Solubility Product of Pu(OH)$_{4(am)}$

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Abstract

For the safety assessment of nuclear waste geological disposal, it is important to know how to calculate the plutonium solubility in reducing conditions. Published values of the solubility product of Pu(OH)$_{4(am)}$, vary by more than 10 orders of magnitude. It is shown in this paper, that Pu(IV) disproportionation, occurring in moderate acidic medium, can induce wide discrepancy in experimental determinations. Typically, the soluble plutonium species in equilibrium with the solid phase Pu(OH)$_{4(am)}$ is PuO$_2^+$ when pH is increased from 0 to 1 by titrating Pu^{4+} acidic solution with NaOH. Only two published works have taken into account this problem in their interpretation, but the extrapolation at the standard state rely only on one experimental value at one ionic strength.

In the present work, the chemical conditions have been chosen to reach a steady state between a Pu(IV) solid phase and PuO$_2^{2+}$, PuO$_2^+$, Pu^{3+} aqueous species in a concentration range high enough to be directly and independently measured by UV/Visible spectrophotometry. The speciation was then controlled. The redox potential of the solution at equilibrium, E, was calculated from the measured [PuO$_2^{2+}$]/[PuO$_2^+$] ratio and the known formal potential of this couple. [Pu^{4+}] was then deduced from E, [Pu^{3+}] and the known Pu^{4+}/Pu^{3+} formal potential. In this way, [Pu^{4+}] is determined without approximation   even if side reactions (for instance hydrolysis) cannot be avoided. pH was measured and *K$_s$ was then obtained at different ionic strength from 0.1 to 3 M in sodium perchlorate solutions. The experimental values were extrapolated to the standard state (I = 0) using the specific interaction theory (S.I.T).

Introduction

In order to assess the safety of radioactive waste disposal in geological formations, one needs to predict the migration of radioelements, especially soluble species of actinides, in groundwater. Plutonium is one of the important elements to consider because of its high toxicity and long half-life. In reducing conditions, tetravalent plutonium chemical species are commonly considered as the most stable ones and used to assess the safety of nuclear waste disposal. The predicted solubility (the total concentration of aqueous species available for

migration) relies on complexation constants, redox potentials and solubility product of the solid phase. This work deals with the determination of the solubility product of $Pu(OH)_{4(am)}$ which will often control the Pu solubility. The ageing of $Pu(OH)_{4(am)}$ might form PuO_2, increasing cristallinity and then decreasing the solubility. Conversely, it seems [1] that autoradiation, depending on Pu isotopic composition, transforms progressively PuO_2 into $Pu(OH)_{4(am)}$ and leads to an intermediary mixed solid phase. It might be one of the reasons why such discrepancy exists in the literature [2-5] on the solubility product of tetravalent plutonium hydroxide. Anyhow, the solubility product of $Pu(OH)_{4(am)}$ is interesting to be known to calcultate an upper limit for the solubility of tetravalent plutonium. In acidic medium, when pH increases and above $pH = 0.3$, Pu^{4+} disproportionates. Controlling the speciation is then essential for a correct interpretation of works dealing with hydrolysis or solubility of tetravalent plutonium, since in the experimental conditions chosen for such experiments, Pu(IV) and above all Pu^{4+} is not the predominant aqueous species. Neglecting the disproportionation of Pu^{4+} or assuming that the total plutonium concentration is only due to tetravalent species leads to a rough overestimation of the solubility product. Moreover the literature review leads to the conclusion that ionic strength influence has not been correctly studied to determine a standard value with reasonable precision.

Our experimental methodology is based on the direct speciation: we have already shown that spectrophotometric technique can be used to measure concentrations of each aquo ion in 0.1M $HClO_4$ even if the Pu(IV) solid phase is in equilibrium [6]. The same experiment is performed at different ionic strengths and the standard solubility product is then evaluated by using the S.I.T.

