , respectively. The value of pH increases from 3.9 to 10.3.

The sample at a near neutral pH which contains the second hydrolysis species as dominant species of Pu(VI) was investigated in a long time-period. The

concentration of Pu(V) absorbing at 569 nm increased and the total Pu(VI) concentration decreased as a function of the time. The formation constant of $\text{PuO}_2(\text{OH})_2$ determined after 1 year of a reaction time will be shown.

4. Conclusions

In the present study, the characteristic features of the absorption spectra for hydrolysis species of hexavalent plutonium, $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, $\text{PuO}_2(\text{OH})_2$ and $\text{PuO}_2(\text{OH})_3^-$ were reported in both visible and NIR ranges. With an aid of a higher detection sensitivity of a 1.0-meter LWCC, the hydrolysis of Pu(VI) was investigated with a weak energy transition in a visible range and it was comparable with the results of a strong absorption in the NIR range. The concentration of Pu(V) was determined precisely by using a 1.0-m LWCC. The determination of the formation constants for the hydrolysis species is in progress.

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