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Complexation parameters for the actinides(IV)-humic acid system: a search for consistency and application to laboratory and field observations

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Summary. The coherence of actinide(IV) complexation by humic substances (HS) is reviewed and new data are proposed. In a first attempt, the values of independent data from literature on Th(IV), U(IV), and Pu(IV) are collected, selected, and compiled. The data obtained follow the "classical" trend of increasing conditional formation "constants" with pH, led both by the increasing ionisation of HS and by the extensive hydrolysis of the tetravalent actinides. Even though a fair agreement is evident, the experimental uncertainties do not permit a full analogy between the actinides(IV) to be ascertained. In a second attempt, the experiments from which the original data are available were reinterpreted using only one hydrolysis constant set for U(IV) as an example, considering that all actinides(IV) have analogous humic complexation behaviour. Hence, the obtained evolution of conditional formation "constants" is much more coherent and the uncertainties do not permit to distinguish an actinide(IV) from one another. The obtained data are then applied to independent laboratory and *in situ* experiments in order to delimit the domain of possible applicability. This exercise demonstrates the treatment of data through analogy in the case of actinides(IV) and would permit to limit and orientate the number of necessary, but difficult, experiment with redox sensitive elements like U, Np, or Pu. It also demonstrates that complexation-only mechanisms may not be sufficient to understand field observations.

Introduction

The extent of tetravalent actinides, or An(IV), complexation by humic substances has puzzled scientists for decades. In natural systems, An(IV) are often associated with natural organic matter in general and with humic substances (HS [1]) in particular [2–4]. Moreover, Pa(V), Np(V), Pu(V) and Pu(VI) are reduced to Pa(IV), Np(IV) and Pu(III)-Pu(IV) by HS [5–10]. Up to now, no reduction of uranium(VI) to uranium(IV) by humic substances has been evidenced [11, 12], except when mediated by bacteria [13, 14]. On the contrary, reoxidation of U(IV) to U(VI) in the presence of HS was observed when the redox conditions are not fully controlled [14]. Nonetheless, the association of U(IV) with HS is suspected in certain groundwaters [15, 16].

It is possible to compare the aqueous chemistry of the different An(IV) through analogy [17–19]. These analogies are often justified as long as relativistic effects are not taking place [20]. For instance, the similarity in the migration behaviour of Pu(IV) and Th(IV) in the presence of HS has been confirmed [21, 22].

Complementary to data obtained in the late seventies and early eighties [23–25], more data were recently obtained on Th(IV) [26–30], U(IV) [31, 32], and Pu(IV) [33]. Transport experiments of U(IV) were also recently obtained [34], evidencing high interaction with HS. Nevertheless, there still maybe a problem with the possible treatment through analogy due to the low numbers of data available. The inherent difficulties of working with An(IV) in general and with redox sensitive actinides in particular, often prevent the obtaining of reliable data. Hence, with due justification, if the majority of the data could be more "simply" obtained with Th(IV) and transferred with a reasonable level of confidence, to the more "difficult" elements namely U(IV), Np(IV) and Pu(IV), this would solve a lot of potential and real problems, and point out the importance of side reaction problems like redox in a first approximation.

The main problem concerning descriptions of humic complexation is the apparent increasing complexation strength with pH. This phenomenon is related to the increasing ionisation of functional groups, namely "carboxylic" and "phenolic", with increasing pH. This increasing complexation strength has been modelled using either global varying complexation coefficients [28], varying the number of sites [35], differential equilibrium function [36], and multi-pK_a approaches, or continuous description, including heterogeneity parameters and electrostatics [37, 38]. The latter types of models could be seen as more representative of the heterogeneous aggregate structure of HS [39]. Nevertheless, more operational types of description have been widely applied to actinides and a large number of data are avail-

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able in the literature for Am(III), Cm(III), Np(V), Th(IV) and U(VI). The parameters that describe the humic complexation can only be considered as averaged empirical values considering the intrinsic heterogeneity of the humic substances [40–42].

The aims of this work are to compare the different data available on tetravalent actinides and to draw out some general complexing properties in order to increase the confidence in complexation parameters estimated by analogy for redox sensitive actinides in their +IV redox state. New data obtained in ultrafiltration are compared to these data and will complement the data basis. Then these data sets are applied to laboratory and field observations.

Experimental

Material

Purified Aldrich humic acid (AHA) is used in a protonated form. Characteristics of this HA are described elsewhere [28, 43]. The proton exchange capacity (PEC) for AHA was determined in [43] by potentiometric titration ($W_{HA} = 5.4$ meq/g).

The initial thorium solution (^{228}Th in 2 M HNO_3) is obtained from Amersham. This solution is diluted in order to obtain a 1.09×10^{-9} M stock solution in 0.9 M $NaClO_4$ and 0.2 M HNO_3. All other chemicals are reagent grade and Milli-Q water is used.

Experimental

The pH measurement were done with a TACUSSEL pH-meter (PHM 220 MeterLab) equipped with a combined TACUSSEL electrode (Radiometer type XC 161, modified $NaClO_4$ 0.1 M, NaCl 10^{-2} M), using $HClO_4$ (0.1 M) or freshly prepared NaOH (0.1 M). The combined electrode was calibrated against commercial pH buffers (pH = 4, 7, 9).

The separation of free Th(IV) from the humate complexes was done by ultrafiltration at pH around 7, 8, and 9 using Amicon MPS YC-05 units. As a problem in the retention of HA at 0.1 M ionic strength was identified in a previous study [44], the efficiency of HA separation was tested with solutions of 50 mg/L of AHA prepared at the desired pH and ionic strength. The rejection of AHA, measured in spectrophotometry (Shimadzu UV-2100), was always higher than 96% at 0.01 and 97% at 0.001 M, between pH 3 and 9. In order to minimize both the effect of ionic strength on the complexation of humics [45], and on the filtration efficiency, ionic strength of 0.01 M $NaClO_4$ was chosen.

The initial solutions were prepared diluting AHA into 0.01 M $NaClO_4$ at the desired pH under careful argon sweeping in order to minimize the CO_2(g) contamination and the formation of hydroxocarbonatothorate(IV) and carbonatothorate(IV) complexes [46, 47]. Enough Th(IV) stock solution is added to obtain a final concentration of 1.15×10^{-12} M, in order to minimize the presence of eigencolloids [48] and the pH is readjusted under careful argon sweeping. The solution is then closed and placed under agitation for 24 h. Under these conditions, carbonate concentration has been shown to be less than 5×10^{-5} M [49]. Three to four 1 mL aliquots were placed in Amicon YC-05 units for 1 h, and 0.5 mL aliquots were sampled for activity measurement by liquid scintillation counting (A_1), in order to get rid of Th(IV) sorption on tube walls as in previous studies [19, 28]. This is also the case here as around 10%–25% of Th(IV) is sorbed on tube walls or filter (data not shown). The units were emptied, filled with another 1 mL aliquot under argon sweeping, and centrifuged (1 h at 5700 rpm). A final 0.5 mL aliquot of the filtrate is then sampled for activity measurements (A_2) by liquid scintillation counting.

The distribution coefficient is calculated as:

$$D = \frac{[\mathrm{Th}]_{\mathrm{filtrate}}}{[\mathrm{Th}]_{\mathrm{solution}}} = \frac{A_1}{A_2} - 1$$

Treatment of data

Only the complexing properties of HS will be considered here, since their reducing properties have not totally been clarified.

Modelling of inorganic and humic substances complexation of An(IV) for this exercise

As this work is a demonstration exercise, we will use the simplest models possible. Humic acids will be considered as homogeneous with no acido-basic properties. Hence, stability parameters will be purely conditional and closely related to pH. The formation of a metal-HS complex MHS can thus be written:

$$\mathrm{An} + \mathrm{HS} \rightleftarrows \mathrm{AnHS} \quad {}^{\mathrm{HA}}\beta(\mathrm{An}) = \frac{[\mathrm{AnHS}]}{[\mathrm{An}]_{\mathrm{total}}[\mathrm{HS}]}\,, \qquad (1)$$

where $[\mathrm{An}]_{\mathrm{total}}$ is the total concentration of An(IV) in solution, [HS] is the concentration of humic sites determined either by titration or $Ca(CH_3CO_2)_2$ and $Ba(OH)_2$.