<u>Notations</u>

I : ionic strength

r : conversion factor $r = I(mol/kg)/I(mol/l)$

F : Faraday constant

R : molar gas constant

z_i : charge of the ion i

a_i , m_i, [i] : activity (mol/kg), molality (mol/kg), molarity (mol/l)

γ_i : activity coefficient of ion i, $\gamma_i = a_i/m_i$

$\varepsilon(i,j)$: specific interaction coefficient between the ions i and j (kg/mol)

$D(T,I)$ $= \dfrac{a(T)\sqrt{I}}{1+ a_j b(T)\sqrt{I}}$: Debye Hückel term,

$a(25°C)=0.5091$ and $b(25°C)=1.5$ [7] and I in molal scale

X^0 : $X(T°,0)$ the standard value of X

$E(I)$: Potential of the working solution at the ionic strength I

$E'^0(I)$: Formal Potential of a Ox/Red couple at the ionic strength I

E^0 : Standard Potential (at I=0) of a Ox/Red couple; $E'^0(0) = E^0$

$^*K_s(I)$: $^*K_s(I) = [Pu^{4+}]/[H^+]^4$

$K_s(I)$: Solubility Product of $Pu(OH)_{4(am)}$; $K_s(I) = [Pu^{4+}] [OH^-]^4$

$K_w(I)$: Water ionic product ; $K_w(I) = [H^+] [OH^-]$

All the thermodynamic constants values ($^*K_s(I)$, $K_s(I)$ or $K_w(I)$) can be given in molal (using m_i) or molar scale (using [i]), but in the S.I.T. equations only the molal scale has to be used.

Method

Speciation in aqueous solution

       We focus here on the choice for convenient experimental conditions (above all pH) for plutonium speciation by spectrophotometric measurement. In acidic medium, the redox potentials of the plutonium system are all quite close to 1 Volt/SHE. It is then possible to prepare solutions where 3 aquo ions are in equilibrium at similar concentrations. In moderate acidic media, at pH about 1, PuO_2^+ disproportionates into PuO_2^{2+} and Pu^{3+} [6] according to the following equilibrium:

$$3\ PuO_2^+ + 4\ H^+ \leftrightarrow 2\ PuO_2^{2+} + Pu^{3+} + 2\ H_2O \tag{1}$$

The reaction progress is followed by UV/visible spectrophotometry. Each aquo ion has a characteristic absorption wavelength [6]. When the equilibrium is attained, PuO_2^{2+}, PuO_2^+ and Pu^{3+} are the major conponents and their concentrations are high enough to be measured by spectrophotometry.

Pu(IV) is quickly hydrolysed (from pH>0.3) and the solubility product of $Pu(OH)_{4(am)}$ is very low. The concentration of Pu^{4+} is too low to be directly measured by spectrophotometry but it is easily calculated using the following classical thermodynamic relation Eq.(7).

According to the Nernst law, the redox potential of a solution containing a redox couple :

$$Ox + ne^- \leftrightarrow Red \tag{2}$$
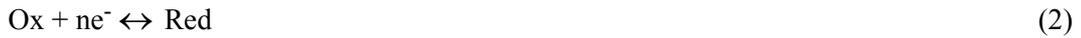
is written as:

$$E(I) = E^0 + \frac{RT}{nF} \lg \frac{a_{Ox}}{a_{Red}} = E'^0(I) + \frac{RT}{nF} \lg \frac{m_{Ox}}{m_{Red}} \tag{3}$$

where $E'^0(I)$, the formal potential of the couple at the ionic strength I, is :

$$E'^0(I) = E^0 + \frac{RT}{nF} \lg \frac{\gamma_{Ox}}{\gamma_{Red}} \tag{4}$$

We apply twice the Nernst law, for PuO_2^{2+}/PuO_2^+ and Pu^{4+}/Pu^{3+} couples:

$$E(I) = E'^0_{6/5}(I) + \frac{RT}{F} \ln \frac{[PuO_2^{2+}]}{[PuO_2^+]} \tag{5}$$

$$E(I) = E'^0_{4/3}(I) + \frac{RT}{F} \ln \frac{[Pu^{4+}]}{[Pu^{3+}]} \tag{6}$$

From Eqs.(5) and (6) we deduce :

$$[Pu^{4+}] = \frac{[Pu^{3+}][PuO_2^{2+}]}{[PuO_2^+]} \exp[\frac{F}{RT}(E'^0_{6/5}(I) - E'^0_{4/3}(I))] \tag{7}$$

