Estimating the stabilities of actinide aqueous species. Influence of sulfoxy-anions on uranium(IV) geochemistry and discussion of Pa(V) first hydrolysis

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Abstract

Qualitative chemical information is used as a guideline for correlations between equilibrium constants or between equilibrium constants and atomic charges (deduced from quantum mechanics calculations). Pa(V) and Nb(V) hydrolysis constants are also recalculated from experimental data. \[ \log K_1^{An^{IV}/RO_2^-} = 6.50 \pm 0.55 \quad (S_2O_3^{2-}), 10.06 \pm 0.88 \quad (SO_3^{2-}), 11.97 \pm 1.07 \quad (CO_2^{2-}) \] and \[ 10.06 \pm 0.88 \quad (HPO_2^{4-}) \] are estimated based on the trend of affinity for An cations in the series \[ CO_2^{2-} > HPO_2^{4-} \approx SO_3^{2-} > SO_4^{2-} \approx S_2O_3^{2-} \]. These ideas and values are used to discuss U(IV) chemistry in S-containing ground-waters. To cite this article: P. Vitorge et al., C. R. Chimie 10 (2007).

Résumé

Des connaissances qualitatives ont été concrétisées sous la forme de corrélations empiriques entre constantes d’équilibres, voire avec les charges atomiques (issues de calculs quantiques) dans la série \[ CO_2^{2-} > HPO_2^{4-} \approx SO_3^{2-} > SO_4^{2-} \approx S_2O_3^{2-} \], pour, par exemple, estimer \[ \log K_1^{An^{IV}/RO_2^-} = 6.50 \pm 0.55 \quad (S_2O_3^{2-}), 10.06 \pm 0.88 \quad (SO_3^{2-}), 11.97 \pm 1.07 \quad (CO_2^{2-}) \] et \[ 10.06 \pm 0.88 \quad (HPO_2^{4-}) \].

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1. Introduction

The geochemical behaviour of actinides have been extensively studied for understanding uranium and thorium ore deposits, and more recently for assessing the environmental impact of the possible disposal of wastes that contain Pa, Np, Pu, Am or Cm. Starting with uranium [1], the Thermochemical Data Base project of the Nuclear Energy Agency (NEA-TDB) organised the reviewing of published experimental data relevant for modelling aqueous chemistries and solubilities of the most important radionuclides. The results of the NEA-TDB project are now well accepted as a reference critical review, essentially for aqueous chemistry and solubility at room temperature, but these reviews proposed data only when convincing experimental validations were published. There is therefore a gap between this restricted set of quantitative validated thermochemical data and qualitative chemical knowledge.

However, besides selected numerical values, the NEA-TDB reviews also provide qualitative information [2,3], which we used together with analogies for estimating the hydrolysis constants and standard potentials [4] needed for drawing Pourbaix' diagrams of actinides [5]. The present paper aims at testing such rough estimates for complexation.

Rules of thumb are currently used by chemists for checking the possible formation of hypothetical chemical species in specific chemical conditions, when these chemical species are not in databases. This might typically be the case for the environmental aqueous chemistry of An(IV), the actinide elements at the +4 oxidation state (An = Th, U, Np and Pu) in the presence of S-containing inorganic ligands; for this reason it is also an aim of the present paper to estimate the stabilities of An(IV) complexes with sulfoxy-anions.

For storing radioactive wastes, several projects are looking for geological sites that are well isolated from surface waters. These often correspond to anoxic conditions, where U, Np and Pu are expected to be stable in the +4 oxidation state [2,4]. Interestingly, chemical analogues are Ce(IV) and Th, and probably Zr and Hf. Selected NEA-TDB equilibrium constants and redox potentials [2] are adequate for reliable modelling of uranium chemistry in most equilibrated groundwaters. Uranium is predicted to be stable in anoxic waters in the form of the U(OH)₄(aq) aqueous species in equilibrium with uraninite, U₃O₈(s), a compound of low solubility [2,5,6]. Similar behaviour is expected for Np and Pu, even though Pu³⁺ might also be stable [4—7].

