

Effect of ionic strength on complexation of Pu(IV) with humic acid

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Summary. Successful geochemical modelling of the migration of radioactive materials, such as the transuranic elements, from nuclear waste repositories is dependent upon an understanding of their interaction with biogeopolymers such as humic acids, the most likely complexing agents in groundwaters. An established silica/humic acid composite has been evaluated as a model substrate for naturally occurring humate-coated minerals that are likely to be present in the vicinity of the repositories. The binding of Pu(IV), the highly likely oxidation state, by the silica/humic substrate was examined at pH 4 in the range 0.02 to 3.00 M NaClO₄ by the titration method. Pu(IV)-humate conditional stability constants have been evaluated from data obtained from these experiments by using non-linear regression of binding isotherms. The results have been interpreted in terms of complexes of 1 : 1 stoichiometry. Analysis of the complex formation dependency with ionic strength shows that the effect of ionic strength on humate complexation of Pu(IV) is not dramatically pronounced. The complexation constants are evaluated for the humate interaction with Pu⁴⁺ and Pu(OH)₃⁺ at pH 4. The complexation constants are found, respectively, to be $\log {}^{\text{HA}}\beta^0(\text{Pu}^{4+}) = 16.6 \pm 0.3$ and $\log \beta_{1,3,1}^0 = 46.6 \pm 2.3$. The estimations through analogy from previous results are in agreement with these new experimental data.

1. Introduction

It is now well established that humic substances play an important role in the geochemical cycling of various metal ions, some of which could be radionuclides of the transuranic series. From the chemical features of humic acids, it was evident that they would influence the speciation of plutonium in the environment. Many investigations have confirmed the suppositions [1–5]. The recovery of chelatable plutonium from humates from a salt marsh soil, which had been radiolabelled by a marine environmental process, was sufficient evidence [4] for a series of *in vitro* investigations of the interaction of transuranic radionuclides with humic acid. The chemistry of the interactions of plutonium with

humic substances needs to be understood in sufficient detail to predict interactions of the transuranic element with humate-coated phases that might mediate its movement out of waste repositories [4, 6–8]. Satisfactory data on tetravalent and redox sensitive actinides, such as plutonium, are scarce and arise from experimental difficulties posed by the low solubility of their oxide-hydroxide [9, 10] and, also, their high affinity for vessel walls [11]. Although pH and ionic strength are the two main factors that affect the complexation of actinides with humic acids, the literature appears to lack a systematic study of the ionic strength effect on the complexation of plutonium ions. The main objectives of this work are to provide equilibrium complexation data for interaction of plutonium with humic acid in controlled systems. Currently, scientifically proven data for Pu-humate complexes are under represented in the literature. An insufficiency might impair computer simulation of the migration of plutonium from waste repositories.

2. Experimental

2.1 Materials and methods

Humic acid was immobilized on silica gel and characterised by using a previously described procedure [12–14] to yield the composite material SiO₂-HA. The proton exchange capacity of the immobilised HA, determined by potentiometric titration, and the specific surface area of the prepared solid phase, determined by the BET method are given in Table 1. C, H and N analyses of SiO₂-HA were conducted on an automatic CHNS-O analyzer. The citrate of ²³⁹Pu was prepared from stock solutions of the nitrates dissolved in 4 M HNO₃. An aliquot of the stock solution was evaporated to dryness and the residue dissolved in 0.01 M HNO₃ to which was added 2% trisodium citrate solution to reach 1 : 1 stoichiometry for Pu : citrate. The resulting solution was adjusted to pH 4 and passed through a membrane of porosity 25 nm (Millipore Ltd.) to minimize the presence of polynuclear plutonium species. ²³⁹Pu were determined by liquid scintillation counting (LSC) in a Packard Tri-Carb 2550 liquid scintillation counter. The oxidation states of plutonium in the stock solution, in the clarified aliquot after the sorption experiment and in the washing solution were determined,

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every 96 h, by the TTA extraction method and NdF_3 coprecipitation method [15, 16]. Plutonium, as Pu(IV), was the dominant oxidation state and was in excess of 90%. The stability of Pu(IV) in humic solution was verified by Marquardt et al. [5] and the slow reduction to Pu(III) was neglected under our conditions. The binding of plutonium(IV) by the immobilized humic acid was examined at pH 4 in 0.02, 0.05, 0.10, 0.20, 0.50, 1.00, 2.00 and 3.00 M NaClO_4 containing 4.2×10^{-8} M concentration of plutonium by the titration method.