that is a thermodynamic realtion an not an approximation. $E'^0_{6/5}(I)$ and $E'^0_{4/3}(I)$ have been measured in the same media in the previous work [8]. $[Pu^{4+}]$ is then deduced using these known formal potentials and $[Pu^{3+}]$, $[PuO_2^{2+}]$, and $[PuO_2^+]$ spectrophotometric determinations. When equilibrium is obtained, the redox potential of the solution is calculated by using Eq. (5) : in fact this is a simple way to measure it with a shorter equilibration time, than when using a classical Pt solid electrode. We assume that the equilibria between Pu^{3+} and Pu^{4+} and also between PuO_2^{2+} and PuO_2^+, are fast enough for each spectrophotometric measurement since it is well known that the electron transfer between two actinide ions of the same structure is rapid and reversible.

Note that, because of the independence of the concentration measurements, Eq.(7) is valid even if Pu(IV) soluble hydrolysed species are formed. It is important to point out that in our methodology, the knowledge of the Pu(IV) hydrolysis behaviour is not necessary to interpret the solubility measurements : this methodology is equivalent to a Pu^{4+} specific electrode.

Solubility Product

At a given time, the ratio $\dfrac{[Pu^{4+}]}{[H^+]^4}$ is called Q(t). When the precipitation occurs and equilibrium is obtained, Q(t) is constant and named $^*K_s$. In our case, the Pu(IV) solid phase is probably $Pu(OH)_{4(am)}$. $[Pu^{4+}]$ is known from Eq.(7) and pH is measured, $^*K_s(I)$ is then easily deduced.
The same experiment performed at different ionic strength, allows us to extrapolate the solubility product $^*K_s(I)$ to the standard state (I = 0) using the Specific Interaction Theory (S.I.T.) [7]. For the S.I.T. model, the ionic strength influence on activity coefficient is :

$$lg\gamma_i = -z_i^2 D(I) + \sum_{z_i z_j < 0} \varepsilon(i,j) \, m_j \tag{8}$$

At I = 0,

$$^*K_s^0 = \frac{a_{Pu^{4+}}(a_{H_2O})^4}{(a_{H^+})^4} \tag{9}$$

and

$$K_s^0 = a_{Pu^{4+}}(a_{OH^-})^4 = {}^*K_s^0 (K_w^0)^4 \tag{10}$$

Using the approximation $a_{H_2O} \approx p \, m_{NaClO_4}$ (p = -0.01502 ± 0.00078) calculated in this work using Pitzer coefficients [9] for $NaClO_4$ electrolyte and Eq.(8)

$$lg \, {}^*K_s(I) = lg \, {}^*K_s^0 + 12 \, D - (\Delta\varepsilon + 4p) \, m_{ClO_4^-} \tag{11}$$

and $\quad \Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - 4 \, \varepsilon(H^+, ClO_4^-) \tag{12}$

[Pu^{4+}] is deduced from Eq.(7), in which [Pu^{3+}], [PuO_2^{2+}] and [PuO_2^+] are measured by spectrophotometry, and the pH meter is calibrated in concentration; then experimental $^*K_s(I)$ are determined in mol/l unit. Conversely in Eq.(11) the concentration unit is mol/kg and a conversion is then needed. The ratio m/M tabulated in [7] for sodium perchlorate is used for this calculation.

When the S.I.T. is satisfied, the plot of (lg $^*K_s(I)$-12D) versus m_{ClO4^-} should be a straight line, whose slope is -($\Delta\varepsilon + 4p$) and the intercept at $m_{ClO4^-} = 0$, lg$^*K_s^0$. Additional treatment of data to deduce $\varepsilon(Pu^{4+}, ClO_4^-)$ estimate is discussed below (see discussion section).

Experimental Section

Solution preparation

The PuO_2^+ starting solution was prepared by electroreduction of a PuO_2^{2+} one at E = 700 mV/ESH. The PuO_2^{2+} solution is prepared by dilution of a carbonate stock solution into a known perchloric medium (xM $HClO_4$, (I-x)M $NaClO_4$ where x is about 0.1 and I = 0.1 , 0.5 , 1 , 2 or , 3M). Electrolysis is performed for each ionic medium. More details have been published in the previous works [6,9].