The values of free $[\mathrm{An}^{4+}]$ depend on the thermodynamic formation constants of the different complexes formed through side reactions. The major problems with An(IV) are their extensive hydrolysis, low solubility, and colloid formation [47, 48, 50–52]. In this exercise, we will use the Davies equation because the specific interaction theory (SIT [47]) parameters are not available to calculate the activity coefficient and formation constant value for some media used (*e.g.* $Na_2S_2O_4$).

The extent of hydrolysis of the metal M, or the proportion of free metal, can then be calculated using:

$$\left.\begin{aligned} [\mathrm{An}]_{\mathrm{total}} &= [\mathrm{An}^{4+}]_{\mathrm{f}} \left(1 + \sum_{n=1}^{4} \frac{{}^{*}\beta_n}{[\mathrm{H}^+]}\right) \\ [\mathrm{An}]_{\mathrm{total}} &= [\mathrm{An}^{4+}]_{\mathrm{f}} \left(1 + \sum_{n=1}^{4} \beta_n [\mathrm{OH}^-]^n\right) \end{aligned}\right\}$$

$$[\mathrm{An}]_{\mathrm{total}} = [\mathrm{An}^{4+}]_{\mathrm{f}} \alpha_{\mathrm{An(IV)}} \qquad (2)$$

where α is the Ringböm, or side reaction, coefficient: the higher α, the lower $[\mathrm{An}^{4+}]_{\mathrm{f}}$. It is then evident that log ${}^{\mathrm{HA}}\beta$ for An(IV)–HS interactions are intimately linked to hydrolysis constants, and cannot be used without proper corrections. Hence, log ${}^{\mathrm{HA}}\beta$ (An^{4+}) can be calculated from the raw data.

Otherwise, the log ${}^{\mathrm{HA}}\beta$ (An) values calculated by the authors can thus be corrected to:

$$\mathrm{An}^{4+} + \mathrm{HS} \rightleftarrows \mathrm{AnHS} \quad {}^{\mathrm{HA}}\beta(\mathrm{An}^{4+}) = \frac{[\mathrm{AnHS}]}{[\mathrm{An}^{4+}]_{\mathrm{f}}[\mathrm{HS}]} \tag{3}$$

Combining Eq. (1) and Eq. (2), then it comes:

$$\log {}^{\mathrm{HA}}\beta(\mathrm{An}^{4+}) \approx \log {}^{\mathrm{HA}}\beta(\mathrm{An}) + \log \alpha_{\mathrm{An(IV)}} \tag{4}$$

using the appropriate hydrolysis constants for $\alpha_{\mathrm{An(IV)}}$.

Acid-base as well as metal complexation properties of HS have been shown to vary with ionic strength [45, 53, 54]. The metal complexation properties for trivalent actinides seem to be more influenced when $I \leq 0.3$ mol/L, than for higher ionic strengths [45, 54], mostly due to the Debye length collapse. Moreover, the extent of this dependence is rather minimal and a generic data independent of ionic strength was proposed in the case of An(III) [45]. The same behaviour can be expected for tetravalent actinides. Henceforth, no quantification of the influence of ionic strength on the behaviour of HS will be used in this exercise.

Charge neutralization model

The charge neutralisation model (CNM) has been shown to be useful for actinide-humic interaction studies. Its concept is fully described elsewhere [35], henceforth we will not enter into the details of the modelling devoted to trace concentration conditions. The log $\beta_{1.n.Z-N}$ values can be obtained to represent the influence of hydrolysis on the complexation of metals by humics:

$$\left.\begin{aligned} \mathrm{M}^{z+} + n\mathrm{OH}^- + \mathrm{HA}(Z{-}N) &\rightleftarrows \mathrm{M(OH)}_n\mathrm{HA}(Z{-}N) \\ \mathrm{M}^{z+} + n\mathrm{H_2O} + \mathrm{HA}(Z{-}N) &\rightleftarrows \mathrm{M(OH)}_n\mathrm{HA}(Z{-}N) + n\mathrm{H}^+ \end{aligned}\right\} \tag{5}$$

with the related constants:

$$\left.\begin{aligned} \beta_{1.\mathrm{n}.Z-N} &= \frac{[\mathrm{M(OH)}_n\mathrm{HA}(Z{-}N)][\mathrm{H}^+]^n}{[\mathrm{M}^{z+}]_{\mathrm{f}}[\mathrm{OH}^-]^n[\mathrm{HA}(Z{-}N)]_{\mathrm{f}}} \\ {}^*\beta_{1.\mathrm{n}.Z-N} &= \frac{[\mathrm{M(OH)}_n\mathrm{HA}(Z{-}N)]}{[\mathrm{M}^{z+}]_{\mathrm{f}}[\mathrm{HA}(Z{-}N)]_{\mathrm{f}}} \end{aligned}\right\} \tag{6}$$

where z is the charge of the metal, $[\mathrm{HA}(Z{-}N)]_{\mathrm{f}}$ and $[\mathrm{M}^{z+}]_{\mathrm{f}}$ are respectively the concentrations of free humic sites and M^{z+} in solution. The total concentration of humic sites available to complex and "neutralize" a metal ion M^{z+} can be written as:

$$[\mathrm{HA}(Z{-}N)]_T(\mathrm{eq/L}) = \frac{(\mathrm{HA})(\mathrm{g/L}) \times \mathrm{PEC(eq/g)}}{Z{-}N} \tag{7}$$

where (HA) is the concentration of HA in g/L and PEC is the proton exchange capacity (eq/g) determined by titration. The free humic site concentration $[\mathrm{HA}(Z{-}N)]_{\mathrm{f}}$ is defined as the difference between the maximum concentration of humic sites available for the metal $\mathrm{LC}(Z{-}N) \times [\mathrm{HA}(Z{-}N)]_{\mathrm{t}}$, where $\mathrm{LC}(Z{-}N)$ is the loading capacity for M^{z+} accompanied by n $\mathrm{H_2O}$ or OH^-, and the actual concentration of humic sites that are involved in the complexation $[\mathrm{M(OH)}_n\mathrm{HA}(Z{-}N)]$.

$$[\mathrm{HA}(Z{-}N)]_{\mathrm{f}} = \mathrm{LC}(Z{-}N) \times [\mathrm{HA}(Z{-}N)]_{\mathrm{t}} - [\mathrm{M(OH)}_n\mathrm{HA}(Z{-}N)] \tag{8}$$

In addition to the original definition, it should be added that when a neutral species is bound to HA, then in Eq. (7) if $n \to z$, then $[\mathrm{HA}(0)] \to \infty$. Hence, the boundary condition is when $n = z$, then $[\mathrm{HA}(0)] = [\mathrm{HA(I)}]$ [19].

The transformation of log ${}^{\mathrm{HA}}\beta$ from the preceding paragraph to log $\beta_{1.n.Z-N}$ is straightforward when only one hydrolysis complex needs to be accounted for:

$$\left.\begin{aligned} \beta_{1.n.Z-N} &= \frac{{}^{\mathrm{HA}}\beta(\mathrm{M}^{z+})}{[\mathrm{OH}^-]^n\mathrm{LC}(Z{-}N)} \\ {}^*\beta_{1.n.Z-N} &= \frac{{}^{\mathrm{HA}}\beta(\mathrm{M}^{z+})[\mathrm{H}^+]^n}{\mathrm{LC}(Z{-}N)} \end{aligned}\right\} \tag{9}$$

where $\mathrm{LC}(Z{-}N)$ is the loading capacity of the metal for HA, reflecting the increasing ionisation of the humic substances and the limited number of available sites. Otherwise, a non linear least square regression would be necessary and $\mathrm{LC}(Z{-}N)$ and log $\beta_{1.n.z-n}$ would be directly linked.

One must also point out that the $\mathrm{M(OH)}_n\mathrm{HA}(Z{-}N)$ species are mostly presupposed, or result from a fit, and are difficult to evidence. CNM surely suffers from severe drawbacks [55] including a lack of an explicit site balance between all the $[\mathrm{HA}(Z{-}N)]$ sites for the same metal, *e.g.* $\mathrm{An(OH)}_n\mathrm{HA}(Z{-}N)$, mostly for pH value at half reaction for hydrolysis where $[\mathrm{M(OH)}_n{}^{z-n}] \approx [\mathrm{M(OH)}_{n+1}{}^{z-(n+1)}]$; the lack of "heterogeneity parameters" could make it difficult to use in competition studies with *e.g.* alkaline earth or copper [38, 53]. Nevertheless, it has been proven to be helpful as an operational model for trace metal concentration.

