

Solubility, Hydrolysis and Colloid Formation of Plutonium(IV)

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Summary

The solubility and hydrolysis behaviour of Pu(IV) is critically reviewed taking into account the effect of colloid formation. Literature data on mononuclear Pu(IV) hydrolysis constants, determined from a solvent extraction study with Pu(IV) trace concentrations, are used to calculate the solubility product of amorphous Pu(OH)₄(am) from the available experimental solubility data. Applying the SIT approach, the thermodynamic constant is calculated to be $\log K_{sp}^{\circ} = -58.7 \pm 0.9$. The evaluated solubility product agrees well with the literature value determined recently by an indirect method, independent of Pu(IV) hydrolysis reactions.

The generation of Pu(IV) colloids is investigated by chemical reduction of Pu(VI) as a function of the Pu concentration in 0.1 M HClO₄. Ultrafiltration and Laser induced breakdown detection (LIBD) measurements demonstrate that colloid formation is the predominant reaction, when the solutions are oversaturated with respect to the thermodynamic solubility of Pu(OH)₄(am). In undersaturated solutions, the contribution of Pu(IV) colloids is negligible. The thermodynamic calculation of the solubility is consistent with the present results on colloid formation.

1. Introduction

Tetravalent actinide ions with their high electric charge have an inordinate tendency toward hydrolysis in aqueous solution. They undergo polynucleation or further to colloid formation [1-3]. Moreover, in acidic solutions Pu(IV) is easily oxidized to Pu(V), which disproportionates into Pu(III) and Pu(VI) [4-6]. Such underlying problems complicate the thermodynamic evaluation of the hydrolysis and solubility constants of Pu(IV).

The chemical nature of fresh or aged Pu(IV) precipitates is not yet clear, either they are assumed as amorphous hydroxide Pu(OH)₄(am) or hydrous oxide PuO₂ · xH₂O(s). A wide scattering of their published solubility products (cf. reviews in [3, 5]) prompts us to reevaluate critically the hitherto available data in the literature. The discrepancies among the published solubility products are mainly ascribed to the following reasons:

(1) The solubility data do not refer to a well-defined solid phase. The degree of crystallinity, particle size, crystal water content and hence the Gibbs free energy of formation for An(IV) hydroxides or oxides

depend on the preparation, pretreatment and alteration [7-10].

(2) As the Pu⁴⁺ ion undergoes hydrolysis reactions even at low pH, the solubility product evaluated from experimental solubilities depends directly on the hydrolysis constants applied to calculate the Pu⁴⁺ concentration.

(3) The Pu(IV) hydrolysis in weakly acidic solutions leads to polynucleation, which grows further to colloidal aggregation [2]. As demonstrated by Kim and Kanellakopoulos [3], colloidal Pu(IV) can be produced even at pH 0-1 for the Pu concentration below 10⁻³ mol/l. Colloids may be considered as long-time metastable amorphous particles. They remain stable in solution, devoid of precipitation from oversaturated solutions, and lead to Pu(IV) concentrations significantly exceeding the thermodynamic solubility.

In order to ascertain the influence of colloids possibly involved in the published solubility and hydrolysis data of Pu(IV), the present study exploits an experimental investigation to quantify the colloid formation as a function of the Pu(IV) concentration in acidic solutions.

2. Discussion of literature data on the hydrolysis of Pu(IV) and thermodynamic evaluation of the solubility product of Pu(OH)₄(am)

2.1 Hydrolysis constants

At low concentrations, the hydrolysis reactions of tetravalent actinide ions An⁴⁺(aq) lead to the formation of mononuclear complexes An(OH)_n⁽⁴⁻ⁿ⁾, with n = 1-4. It is not yet confirmed whether or not the anionic species An(OH)₄⁻ is formed in strongly alkaline solutions. At higher An(IV) concentrations, polynuclear species are formed. The hydrolysis constants K'_{1n} (in a given medium) and K^o_{1n} (at infinite dilution), and the corresponding formation constants β_{1n} and β^o_{1n} for the species An_n(OH)_n⁽⁴⁻ⁿ⁾ are given by

$$K'_{1n} = \frac{[An_n(OH)_n]^{(4-n)} [H^+]^n}{[An^{4+}]^n} = K^o_{1n} (\gamma_{An})^n (a_w)^n / (\gamma_{An(OH)_n}) (\gamma_H)^n \quad (1)$$

and

$$\beta_{1n} = \frac{[An_n(OH)_n]^{(4-n)}}{[An^{4+}]^n [OH^-]^n} = \beta^o_{1n} (\gamma_{An})^n (\gamma_{OH})^n / (\gamma_{An(OH)_n}) \quad (2)$$

respectively. [i] is the concentration of species i, γ_i its activity coefficient and a_w the activity of water.

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Table 1. Literature data for Pu(IV) hydrolysis constants at 20–25°C (molar scale) and the values converted to $I = 0$ with the SIT approach.