Spectrophotometry

Absorption spectra were recorded by a Cary 17D spectrophotometer. Molar absorptivities are already published [6,9].

pH measurement

Precise pH measurements are needed since a_{H^+} appears at power 4 in $^*K_s^0$ expression Eq.(9). A combined glass electrode (Tacussel XC 161) was used. For each experiment, the Ag/AgCl reference electrode compartment was filled with a new solution {0.01 M NaCl + (I-0.01) M $NaClO_4$}, and new buffers {$HClO_4$ x M + $NaClO_4$ (I-x) M} were prepared. All these solutions had the same ionic strength I that minimizes then the junction. pH was measured when the equilibrium was achieved. To calculate Q(t) at given time it was assumed that a variation of pH due to the reaction (1) or radiolysis could be neglected, since there was 2 orders of magnitude between the total plutonium concentration and the initial $HClO_4$ concentration. This assumption has been verified on the experiment performed at I = 0.5M : there was no pH difference between the starting pure PuO_2^+ solution and the mixed solution when the equilibrium is achieved. Since the pH-meter was calibrated in concentration using two perchoric buffers, -lg[H^+] and not pH was measured. The -lg[H^+] values measured for the working solutions at I = 0.1, 0.5, 1, 2 and 3M were 1.00, 0.88, 1.04, 0.97, 1.10 respectively.

Results

Concentration variation versus time

$[Pu^{3+}]$, $[PuO_2^{2+}]$, and $[PuO_2^+]$ were used previously [6] to measure the Pu(V) disproportionation constant (Eq.(1)). The data of the same experiments are used here. These original data are published elsewhere [6,10]. At I = 0.1 M the time dependence of $[PuO_2^{2+}]$, $[PuO_2^+]$, and $[Pu^{3+}]$ and $[Pu^{4+}]$ were found fast during the first few hours, then slowed down. $[PuO_2^{2+}]$ reached a maximum, while $[PuO_2^+]$ decreased and $[Pu^{3+}]$ increased along the experiment. In fact, the variation of the concentrations versus time was the result of two simultaneous phenomena : the disproportionation of PuO_2^+ and the autoradiolysis that led in perchoric media to the reduction of all aqueous Pu species into Pu^{3+}.

For I $\neq$ 0.1M, the variations were similar. Only the time needed to obtain the equilibrium varied with I : it decreased from a few tens to 1 day when I increased. This might be due to the stabilisation of the products of the reaction (7) when I increases since Pu^{3+} and PuO_2^{2+} are highly charged species compared to PuO_2^+.

It has been controlled from time to time that Pu^{4+} was not detected and this is in agreement with the calculation using Eq.(7) that leads to $[Pu^{4+}]$ values always smaller than 10^{-4} M which was lower than the detection limit.

K_s and ionic strength influence

We noticed that the sum $[PuO_2^{2+}]+[PuO_2^+]+[Pu^{4+}]+[Pu^{3+}]$ decreased with time by about 10%. Since the experiments have been performed at pH about 1 only tetravalent plutonium might be hydrolysed. All along the experiment, only PuO_2^{2+}, PuO_2^+ and Pu^{3+} could be detected, and there was no evidence of any other soluble species. We then assumed that the $Pu(OH)_{4(am)}$ precipitation occurs. The plot of lgQ(t) (Fig. 1) or $[Pu^{4+}]$ versus time showed a stabilisation after a few days : up to this time the solution was undersaturated and over this time there was precipitation. For I = 0.1M the experiment was followed during 100 days: after 10 days and up to the end lgQ(t) remained constant. It was then supposed first that equilibrium precipitation was achieved and secondly that there was no modification of the cristallinity of the solid phase controlling the solubility. $^*K_s$(I) was calculated as the mean of the Q(t) values measured when equilibrium was reached as summarized in Table (2). The statistical uncertainty (1.96σ) appears to be too small for the reasons enumerated below : it does not account for the uncertainty of spectrophotometric measurements, the equilibrium is perhaps not reached, we do not characterised the solid phase and the measurements have been carried out only at one pH value. Finally the uncertainty is increased and set arbitrary at 0.3 for experimental $^*K_s$ and 0.5 for the standard value deduced from S.I.T. extrapolation.