Determination of maximal complexing capacity (B_{\max}) and conditional interaction constants of SiO_2 -HA (${}^{\text{HA}}\beta$) for Pu_{total}

The complexing capacity (B_{\max}) of SiO_2 -HA was determined for Pu(IV). Accurately weighed quantities of the gels, typically about 10 or 20 mg, were added to 9 ml of 0.02, 0.05, 0.10, 0.20, 0.50, 1.00, 2.00 and 3.00 M NaClO_4 solutions (pH 4). The resulting suspensions were titrated by adding 1 mL of the plutonium stock solution (C_0 : 4.2×10^{-8} M) and shaken at room temperature for 48 h. The suspension was clarified after 48 h by centrifugation at 4000 rpm. Aliquots, 1 mL, from the supernatant were taken for measurement of ${}^{239}\text{Pu}$ by LSC. After removal of these aliquots an equal volume of the same stock solution was added. This step was repeated 21 times. The amount of Pu(IV) retained by the suspended gel at each step was calculated according to the following equation:

$$q_i = q_{i-1} + \frac{C_0 + 9C_{i-1} - 10C_i}{W}, \quad (1)$$

where q_i is the concentration of Pu(IV) bound on the gel at the end of i th titration step (mol/g); q_{i-1} is the concentration of Pu(IV) remaining on the gel at the end of $(i-1)$ th titration step (mol/g); C_i is Pu(IV) concentration in the solution at the end of the i th step (mol/L); C_{i-1} is Pu(IV) concentration in the solution at the end of the $(i-1)$ th step (mol/L); C_0 is the concentration of the stock solution (mol/L) and W is the solid concentration in the suspension (g/L).

A parallel titration study evaluated the sorption of Pu(IV), in the absence of SiO_2 -HA on to vial walls. The amount of Pu(IV) bound by SiO_2 -HA was calculated by using the difference between the Pu(IV) concentrations measured in titration experiment and the concentration of Pu(IV) remaining in solution in the foregoing parallel study. Isotherms were then plotted.

It is important to note that the proportion of Pu(IV)-citrate complex should be very low under these conditions, i.e., less than 3% using the data in Kantar and Honeyman [17] at 0.101 mol/kg_w. Recent studies on Np(IV) seem to show that a di-citrate complex should occur around pH 4 [18], but given the large extent of hydrolysis, these species were not considered important in the following.

Calculation of maximal binding capacity (B_{\max}) and conditional interaction constants (${}^{\text{HA}}\beta$) of Pu_{total} from binding isotherm

The conditional interaction constant ${}^{\text{HA}}\beta$ is relative to the following equilibrium:



$$\text{with } {}^{\text{HA}}\beta = \frac{[\text{Pu-HA}]_{\text{total}}}{[\text{Pu(IV)}_{\text{total}}]_{\text{f}} [\text{HA}]_{\text{f}}}, \quad (3)$$

where $\text{Pu(IV)}_{\text{total}}$ is the Pu(IV) cations at the given pH, HA is the humic acid, $[\text{HA}]_{\text{f}}$ is the concentration of the free humic acid, $[\text{Pu(IV)}_{\text{total}}]_{\text{f}}$ is the concentration of the free Pu(IV) ion. The concentration of total Pu-HA species is given by the sum:

$$[\text{Pu-HA}]_{\text{total}} = [\text{PuHA}] + [\text{Pu(OH)HA}] + [\text{Pu(OH)}_2\text{HA}] + [\text{Pu(OH)}_3\text{HA}].$$

The assumption is made that the macromolecule is the central group and the complexation can be described in terms of a Langmuir-type adsorption equation. The free ligand concentration can be calculated in Eq. (3) by introducing B_{\max}

$$[\text{HA}]_{\text{f}} = B_{\max} - [\text{Pu(IV)-HA}]_{\text{total}}, \quad (4)$$

where B_{\max} is the maximal complexing capacity of humic acid.

