

Speciation of Pu(VI)-OH Complexes in an Aqueous Media

H.-R. Cho, E. C. Jung, M. H. Lee, K. K. Park, Y. J. Park, W. H. Kim, and K. Y. Jee
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute
P.O. Box 105, Yuseong, Daejeon, Korea, 305-353
hrcho@kaeri.re.kr

1. Introduction

The chemical behaviors of actinides in an aqueous media are of great interest in the research field for the migration of radionuclides. They form complexes with inorganic or organic ligands such as OH⁻, CO₃²⁻ and humic substances, etc. in a natural aquatic system [1]. These chemical behaviors depend on the oxidation state of actinides and, normally, the chemical behaviors of hexavalent actinides are represented as U(VI) because of its redox stability. The hydrolysis of Pu(VI) are not well defined until now due to the complicated redox behaviors of plutonium in a solution [2].

In this paper, we report on the characteristic features of absorption spectra for the hydrolysis species of Pu(VI) by using a UV/Vis spectrophotometer. By varying the pH and plutonium concentration at a fixed ionic strength, the identification of various species such as PuO₂²⁺, PuO₂OH₂ and (PuO₂)₂(OH)₂²⁺ has been performed. With an aid of a higher detection sensitivity of a 1.0-m liquid waveguide capillary cell (LWCC), we could directly monitor the increase of aqueous Pu(V) due to the reduction of Pu(VI).

2. Experimental

²⁴²Pu (99.932%) were purchased from Oak Ridge National Laboratory as an oxide form. The plutonium oxide was dissolved with concentrated HNO₃ and HF and oxidized to Pu(VI) by fuming several times with a small amount of concentrated HClO₄ to a near dryness. At the last step, the Pu solution was totally dried and then dissolved in 0.3 M HClO₄ and softly heated to minimize the insoluble Pu. The concentration of this Pu solution was 3.94 mM which was determined by using a liquid scintillation counting (LSC) and an α -spectrometer. The concentrations of the other oxidation states (Pu(III), Pu(IV), Pu(V)) are lower than the detection limit of a UV/Vis spectrometer (Cary 5, Varian) being about 5 μ M for Pu(III), 4 μ M for Pu(IV) and 10 μ M for Pu(V).

In order to obtain the calibration curve for the measurement of a PuO₂²⁺ ion concentration, Pu(VI) samples were prepared in 1 M HClO₄. For the investigation of Pu(VI) hydrolysis species, samples with concentrations less than 10⁻⁴ M at a pH range of 2.0-12.0 were prepared at 21 \pm 1 $^{\circ}$ C in an Ar atmosphere. An aliquot of a stock solution was appropriately diluted with ultra-pure water (Millipore) or 0.01 M NaClO₄ solution to maintain a 0.01 M ionic strength and NaOH (99.99%, Aldrich) solutions to adjust the pH. For a

purification, NaClO₄ · H₂O (analysis grade, Merck) was carefully recrystallized and then dissolved in ultra-pure water. The pH measurement was carried out by a Ross-type combination glass electrode calibrated with several pH buffer solutions.

The UV/Vis absorption spectra of aqueous plutonium species were measured as a function of the time by using a sealable 1.0-cm cell (Hellma) out of a glove-box and a 1.0-m LWCC in a glove-box [3].

3. Results and Discussion

For a calibration purpose several absorption spectra were measured in the concentration range from 10⁻⁶ M to 10⁻⁴ M in 1 M HClO₄. The results are shown in Fig. 1. A narrow absorption peak is observed at 830.7 nm with its molar absorption coefficient of 545 \pm 27 M⁻¹cm⁻¹. In the inset of Fig. 1, the calibration curve designated as a dotted line illustrates a precise linear dependency with a regression coefficient better than 0.99.

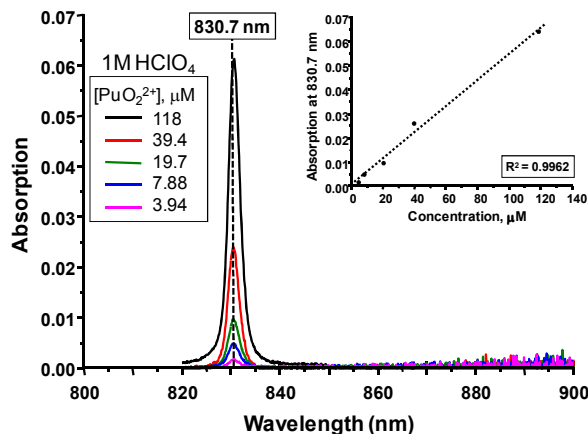


Figure 1. Absorption spectra and a calibration curve (inset) for the measurement of PuO₂²⁺ ion concentration in 1 M HClO₄.

Figure 2 shows the absorption spectra at various values of pH for the two different total plutonium concentrations, 118 μ M (top) and 16 μ M (bottom). For the case of Fig. 2(a), the absorption peak at 830.7 nm gradually decreases with an increasing pH. Whereas, the absorption peak at 846.7 nm, corresponding to the first hydrolysis species of (PuO₂)₂(OH)₂²⁺, increases simultaneously at pH values higher than 5.20. The second hydrolysis species, PuO₂(OH)₂, is observed at the wavelength of 850 nm and pH 7.73.