Experimental points (lg$^*K_s$(I) - 12D) versus $m_{ClO_4^-}$ fall quite well on a straight line Fig.(2a) whose slope has a reasonable numerical value (see discussion section): the S.I.T. seems to be satisfied up to 3M. The plot of lg$^*K_s$(I) versus $m_{ClO_4^-}$ shows a sharp increase from 0 to 1 molal, then up to 3 molal, its variations are quite negligible Fig.(2b). As explained in the method section, the standard solubility product and interaction coefficient were deduced from linear regression and the following values were obtained:

$$\lg {}^*K_s^0 = -2.26 \pm 0.5 \tag{13}$$

$$\lg K_s^0 = -58.3 \pm 0.5 \tag{13'}$$

$$\Delta\varepsilon + 4p = 0.23 \pm 0.20 \tag{14}$$

$\varepsilon(Pu^{4+}, ClO_4^-)$ value is then deduced from this $(\Delta\varepsilon + 4p)$ determination, p value, and the $\varepsilon(H^+, ClO_4^-)$ auxiliary data selected by the Thermodynamic Data Base (T.D.B.) [7].

$$\varepsilon(Pu^{4+}, ClO_4^-) = 0.85 \pm 0.20 \tag{15}$$

Discussion

Pu(OH)₄ solubility product

Published data for the $Pu(OH)_{4(am)}$ solubility product (Table 3) show a great discrepancy from $K_s = 10^{-47}$ to 10^{-53} $(mol/kg)^{-3}$. In only two works [2,3] the aqueous speciation was controlled and taken into account in the interpretation. In the other ones, plutonium in solution is assumed to be at the +4 oxydation state, the Pu(IV) disproportionation was then neglected and the solubility product overestimated. The results from [2,3] and present work are compared and the extrapolation to zero ionic strength is discussed below.

Kim and Kanellakopulos [3] and Rai [2] studies are in qualitative agreement with the present work: Pu^{4+} disproportionation cannot be neglected. It is an important phenomenon in such conditions (moderate acidic medium) since Pu^{4+} is not the major aqueous species in equilibrium with $Pu(OH)_{4(am)}$. The standard values proposed by Kim [3] and Rai [2] are in fair agreement with the one determined in present work (Table 3). But, the consistency is not so straightforward, since the experimental results (i.e. K_s at $I \neq 0$) are not in accordance within the uncertainty.

Kim and Kanellakopulos [3] measured directly by spectrophotometry the Pu^{4+} concentration in equilibrium with a solid phase $Pu(OH)_{4(am)}$. On one hand, as the authors said, the measurement was not very precise because of the interference with the Pu(IV) polymer. On the other hand, the very high proportion of colloidal Pu(IV) (80%) might have been formed when the filtration was performed and then the equilibrium might have shiftted at the expense of Pu^{4+}. This methodology might lead to an underestimated K_s value. Concerning the estimation of standard value, this extrapolation relies only on one experiment performed at $I = 1$ and the calculations are not sufficiently documented to understand how the Pu^{4+} activity coefficient was evaluated.

Rai [2], performed measurements of the $Pu(OH)_{4(am)}$ solubility from oversaturated solutions at pH = 0.5 to 4.9. The redox potential of the solution and the concentration of aquo ions, when these ones were high enough, were measured to control the speciation in solution. However, it is difficult to compare these results with ours or those of Kim because experiments are carried out in nitrate medium. Then the interpretation needs hydroxyde and nitrate complexation constants : the selection and the accuracy of these thermodynamic constants were not discussed and because of the lack of data to extrapolate them in the studied medium, the authors used them sometimes, without ionic strength corrections. To sum up, experimental K_s

can not be directly compared with other works and the extrapolation calculated by Rai increases markedly the uncertainty.

There is a real lack of ionic strength influence study, that induces a poor precision on the standard value. In the present work the $Pu(OH)_{4(am)}$ solubility product has been measured at different ionic strengths, and extrapolation to the standard state is performed without using auxiliary data. Moreover, the numerical value obtained for Pu^{4+} interaction coefficient, in agreement with those of ions charged +4, seems to proove that the extrapolation to the standard state is realistic as discussed below.