Combination of Eqs. (3) and (4) gives the relationship that could be used for calculation of conditional interaction constants:

$${}^{\text{HA}}\beta = \frac{[\text{Pu-HA}]_{\text{total}}}{[\text{Pu(IV)}_{\text{total}}]_{\text{f}} (B_{\max} - [\text{Pu-HA}]_{\text{total}})} \quad (5)$$

or after alteration

$$[\text{Pu-HA}]_{\text{total}} = \frac{{}^{\text{HA}}\beta [\text{Pu(IV)}_{\text{total}}]_{\text{f}} B_{\max}}{1 + {}^{\text{HA}}\beta [\text{Pu(IV)}_{\text{total}}]_{\text{f}}}. \quad (6)$$

After plotting $[\text{Pu-HA}]_{\text{total}}$ vs. $[\text{Pu(IV)}_{\text{total}}]_{\text{f}}$ and using the binding isotherms, the maximal binding capacity and ${}^{\text{HA}}\beta$ of $\text{Pu(IV)}_{\text{total}}$ could be determined.

Calculation of conditional interaction constants (${}^{\text{HA}}\beta$) of Pu^{4+} with humic acid

Accounting for the Pu(IV) hydrolysis, the reaction between Pu^{4+} and HA can be written:



$${}^{\text{HA}}\beta (\text{Pu}^{4+}) = \frac{[\text{Pu-HA}]_{\text{total}}}{[\text{Pu}^{4+}]_{\text{f}} [\text{HA}]_{\text{f}}}. \quad (8)$$

Pu^{4+} is readily hydrolysed and it is not expected that only Pu^{4+} ions exist in solution at pH 4. From the $\text{Pu(IV)}_{\text{total}}$ the $[\text{Pu}^{4+}]$ can be calculated by using the stability constants of the hydroxo complexes Pu(OH)^{3+} , Pu(OH)_2^{2+} , Pu(OH)_3^+ and $\text{Pu(OH)}_{4(aq)}$ [9, 19]:

$$[\text{Pu(IV)}]_{\text{total}} = \sum_{i=0}^4 [\text{Pu(OH)}_i^{4-i}], \quad (9)$$

$$[\text{Pu(IV)}]_{\text{total}} = [\text{Pu}^{4+}] \alpha_{\text{Pu}}, \quad (10)$$

where α_{Pu} and ${}^*\beta$ are the side reaction coefficient and hydrolysis constants, respectively [20]:

$$\alpha_{\text{Pu}} = 1 + \sum \frac{{}^*\beta_i}{[\text{H}^+]^i} \quad (11)$$

After measuring the total Pu(IV) concentration in the liquid phase, it becomes possible to calculate the conditional interaction constants ${}^{\text{HA}}\beta(\text{Pu}^{4+})$ using the following equation:

$$\log {}^{\text{HA}}\beta(\text{Pu}_{\text{total}}) + \log \alpha_{\text{Pu}} = \log {}^{\text{HA}}\beta(\text{Pu}^{4+}). \quad (12)$$

3. Results and discussion

The main characteristics of SiO₂-HA are reported in Table 1.

