

# A study of colloid generation and disproportionation of Pu(IV) in aquatic solutions by LIBD and LPAS

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The tetravalent plutonium ion in aquatic solutions is known to be unstable even at low pH in dilute concentrations, because of its tendency towards colloid formation and/or disproportionation. Such particular properties of Pu(IV) have caused large difficulties in the assessment of its thermodynamic solubility in aquatic systems and thus resulted in a large number of controversial results [1]. Undergoing chemical reactions of Pu(IV) in dilute concentrations in the low pH region can only be recognized by sensitive speciation approaches.

The present work describes the combination of laser-induced breakdown detection (LIBD) [2] for colloid quantification and laser-induced photoacoustic spectroscopy (LPAS) [3] for measuring optical properties of the ionic state in order to study the aquatic chemical reactions of Pu(IV) in dilute concentrations. The chemical behaviour of the Pu<sup>4+</sup> ion is investigated below 10<sup>-4</sup> mol/l at low pH (0.3 – 2.0) for the colloid formation or disproportionation. The results allow to evaluate the solubility of Pu(IV) colloids, which corresponds very closely to the solubility of Pu(IV) hydroxide or oxy-hydrate, as is the case with Np(IV) [3].

The <sup>242</sup>Pu solution is prepared in 0.5 M HCl by electrochemical reduction of a mixture of oxidation states to Pu(III) and subsequent oxidation to Pu(IV) under UV spectroscopic control. The Pu concentration is assayed by liquid scintillation spectrometry. The solution pH is varied from 0.3 to 2.0 by appropriate dilution with 0.5 M NaCl to a desired value. Use of NaOH is avoided, because it contains latent colloidal impurities. The experiment is performed under ambient atmosphere at room temperature.

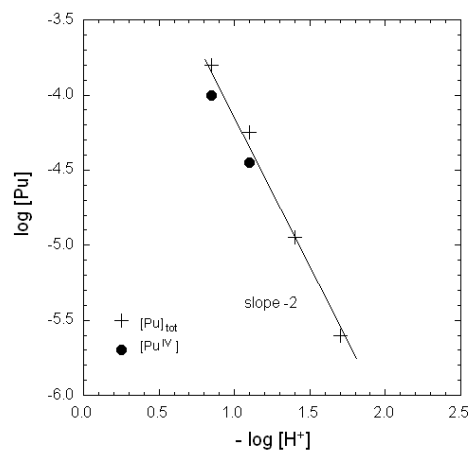


Fig.1: For decreasing Pu concentration the point of colloid formation is shifted to higher pH. From the slope -2 we infer the Pu(IV) to be present as dihydroxo-complex in equilibrium with colloids (solubility product  $\log K_{sp} = -59.0 \pm 0.3$ ).

The formation of Pu(IV) colloids is observed by LIBD at a certain pH when increasing the pH gradually to higher values. The breakdown events detected by acoustical monitoring of plasma generation on colloids [2] remains at a background level as in pure water at low pH. Once the pH is reached at which Pu(IV) colloids are beginning to form, the breakdown events become distinctively noticeable at  $\geq 1\%$  breakdown probability.

When the Pu(IV) concentration is gradually diluted, the pH of colloid-formation is increased accordingly. The points of Pu(IV) colloid formation as a function of pH, illustrated in Fig. 1, are narrowly scattered around a slope of -2. This particular slope suggests the reaction  $\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{Pu}(\text{OH})_2^{2+} + 2\text{H}^+$  to occur, which further undergoes colloid formation and thus  $\text{Pu}(\text{OH})_2^{2+}$  is in equilibrium with colloids. Knowing the hydrolysis constant of  $\text{Pu}(\text{OH})_2^{2+}$  [1], the solubility product of Pu colloids (presumably oxy-hydrate) can be derived from Fig. 1, which appears to be:  $\log K_{sp} = -59.0 \pm 0.3$  at zero ionic strength.

As the amount of Pu(IV) colloids is relatively small ( $< 5\%$  of the total Pu concentration) at a given pH of colloid formation, the remainder of the Pu(IV) ionic species undergoes disproportionation with time, i.e.  $3\text{Pu}(\text{IV}) + 2\text{H}_2\text{O} = 2\text{Pu}(\text{III}) + \text{Pu}(\text{VI}) + 4\text{H}^+$ . This reaction is observed then in situ by LPAS for Pu(IV) and Pu(III). Whereas a relatively small amount of Pu(IV) colloids present in this solution at pH 1.2 cannot be assessed by LPAS, such a minute concentration of colloids ( $< 10^{-6}$  mol/l Pu(IV)) can be on the other hand detected by LIBD. Therefore, a combination of LIBD and LPAS facilitates a sound assessment of chemical reactions of Pu(IV) involved at the rim of its solubility constrained pH for the total Pu(IV) concentration down to  $10^{-6}$  mol/l and for its colloids about 100 times less (down to a particle concentration of  $10^{-8}$  mol/l). In the literature, there is a wide scattering of values of the Pu(IV) solubility product published either for its oxide or for its hydroxide, the difference being a few orders of magnitude [1]. As a consequence, the solubility assessment of Pu(IV) remained with considerable uncertainties. The present experiment demonstrates how to avoid such uncertainties with the assistance of novel spectroscopic approaches.

## References:

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