Medium/Species	$\log K'_1$	$\log K'_2$	$\log \beta^0$	Method ^a	Ref.
1.0 M HClO ₄ /LiClO ₄ , room temp., 10^{-2} – 10^{-3} M H ⁺ , 10^{-3} M ²³⁸ Pu(IV)				extr	[16, 17]
Pu(OH) ³⁺	-0.45	0.60	14.6 ± 0.2		
Pu(OH) ₂ ²⁺	-1.2	0.63	28.6 ± 0.3		
Pu(OH) ₃ ⁺	-4.5	-2.25	39.7 ± 0.4		
Pu(OH) ₄ (aq)	-10.8	-8.54	47.5 ± 0.5		
Pu(OH) ₃ ⁺					
0.5 M HCl/NaCl, 25°C, 0.01–0.5 M H ⁺ , $7.2 \cdot 10^{-4}$ M Pu(IV)	-1.65	-0.63	13.37	spec	[11]
0.5 M HClO ₄ /NaClO ₄ , 25°C, 0.01–0.5 M H ⁺ , $7.2 \cdot 10^{-4}$ M Pu(IV)	-1.60	-0.64	13.36	spec	[11]
2.0 M HClO ₄ /NaClO ₄ , 25°C, 0.01–2.0 M H ⁺ , 10^{-3} M Pu(IV)	-1.73	-0.70	13.30	spec	[12]
0.19 M HClO ₄ , 23°C, $1.8 \cdot 10^{-3}$ M Pu(IV)	-1.96	-1.19	12.81	spec	[13]
0.06 M HClO ₄ , 23°C, $1.6 \cdot 10^{-3}$ M Pu(IV)	-1.48	-0.94	13.06	spec	[13]
1.0 M HClO ₄ /NaClO ₄ , 25°C, 0.1–0.2 M H ⁺ , 10^{-3} M Pu(IV)	-1.51	-0.45	13.55	redox	[14]
2.0 M HClO ₄ /LiClO ₄ , 25°C, 0.1–2.0 M H ⁺ , $8 \cdot 10^{-3}$ M Pu(IV)	-1.27	-0.24	13.76	redox	[15]

^a extr = solvent extraction; spec = spectroscopy; redox = Pu(III)/Pu(IV) redox potential.

The hydrolysis constants reported in the literature for Pu(IV) are summarized in Table 1. A number of spectroscopic studies are performed in the range pH 0–2 [11–13], and the decrease of the characteristic Pu(IV) absorption bands is ascribed to the initial mononuclear hydrolysis step ($\text{Pu}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{3+}$). However, the total Pu(IV) concentrations used in these studies ($[\text{Pu(IV)}] = 7 \cdot 10^{-4}$ – $2 \cdot 10^{-3}$ M) considerably exceed the solubility limit of Pu(OH)₄(am) at pH 1–2 (cf. section 2.3). According to the present investigation, the colloid formation is expected to be the predominant reaction in these studies, and hence the reported data are disregarded. The same holds for the two studies on the Pu(III)/Pu(IV) redox couples [14, 15]. Solely the stepwise hydrolysis constants reported by Metivier and Guillaumont [16, 17] are determined in undersaturated solutions, by solvent extraction using Pu-238 in trace concentrations. These constants ($\log K^*_1 = -0.45$, $\log K^*_2 = -0.75$, $\log K^*_3 = -3.3$ and $\log K^*_4 = -6.3$ in 1.0 M HClO₄/LiClO₄ [16, 17]) are considered to be the most reliable data on the hydrolysis of Pu(IV). As no experimental uncertainties are given in these papers [16, 17], they are estimated to be about 0.2 logarithmic units for each hydrolysis step. Fig. 1 shows the corresponding speciation of Pu(IV). Even in 1 M HClO₄, the Pu⁴⁺ aquo ion is partially hydrolysed. In neutral to alkaline solutions, the complex Pu(OH)₄⁰(aq) is predominant.

2.2 Ionic strength corrections and ion interaction (SIT) coefficients

In the present study, the specific ion interaction theory (SIT) [18] is applied for the calculation of activity coefficients. The simple SIT equation is preferred to the more elaborated Pitzer approach [19], because with the present knowledge and experimental data, it is not possible to evaluate the Pitzer parameters necessary to calculate activity coefficients for Pu(IV) hydrolysis