Determination of maximal binding capacity (B_{max}) of SiO₂-HA and conditional interaction constants (${}^{\text{HA}}\beta$) of Pu_{total} from binding isotherm

Typical binding isotherms, solid phase concentration vs. liquid phase concentration in equilibrium, of Pu(IV) by SiO₂-HA at different ionic strengths at pH 4 are presented in Fig. 1. As seen from the Fig. 1, a high reproducibility in the isotherms was obtained. From these binding isotherms it has been possible to calculate, see Table 2, the complexing capacity (B_{max}) expressed in mol g⁻¹ solid phase. As seen in Table 2 and Fig. 2, the complexing capacities of the immobilized humic substances on silica gel decrease exponentially with increasing ionic strength. A similar phenomenon has been reported by others [21]. This has been related to the increase of the electrostatic potential of the humic substances with the ionic strength [22].

The conditional interaction constants can be calculated from the sorption data. The calculated values of conditional interaction constants (${}^{\text{HA}}\beta$) of Pu_{total} with HA on SiO₂-HA, at different ionic strengths of the perchlorate solutions, at pH 4, are presented in Table 3 and Fig. 3. Table 3 contains the $\log {}^{\text{HA}}\beta(\text{Pu}_{\text{total}})$ values obtained from the binding isotherms (Eq. (6)). From Fig. 3, it is apparent that the conditional interaction constants slightly increase with increasing ionic strength. In the literature, the ionic strength

effect on the interaction constants has been debated. In some cases, conditional interaction constants appear to increase with ionic strength. A similar feature was noted by Fukushima *et al.* [23] with Cu(II). However, in other cases, a decrease with increasing ionic strength is evident as observed for actinide(III) [21]. It should be also emphasized that the technique and calculation method used may greatly affect the variation of the interaction constants with ionic strength.

Table 2. Binding capacity (B_{max}) and loading capacity (LC(I)) of humic substances immobilized on silica gel with plutonium as a function of ionic strength.

Ionic strength M	B_{max} (10 ⁻⁸ mol/g) on 10 mg gel	LC _{calc} (%)	B_{max} (10 ⁻⁸ mol/g) on 20 mg gel	LC _{calc} (%)
0.02	157.2 ± 40.4	2.34 ± 0.60		
0.05	113.8 ± 17.2	1.69 ± 0.25	111.4 ± 28.6	1.66 ± 0.57
0.10	86.2 ± 7.8	1.28 ± 0.12	93.6 ± 24.4	1.39 ± 0.36
0.20	53.8 ± 5.8	0.80 ± 0.09	37.4 ± 4.2	0.56 ± 0.07
0.50	27.6 ± 3.6	0.41 ± 0.05	20.2 ± 2.2	0.30 ± 0.03
1.00	16.2 ± 1.2	0.24 ± 0.01	13.6 ± 0.8	0.20 ± 0.01
2.00	24.1 ± 1.4	0.35 ± 0.02	19.1 ± 1.2	0.28 ± 0.02
3.00	27.2 ± 4.2	0.40 ± 0.06	23.4 ± 3.7	0.35 ± 0.05

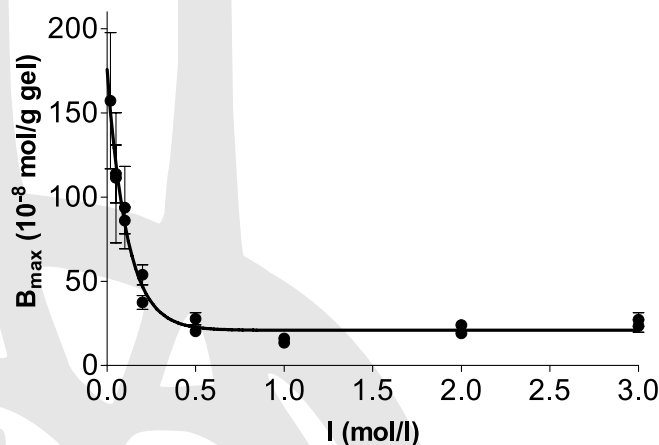


Fig. 2. Effect of ionic strength on the maximal binding capacity (B_{max}) of SiO₂-HA.

Table 1. Characteristics of SiO₂-HA.