Proposition of complementary data

The mean results from 4 replicates obtained in ultrafiltration are monitored in Table 1. As the activities in the filtrate are weak, this evidences the already well known high interaction between Th(IV) and HA. Considering that

Table 1. Complexation study of Th(IV) with Aldrich humic acid at varying pH in 0.01 M $\mathrm{NaClO_4}$ by ultrafiltration. The loading capacity of AHA was estimated from [56] for log ${}^*\beta_{1.4.I}$ calculation. $\mathrm{Th(OH)_4HA(I)}$ was hypothesized to be the major complex. Global interaction parameter log ${}^{\mathrm{HA}}\beta$ and CNM constant are linked to hydrolysis in [52].

pH[a]	*A*1	*A*2	*R*	log D_{mes}	log ${}^{\mathrm{HA}}\beta$	log ${}^*\beta_{1.4.I}$
7.04	6802 ± 86	58 ± 37	0.991 ± 0.005	2.07 ± 0.28	15.0	−12.3
8.04	6885 ± 158	43 ± 32	0.994 ± 0.005	2.21 ± 0.33	19.1	−12.4
9.26	6878 ± 71	74 ± 50	0.995 ± 0.006	1.96 ± 0.29	24.0	−13.0
						−12.6 ± 0.4

Table 2. Formation constants used in this study referring to [51, 52], extrapolated using Davies equation[a].

Reaction	$\log K_w^\circ$	$\log K_w$ 0.010 m	$\log K_w$ 0.101 m	$\log K_w$ 0.202 m			
$H_2O \rightleftarrows H^+ + OH^-$	−14	−13.9	−13.8	−13.7			
γ^+	1.000	0.902	0.781	0.746			
	U [51]				Th [52]		
	$\log \beta^\circ$	$\log \beta$ 0.010 m	$\log \beta$ 0.101 m	$\log \beta$ 0.202 m	$\log \beta^\circ$	$\log \beta$ 0.010 m	$\log \beta$ 0.101 m
$An^{4+} + H_2O \rightleftarrows AnOH^{3+} + H^+$	−0.4	−0.7	−1.0	−1.2	−2.2	−2.5	−2.8
$An^{4+} + 2H_2O \rightleftarrows An(OH)_2^{2+} + 2H^+$	−1.1	−1.5	−2.2	−2.4	−6.6	−7.0	−7.7
$An^{4+} + 3H_2O \rightleftarrows An(OH)_3^{+} + 3H^+$	−4.7	−5.2	−6.0	−6.2	−11.4	−11.9	−12.7
$An^{4+} + 4H_2O \rightleftarrows An(OH)_4(aq) + 4H^+$	−10.0	−10.5	−11.3	−11.5	−17.0	−17.5	−18.3
$AnO_2^{2+} + \mathit{0.5H_2(g)} \rightleftarrows AnO_2^{+} + \mathit{H^+}$	1.48	1.35	1.16	1.19			
$AnO_2^{2+} + 4H^+ + \mathit{H_2(g)} \rightleftarrows An^{4+} + 2H_2O + \mathit{2H^+}$	9.04	9.40	9.90	10.06			
$AnO_2(am,hyd) + 2H_2O \rightleftarrows An^{4+} + 4OH^-$	−54.5	−53.6	−52.4	−52.0	−47.8		−45.6
$AnO_2(am,hyd) + 4H^+ \rightleftarrows An^{4+} + 2H_2O$	1.5	2.0	2.8	3.0	8.2		9.5
$AnO_2(cr) + 4H^+ \rightleftarrows An^{4+} + 2H_2O$	−4.85	−4.31	−3.56	−3.32			
$AnO_2^{2+} + H_2O \rightleftarrows AnO_2OH^+ + H^+$	−5.25	−5.34	−5.47	−5.50			
$AnO_2^{2+} + 2H_2O \rightleftarrows AnO_2(OH)_2(aq) + 2H^+$	−12.15	−12.24	−12.36	−12.40			
$AnO_2^{2+} + 3H_2O \rightleftarrows AnO_2(OH)_3^- + 3H^+$	−20.25	−20.25	−20.25	−20.25			
$AnO_2^{2+} + CO_3^{2-} \rightleftarrows AnO_2CO_3(aq)$	9.94	9.58	9.08	8.92			
$AnO_2^{2+} + 2CO_3^{2-} \rightleftarrows AnO_2(CO_3)_2^{2-}$	16.61	16.25	15.75	15.59			
$AnO_2^{2+} + 3CO_3^{2-} \rightleftarrows AnO_2(CO_3)_3^{4-}$	21.84	21.84	21.84	21.84			
$2AnO_2^{2+} + 3H_2O + CO_3^{2-} \rightleftharpoons (AnO_2)_2CO_3(OH^-)_3^- + 3H^+$	−0.86	−1.22	−1.72	−1.88			
$AnO_3 \cdot 2H_2O(cr) + 2H^+ \rightleftarrows UO_2^{2+} + 3H_2O$	4.81		5.3				

a: Following the recommendation in [47, p. 719], H^+ issued from the hydrogen oxidation are not taken into account in Δz^2, and are thus written in *italic*.

only $Th(OH)_4(aq)$ exists under these conditions, only the $Th(OH)_4HA(I)$ species was taken into account as in [19], and $\log {}^*\beta_{1.4.I}$ using the CNM can be calculated at each pH using:

$$D = \frac{[Th]_{filtrate}}{[Th]_{solution}} \equiv \frac{{}^*\beta_{1.4.I}[HA(I)][H^+]^{-4}}{\alpha_{TH(IV)}} \quad (10)$$

were HA(I) is calculated from [56, Eq. (14)], $\alpha_{Th(IV)}$ from the hydrolysis constants in Table 2 at ionic strength 0.01 mol/kg_w.

Using the hydrolysis data from [52], the mean value obtained from the three pH's in Table 1 leads to $\log {}^*\beta_{1.4.I} = -12.6 \pm 0.4$ ($\log \beta_{1.4.I} = 43.1 \pm 1.6$) with 95% confidence interval. This value is in agreement with previously obtained data on comparable systems, where $\log \beta_{1.4.I} = 41.6 \pm 0.6$ was obtained in [19] with SIT and hydrolysis in [51], which can be recalculated to $\log \beta_{1.4.I} = 42.1 \pm 0.6$ using the Davies equation and [52].

The transformation to global conditional constant is done by using Eq. (9) and will permit comparison of these values with literature data.

Compilation of data

Up to now there is not a lot of data on the quantification of An(IV) complexation by humic substances in the literature [19, 23, 24, 26, 28–30, 32, 33, 57]. We proposed hereafter to review these data and compile them if possible.

Li *et al.* have proposed a $\log {}^{HA}\beta(U(IV)) = 6.98$ at pH 6 for the strong sites on humic acids, which was apparently not corrected for U(IV) hydrolysis [24]. As the control of the chemistry of U(IV) is not reported, the study should be considered with care. Moreover, total concentration of U(IV) in solution is between 0.1 and 10 mg/L[1] for a total humic acid concentration of 20 mg/L. The lower U(IV) concentration is 133 times higher than total inorganic solubility of UO_2 at this pH, *i.e.* 3.2×10^{-9} mol_U/kg_w using thermodynamic data in [47]. Using the results of a preceding calculation exercise [19], the solubility of amorphous $ThO_2(am)$ would be enhanced at pH 6 by a factor of *ca.* 60 in the presence of humic acid. As a comparison, the solubility enhancement observed for UO_2 in the presence of HA was a factor of *ca.* 2 when $6.5 \leq pH \leq 9$ [32]. For lower uranium concentrations, the results could thus be used for comparison, but with great care.

The study of Zuyi and Huanxin is not reliable as it suffers from a mass balance problem [Table 1 in 57], and the raw results from Murphy *et al.* in [26] on Suwannee River Humic acid (SRHA) are only available in [27].

Nash and Choppin determined complexation constants for Th(IV) at different pH values with different humic and fulvic acid samples, *i.e.* a lacustrine (Lake Bradford, Tallahassee, FL, USA), a soil (Joliet, IL, USA), and a commercial sample (Aldrich Chemical Co.) [23, 58]. They used

[1] $4.2 \times 10^{-7} \leq [U]_{total} \leq 4.2 \times 10^{-5}$ mol/L.

Table 3. Generic formation parameters for humic complexes proposed for humic complexation in the framework of this study and [19, 35 and references therein].