Specific interaction coefficient

The value of $\varepsilon(Pu^{4+}, ClO_4^-) = 0.85 \pm 0.2$ Eq.(15) calculated in the present work, using the $\varepsilon(H^+, ClO_4^-)$ [7] and p values, is to be compared with the value proposed by the T.D.B. [7], $\varepsilon(Pu^{4+}, ClO_4^-) = 1.03 \pm 0.05$. This last value was deduced from

$$\Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - \varepsilon(Pu^{3+}, ClO_4^-) = 0.54 \pm 0.03 \text{ [11]} \tag{16}$$

experimental determination (S.I.T. extrapolation to zero ionic strength of the Pu^{4+}/ Pu^{3+} redox potential measured in perchlorate media) and from the following analogy between lanthanide(III) and Pu^{3+} :

$$\varepsilon(Pu^{3+}, ClO_4^-) = \varepsilon(Nd^{3+}, ClO_4^-) = 0.49 \pm 0.03 \tag{17}$$

We have previously [8] redetermined this $\Delta\varepsilon$ value relating it to the two Pu reversible couples. This new value $\Delta\varepsilon$ value:

$$\Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - \varepsilon(Pu^{3+}, ClO_4^-) = 0.33 \pm 0.05 \text{ [8]} \tag{18}$$

which is now in fair agreement with the corresponding value of other actinides leads in analogy to Eq.(17), to :

$$\varepsilon(Pu^{4+}, ClO_4^-) = 0.82 \pm 0.07 \tag{19}$$

This analogy between actinide and lanthanide is based on the ionic radii. However we have determined the specific interaction coefficients from published Pitzer coefficients [9] and found numerical values very close within the lanthanide series. Then the choice of the lanthanide for the analogy does not induce significant difference on the final $\varepsilon(Pu^{4+}, ClO_4^-)$ final result. For consistency with TDB and then CODATA recommended value, we keep the same Pu^{3+}/Nd^{3+} analogy.

Finally our $\varepsilon(Pu^{4+}, ClO_4^-)$ value in Eq.(15) is consistent with the value already known for other cations charged 4+ [7] and particularly with the independent estimation for Pu using well established analogy. This result verifies once more the analogy in the behaviour of actinides at the same oxydation state and on the other hand it verifies also the assumption of our interpretation, i.e., the achievement of the solubility equilibrium.`

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Table 1 Auxiliary Data : Redox Potentials of PuO_2^{2+}/PuO_2^+ et Pu^{4+}/Pu^{3+} couples

The potentials in the two last columns are calculated versus ionic strength using standard potentials, $E(0)$, specific interaction coefficient $\Delta\varepsilon$ [8], and the following S.I.T. equation : $E(I) = E(0) + 59.16 [-\Delta z^2 D(I) + \Delta\varepsilon\, m_{ClO_4}^-]$ (mV). These potentials values are used to deduce $[Pu^{4+}]$ in Eq. (7). r is the conversion factor molality/molarity for $NaClO_4$ [7].

I (Mol/l)	r = m/M (kg/l)	I (mol/kg)	$E_{6/5}$ (mV/SHE)	$E_{4/3}$ (mV/SHE)
0			938 ± 10	1044 ± 10
0.1	1.007	0.101	920 ± 10	1001 ± 10
0.5	1.026	0.513	913 ± 10	981 ± 10
1	1.050	1.050	915 ± 10	979 ± 10
2	1.102	2.205	925 ± 11	989 ± 12
3	1.162	3.487	939 ± 12	1007 ± 14

Table 2 : Experimental solubility product of Pu(OH)$_{4(am)}$ in percloric and extrapolation to I=0. $lg^*Ks(I\neq0)$(column 2) is deduced from Eq.(7) and measured values of $lg[H^+]$. The values in bold face are the results of the SIT extrapolation Eq. (11). lgK_s is calculated to be compared with published works in Table 3 using K_w values [7, 12].