In natural underground waters CO₃⁻, the carbonate anion is often the dominating ligand among the inorganic ligands (for actinide cations). However, carbonate complexes are predicted to be of little importance for An(IV) [2,4,7]. Nevertheless, many An(CO₃)₃(OH)₄⁻⁻⁻⁻⁻ complexes have been proposed, but no reliable values could be validated for most of the corresponding formation constants [2,4], for which maximum possible values have been estimated from experimental observations, that also confirmed the similar behaviour of Th, U(IV), Np(IV) and Pu(IV) in carbonate/bicarbonate aqueous solutions [4,5,8]. Values have recently been proposed for the formation constants of several Th(CO₃)₄(OH)₄⁻⁻⁻⁻⁻ complexes in an attempt to interpret a solubility study of ThO₂(s) [8,9], but the Th(CO₃)₄³⁺ species were not included in the interpretation, even though we shall see it should not be completely negligible according to the NEA-TDB data [4]. For probing such competition between the HO⁻ and CO₃⁻ ligands, the relative stabilities of the corresponding 1:1 complexes of An⁺³ will be compared. In this framework, the stability of AnCO₃⁺³⁻ will be estimated: its existence has never been demonstrated, since it is always hidden by hydrolysed species. This over-stabilisation of hydrolysis is specific to the +4 oxidation state: the 1:1 carbonate complexes are well known, and their stabilities were well established for An(III), An(V) and An(VI) (it is not known for Pa(V), which is known to have a very different aqueous chemical behaviour from the other An(V)).

Several other inorganic hard anions are quite reactive toward actinide cations, especially those of high charge (PO₄³⁻), of small size (F⁻), or polydentate (HPO₄²⁻): depending on their content in groundwaters they might form complexes with actinide cations. For example, it
was recently proposed that the pore-waters of Callovo-Oxfordian clay minerals, where an underground research laboratory is being built to study the feasibility of a deep geological repository for radioactive wastes in France [10], contain quite large amounts of $\text{SO}_4^{2-}$. The pore-water composition is approximately at the $\text{SO}_2^-/\text{CO}_3^2-$ frontier point (Fig. 1). Although the most stable aqueous sulfur species - those bolded on Pourbaix’ diagrams - are sulfide ($\text{HS}^-$) and sulfate ($\text{SO}_4^{2-}$), some other sulfoxy-anions are often detected in natural environments, typically as thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and sulfite ($\text{SO}_3^{2-}$) ions. For example, about 25% of the total S content has been reported to be $\text{S}_2\text{O}_3^{2-}$ in a reducing groundwater [11], and even in more oxidizing conditions [12]. Sulfoxy-anions are also suspected to form in the course of the oxidative dissolution of pyrite ($\text{FeS}_2$) [13], a mineral often associated with the redox regulation of ground-waters. For this reason, we focus on sulfoxy-anion ligands, specially on $\text{S}_2\text{O}_3^{2-}$.

Grenthe et al. have selected complexing constants for U(VI) complexes with these anions [2], but they wrote in their review that confirmation is needed: “The only quantitative information about aqueous uranium thiosulfate complexes is the study by Melton and Amis […] This review tentatively accepts [their] value, (although confirmation of the results from another study would be useful)”. Furthermore: “The solid formed seems to be a mixture indicating decomposition of thiosulfate into sulfate and elemental sulfur. This review finds no reliable evidence for the formation of solid uranium thiosulfate compounds.” This decomposition might very well be the result of redox reactions (disproportionation), since both uranium and sulfur have a wide range of possible oxidation states, and their stability domains are not well established in mixtures of uranium and sulfur. This might in fact be a problem for other uranium compounds and complexes with sulfur-containing ligands. Unfortunately the NEA-TDB reviews could not validate such data for the Th and Zr analogues [14,15]. Since the NEA-TDB review has selected data for a thiosulfate complex of U(VI) [2], one might very well expect thiosulfate complexes of U(IV) in more reducing conditions — unless thiosulfate is strongly reduced, when U(IV) is formed — because the $\text{U}^{4+}$ hard cation is usually more reactive (than $\text{UO}_2^{2+}$) toward oxygen-donor ligands. Based on the same hardness rule, thiosulfate should bind to hard cations via the O rather than the S atom of the sulfoxy-anion ligands. The same problem holds for the $\text{U}/\text{SO}_4^{2-}$ system: the NEA-TDB review has selected data for sulfate complexes of U(VI); but not for U(IV): “Formation of