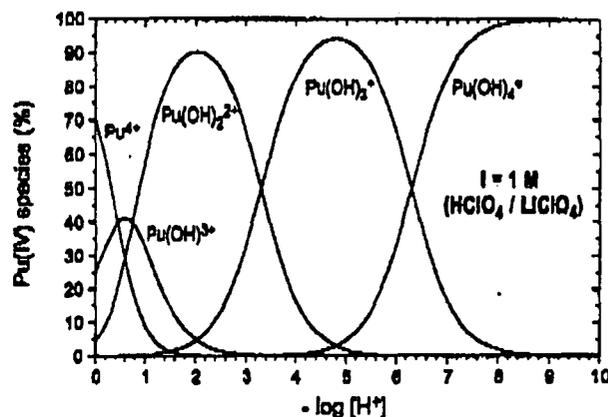


Fig. 1. The Pu(IV) speciation in carbonate-free 1 M HClO₄/LiClO₄ at 25°C, calculated for Pu(IV) trace concentrations with the hydrolysis constants from Metivier and Guillaumont [16].

species. According to the SIT approach, activity coefficients γ_i are given by

$$\log \gamma_i = -z_i^2 D + \sum \epsilon_{ij} m_j \quad (3)$$

where z_i is the charge of ion i , m_j (mol/kg H₂O) the molal concentration of ion j , and D the Debye-Hückel term, at 25°C: $D = 0.509 \sqrt{I} / (1 + B \bar{a} \sqrt{I})$, with $B \bar{a} = 1.5$. I is the molal ionic strength and ϵ_{ij} the ion-ion interaction parameter for a pair of oppositely charged ions. The coefficients ϵ_{ij} used in the present study are summarized in Table 2. Unknown interaction coefficients are estimated according to known analog ions of similar charge, structure and size, systematics in the series of tetravalent actinides, and differences between the interaction coefficients for $M^{4+}\text{Cl}^-$ and $M^{4+}\text{ClO}_4^-$ (cf. ϵ_{ij} values given in the NEA review on uranium [10]). In order to minimize uncertainties arising from the estimated SIT coefficients, the present calculations are restricted to $I \leq 1$ mol/kg.

Table 2. Ion interaction (SIT) coefficients at 25°C used in the present study.

i	j	ϵ_{ij}
H ⁺	ClO ₄ ⁻	0.14 ± 0.02 ^a
H ⁺	Cl ⁻	0.12 ± 0.01 ^a
OH ⁻	Na ⁺	0.04 ± 0.01 ^a
Pu ⁴⁺	ClO ₄ ⁻	0.83 ± 0.1 ^b
Pu(OH) ³⁺	ClO ₄ ⁻	0.5 ± 0.1 ^b
Pu(OH) ₂ ²⁺	ClO ₄ ⁻	0.3 ± 0.1 ^c
Pu(OH) ₃ ⁺	ClO ₄ ⁻	0.15 ± 0.1 ^c
Pu ⁴⁺	Cl ⁻	0.4 ± 0.1 ^c
Pu(OH) ³⁺	Cl ⁻	0.2 ± 0.1 ^c
Pu(OH) ₂ ²⁺	Cl ⁻	0.1 ± 0.1 ^c
Pu(OH) ₃ ⁺	Cl ⁻	0.05 ± 0.1 ^c
Pu(OH) ₄ ⁰	j	0

^a From the NEA-TDB [10].

^b Capdevila and Vitorge [5] reported two independently determined values: 0.85 ± 0.20 and 0.82 ± 0.07. The value of 1.03 ± 0.05 given in the NEA-TDB [10] (from the previous work of Vitorge *et al.*) has to be revised.

^c Estimated in the present study according to the analogies and systematics pointed out in the NEA-TDB [10].

2.3 Solubility product of Pu(IV) hydroxide/hydrous oxide

The solubility of Pu(OH)₄(am) or PuO₂ · xH₂O(s) has been investigated over several decades [3, 5–7, 20–24]. Figs. 2a and b show the experimental Pu(IV) concentrations reported in 1 M HClO₄/NaClO₄ and in acidic solutions of low ionic strength, respectively. As already mentioned, the scattering of the reported data may be ascribed to different solid phases used. The most striking example is a large difference between the solubilities measured by Kim and Kanellakopoulos [3] in 1 M HClO₄ with PuO₂(cr) sintered at 900°C and an amorphous precipitate of Pu(OH)₄(am). Contributions from colloids are another possible source of uncertainties. However, the reported solubility data are usually measured after filtration in order to minimize this effect. Particularly at pH > 1.5, Pu(IV) is easily oxidized to Pu(V), and disproportionation reactions lead to Pu(III) and Pu(VI) [3–7]. Therefore, the oxidation state of the aqueous species has to be controlled by solvent extraction or spectroscopic methods as done in a number of studies [3, 5, 6, 20, 21]. The data of Pérez-Bustamante [22] in 0.001–0.03 M HClO₄ (Fig. 2b) represent a typical example for the solubility increase due to aqueous species of other oxidation states. Similar data are reported in other papers [7, 21, 23, 24], with aqueous species of different oxidation states being predominant and the fraction of Pu(IV) not known. They are disregarded in the present discussion. The solubility product of Pu(OH)₄(am) or PuO₂ · xH₂O(s) is defined by

$$K'_{sp} = [\text{Pu}^{4+}][\text{OH}^-]^4 \quad (4)$$

with

$$K^{\circ}_{sp} = K'_{sp} (\gamma_{\text{Pu}}) (\gamma_{\text{OH}})^4 \quad (\text{for Pu(OH)}_4(\text{am})) \quad (5)$$