Equilibrium	$\log {}^{HA}\beta$	
	Th	U
$An^{4+} + 4H_2O + HA(I) \rightleftarrows An(OH)_4HA(I) + 4H^+$	-12.1 ± 1.9	-3.8 (BCHA) -5.2
$AnO_2^+ + HA(I) \rightleftarrows AnO_2HA(I)$		4.6 [7]
$AnO_2^{2+} + HA(II) \rightleftarrows AnO_2HA(II)$		6.2 [11]
$AnO_2^{2+} + H_2O + HA(I) \rightleftarrows AnO_2OHHA(I) + H^+$		1.1 [78]

a solvent extraction technique in acetate medium and the Schubert method [59]. The authors noted a "linear" evolution of the partition coefficient (D) without humic acid, between pH 3.5 and 4 with a slope of +3, which they attributed to $Th(CH_3CO_2)^{3+}$. At pH 4.5–5, a deviation from linearity in the value of D was observed, which was attributed to eigencolloid formation [Fig. 21, in 58], which could be the formation of ThO_2 colloids as noted in [48]. The authors assumed that under these pH conditions, and in the presence of a large excess of humic substances, the formation of these colloids would be hindered. This can also be assumed from the calculation results [19]. Under these pH conditions, D_0 values were not the actual experimental values but the ones extrapolated from the line with slope +3 between pH 3.5 and 4. The only raw data available are for the Aldrich sample at pH $\approx$ 4. The other data will be treated using Eq. (7). The total concentration of Th(IV) in solution is not reported, so an estimation of solubility is not possible.

In [25], measurements were made from a Pu(IV)-citrate stock solution where the final oxidation state was controlled. The technique was comparable to the one used in [58] but the D_0 values were approximated from Th(IV) through analogy. The $\log {}^{HA}\beta = 12.4$ relative to hydrolysis constants for $Pu(OH)_n^{4-n}$ – $\log {}^*\beta^\circ{}_4 = -9.5$ and $\log {}^*\beta^\circ{}_5 = -15$ – was estimated. Even if the raw data are available in the document, the D_0 value cannot be used as stressed by the author. The value is only taken for comparison and treated through Eq. (7).

Reiller *et al.* determined conditional formation constants between pH 6.5 and 8 using the Schubert method in competition between HA and SiO_2 [28]. Total thorium concentration was always lower than 10^{-10} mol/L so no precipitation of ThO_2 or colloid formation was anticipated. The determination of the constants was either from pH isotherms or from humic acid isotherms. Only the points above pH 6.5 can be used in the pH isotherm in [28] in order to reduce the interference from HA sorption on SiO_2. The data from pH isotherms will be estimated using Eq. (7), because it would need a total calculation of the Th-SiO_2 system, which is not the goal of this study.

Szabó *et al.* worked in a wider pH range using silica grafted humic acids [29, 30, 33]. The isotherms were constructed varying the ratio An(IV), *i.e.* Th and Pu, to the number of available humic sites. The modification induced by grafting was quantified and the complexation properties of HA was not altered [60, 61]. Sorption of An(IV) onto tube walls has been taken into account and total concentration is always under the solubility limit. Pu(IV) was added as Pu(IV) citrate, and the total citrate concentration added did not control the speciation [62]. The data at pH < 3 were discarded because HA are not supposed to be soluble.

Recently, Warwick *et al.* published conditional stability constants obtained from uranium concentration enhancement from UO_2 by AHA, and from Boom Clay humic acid, or BCHA (Belgium) [32]. The stability of U(IV) was "fixed" by adding sodium dithionite ($Na_2S_2O_4$), also used to hinder oxidation of Np(IV) [63]. In this work, the inevitable sorption of humic acids to UO_2 was not taken into account. The UO_2 surface zero point of charge has been determined as being between 5–5.5 [64]. The sorption was thus likely to be higher at pH 6.5–8 than for SiO_2 [28], but no data are available.

The authors did not correct the water protolysis for ionic strength in [32]. Henceforth, all thermodynamic constants have been re-determined from experimental data. The recalculated solubility constants from [32, Table 4] presented in Table 4, *i.e.* $\log K_{sp}(0.202\ \text{m}) = -51.1 \pm 0.8$, is more in agreement with the value extrapolated from [51] in Table 2, and no eigencolloids formation were anticipated.

The results on uranium concentration enhancement by humics are reinterpreted and presented in Table 5 for BCHA from [Table 5 in 32], and for AHA from [Tables 6, 7, and 8 in 32]. The constants $\log {}^{HA}\beta$ accounting for the solubility of UO_2(am, hyd) recommended in [47], which is consistent with hydrolysis data in Table 2 [51], are also reported in Table 5. These latter values will be use hereafter.

The compiled data are represented together on Fig. 1. For Th(IV), the data were not corrected for hydrolysis in the same way: data from [23, 58] were reported as they are [65] because they mainly depend on acetate complexation [66];

Table 4. Data for measurement of solubility product of UO_2(am) and recalculation from [32, Table 4].

pH	$[OH^-]$	α	$\log K_{sp}$
10.17	1.96×10^{-4}	4.28×10^{28}	−51.3
8.90	1.05×10^{-5}	3.56×10^{23}	−51.2
10.45	3.74×10^{-4}	5.64×10^{29}	−50.6
8.18	2.01×10^{-6}	4.70×10^{20}	−51.2
7.04	1.45×10^{-7}	1.32×10^{16}	−50.8
6.97	1.24×10^{-7}	6.97×10^{15}	−51.2
8.20	2.10×10^{-6}	5.65×10^{20}	−51.5
		Mean	−51.1
		SD	0.3
		95% conf. int.	0.8

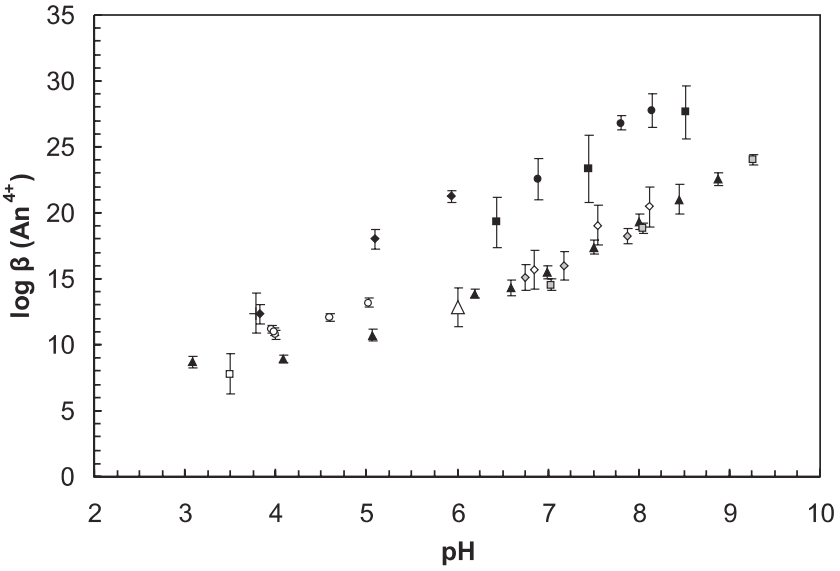


Fig. 1. Compilation of data for the An(IV)-HA systems; for Th(IV), ○ [23], △ [24], □ [26] referring to hydrolysis in [65], ◇ and ◈ [28], and ▲ [29, 30], ▣ this study referring to hydrolysis in [52]; for uranium(IV), ● and ■ U(IV) [32] referring to hydrolysis in [51]; for Pu(IV) + LBHA [25], ◆ Pu(IV) on SiO_2-HA [33] referring to hydrolysis in [47].

Table 5. Conditional formation constants for U(IV)-HA system recalculated from [Tables 5 to 8 in 32].

	pH	log $^{HA}\beta$ from solubility recalculated in Table 4	log $^{HA}\beta$ from solubility in [51], see Table 2	log $\beta_{1.4.1}$ [a]	log $^{*}\beta_{1.4.1}$ [a]
			BCHA		
Mean:	7.81	25.6	26.5	51.4	−3.5
S.D.:	0.02	0.2	0.2	0.3	0.3
Mean:	8.15	26.3	27.5	51.0	−4.0
S.D.:	0.04	0.5	0.5	0.5	0.5
Mean:	6.90	21.4	22.2	51.1	−3.9
S.D.:	0.10	0.7	0.7	0.2	0.2
			Grand mean	51.2	−3.8
			s.d.	0.4	0.4
			AHA		
Mean:	8.52	26.6	27.6	49.5	−5.5
S.D.:	0.23	1.0	1.0	0.5	0.5
	7.45	22.4	23.3	49.8	−5.2
	0.24	1.3	1.2	0.4	0.4
	6.43	18.3	19.3	50.1	−4.9
	0.24	0.9	0.9	0.3	0.3
			Grand mean	49.8	−5.2
			s.d.	0.5	0.5

a: LC calculated using $\log \mathrm{LC(I)} = 0.26\,\mathrm{pH} - 2.72$ [56, Eq. 14].

the other Th(IV) were recalculated referring to [52]. For Pu(IV) and U(IV) the hydrolysis constants from [47] were used.