$^*K_s = [Pu^{4+}]/[H^+]^4$; $K_s = [Pu^{4+}] [OH^-]^4 = K_s K_w^4$;

$lg^*K_s(m) = lg^*K_s(M) - 3 lgr$ (for r values see Table 1)

I (Mol/l)	lg^*K_s $^*K_s$ in (Mol/l)$^{-3}$	lg^*K_s $^*K_s$ in (Mol/kg)$^{-3}$	lgK_s K_s in (Mol/kg)^5	$-lgK_w$ K_w in (Mol/kg)$^{-2}$
0		**-2.26 ± 0.50**	-58.26 ± 0.51	14.00 ± 0.02
0.1	-0.72 ± 0.30	-0.73 ± 0.30	-55.93 ± 0.31	13.80 ± 0.02
0.5	-0.63 ± 0.30	-0.66 ± 0.30	-55.62 ± 0.31	13.74 ± 0.02
1	0.26 ± 0.30	0.20 ± 0.30	-54.92 ± 0.32	13.78 ± 0.03
2	-0.04 ± 0.30	-0.17 ± 0.30	-55.88 ± 0.36	13.93 ± 0.05
3	0.23 ± 0.30	0.03 ± 0.30	-56.48 ± 0.44	14.13 ± 0.08

Table 3 : Review of Pu(OH)$_{4(am)}$ solubility product. In Ref. [4,5] the aqueous speciation was not taken into account in the interpretation (last lines). * means value calculated in this work from published original experimental results to allow comparison before extrapolation to I = 0.

	lgK$_s$	lg*K$_s$	Media
[2]	-56.85 ± 0.36		I = 0
[3]	-57.85 ± 0.05		I = 0
This work	-58.3 ± 0.5	-2.26 ± 0.50	I = 0
[2]		0.138*	I = 0.064, pH = 1.2 nitric medium
[2]		0.518*	I = 0.112, pH = 1 nitric medium
This work	-55.93 ± 0.3	-0.73 ± 0.30	0.1 M HClO$_4$
This work	-55.66 ± 0.3	-0.66 ± 0.30	0.1 M HClO$_4$ + 0.4 M NaClO$_4$
This work	-54.96 ± 0.3	0.20 ± 0.30	0.1 M HClO$_4$ + 0.9 M NaClO$_4$
[3]	-57.4*		1M HClO$_4$
This work	-56.01 ± 0.3	-0.17 ± 0.30	0.1 M HClO$_4$ + 1.9 M NaClO$_4$
This work	-56.69 ± 0.3	0.03 ± 0.30	0.1 M HClO$_4$ + 2.9 M NaClO$_4$
[4]	*-55.1*		0.062 M HCl
[4]	*-55.2*		(0.052 M NaClO$_4$+ 0.95 M HClO$_4$)
[5]	*-47.3 à 56.3*		
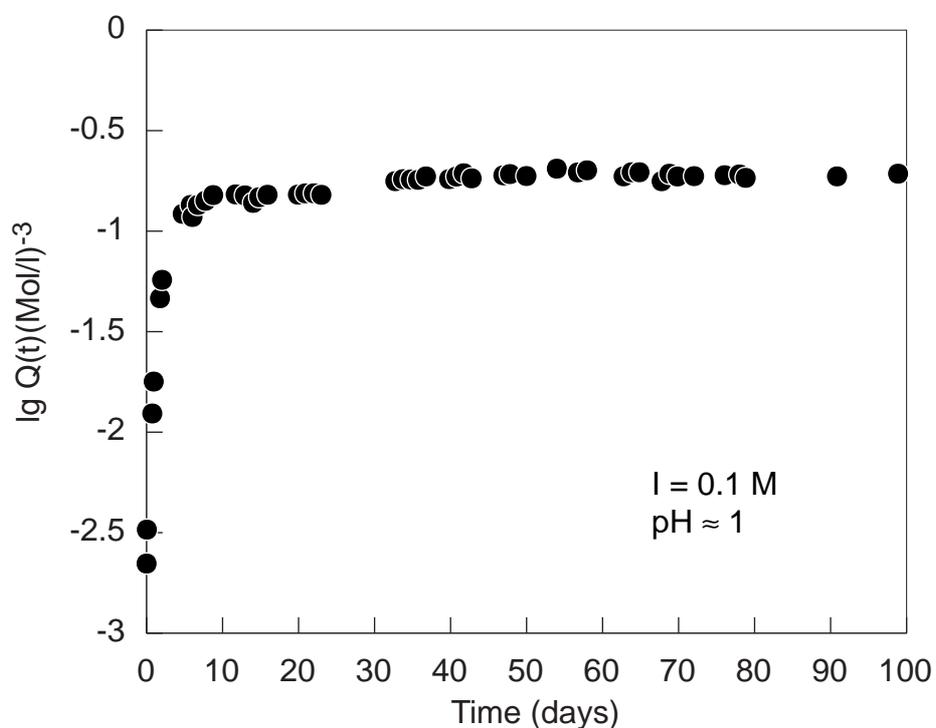
Fig 1 : Variation of Q = [Pu^{4+}]/[H$^+$]^4 versus time.