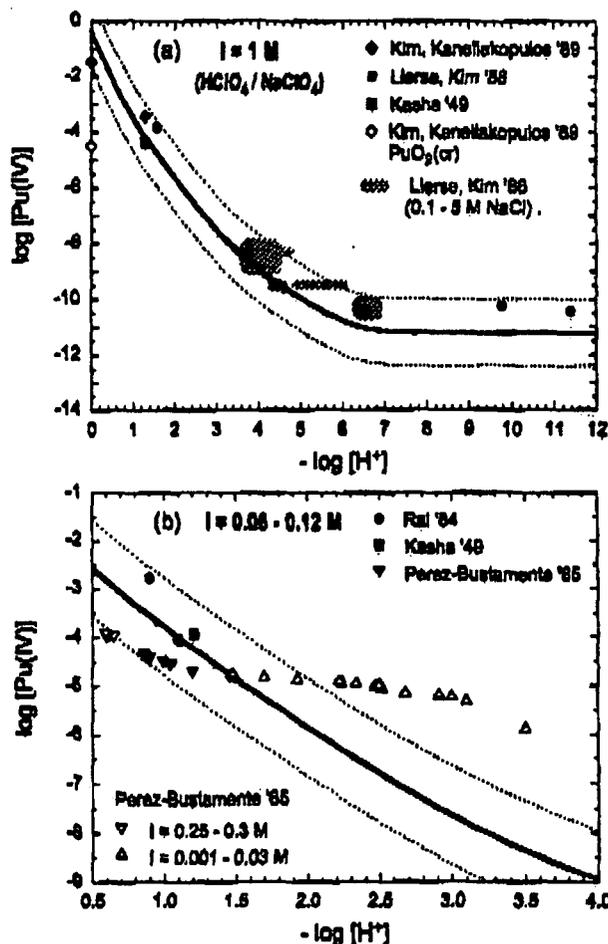


Fig. 2. Solubility of Pu(IV) hydroxide as a function of the H⁺ concentration at 20–25°C, (a) in 1 M HClO₄/NaClO₄ (above), (b) in acidic solutions at low ionic strength (below). The experimental data are from [3, 6, 20–22]. The solid line is calculated for I = 1 and 0.1 mol/l, respectively, with log K[°]_{sp} = -58.7 and the hydrolysis constants from [16]. The dotted lines show the range of uncertainty.

or

$$K^{\circ}_{sp} = K'_{sp} (\gamma_{\text{Pu}}) (\gamma_{\text{OH}})^4 (\alpha_{\text{H}})^{4-2j} \quad (\text{for PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})). \quad (6)$$

If the Pu(IV) concentration of polynuclear and colloidal species is small compared to that of mononuclear hydrolysis species, the solubility is given by

$$[\text{Pu(IV)}]_{\text{tot}} = (K'_{sp}/[\text{OH}^-]^4) (1 + \sum K'_{sp} \beta'_{ij} [\text{OH}^-]^j). \quad (7)$$

Applying Eq. (7) and the hydrolysis constants of Metivier and Guillaumont [16], the solubility product of Pu(IV) hydroxide or hydrous oxide is calculated from the published solubility data. The results are summarized in Table 3. An overall mean value is found to be

$$\log K^{\circ}_{sp} = -58.7 \pm 0.9.$$

Fig. 2 shows the pH-dependent solubility calculated with the hydrolysis constants of Metivier and Guillaumont [16] (solid line) together with experimental solubilities. Within the range of uncertainty, the calculated

Table 3. Experimental solubility data for Pu(IV) hydroxide/hydrous oxide at 20–25 °C, and the solubility products $\log K'_{sp}$ (molar scale) and $\log K^{\circ}_{sp}$ calculated with the hydrolysis constants and SIT coefficients selected in the present study.

