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# The Chemistry of Pu in Concentrated Aqueous NaCl Solution: Effects of Alpha Self-Radiolysis and the Interaction between Hypochlorite and Dioxoplutonium(VI) [1]

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*Plutonium / Complexation / Hypochlorite / Radiolysis / Oxidation / Spectrophotometry*

## Abstract

The reactions between dioxoplutonium(VI) and hypochlorite in aqueous solution produce the species  $\text{PuO}_2(\text{OH})(\text{ClO})$  and  $\text{PuO}_2(\text{ClO})_2$ . The results of spectrophotometric observations are presented and the data used to calculate values of  $\log K = 14.0$  at  $\text{pH} = 6.7$  and  $14.5$  at  $\text{pH} = 8.4$  for the former complex and a value of  $10.3$  for the latter. The possible participation of  $6d$  orbitals in these reactions is noted.

## Introduction

The  $\alpha$  particles from the radioactive decay of Pu in concentrated aqueous NaCl solutions produce (among other products) a steady state concentration of oxidized chlorine species including the hypochlorite ion [2]. The subsequent electron transfer reactions of these species with plutonium ions [2, 3] result in a system wherein Pu(VI) is the sole oxidation state of the metal ion.

The reactions of the hypochlorite ion with  $d$  transition metal ions are for the most part oxidation-reduction reactions [4–6]. The detailed mechanisms of such reactions postulate a metal ion hypochlorite complex as an intermediate. The existence of such an intermediate complex in the oxidation of tetracyanoplatinate(II) has been experimentally demonstrated [7].

The preliminary results of a solubility study were consistent with the postulate that a stable complex was formed between Pu(VI) and hypochlorite ions [2]. The possibility of the formation of such a unique complex prompted a detailed study of the reaction between hypochlorite and Pu(VI), the results of which are presented in this communication.

## Experimental

The Pu(VI) stock solution was prepared by dissolving reactor grade  $\text{PuO}_2$  (0.04%  $^{238}\text{Pu}$ , 90.57%  $^{239}\text{Pu}$ ,

8.88%  $^{240}\text{Pu}$ , 0.40%  $^{241}\text{Pu}$ , 0.11%  $^{242}\text{Pu}$ ) in  $\text{HNO}_3/\text{HF}$ , fuming several times with concentrated perchloric acid until near dryness and dissolving in bidistilled water resulting in a solution of  $\text{pH} 4$  containing all Pu in the hexavalent state. The purity of the oxidation state of this solution was verified by measuring the absorbance of an acidified aliquot at  $830 \text{ nm}$  ( $\epsilon = 555 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  [8]) and counting for total Pu. Weight amounts of sodium perchlorate were dissolved in bidistilled water. NaOH ( $\text{CO}_2$ -free) and  $\text{HClO}_4$  solutions were prepared by dilution of analytical grade reagents. The solutions were subsequently standardized by conventional acid/base titrations. The sodium hypochlorite solutions were prepared from  $\text{HClO}$  [9] and standardized spectrophotometrically at  $290 \text{ nm}$  ( $\epsilon = 290 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  [10]).

A ROSS electrode with  $3 \text{ M NaClO}_4$  as filling solution was used for all pH measurements and calibrated daily with 6 different buffer solutions in the range from  $\text{pH} 2$  to  $\text{pH} 8$ . A Perkin-Elmer recording spectrophotometer (Lambda 9) was used for all absorbance measurements.

The test solutions were prepared by equilibrating an aqueous phase of the appropriate composition with a freshly precipitated and washed Pu(VI) hydroxide. A portion of the supernatant solutions was acidified and analyzed for Pu(VI) spectrophotometrically.

## Results and discussion

The results obtained in a preliminary set of observations ( $1.4 \cdot 10^{-3} \text{ M Pu(VI)}$ ,  $[\text{NaClO}] = 0.55 \text{ M}$ ,  $\text{pH} 7.3–9.4$ ,  $22^\circ\text{C}$ ) were used to assign the absorption band at  $852 \text{ nm}$  as characteristic of the monohypochlorite complex and the band at  $862 \text{ nm}$  as that of the bis-hypochlorite Pu(VI) complex. Fig. 1 shows the absorption spectrum of Pu(VI) in perchlorate and hypochlorite medium. In Fig. 2 the pH dependence of the two characteristic absorption bands are presented. These results were used to calculate the molar absorptivities for the bands at  $852 \text{ nm}$  ( $\epsilon = 190 \pm 5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and  $862 \text{ nm}$  ( $\epsilon = 145 \pm 5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and to fix the experimental constraints of  $\text{pH}$ ,  $[\text{Pu(VI)}]$  and  $[\text{NaClO}]$  for two separate series of studies, wherein the  $\text{ClO}^-$  concentrations were varied at constant  $\text{pH} = 6.7$  and  $\text{pH} = 8.4$ .