The classic increase in the metal-humic "formation constants" has been obtained throughout the pH range. The uncertainties are either calculated from the mean of different determinations when raw data are available, *i.e.* $t_{0.05} \times \sigma$, or estimated as ±1.5 when the data are not available. The different log $^{HA}\beta$ (An^{4+}) values cannot be rigorously assumed as equal, with the exception of some values, *e.g.* pH ≈ 4, 7 and 7.5. Nevertheless, the values are in reasonable agreement.

Values determined in ultrafiltration at 0.01 mol/kg_w in $NaClO_4$ in this study are also in agreement with the Th(IV) data.

More generally, the data on Th(IV) are more consistent with each other, with the exception of data from [23, 58] for a reason we will discuss later.

Reinterpretation of data

Conditional stability constants

The only data that can be reinterpreted with a reasonable level of confidence are the ones that are documented in the

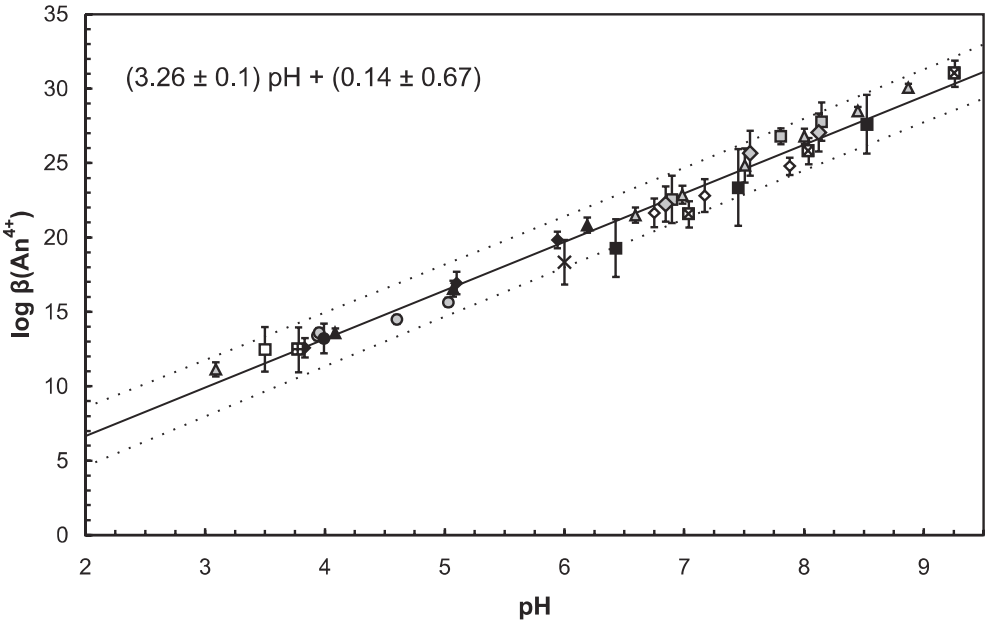


Fig. 2. Comparison of the log $\beta(An^{4+})$ values obtained for different actinides corrected for U(IV) hydrolysis [51]: ■ U-Aldrich HA, and ▩ U-Boom Clay HA [32]; ◇ Th-SiO_2-Aldrich HA, Schubert, and ◈ Th-SiO_2-Aldrich HA, pH isotherm [28]; ▲ Th-SiO_2 grafted HA [29, 30], △ [30]; ◆ Pu-SiO_2 grafted HA [33]; ○ Th-Aldrich HA, ◍ Lake Bradford HA, and ● IHA [23]; □ Th-SRHA [26]; ⊠ Th-Aldrich HA (this study); ⊞ Pu Lake Bradford HA [25]; × U-HA [24].

original articles or PhD theses. It means that only the data for Aldrich HA in [23, 58], and the data from [19, 28, 29, 32], and the data proposed here can be used for these calculations. For the other data, estimation can be proposed assuming that:

$$\log {}^{HA}\beta(An^{4+}) = \log {}^{HA}\beta(Th^{4+}) + \log \frac{\alpha_{An(IV)}}{\alpha_{Th(IV)}} \quad (11)$$

Should one particular species dominate the speciation, as it is the case for $An(OH)_4(aq)$ above pH 7, then the preceding equation can be written as:

$$\log \beta(An^{4+}) = \log \beta(Th^{4+}) + \log \frac{\beta_{An(IV)}}{\beta_{Th(IV)}} \quad (12)$$

As in a previous exercise [19], these conditional constants are only estimates and should be used with caution as guidelines for further studies.

All the data on Th(IV) [28–30], U(IV) [32], and Pu(IV) [33] were treated using the Davies equation and the data for the hydrolysis of U(IV) in [51]. The correlation hypothesised in Fig. 1, is now evident in Fig. 2. It can be seen that all the data are now more coherent with each other for the three different An(IV). A linear relationship has been obtained using a classical linear regression, using only the log ${}^{HA}\beta$ from which the raw data are available between pH 3 and 9.3:

$$\log {}^{HA}\beta(An^{4+}) = (3.26 \pm 0.10)\text{pH} + (0.14 \pm 0.67) \quad (13)$$

Using this kind of correlation, a log ${}^{HA}\beta$ value can be given with a 95% uncertainty of ± 1.96 ($r^2 = 0.9726$) in the pH range. It is worthy to notice that other values, estimated using Eq. (11), are in agreement with the regression. No weighted regressions were used because different kinds of uncertainties are represented in Fig. 2: either from fits or truly experimental ones. This kind of correlation can be sufficient for operational model, as for performance assessment, but not for a detailed understanding of the complexation processes including competition [67, 68].

Charge neutralization model

The $\log \beta_{1.n.Z-N}$ values across a pH range can be obtained for the individual sets of data by non-linear least square regression. The Th(IV) isotherms from [29, 30] were treated in a comparable manner as [19]. As there is no dominant Th(IV) species between pH 3 and 6.5, the $Th(OH)_nHA(Z-N)$ species were chosen arbitrarily, *i.e.* ThHA(IV) and ThOHHA(III), $Th(OH)_3HA(I)$ and the already assumed $Th(OH)_4HA(I)$ [19]. The best fits were adjusted at each pH minimising the number of needed species. The uncertainties were estimated using the SolverAid Microsoft Excel macro [69]. The values of LC($Z-N$) were taken as LC(III) for ThHA(IV) and ThOHHA(III) [19] and as LC(I) for $Th(OH)_3HA(I)$, and $Th(OH)_4HA(I)$ from [56]. Hence the data at pH < 3 were not used because LC(III) becomes negative [35].

On Fig. 3 is represented the log ${}^{*}\beta_{1.n.Z-N}$ values; the equilibria and constants reported in Table 6. From these constants, $\log {}^{*}\beta_{1.4.I} = -11.4 \pm 0.4$ ($\log \beta_{1.4.I} = 43.6 \pm 1.5$) for $Th(OH)_4HA(I)$ is in reasonable agreement both with the data proposed in this study and with a previous determination of $\log \beta_{1.4.I} = 41.6 \pm 0.6$ in [19] on a narrower pH range with SIT and [51], which corresponds to $\log \beta_{1.4.I} = 42.1 \pm 0.6$ using the Davies equation and [52].

From the evolution in Fig. 3, the ionic strength does not seem to be a critical parameter. Nevertheless, one must not forget that activity variation was accounted for in $[H^+]$ calculation. Combining the data gives a grand mean generic value of $\log {}^{*}\beta_{1.4.I} = -12.1 \pm 1.9$ (Table 3).