Authors/Medium	$\log [\text{Pu(IV)}]_{\text{ex}}$	$\log K'_{sp}$	$\log K^{\circ}_{sp}$
Kasha (1949) [20] 1 M NaClO ₄ /0.05 M H ⁺ 0.06 M HCl	-4.34	-55.9 ± 0.3	-58.9 ± 0.3
	-3.95	-56.6 ± 0.3	-58.4 ± 0.3
Pérez-Bustamente (1965) [22] 0.06–0.12 M HClO ₄ 0.25–0.29 M HClO ₄	-4.72 to -4.35	-57.4 ± 0.4	-59.4 ± 0.4
	-3.96 ± 0.03	-57.3 ± 0.3	-59.9 ± 0.3
Rai (1984) [6] I = 0.112 M, pH = 1.00 ^a I = 0.064 M, pH = 1.20 ^a	-2.77	-55.8 ± 0.3	-58.0 ± 0.3
	-4.03	-56.9 ± 0.3	-58.7 ± 0.3
Lierse and Kim (1986) [21] 1 M NaClO ₄ , pH _{exp} = 1.38 ^b 1 M NaClO ₄ , pH _{exp} = 9–12	-3.83	-54.8 ± 0.3	-57.8 ± 0.3
	-10.4 ± 0.4	-54.9 ± 0.6	-57.9 ± 0.6
Kim and Kanellakopoulos (1989) [3] 1 M HClO ₄ 1 M NaClO ₄ , pH _{exp} = 1.09 ^a	-1.48	-56.9 ± 0.2	-59.9 ± 0.3
	(-2.20) -3.44	-57.4 ± 0.2 -55.0 ± 0.3	-60.4 ± 0.3) ^c -58.0 ± 0.3
Capdevila and Vitorge (1998) [5] I = 0 0.1 M HClO ₄ 0.1 M HClO ₄ /0.4 M NaClO ₄ 0.1 M HClO ₄ /0.9 M NaClO ₄ 0.1 M HClO ₄ /1.9 M NaClO ₄ 0.1 M HClO ₄ /2.9 M NaClO ₄			-58.3 ± 0.5
		-55.9 ± 0.3 ^d	-58.0 ± 0.3
		-55.7 ± 0.3 ^d	-58.7 ± 0.3
		-55.0 ± 0.3 ^d	-58.0 ± 0.3
		-56.0 ± 0.3 ^d	-58.4 ± 0.3
		-56.7 ± 0.3 ^d	-58.1 ± 0.3

^a The H⁺ concentration is derived from $\text{pH} = -\log [\text{H}^+] - \log \gamma_{\text{H}^+}$ by calculating the activity coefficients γ_{H^+} with the SIT equation.

^b The H⁺ concentration is calculated with the relation: $\log [\text{H}^+] = -\text{pH}_{\text{exp}} - 0.23$ [31] for pH measurements with Ross electrodes (3 M NaCl junction) in 1 M NaClO₄.

^c Calculated with the spectroscopically determined value of $\log [\text{Pu}^{4+}] = -2.20$.

^d Determined by an indirect method, independent of Pu(IV) hydrolysis reactions (see text).

solubility curve covers many experimental data, even a couple of data reported by Lierse and Kim [21] for ²³⁹PuO₂(s) in 0.1–5 M NaCl in the range pH = 3–7. From the experimental solubility determined by Kim and Kanellakopoulos [3] with a crystalline PuO₂(cr) equilibrated for 3 years in 1 M HClO₄ ($\log [\text{Pu(IV)}] = -4.5 \pm 0.2$, Fig. 2a), a solubility product of $\log K^{\circ}_{sp} = -62.9 \pm 0.4$ is calculated. This value differs somewhat from those calculated from thermochemical data ($\log K^{\circ}_{sp}(\text{PuO}_2(\text{cr})) = -63.8 \pm 1.0$ [3] and -64.1 ± 0.7 [25]).

Recently, the solubility product of amorphous Pu(IV) hydroxide has been evaluated with an indirect method (Capdevila and Vitorge [5]). In that study, the solubility of Pu(OH)₄(am) is investigated under conditions, where PuO₂⁺, PuO₂²⁺ and Pu³⁺ are the predominant aqueous species. Their concentrations are determined spectroscopically. When the disproportionation reaction reaches the equilibrium state, the Pu⁴⁺ concentration can be calculated from the known redox potentials $E(\text{Pu}^{4+}/\text{Pu}^{3+})$ and $E(\text{PuO}_2^{2+}/\text{PuO}_2^+)$. The thermodynamic solubility product of Pu(OH)₄(am) is then obtained from the experimental data in 0.1–3 M NaClO₄ by extrapolation to I = 0 with the SIT: $\log K^{\circ}_{sp} = -58.3 \pm 0.5$ [5]. This value agrees very

well with the present result, although it is evaluated by a completely different method, which is independent of Pu(IV) hydrolysis reactions.