Substrate content (mg HA g ⁻¹)	19.9 ± 1.2
Proton exchange capacity (μeq g ⁻¹ solid matter)	67.3
BET surface area ^a (m ² g ⁻¹)	74 ± 8

a: The surface area of the parent silica gel is 100 m² g⁻¹.

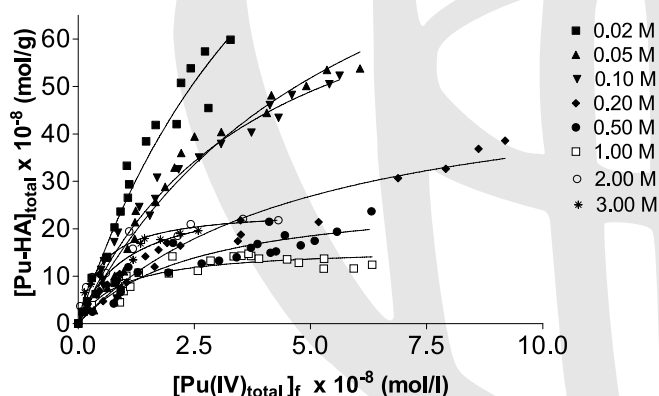


Fig. 1. Binding isotherms of Pu(IV) on SiO₂-HA in different ionic strengths at pH 4.

Table 3. Calculated conditional interaction constants, $\log {}^{\text{HA}}\beta(\text{Pu}_{\text{total}})$, side reaction coefficient ($\log \alpha_{\text{Pu}}$) and conditional interaction constants, $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ of SiO₂-HA with plutonium as a function of molal ionic strength.

Ionic strength mol/kg _{water}	$\log {}^{\text{HA}}\beta(\text{Pu}_{\text{total}})$ calculated from binding isotherms data use of Eq. (6)	$\log \alpha_{\text{Pu}}$	$\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ calculated using of Eq. (12)
0.020	7.28 ± 0.44	8.87	16.15 ± 0.44
0.050	7.22 ± 0.63	8.51	15.73 ± 0.63
0.101	7.42 ± 0.77	8.19	15.61 ± 0.77
0.202	7.29 ± 0.67	7.85	15.14 ± 0.67
0.513	7.61 ± 0.51	7.46	15.07 ± 0.51
1.051	8.05 ± 0.56	7.35	15.40 ± 0.56
2.212	8.32 ± 0.41	7.63	15.95 ± 0.41
3.502	7.99 ± 0.45	8.19	16.18 ± 0.45

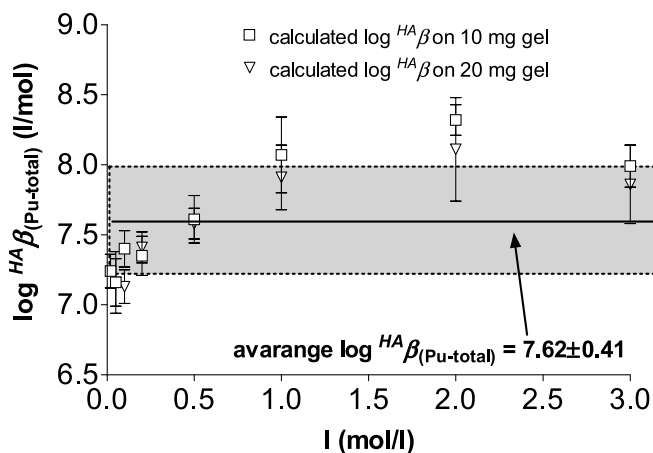


Fig. 3. Effect of ionic strength on the calculated conditional stability constant ($\log {}^{\text{HA}}\beta$) of Pu_{total} .

Determination of the conditional interaction constants of $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$

The $\log {}^{\text{HA}}\beta$ values for Pu_{total} with humic acid are presented in Table 3. From this table the conditional interaction constants of Pu^{4+} with humic acid, ${}^{\text{HA}}\beta(\text{Pu}^{4+})$, can be calculated by using Eq. (12) and the hydrolysis constants from Guillaumont *et al.* [19]. The $\log \alpha_{\text{Pu}}$ values were calculated using the specific ion interaction theory, SIT [24], on the molality scale. Table 3 and Fig. 4 shows the effect of ionic strength on $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$.