![Pourbaix diagram of sulfur](image-url)

Fig. 1. Pourbaix diagram of sulfur. (a) The names of the major species ($\text{HS}^-$, $\text{H}_2\text{S}$, $\text{SO}_4^{2-}$, $\text{HSO}_3^-$ and solid S) are in bold, and their predominance domains are drawn with thick lines. The domains (thin dashed lines) of the other (minor sulfur) species are obtained by suppressing $\text{SO}_4^{2-}$, $\text{HSO}_3^-$ and $\text{H}_2\text{SO}_4$. (b and c) The speciation (namely $\log([\text{H}_2\text{S},\text{O}_2]/[\text{S}_{\text{total}}]$) of each species ($\text{H}_2\text{S},\text{O}_2$) is represented for two kinetic assumptions (see text) in redox conditions corresponding to line B of Fig. 6.
aqueous uranium(IV) sulfite complexes was reported in a preliminary study by Rosenheim and Kelmy. However, no experimental chemical thermodynamic data on these species are available.” As a probe for ligand competition (between S₂O₃²⁻ or SO₃²⁻ and typically OH⁻ or CO₃²⁻), we shall estimate the formation constants of the corresponding 1:1 An(IV) complexes, namely AnS₂O₃³⁺ and AnSO₂³⁻.

Various methods are commonly used for estimating equilibrium constants, typically as empirical correlations with physical (or phenomenological) parameters (atomic radii and charges, solvent interactions...). They can also be obtained from molecular modelling methods. Indeed we recently estimated an uncertainty of 10 kJ mol⁻¹ on Δ_G for Pa(V) hydrolysis [16], which is about 20 times higher than the uncertainty of the experimental determinations of equilibrium constants and standard redox potentials in aqueous solutions. Furthermore, such methods need caution, when using calculated standard redox potentials in aqueous solutions. Experimental determinations of equilibrium constants and uncertainties of the experimentally determined equilibrium constants and standard redox potentials in aqueous solutions. Furthermore, such methods need caution, when using calculated energies [17]. After others [18,19] (with a comment in Ref. [7]) we also tested empirical correlations, which appear to work surprisingly well for some of them: they actually help in putting numbers for quite encyclopedic qualitative knowledge. It is also a way to check such knowledge and corresponding chemical intuition. We use such correlations here, hoping this special issue will help such rules of thumb used by actinide chemistry specialists to become less mysterious. The rough estimates are only guidelines, which need experimental confirmation. They often originate in geometrical and electrostatics reasoning. Indeed, the chemical stabilities of hard cations are often correlated with the charge²/radius ratios of the reactants. Nevertheless, we shall see that the best correlations are not specially with the atomic charges; correlations between measured equilibrium constants will often appear to fit better: several physical contributions probably cancel out in those cases.

The present paper is organised as follows. First, definitions are given, together with features and explanations of methodologies from the NEA-TDB reviews. Results are first reported for correlations between U(VI) (or analogous An(VI)) 1:1 (1 cation with 1 ligand) complexes and protonation of the corresponding ligands, two types of reactions for which many published data are available. In a next step, such correlations are extended to An(III) and An(V). There are virtually no reliable published 1:1 complexing constants of An(IV), since An⁴⁺ hydrolysis usually overcomes complexation. Consequently we shall estimate An(IV) 1:1 complexing constants. We shall also consider the position of Pa(V) in our correlations, since its chemical behaviour is an exception as compared to that of the other An(V): this comparison will be based only on hydrolysis data, since there are very few other published equilibrium constants for Pa(V) aqueous complexes. Prior to this comparison, we shall examine the impact of our estimated complexing constants on the geochemical behaviour of U(IV).