3. Investigations on the formation of Pu(IV) colloids

The generation of Pu(IV) colloids is investigated by chemical reduction of Pu(VI) to Pu(IV) as a function of the Pu concentration in 0.1 M HClO₄. Besides concentration measurements after filtration at different filter pore sizes (400 nm and 1 nm), the colloid formation is investigated by means of Laser Induced Breakdown Detection (LIBD). The principle of the LIBD is described in detail by Kitamori *et al.* [26, 27] and Scherbaum *et al.* [28]. The method is based on the plasma generation on colloids in the focal volume of a pulsed laser beam. Because the critical power density needed to produce plasma is lower on solids than on liquids, the plasma can be generated selectively on dispersed particles, by adjusting the laser pulse power density below the breakdown threshold of water. Detecting the number of breakdown events per number of laser pulses, a breakdown probability can be calcu-

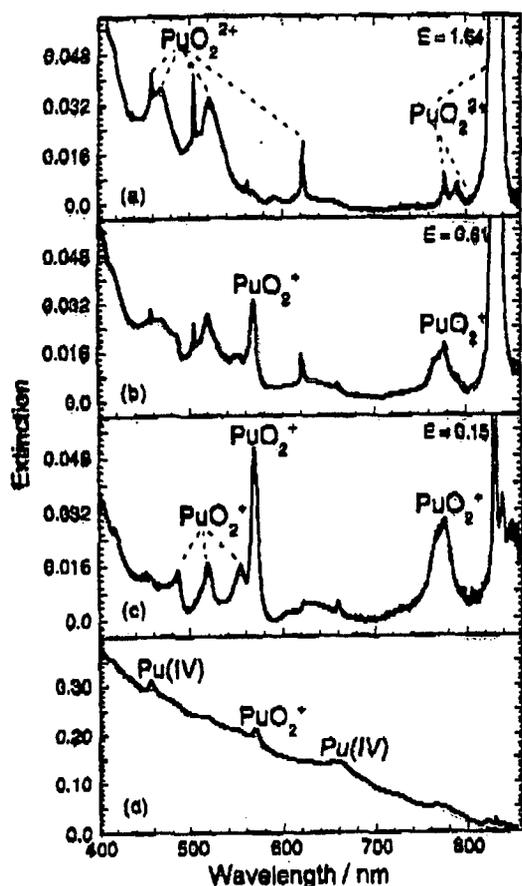


Fig. 3. Absorption spectra of the $3 \cdot 10^{-3}$ M Pu(VI) stock solution in 0.1 M HClO_4 (a), and 5 min, 60 min and 40 hours after adding an appropriate amount of H_2O_2 (b, c and d, respectively). In spectrum d), the continuous increase of the extinction at lower wavelength is caused by light scattering due to the presence of Pu(IV) colloids.

lated, which correlates with the mass concentration of colloids of given particle size and material. The method is very sensitive for small colloids of some nm in diameter [28]. The detection limit is found to be in the ppt range [29]. The applicability of LIBD for actinide colloids has been verified by direct measurement of Th(IV) colloids with a diameter ≈ 20 nm [30]. The colloidal Th(IV) concentration of $[\text{Th}]_{\text{coll}} = 4 \cdot 10^{-10}$ mol/l can be detected, and hence the corresponding concentration of Pu colloids is detectable as well.

3.1 Experimental

A $3 \cdot 10^{-3}$ M Pu(VI) stock solution ($>99\%$ Pu-242) is prepared by dissolving $\text{PuO}_2\text{CO}_3(\text{s})$ in 0.1 M HClO_4 . Traces of Pu(III), Pu(IV) and Pu(V) are oxidized by bubbling ozone through the solution, which is then filtered through an ultrafilter of 1 nm pore size. Aliquots of the stock solution are diluted with 0.1 M HClO_4 to obtain Pu concentrations in the range $1.7 \cdot 10^{-2}$ – $3.5 \cdot 10^{-6}$ mol/l, and reduced at room temperature by adding a small amount of H_2O_2 (30% in H_2O , p.a. from Merck Co.). The reduction of Pu(VI), via Pu(V),

to Pu(IV) is monitored by UV/VIS absorption spectroscopy, recording spectra after 5 min, 60 min and 40 hours (Fig. 3). After 3–5 days, the absorption spectra show only the mononuclear and colloidal Pu(IV) species. Species of other oxidation states cannot be detected. In order to ensure the complete reduction, filtration experiments are performed ten days after reduction. For the colloid size classification, the solutions are filtered in triplicate, using filters of pore size 400 nm (Nucleopore 110407 PC) and 1 nm (Amicon YM1). The concentrations of ^{242}Pu in the initial solutions and filtered fractions are determined radiometrically with a Beckman LS 6800 liquid scintillation counter, and the laser induced photoacoustic breakdown detection (LIBD) is used for colloid detection. The experimental setup of the LIBD and its calibration with reference colloids have been described previously [28].