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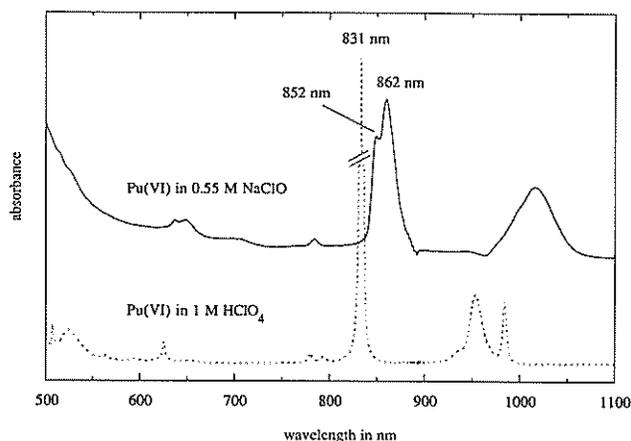


Fig. 1. Absorption spectrum of  $1.4 \cdot 10^{-3}$  M Pu(VI) in 0.55 M NaClO solution at pH 9.42; the standard spectrum of  $5 \cdot 10^{-3}$  M Pu(VI) in 1 M HClO<sub>4</sub> is also given for the purpose of comparison.

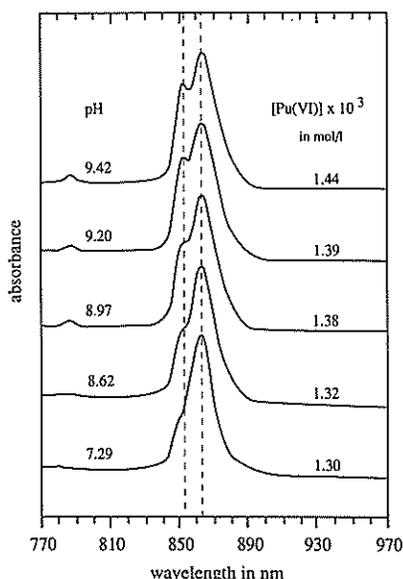
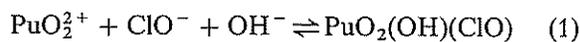


Fig. 2. Influence of pH on the absorption bands of Pu(VI) at 852 and 862 nm in 0.55 M NaClO solution.

The formation of the  $\text{PuO}_2(\text{OH})(\text{ClO})$  can be written as reaction (1) and its concentration given by Eq. (2) where  $K_{111}$  is the corresponding formation constant.



$$[\text{PuO}_2(\text{OH})(\text{ClO})] = K_{111} \cdot [\text{PuO}_2^{2+}] \cdot [\text{OH}^-] \cdot [\text{ClO}^-] \quad (2)$$

The plutonyl aquo-ion concentration  $[\text{PuO}_2^{2+}]$  can be described by  $K_{sp}/[\text{OH}^-]^2$ . From the absorbance at 852 nm and substituting  $K_w/[\text{H}^+]$  for  $[\text{OH}^-]$  the linear relation between the logarithm of the measured absorbance data and the logarithm of the free hypochlorite concentration  $[\text{ClO}^-]$  is:

$$\log A_{852} = \log(K_{111} \cdot K_{sp}/K_w) - \text{pH} + \log \epsilon_{852} + \log[\text{ClO}^-] \quad (3)$$

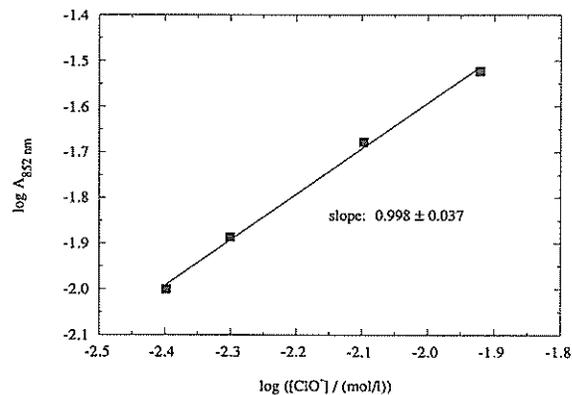


Fig. 3. Variation of the absorptivity at 852 nm with change of the  $\text{ClO}^-$  concentration at pH 6.7.