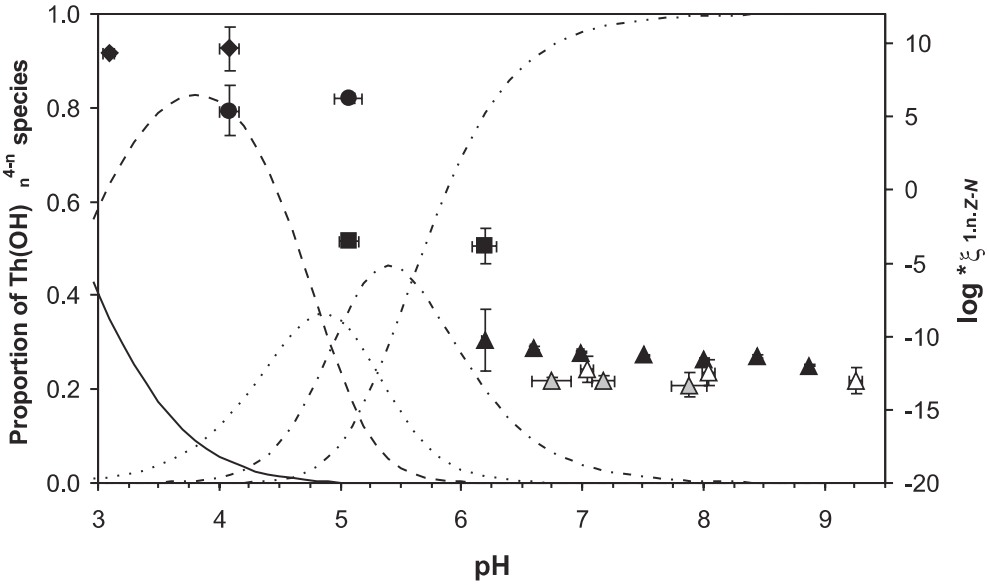


Fig. 3. Value of log ${}^{*}\beta_{1.n.Z-N}$ for the Th(IV) HA grafted SiO_2 from [29, 30], black symbols, compared to the Th(IV) speciation [52]: plain line Th^{4+}, dashed line $ThOH^{3+}$, dotted line $Th(OH)_2{}^{2+}$, dot-dash $Th(OH)_3{}^{+}$, dash-dot-dot $Th(OH)_4$(aq); diamond ThHA(IV), square $Th(OH)_2$HA(II), and triangles $Th(OH)_4$HA(I); open symbols this study, grey symbols [19] adapted to hydrolysis in [52].

Table 6. Formation constants for the Th(IV)-GraftedHA system recalculated from [29, 30] in the pH range 3–9. Uncertainties of mean log ${}^{*}\beta_{1.n.Z-N}$ are calculated from the propagation of error of fitting uncertainties at each pH in Fig. 3.

Equilibrium	log ${}^{*}\beta_{1.n.Z-N}{}^{a}$
$Th^{4+} + HA(IV) \rightleftarrows ThHA(IV)$	9.6 ± 1.5
$Th^{4+} + H_2O + HA(III) \rightleftarrows ThOHHA(III)$	5.4 ± 1.7
$Th^{4+} + 3H_2O + HA(I) \rightleftarrows Th(OH)_3HA(I) + 2H^+$	-3.6 ± 1.2
$Th^{4+} + 4H_2O + HA(I) \rightleftarrows Th(OH)_4HA(I) + 4H^+$	-11.4 ± 2.1

a: $n \rightarrow z$, then $N-Z \rightarrow 1$, and [HA(0)] $\rightarrow$ [HA(I)], see text.

The value of $\log \beta_{1.IV} = 9.5 \pm 1.5$ for ThHA(IV) is significantly lower that the estimated value in [19] from the data in [23, 58], *i.e.* $\log(\beta_{1.IV} \times LC) = 11.7 \pm 0.3$. This may be due to the hydrolysis of Th(IV) at pH 3 and 4, which was hindered by CH_3COOH complexation in [23, 58]. These values may also not be compared directly as the data in [23, 58] are mostly linked to acetate complexation constants in [66], and the data calculated in this study are linked to hydrolysis data in [52]. Moreover, acetate data from [66], obtained in 1 M $NaClO_4$ were corrected to 0.1 M $NaClO_4$ in [23, 58] using a modified Debye–Hückel expression [70, 71] that differs from the Davies equation, which is not valid at 1 M. Considering the differences in the techniques, extrapolation models, and complexation data sets, these data are in fair agreement. This new value may be more representative of the model used for non-ideality.

The large uncertainty for log ${}^{*}\beta_{1.1.III}$ is due to the lack of data in pH range were this species can be considered as dominant.

Using Eq. (13), when $An(OH)_4$(aq) is the only species present, *i.e.* when pH ≥ 7 according to [51], then $\log {}^{*}\beta_{1.4.I} = -5.2 \pm 0.4$ ($\log \beta_{1.4.I} = 49.8 \pm 3.6$) can be calculated with 95% confidence interval for $U(OH)_4$HA(I) (Table 3). These uncertainties and differences come both from combining data on different elements, at different ionic strengths, and from different humic substrates.

For the sake of consistency in the following exercise on independent data, the constant for BCHA and AHA obtained in [32] can be calculated relative to [47]. When only BCHA data are used, $\log {}^{*}\beta_{1.4.I} = -3.8 \pm 1.1$ (Table 3), corresponding to the formation of the complex $U(OH)_4$AH(I). In the case of AHA, $\log {}^{*}\beta_{1.4.I} = -5.2 \pm 1.3$ using a 95% confidence interval is obtained. Even if the confidence intervals overlap, the differences in humic extracts are evident. These data can be compared with the one that was proposed in [19] originally relative to hydrolysis data in [72], *i.e.* $\log \beta_{1.4.I} = 54.4$, and corrected relative to hydrolysis data in [47], *i.e.* $\log \beta_{1.4.I} = 49.1$ or $\log {}^{*}\beta_{1.4.I} = -6.1$, which is in good agreement with the AHA data. It is to be noted that in the Boom clay water conditions, *i.e.*, pH 8.2, hydrolysis data in [47] and in [51] result in the only presence of $U(OH)_4$(aq).[2]

In conclusion, even if the analogy treatment is justified when it comes to estimating humic "complexation constant", it should not prevent from direct acquisition of data to minimize uncertainties.

Comparison with independent data

Uranium(IV) laboratory data

An independent set of data was obtained by the Belgian SCK-CEN on the increase of available uranium concentration from UO_2 in various water compositions [31, 73]. In the study of Cachoir *et al.*, real interstitial water from the Mol formation (RIC), synthetic clay water (SCW), synthetic clay water with humic acid (SCWHA), and synthetic clay water with humic acid but with low carbonate content (SCWHA/C) were used [31]. The authors intended to keep the E_h of their solutions as low as possible by adding Na_2S.

[2] $\log \alpha = 20.76$ in both cases as $\log \beta_4$ are identical.

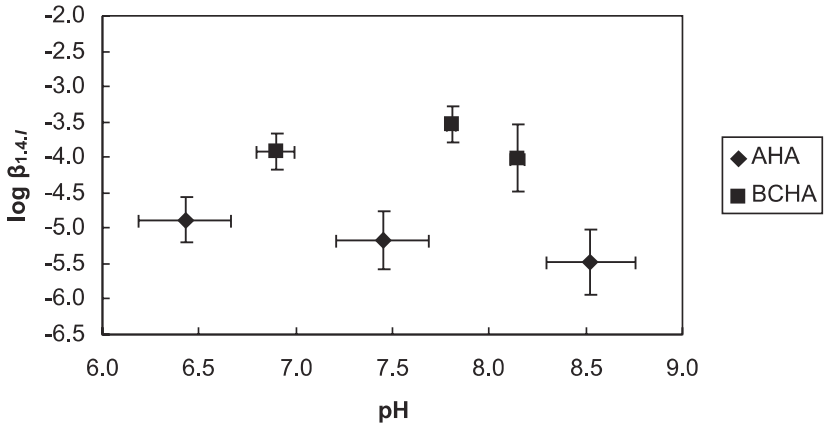


Fig. 4. Evolution of mean $\log \beta_{1.4.I}$ for $U(OH)_4HA(I)$ complex with Aldrich (AHA) and Boom Clay (BCHA) humic acid from data in [32] (Table 5).

The kinetics of the dissolution was followed for a period of *ca.* one year.