3.2 Results

The filtration results, the Pu(IV) concentrations and breakdown probabilities for the initial solutions and filtered fractions are shown in Table 4. In the experiments A and B, with the respective initial Pu concentrations of $1.73 \cdot 10^{-2}$ mol/l and $3.11 \cdot 10^{-4}$ mol/l, a significant filtration effect is observed. In the case of the solution A, which is considerably oversaturated with respect to the thermodynamic solubility of $\text{Pu}(\text{OH})_4(\text{am})$ (cf. Fig. 2), about 63% of the Pu(IV) is removed by 400 nm filtration. The rest of the plutonium passes almost completely through the 1 nm filter. The formation of a filter cake is observed visually, which may explain the relatively large standard deviation for the Pu concentration in the filtrates. Because of the relatively large uncertainties of the Pu concentration in the filtrates, $\pm 8.0\%$ and $\pm 10\%$, respectively, the contribution of colloids to the Pu concentration in the filtrates cannot be distinguished. However, the LIBD measurements indicate the presence of a relatively small amount of Pu colloids in the 400 nm filter fraction, which is then removed by filtration at 1 nm pore size. In experiment B with $[\text{Pu}] = 3.11 \cdot 10^{-4}$ mol/l, only 13% Pu is removed by 400 nm filtration and 22% by 1 nm filtration. Fig. 4 illustrates the proportionality between the Pu(IV) concentration in the filter fractions and the colloids detected by LIBD. Nearly equal breakdown probabilities are found in the fractions smaller and larger than 400 nm, whereas in experiment A, about 98% of the breakdown events in the initial solution are caused by colloids larger than 400 nm in diameter (Table 4). After 1 nm filtration, the breakdown probabilities are in the range of those measured in 0.1 M HClO_4 (without Pu), i.e. the remaining amount of colloidal particles is negligible.

In experiments C ($[\text{Pu}] = 3.33 \cdot 10^{-6}$ mol/l) and D ($[\text{Pu}] = 3.54 \cdot 10^{-6}$ mol/l), no decrease in the Pu concentration can be recognized after filtration. The accuracy of the LSC measurements sets an upper limit for

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Table 4. Filtration and LIBD experiments for Pu(IV) solutions in 0.1 M HClO₄: the effect of filter pore size on the Pu concentration and breakdown probability.

Experiment	[Pu] (mol/l) ^a	Breakdown probability	
		all colloids	Pu colloids ^b
A	prior to filtration	$(1.73 \pm 0.05) \cdot 10^{-3}$	135.7 ± 15.0^b
	after 400 nm filtration	$(6.38 \pm 0.51) \cdot 10^{-4}$	3.23 ± 0.46^b
	after 1 nm filtration	$(6.51 \pm 0.66) \cdot 10^{-4}$	0.025 ± 0.012
B	prior to filtration	$(3.11 \pm 0.01) \cdot 10^{-4}$	1.77 ± 0.12^b
	after 400 nm filtration	$(2.72 \pm 0.06) \cdot 10^{-4}$	0.89 ± 0.03
	after 1 nm filtration	$(2.04 \pm 0.14) \cdot 10^{-4}$	0.018 ± 0.008
C	prior to filtration	$(3.33 \pm 0.04) \cdot 10^{-4}$	0.208 ± 0.029
	after 400 nm filtration	$(3.35 \pm 0.02) \cdot 10^{-4}$	0.121 ± 0.012
	after 1 nm filtration	$(3.35 \pm 0.06) \cdot 10^{-4}$	0.015 ± 0.007
D	prior to filtration	$(3.54 \pm 0.07) \cdot 10^{-4}$	0.175 ± 0.015
	after 400 nm filtration	$(3.52 \pm 0.05) \cdot 10^{-4}$	0.140 ± 0.019
	after 1 nm filtration	$(3.52 \pm 0.08) \cdot 10^{-4}$	0.016 ± 0.012

^a Mean values and standard deviation of three independent experiments.

^b In order to measure the breakdown probability, the solution was diluted and the measured values are summed up.

^c The breakdown probabilities caused by Pu colloids is calculated from the total value by subtracting the mean value observed in the corresponding fractions in C and D.

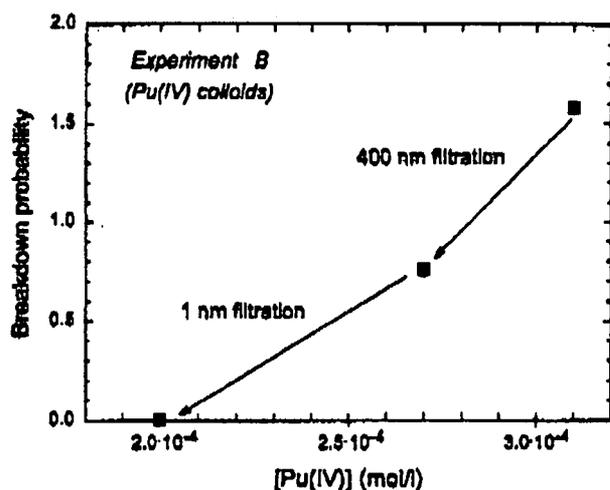


Fig. 4. The effect of filtration on the Pu concentration and breakdown probability caused by Pu(IV) colloids in the experiment B.

the colloidal Pu concentration in these samples, which is less than 1% of the initial concentration. The breakdown probabilities in the unfiltered solutions and the fractions 1–400 nm indicate the presence of small amounts of colloids. Although the Pu concentration is decreased one order of magnitude from C to D, the breakdown probabilities in the corresponding fractions remain constant. Therefore, the measured breakdown probabilities cannot be ascribed to Pu colloids but rather to artefacts, i.e. to colloids generated in the solutions during the experimental procedure. In order to distinguish between these artefacts and Pu colloids, the mean values observed in the corresponding fractions of the experiments C and D are subtracted from the total breakdown signals (Table 4).