As was done by Czerwinski *et al.* [21], one can propose the apparent variation of $\log {}^{\text{HA}}\beta$ as a function of $\sqrt{I_m}$ following the SIT:

$$\log \beta(I_m) = \log \beta(0) - \Delta z^2 \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + \Delta \varepsilon I_m. \quad (13)$$

As neither the definitions of Δz^2 nor of $\Delta \varepsilon$ for a humic acid complexation process are straightforward, the $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ for zero ionic strength can be calculated from Eq. (13) using a non-linear least square fitting procedure, which gives:

$$\log {}^{\text{HA}}\beta^0(\text{Pu}^{4+}) = 16.6 \pm 0.3.$$

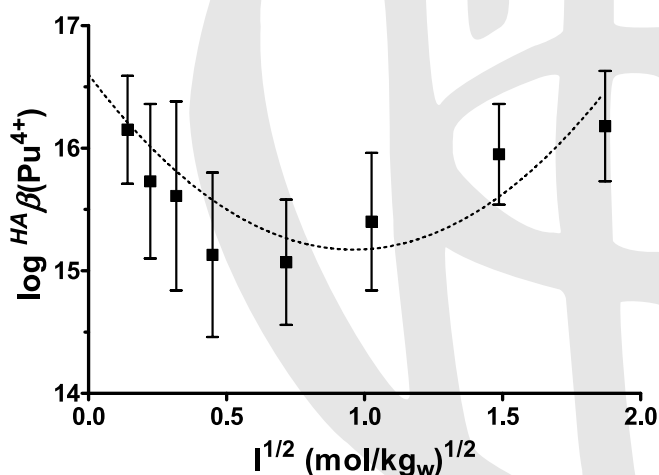


Fig. 4. Effect of ionic strength on the calculated conditional stability constant $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ and fitting to Eq. (13).

The physical meaning of the values of $\Delta z^2 = 9.5 \pm 2.2$, and $\Delta \varepsilon = 0.6 \pm 0.1$ in the case of humic complexation are evidently arguable as conformation changes with ionic strength occurs [22]. They can only be treated here as adjustment operational parameters. Similar observations have been reported for actinides(III) by Czerwinski *et al.* [21] but with half a logarithmic unit intensity for $\log {}^{\text{HA}}\beta_{\text{I,II,III}}$.

Comparison with the compilation of data in reference [25] is also informative. The authors proposed that the evolution of $\log {}^{\text{HA}}\beta(\text{An}^{4+})$ is following a linear relationship (Eq. (11) in [25]) which can be shifted from one actinide(IV) to another by analogy using the relation:

$$\log {}^{\text{HA}}\beta(\text{An}_1^{4+}) = \log {}^{\text{HA}}\beta(\text{An}_2^{4+}) + \log \frac{\alpha_{\text{An}_1(\text{IV})}}{\alpha_{\text{An}_2(\text{IV})}}, \quad (14)$$

where $\alpha_{\text{An}(\text{IV})}$ is the side reaction coefficient for actinide(IV).

For U(IV), using the hydrolysis constant of Neck and Kim [9] and the Davies correction for non-ideality, the relation