The authors added around 40 mg/L of Na_2S to solutions that already contained 20 mg/L of SO_4^{2-}, which leads to $[S^{2-}] = 5.13 \times 10^{-4}$ mol$_S$/L and $[SO_4^{2-}] = 2.08 \times 10^{-4}$ mol$_S$/L. The authors did not note an increase in SO_4^{2-} concentration, which means that either S(–II) was not oxidized to S(VI), or it may have been oxidized to another oxidation state of sulphur. Should there have been a coexistence of S(–II)/S(VI), the redox couple would lead finally to a minimum potential value of $E_h = -288.8$ mV/SHE at 20 °C. The authors reported a maximum measured value of −150 mV, pointing out that it is difficult to assess a redox potential under these conditions.

Knowing the complexity of the water compositions, the speciation of uranium can be calculated using PHREEQC [74]. As some $\Delta_f H°$ values are missing in [47], the most critical being UO_2(am, hyd) and $UO_2(OH)_3^-$, we will consider the difference between 20 and 25 °C negligible, as an increase in solubility of *ca.* 20% is awaited for UO_2(cr). All the calculations done afterwards were performed at 25 °C.

Nevertheless, as it was noted earlier, the formation "constants" of humic complexes are closely related to the ionic strength of their determinations. These "constants" must be decoupled form the ionic strength extrapolation performed in PHREEQC, using either the Davies (Eq. (4)) or the Debye–Hückel equation (Eq. (14)):

$$-\log \gamma = \frac{Az^2\sqrt{I}}{1 + Ba_i^0\sqrt{I}} - b_i I \qquad (14)$$

In order to "fix" the humic "constants" to their values and hinder the ionic strength correction, a_i^0 was fixed to 10^{14} and b_i was fixed to 0 [74, page 156]. As in these experiments Boom clay humic acids were used, only the $\log {}^*\beta_{1.4.I} = -3.8 \pm 0.8$ for $U(OH)_4HA(I)$ determined using data in [32] will be used in the following calculations (Table 3).

The solubility of An(IV) is not an easy task to tackle. For most of the studies, log(solubility) values are between −9 to −8, when for crystalline forms log S are *ca.* −14 [75]. The development of a hydration layer at the surface of the MO_2 oxides, as in the case of ZrO_2 seems to be inevitable, even when the solid is produced *via* a hydrothermal route [76, 77] in neutral media [75]. The formation of colloids was also shown in the case of Th(IV) [48].

Cachoir *et al.* characterised their uranium oxide samples after leaching in RIC, SCW, and SCWHA as mixtures of UO_2 and U_4O_9 [31]. The final uranium concentrations in solution at 20 °C were between 3×10^{-8} and 5×10^{-8} mol$_U$/L for RIC, SCW, and SCWHA, which is an order of magnitude above the UO_2(am) solubility. In the case of SCWHA/C, the $[U]_{max}$ increased up to 1.5×10^{-6} mol$_U$/L which represents 30 times the initial concentration.

Using the $\log {}^*\beta°_n$ in [47] for hydrolysis and $\log {}^*\beta_{1.4.I} = -3.8$ for $U(OH)_4HA(I)$, and other constants in Table 3 for UO_2^+, using analogy with NpO_2^+ [56], and UO_2^{2+} [11, 78], speciation calculations can be done under the conditions given in [31, Table 1] for SCWHA and SCWHA/C.

In the case of SCWHA/C, if the calculation is done from the solubility of UO_2(am, hyd) in [47] at $E = -150$ mV and -288.8 mV, $[U]_{max} = 3.96 \times 10^{-8}$ mol$_u$/kg$_w$, 85.5% being U(VI) species, and $3.16 - 9$ mol$_u$/kg$_w$, 99.7% being U(IV) species, should be obtained respectively at 25 °C, with U_4O_9(cr) oversaturated (Fig. 5). The fact that the $[U]_{max}$ value at −150 mV is in line with the observed value for RCI, SCW, and SCWHA is noteworthy, even if the authors carefully worked with a cristalline UO_2.

The calculation of the humic complexation can be done considering that the total number of humic sites is $[BCHA] = 2.9$ meq/g $\times$ 177 mg/L $= 5.13 \times 10^{-4}$ eq/L. The proportion of accessible sites at pH = 8.2 is estimated from [7, 35]:

$$\left.\begin{array}{l} LC(I) = 10^{0.26.pH-2.72} = 0.255 \\ LC(II) = 1 \end{array}\right\} \qquad (15)$$

Hence, $[BCHA(I)] = 1.33 \times 10^{-4}$ eq/L, and $[BCHA(II)] = 2.54 \times 10^{-4}$ eq/L.

The calculated $[U]_{max}$ is increased to 6.5×10^{-7} and 6.4×10^{-7} mol$_U$/L respectively for the two E_h values. This represents an increase by a factor of *ca.* 17 and 200 respectively. This increase is either the half or 6 times the experimental one *i.e.* 30. The agreement between experiment and modelling is reasonable (Fig. 5).

The formation of UO_2 amorphous eigencolloids as in the case of ThO_2 [48] or nano-phase entrapment in HA as in the case of iron [79], can also be taken into account.

The hypothesis concerning the complexation of U(VI) by humics under these conditions is unlikely for different reasons. Firstly, under these conditions, the U(VI) species are

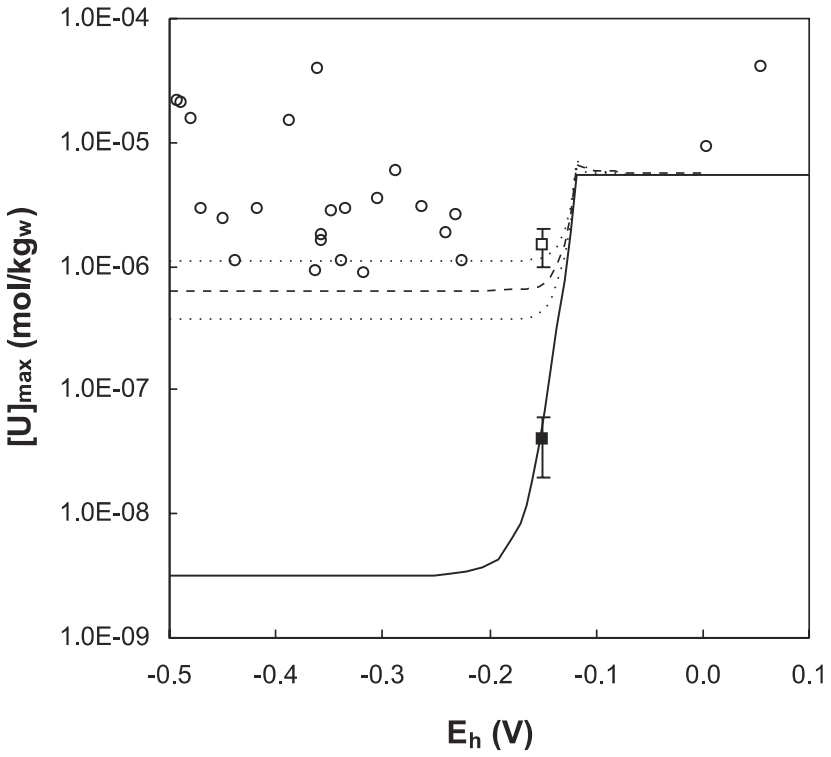


Fig. 5. Evolution of the available uranium concentration from UO_2(am,hyd) to $UO_3{:}2H_2O$ *vs.* E_H at pH 8.2, under the conditions of the SCWHA/C [31], considering the chemistry in [47]: plain line without HA, dashed line with HA, dotted line uncertainties; ■ approximate value of final uranium concentration in RIC, SCW, and SCWHA in [31]; □ approximate final uranium concentration in SCWHA/C in [31]; ○ data from [73]; value from BCHA $\log {}^{*}\beta_{1.4.1} = -3.8$ (Table 3).

anionic[3] and will be repelled by the negative potential existing at the "surface" of humic particles unless redox reaction occurs [44, 80]. Secondly, it has undoubtedly been shown that the carbonate system competes effectively with the humic complexation of uranium(VI): for $\log p(CO_2) \geq -3.5$, no humic complexes of U(VI) could be obtained at pH $\geq$ 8 [15, 68, 81, 82]. In the Boom clay water, $\log p(CO_2) \approx -2.3$ (total inorganic carbon 900 mg/L [31]), hence no U(VI) humic complexation could be anticipated. Furthermore, Glaus *et al.* only evidenced a weak mixed complex between $UO_2{}^{2+}$, $CO_3{}^{2-}$, and HA [83]. Finally, in all our calculations, neither UO_2HA(II) nor UO_2OHHA(I) attained more than 0.5% of the total uranium speciation. Noteworthy is the fact that using data in Table 3, an hypothetic UO_2HA(I), *i.e.*, an $UO_2{}^{+}$ humic complex, even minor should be more important than both UO_2HA(II) and UO_2OHHA(I) in the two hypotheses.