4. Comparison between thermodynamic calculations and the present investigations on Pu(IV) colloid formation

In Fig. 5 the results of the filtration experiments in 0.1 M HClO₄ are compared with the solubility calculated for Pu(OH)₄(am) at I = 0.1 mol/l using the selected thermodynamic constants as mentioned above. In experiments A and B, where the initial Pu concentration exceeds the calculated solubility, appreciable amounts of colloids have been detected. In experiments C and D, where the initial Pu concentration is below the calculated solubility, the Pu concentration is not affected by 1 nm filtration, and the amount of colloidal Pu(IV) is found to be less than 1%. Considering colloids as small amorphous solid particles, the filtration experiments provide information on the Pu(IV) saturation concentration (excluding colloids). By calculating the Pu(IV) speciation in 0.1 M HClO₄ (log [OH⁻] = -12.80) with the hydrolysis constants of Metivier and Guillaumont [16] converted to I = 0.1 mol/l: 2.3% Pu⁴⁺, 20.6% Pu(OH)³⁺, 76.5% Pu(OH)₂²⁺, 0.6% Pu(OH)₃⁺, the following values are obtained for the solubility product of amorphous colloidal Pu(IV) particles:

$$\text{Exp. A: } \log [\text{Pu(IV)}] < -3.19 \\ \Rightarrow \log K'_{sp} < -56.0; \log K^{\circ}_{sp} < -58.1$$

$$\text{Exp. B: } \log [\text{Pu(IV)}] \approx -3.69 \\ \Rightarrow \log K'_{sp} \approx -56.5; \log K^{\circ}_{sp} \approx -58.6$$

$$\text{Exp. C: } \log [\text{Pu(IV)}] > -4.48 \\ \Rightarrow \log K'_{sp} > -57.3; \log K^{\circ}_{sp} > -59.4.$$

These upper and lower limits are consistent with $\log K^{\circ}_{sp} = -58.7 \pm 0.9$, the grand average value evaluated from the solubility data given in Table 3. This indicates that the estimation of the solubility

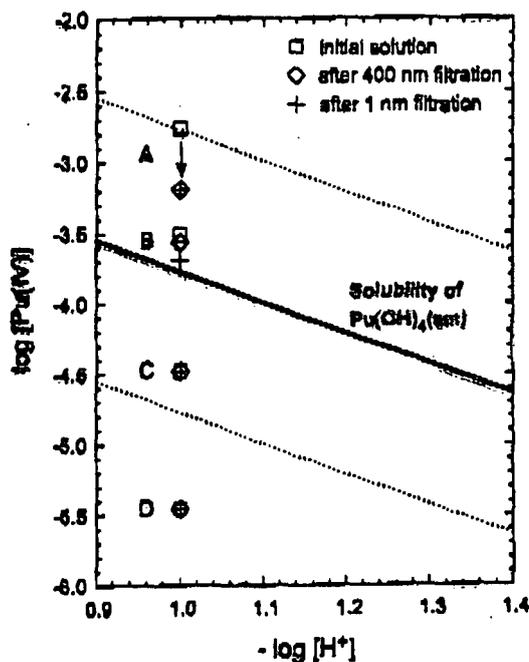


Fig. 5. The results of the filtration experiments in comparison with the calculated thermodynamic solubility of $\text{Pu}(\text{OH})_4(\text{am})$ (solid line).

product, including a minor amount of colloids possibly present, does not exceed the range of other uncertainties, e.g. different degrees of crystallinity of amorphous solid phases. Small polynuclear species like oligomers and colloids with diameters < 1 nm are not detectable by LIBD. However, the difference in $[\text{Pu}(\text{IV})]$ after 1 nm filtration in the experiments A through B is relatively small. Moreover, the pH-dependent solubility is well described by the mononuclear hydrolysis constants from Metivier and Guillaumont [16], as shown by

the solid line in Fig. 2a. This leads to the conclusion that small polynuclear or colloidal species < 1 nm do not contribute considerably to the solubility of $\text{Pu}(\text{OH})_4(\text{am})$.

Fig. 5 indicates that a systematic investigation on the initial colloid formation as a function of pH and the total actinide concentration provides the possibility to evaluate thermodynamic data for amorphous precipitates. Therefore, the LIBD investigations reported for Th(IV) [29, 30] might be helpful to evaluate the thermodynamic solubility of Th(IV) hydroxide or hydrous oxide, for which the published thermodynamic constants are extremely scattered.

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