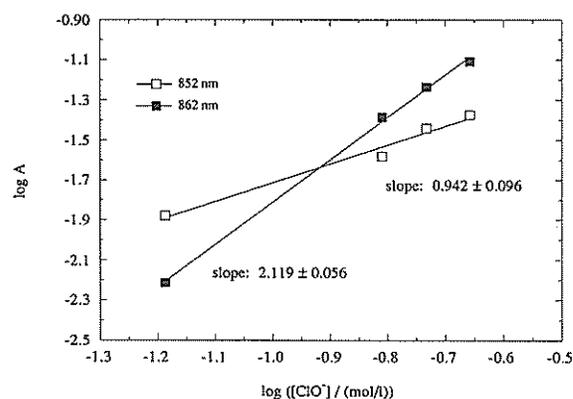
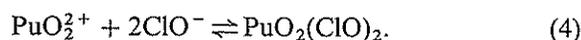


Fig. 4. Variation of the absorptivity at 852 and 862 nm with change of the  $\text{ClO}^-$  concentration at pH 8.4.

The variation of the absorptivity at 852 nm with change in the concentration of  $\text{ClO}^-$  at a constant pH 6.7 is presented in Fig. 3. From these data the logarithm of the formation constant  $K_{111}$  for reaction (1) is calculated to be 14.0 where  $\log K_{sp} = -23.0$  [11],  $\log K_w = 13.8$  in 0.55 M NaClO<sub>4</sub> [12] and  $\log \epsilon_{852} = 2.3$  in Eq. (3).

The results obtained at pH 8.4 for 852 and 862 nm are presented in Fig. 4. The treatment of the data at 852 nm yields a value of  $\log K_{111} = 14.5$  for reaction (1) in substantial agreement with the result at pH 6.7.

The data in Fig. 4 also demonstrate the second order  $[\text{ClO}^-]$  dependence of the absorptivity change at 862 nm. The formation of the  $\text{PuO}_2(\text{ClO})_2$  complex can be written as



The logarithm of the absorbance at 862 nm is linearly related to the  $\text{ClO}^-$  concentration via Eq. (5):

$$\log A_{862} = \log(K_{102} \cdot K_{sp}/K_w^2) - 2\text{pH} + \log \epsilon_{862} + 2\log[\text{ClO}^-] \quad (5)$$

From the data given in Fig. 4  $\log K_{102}$  is calculated to be 10.3 using the values noted above for the solu-

bility product of Pu(VI) hydroxide and ionization product of water and  $\log \varepsilon_{862} = 2.16$ .

The magnitude of the reaction between Pu(VI) and  $\text{ClO}^-$  is somewhat surprising since the predominant binding forces in the equatorial plane of the linear dioxoactinide cations are primarily electrostatic in nature. The electronic structure of  $\text{ClO}^-$  [13] may provide, in addition, an energetically feasible configuration for electron density transfer to an available  $6d$  orbital. This postulated orbital overlap is also consistent with the previous results on the redox reaction of the Pt complex [7]. In addition it provides an useful rationale for the facile kinetic behaviour of hypochlorite in the electron transfer reactions with a variety of transition metal ions [4–6].

### References

1. A part of the work is performed under the auspices of the Office of Basic Energy Sciences, USDOE under contract no. W-31-109-Eng38.
2. Büppelmann, K., Kim, J. I., Lierse, Ch.: *Radiochim. Acta* **44/45**, 65 (1988).
3. Connick, R. E.: *Oxidation, States, Potentials, Equilibria, and Oxidation-Reduction Reactions of Plutonium*. In: *The Transuranium Elements*, Chap. 8, Division IV, Vol. 14A, National Nuclear Series, McGraw Hill, New York 1954.
4. Lister, M. W.: *Can. J. Chem.* **31**, 638 (1953).
5. Lister, M. W.: *Can. J. Chem.* **34**, 575 (1956).
6. Zenker, G. I.: Dissertation, TU Berlin, pp. 35–38 (1954).
7. Drougge, L., Elding, L. I.: *Inorg. Chem.* **24**, 2292 (1985).
8. Cohen, D.: *J. Inorg. Nucl. Chem.* **18**, 217 (1961).
9. Gady, G. H., Naughton, J. M., Dexter, T. H.: *Inorg. Synth.* **5**, 156 (1957).
10. Friedman, H. L.: *J. Chem. Phys.* **21**, 319 (1953).
11. Kim, J. I., Bernkopf, M., Lierse, Ch., Koppold, F.: *Hydrolysis Reactions of Am(III) and Pu(VI) Ions in Near-Neutral Solutions*. In: *Geochemical Behavior of Disposed Radioactive Waste*, ed. by Barney, G. S., Navratil, J. D., Schulz, W. W., ACS Symposium Series **246**, 115 (1984).
12. Baes, Jr., C. F., Mesmer, R. E.: *Hydrolysis of Cations*, John Wiley and Sons, New York 1976.
13. Mulliken, R. S.: *J. Chem. Phys.* **3**, 577 (1935).