[Pu^{4+}] is deduced from [PuO$_2^{2+}$], [PuO^{2+}], [Pu^{3+}] spectrophotometric measurements and normal redox potentails in Table 1 (Eq.(7)). -lg[H$^+$] is also measured. When Q(t) is constant Q(t) = *K$_s$ (Table 2). The same treatment is used for I = 0.5, 1, 2, 3M (H$^+$, Na$^+$, ClO$_4^-$)
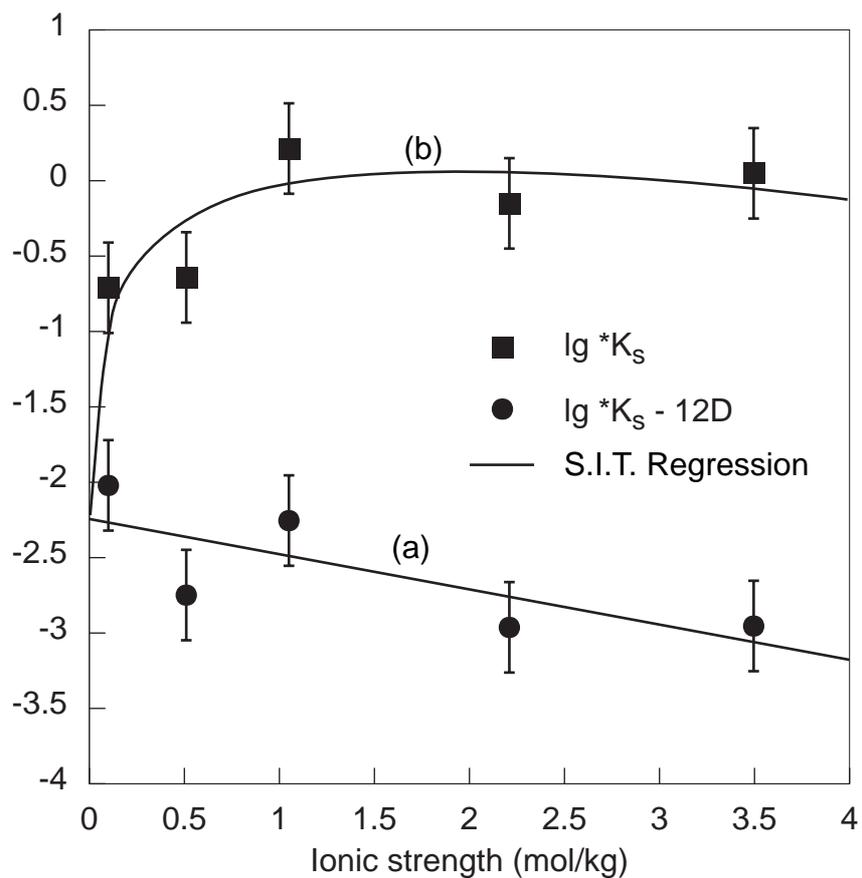
Fig 2 : Ionic Strength Influence on the Pu(OH)$_{4(am)}$ solubility product.

*K$_s$(I) is measured in perchloric media at different ionic strength (Fig.1 for I = 0.1M) and extrapolated to I = 0 using the S.I.T. formula Eq.(11). The intercept at I = 0 of curve (a) is lg *K$_s$(0) and the slope -($\Delta\varepsilon$ + 4p). These numerical values are used to calculate the curve (b).