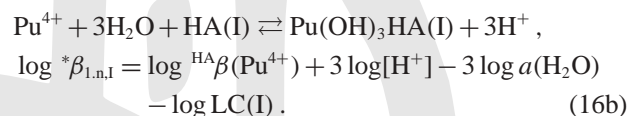
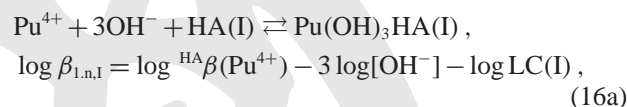
$$\log {}^{\text{HA}}\beta(\text{U}^{4+}) = (3.26 \pm 0.10)\text{pH} + (0.14 \pm 0.67) \quad (15)$$

was proposed. A value of $\log \alpha_{\text{U}(\text{IV})} = 5.95 \pm 1.05^1$ can be calculated with Neck and Kim [9] and the Davies correction for non-ideality at 0.101 m, and $\log \alpha_{\text{Pu}(\text{IV})} = 8.19 \pm 0.37^*$, using data in Guillaumont *et al.* [19] with SIT. Applying the shift to the previous relation, one can wait at 0.101 m for Pu^{4+} :

$$\begin{aligned} \log {}^{\text{HA}}\beta(\text{Pu}^{4+}) &= (13.18 \pm 0.66) - (5.95 \pm 1.05) \\ &+ (8.19 \pm 0.37) = 15.4 \pm 1.3, \end{aligned}$$

which is in fair agreement with the experimental data in Table 3.

At pH 4 Pu(IV) is hydrolysed mainly to $\text{Pu}(\text{OH})_3^+$ with a speciation range of 89% at 0.02 mol/kg_w down to 84.2% at 0.5 mol/kg_w and then up to 95.6% at 3.5 mol/kg_w [19]. $\text{Pu}(\text{OH})_3\text{HA}(\text{I})$, following [25–27], can be proposed:



The loading capacity factor $\text{LC}(\text{Z})$ defined in [26], which in fact is already accounted in $\log {}^{\text{HA}}\beta(\text{Pu}^{4+})$ as $B_{\text{max}} = \text{PEC} \times \text{LC}(\text{I})$, can be calculated from Tables 1 and 2. The B_{max} values are divided by the number of available sites in the grafted humic, *i.e.*, $\text{PEC} = 67.3 \mu\text{mol/g}$ solid, and are reported in Table 2. Hypothetical $\text{LC}(\text{I})$ at $I_m = 0$ mol/kg_w can be extrapolated using a weighted linear regression:

$$\text{LC}(\text{I}) = (0.028 \pm 0.003) - (0.049 \pm 0.007)\sqrt{I_m} \quad (17)$$

in the range $0.02 \leq I_m(\text{mol/kg}_w) \leq 0.202$ (Fig. 5). This yields in turn $\text{LC}(\text{I}) = 0.023 \pm 0.002$ at 0.101 mol/kg_w,

¹ $\sigma(\log \alpha)$ estimated using a finite difference calculation.

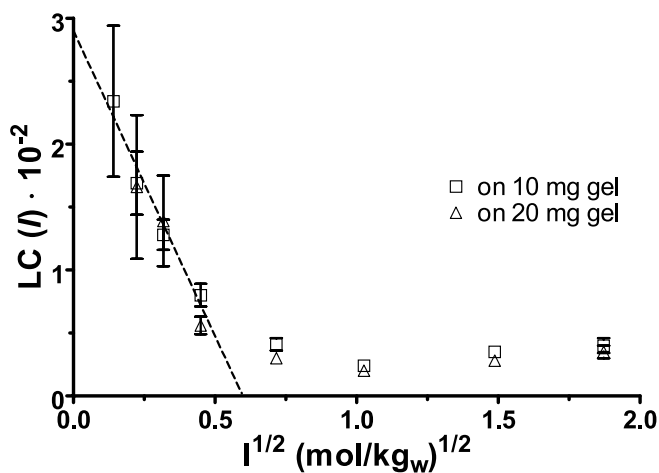


Fig. 5. Effect of ionic strength at pH 4 on the calculated loading capacity of SiO₂-HA gel for Pu(OH)₃⁺, and weighted least square fitted linear relationship between 0.02 and 0.101 mol/kg_w.