2. Methods

2.1. Equilibrium constants

For consistency, we used reaction data — i.e. Δ_G° (equivalently standard equilibrium constants and potentials of redox couples) — they were preferred to formation data (Δ_H°) [2].

K̃ₐ = |MLₓ⁻¹⁺L|/|M|²ₓ|L|₂⁻ (1)

where |A| is the activity of species A.

pKₐ = −log Kₐ⁺ is pH at the half-point reaction (where |L|²⁻ = |HL|¹⁺). pKₐ appears to be the ionic product of water, when L²⁻ = OH⁻ and when using |H₂O| = 1; but when comparing the complexing strengths of various ligands we used the concentration of liquid water: |H₂O| = CH₂O (55.34 mol kg⁻¹). Superscript ° stands for infinite dilution (ionic strength, I = 0), the standard conditions (see Section 2.2)

log K°₁ values were plotted as a function of pKₐ, for example when K₁ is the formation constant of AnCO₃⁺, 1/Kₐ is the protonation constant of CO₃²⁻.

We observed

log K°₁⁺ = aₙ + bₙpKₐ (3)

linear correlations, where we fitted the aₙ and bₙ parameters for a series of actinides (or analogues) of the same oxidation number X: An(X) = Mₓ⁻ = An₃⁺, An₄⁺, AnO₂⁺ or AnO₂²⁺. 10ᵇₙ = K₁(Kₐ)ᵇₙ = |MLₓ⁻¹⁺|/|M|²ₓ|L|₂⁻|H|¹⁺/(|ML|²⁺|L|₁⁻|H|₁⁺|L|₅⁻) is obtained from Eqs. (1)–(3): it is actually an equilibrium constant. When b = 1, it simplifies into the 10ᵃₙ = K₁Kₐ = |MLₓ⁻¹⁺|/|M|²ₓ|H|¹⁺/(|ML|²⁺|H|₁⁺|L|₅⁻), the

Mₓ⁻ + HL₁⁻|L|₅⁻ ⇌ MLₓ⁻¹⁺ + H⁺ (4)

exchange equilibrium constant: |L|²⁻ cancels out in K₁Kₐ ( = 10ᵃₙ), which is now the same for all the reactions; it also only depends on a, not on each Kₐ (or equivalently K₁). In that case, the half-point reaction definition is |H|¹⁺/|M|²⁺|H|₁⁺ = K₁Kₐ; a solution of
activity $[H^+]$ has the same reactivity (for the $L^2_-$ ligand) as a solution of activity $[M^{2+}]^{10^9}$. Conversely, when the (b) slope is not 1, this simple equivalent solution definition is no longer relevant: the general half-point reaction definition is $10^a = K_1^{a}(K_a)^b = \frac{|[H^+]|L^z_a|^b}{(|M^{2+}|L^z_a)|^{1-1/b}}$, whose interpretation is less intuitive. Furthermore the constant of the exchange equilibrium (Eq. (4)) is now specific for each reaction: $K_1^{a}(K_a)^b = 10^a/K_1^{a}$, and $K_1^{a}$ (or equivalently $K_1$), not only on $a$ and $b$.

Since $b_2$ did not seem to strongly depend on $X$, we finally used the same $b_2 (= b)$ value for all the oxidation states; in that case, for comparing $An(X)$ complexes with $An(VI)$ ones, we used:

$$10^{\text{pK}_{\text{avI}}} = \frac{K_1^{X}}{K_1^{	ext{VI}}} = \frac{K_1^{X}}{K_1^{	ext{VI}}} = \frac{\text{ML}^{2+\text{L}^2_2}\text{M}^{2+}}{\text{ML}^{2+\text{L}^2_2}\text{M}^{2+}}$$