In both cases, if U_4O_9(cr) is allowed to precipitate, $[U]_{max}$ should be lowered to 9.2×10^{-14} mol_U/kg_w and 2.4×10^{-13} mol_U/kg_w respectively without HA. The presence of HA would lead to $[U]_{max}$ values of 3.4×10^{-12} mol_U/kg_w and 5.1×10^{-11} mol_U/kg_w. This is not in agreement with any of the measured values. As for ThO_2(cr) or ZrO_2, even in the case of crystalline UO_2, the solubility is controlled by the formation of an amorphous layer [75–77]

For SCW and SCWHA, the uranium concentration changes in [Fig. 3 in 31] *vs.* time are remarkable. After a first increase up to 5×10^{-7} mol_U/L after 75 days, the uranium concentration decreased around 5×10^{-8} mol_U/L after 200 days. If a calculation is done from the solubility of UO_2(am, hyd) in [47] at $E_h = -150$ mV, a maximum value of $[U] = 1.45 \times 10^{-3}$ mol_U/kg_w should be obtained at 25 °C, 98.6% $UO_2(CO_3)_3{}^{4-}$ with U_4O_9(cr) oversaturated. If U_4O_9(cr) is allowed to precipitate afterwards, the equilibrium uranium concentration decrease to 3.0×10^{-8} mol_U/kg_w at 25 °C, 99% $UO_2(CO_3)_3{}^{4-}$ as in [31], with a very low $U(OH)_4$HA(I) concentration, *i.e.* 3.3×10^{-12} mol_U/kg_w, which is in agreement with the experimental uranium concentration. The interpretation is not straightforward, but the precipitation of the U(VI) dissolved in carbonate form, and not as uranium(IV) hydroxide, as U_4O_9(cr) seems likely.

When the $E_h = -288.8$ mV, the equilibrium concentration of uranium would be 8.9×10^{-8} mol_U/kg_w with UO_2(am, hyd) at 25 °C; 95.2% $UO_2(CO_3)_4{}^{4-}$, and 3.9% $U(OH)_4$(aq). In the presence of HA, the final calculated concentration is 7.2×10^{-7} mol_U/kg_w, 88.4% of $U(OH)_4$HA(I), and is in agreement with the "transient state" between 50 and 100 days, *viz.* 5×10^{-7} mol/L. Inasmuch, as the final uranium concentration, *viz.* $\leq 5 \times 10^{-8}$ mol/L, is not in agreement with the calculated solubility, this hypothesis can only explain part of the data.

Another possibility would be an increase in U(IV) concentration in solution due to carbonate complexes similar to hydroxocarbonatothorate(IV) [46, 84]. These complexes can be postulated for U(IV) but up to now cannot be accounted for in the present calculation for the sake of data consistency relative to other uranium thermodynamic data. As an example, under these conditions, an increase of ThO_2(am) solubility from 1.5×10^{-9} mol/kg_w in aqueous solution to 1×10^{-7} mol/kg_w is awaited in the water RIC given in [Tables 1 in 31] using thermodynamic data in [46, 52]. This could also partly explain the initial increase in solubility for RIC, SCW and SCWHA.

Should U_4O_9(cr) control the solubility of the samples, the equilibrium uranium concentration without HA would be 8.1×10^{-12} mol_U/kg at 25 °C, and to $[U]_{max} = 5.9 \times 10^{-11}$ mol_U/kg_w with HA, and is not in agreement with the data.

[3] mainly $(UO_2)_2CO_3(OH)_3{}^{-}$, $UO_2(OH)_3{}^{-}$, and $UO_2(CO_3)_3{}^{4-}$.

Hence, these data do not permit a thorough understanding of the decrease in uranium concentration in the carbonated reducing waters. The only plausible explanation would be a UO_2(am, hyd) control of the solubility of the samples through the formation of a hydrated amorphous layer at the surface of the crystalline sample. The presence of carbonate in the solution would permit the solubilisation through the formation of U(VI) carbonate complexes, that can precipitate as U_4O_9(cr) afterwards. The existence of hydroxocarbonatouranate(IV) cannot be excluded.

In the presence of humic substances and high concentration of carbonate, the formation of humic complexes of U(VI) is suppressed and the formation of uranium(IV) humic complexes is unlikely, but nevertheless delays the formation of U_4O_9(cr). One can also think that the eventual formation of negative hydroxocarbonatouranate(IV), and carbonatouranate(IV), would also hinder the formation of humic complexes. Lastly, under low carbonate conditions, the formation of uranium(IV) humic complexes is possible and hinders the formation of U_4O_9(cr). The stabilization of uranium hydroxide colloids, as for Th(IV) [48], or nanophases as for Fe, is also likely when sorbed on humic substances as for iron oxides [79, 85–88], that could lead to an enhancement in mobility [89].

Another point is the redox capacities of HA, especially the possibility of UO_2 oxidation if the reducing conditions are not strictly controlled [14]. This argument is also questionable regarding these experiments because it has been shown in [14, Fig. 5b] that the reoxidation of UO_2, synthesised in the absence of humics, is comparable in Milli Q water, in 0.03 M $NaHCO_3$, and with two different HA samples. Furthermore, the final concentration obtained in RIC, SCW, and SCWHA [31], are in agreement with a fairly good redox control.

It seems that humic substances can complex U(IV) at low carbonate concentration, but do not seem efficient to effectively dissolve reduced uranium phases in the presence of carbonate in groundwaters in the long term. Nevertheless, in transient state the role of humics in the reoxidation of UO_2 is evident.

An increase of uranium concentration was also observed for amorphous UO_2 in Boom Clay water [73]. The original data [Table 3 in 73] are also in reasonable agreement with the calculation in Fig. 5. Nevertheless, the quantitative description is underestimated for most of the point. One must not forget that the determination in [32] was done in enhancing the uranium concentration with HA and that sorption of HA to UO_2, which is not easy to account for, was not taken into account. All the preceding arguments can be repeated here.

Uranium(IV) field data

The strong affinity of uranium for natural organic colloids was also evidenced in the Gorleben groundwaters [15, 16]. The authors stated that accounting only for U(VI) humic complexation cannot represent the repartition of uranium in humic colloids, regarding to the high concentration of carbonate, and that U(IV) humic complexation "would explain the propensity of uranium binding to humic colloids ...".

Using our laboratory data and the composition of the groundwater from Gorleben site (Gohy-532) given in [12], no humic complexation could be awaited as uranium speciation would largely be dominated by $UO_2(CO_3)_n^{2-2n}$ complexes: this calculation is not in agreement with the experimental results obtained in [15, 16].

Some hypotheses can then be proposed. Firstly, the redox potentials proposed in [15] are underestimated has reported in [90]. But the carbonate concentration and pH values should then still lead to the stabilisation of tricarbonatouranyl(VI) complex in the uncertainty range proposed.

Secondly, the uranium humic colloids are formed by a more complicated path than direct complexation in the formation. This hypothesis is more likely in view of the complexity of water fluxes and HS origin from the Gorleben area [91]. It is reported that the formation of these HS is due partly to the humus horizon with recharge water, and mainly from the oxidation of sedimentary organic carbon by microbial activity [92]. Humic substances can enhance both the biological reduction of U(VI) to U(IV), and the reoxidation of U(IV) to U(VI) [13, 14]. Nonetheless, stabilization of U(IV)-humic complexes demand a strict anaerobic condition, otherwise the stabilisation of U(VI) as carbonate complexes would be favoured [14]. Knowing the slow dissociation kinetics of An(IV) humic complexes [16, 93, 94], should the uranium pool in the Gorleben groundwater be associated to humics in the colloidal fraction, it is possible to propose that it comes from a bioreduction mechanism, may be during the bio-oxidation of the sedimentary organic carbon, and not from a direct complexation.

Conclusions

The treatment of humic complexation of tetravalent actinides has been shown to be useful in estimating humic complexation constants. Indeed, it permits to visualise the good correlation of the experimental data when consistent hydrolysis constants sets are taken into account. A first estimation of the available tetravalent actinide concentration in the presence of humic acids can be obtained through this treatment. Nevertheless, for accurate determination direct and specific experiments are still needed. The comparison with field and laboratory data also evidences the possible effect of redox processes that are difficult to account for the moment being.

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