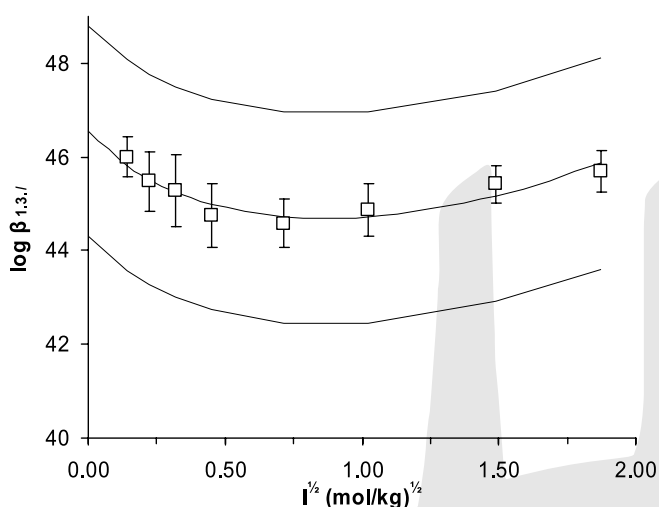


Fig. 6. Effect of ionic strength at pH 4 on log ^{HA}β_{1.3,i} for experimental data (□), data obtained from fitting of Eq. (13) (solid), and associated standard deviation (dotted).

a value which is in agreement with the case of NpO₂⁺ [28], *i.e.*, LC(I) = 0.021 at pH 4 and *I* = 0.1 M. Calculation by using of Eq. (16a) and (16b) results in log β_{1.3,1}⁰ = 46.6 ± 2.3 (log *β_{1.3,1}⁰ = 4.6 ± 2.3). One can remark that both the amplitude and the validity of the linear domain of LC(I) vs. $\sqrt{I_m}$ is far less important compared to the results on LC(III) for actinides(III) [21]. This could be the results of a more constrained structure due to the grafting that might change the conformation of humic acid.

From a comparison with previous data [29,30], further analysis, as indicated in Ref. [25] can be done. A value of log ^{HA}β_{1.3,1} = 38 ± 1.2 for Th(IV) was proposed (log *^{HA}β_{1.3,1} = -3.6 ± 1.2), which can be adapted to Pu(IV) using Eq. (14):

$$\log {}^{\text{HA}}\beta_{1.3,1}(0.101 \text{ m}) = (38 \pm 1.2) - (1.24 \pm 0.31) + (8.19 \pm 0.37) = 44.95 \pm 1.29.$$

By using Eq. (13), the value for log ^{HA}β_{1.3,1} = 45.3 ± 2.3² at 0.101 *m* can be calculated (Fig. 6). The 2σ confidence

$${}^2 \sigma(\log \beta_{1.3,1}) = (\sigma^2(\log {}^{\text{HA}}\beta^0(\text{Pu}^{4+})) + \sigma^2(\Delta z^2) + \sigma^2(\Delta \epsilon^2))^{-1/2}.$$

intervals of these constants clearly overlap and cannot be considered different.

4. Summary and conclusions

The potential of SiO₂-HA as a model substrate for predicting the complexation of species such as Pu⁴⁺ by humate-coated minerals has been demonstrated. From an examination of the sorption isotherms of Pu(IV) at different ionic strengths, it is apparent that conditional stability constants log ^{HA}β(Pu_{total}) and log β_{1.n.z} through the charge neutralization model can be easily calculated. Using these values and the side reaction coefficients (α_{Pu}) the conditional stability constants ^{HA}β(Pu⁴⁺) can be calculated. A comparison of log ^{HA}β(Pu⁴⁺) at different ionic strength with log ^{HA}β⁰(Pu⁴⁺) indicates that the effect of ionic strength on humate complexation of Pu(IV) is not dramatically pronounced over part of the range but becomes clearly pronounced for ionic strength less than 0.15 mol/kg_w. The effect of ionic strength on maximal binding capacity (*B*_{max}) appears to be significant. The *B*_{max} and thus loading capacity factor LC(I), decreases gradually with increasing ionic strength. The experimentally determined log ^{HA}β values obtained here are in fair agreement, although slightly higher than expected, with previous estimations.

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