For the lower [Pu]_{tot}, as shown in Fig. 2(b), the dimer species is not observed but PuO₂(OH)₂ species is

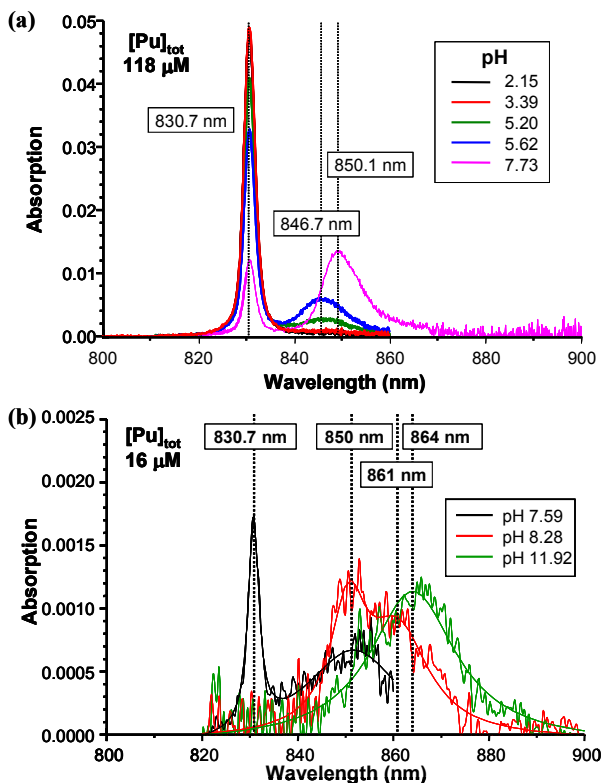


Figure 2. Absorption spectra of Pu solutions at various pH with concentration of $[Pu]_{tot}=118 \mu M$ (a) and $16 \mu M$ (b).

formed at pH 7.59. However, the absorption peak at 850 nm disappears with an increasing pH and an absorption peak at 864 nm is observed at pH values higher than 8.28. We speculate that this peak is probably due to the formation of a third hydrolysis such as anionic species, $PuO_2(OH)_3^-$ and $PuO_2(OH)_4^{2-}$.

The absorption peak at 841 nm for PuO_2OH^+ species, reported in a previous work [4], was not observed in these experimental conditions. We do not know the reason exactly. One of the possible reasons is that the monomer species cannot be formed because of a local over-saturation which occurred during the pH titration with NaOH. However, we observed that the sample of pH 5.62 was changed to pH 5.33 after 1 month due to the reduction of Pu(VI). As a result, the $PuO_2(OH)_2$ species disappeared. This behavior agrees well with the distribution of hydrolysis species estimated by using the formation constants in the literature [2] which shows 80% for PuO_2^{2+} and 20% PuO_2OH^+ without $PuO_2(OH)_2$ at about pH 5 and $[Pu(VI)]$ of $100 \mu M$. However, the absorption of PuO_2OH^+ at 841 nm was not observed in this condition, too. Thus, the absorption band for PuO_2OH^+ should be investigated more carefully.

With an increasing $[Pu(V)]$ due to the reduction of Pu(VI), the concentrations of Pu(V) have to be determined for a precise interpretation of the chemical behaviors of Pu(VI). For this purpose, absorption spectra of Pu(V) were measured by using a 1.0-m LWCC. Figure 3 illustrates the representative example for the change of the absorption spectra with time. The

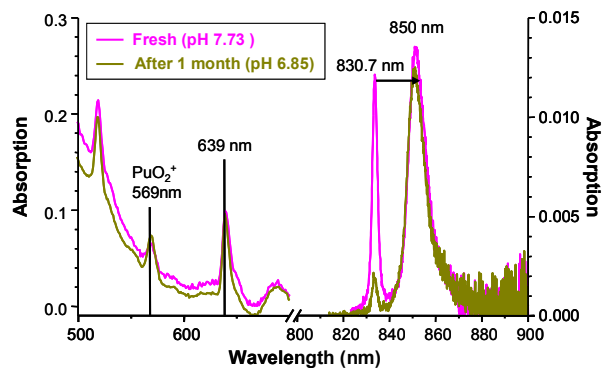


Figure 3. Absorption spectra of Pu samples changed with time.

absorption spectra in the wavelength ranging from 500 to 800 nm and the spectra ranging from 800 to 900 nm were measured by using a 1.0-m LWCC and 1.0-cm cell, respectively. The peaks observed at 639 nm and 850 nm are due to the absorption of $PuO_2(OH)_2$ species [4,5]. As the time elapsed with the pH change from 7.73 to 6.85, the absorption at 830.7 nm for the PuO_2^{2+} decreased with an increase of the absorption at 569 nm for PuO_2^+ .

4. Conclusions

In the present study, the characteristic features of absorption spectra for hydrolyzed plutonium, $(PuO_2)_2(OH)_2^{2+}$ and $PuO_2(OH)_2$, are reported. Unidentified absorption bands at about 864 nm were observed in the basic solution. It can be interpreted as the absorption bands due to the soluble anionic hydrolysis species. The concentration of Pu(V) was determined precisely by using a 1.0-m LWCC. The formation constant of $\log \beta_{22}^{\circ} = -7.63$ for $(PuO_2)_2(OH)_2^{2+}$ was obtained from the measured absorption spectra. It agrees well with the $\log \beta_{22}^{\circ} = -7.5$ in literature [2]. Researches on the formation constants for other hydrolysis species are in progress.

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