(5)

the constant of the exchange equilibrium. This $AnO_2^+/M^{2+}$ exchange equilibrium is similar to the $H^+/M^{2+}$ one (Eq. (4)), where now the half-point reaction definition is $\frac{|[AnO_2^+]^b|/|M^{2+}|_{1/2}}{K_1^a}$: a solution of activity $|AnO_2^+]$ has the same reactivity (for the $L^2_-$ ligand) as a solution of activity $|M^{2+}|K_1^a$. Similarly, for comparing hydrolysis equilibria, we used the $AnO_2OH^+ + M^{2+} \rightleftharpoons MOH + AnO_2^2+$

(6)

hydrolysis competition equilibrium of constant

$$\frac{K_1^{X}}{K_1^{	ext{VI}}} = \frac{\text{MOH}^{\text{VI}}}{[\text{AnO}_2^2+]} \frac{|\text{AnO}_2^{2+}|}{|\text{AnO}_2OH^+|^2}$$

(7)

where

$$\frac{K_1^{X}}{K_1^{	ext{VI}}} = \frac{|\text{M(OH)}^{2-}\text{H}^+|^2}{|\text{M(OH)}^{2-}|^{2}}$$

(8)

is a classical stepwise standard equilibrium constant.

$$-\log K_1^{X} = \text{pH}_{1/2}$$

2.2. Activity coefficients

For ionic strength corrections, we used $\gamma_0$, the molal activity coefficient of ion $i$ calculated with the "Specific Interaction Theory", the SIT formula [2,4]. The corresponding $\epsilon_{ij}$ empirical (pair interaction) coefficients are taken from the NEA-TDB reviews [4]:

$$\log \gamma_i = -\varepsilon_i^2 D + \sum_j \epsilon_{ij} m_j$$

(9)

In most cases, the summation could here be restricted to the $\text{ClO}_4^-$ and $\text{Na}^+$ (dominating) counter-ions ($= j$). $m_j$ is $j$ (molal) concentration (mol per kg of pure water). Molar ($M = \text{mol L}^{-1}$) to molal conversion coefficients are tabulated in Handbooks (including the cited NEA-TDB books):

$$D = \frac{A\sqrt{T_m}}{1 + B_1\sqrt{T_m}}$$

(11)

is a Debye–Hückel term, where $I_m$ is molal $I$, $A = 0.509 [298 \varepsilon_{298}/T_{\varepsilon_{298}}]^{1/2} [d_{298}/d_T]^{0.5}$ kg$^{1/2}$ mol$^{-1/2}$, and $B = 3.28 \times 10^9 [298 \varepsilon_{298} d_T/(T_{\varepsilon_{298}} d_{298})]^{0.5}$ kg$^{1/2}$ mol$^{-1/2}$ m$^{-1}$ are calculated from physical constants, and $\varepsilon_{i,T}$ the relative dielectric constant of the solvent (water) and $d_T$ the density at absolute temperature. $T$ accounts for geometric exclusion about ion $i$. $r$ is assumed to be constant, $B r = 1.5$ kg$^{1/2}$ mol$^{-1/2}$ at $25^\circ$C, an approximation that enables many measured mean activity coefficients of strong inorganic aqueous electrolytes to be fitted [2]: it corresponds to $r = 4.57 \times 10^{-10} m$, which appears to be of the correct order of magnitude for most inorganic hydrated ions including their first hydration sphere (by definition if a counter-ion stays in the first hydration sphere, it is treated as complex formation, not non-ideality). Furthermore, $B\sqrt{T} = 1$, where $b_D$ is the Debye distance, the distance between an ion and its counter-ion atmosphere: $3.05 \times 10^{-10} m$ (at $25^\circ$C and $I = 1$ M) in the SIT approximation. The Debye–Hückel formula is valid for large $b_D$ namely for $b_D >> r$: $B r = 1.5$ kg$^{1/2}$ mol$^{-1/2}$ corresponds to $r/b_D = 1.5 \sqrt{T_m} << 1$. Indeed the Debye–Hückel formula ($D$ term alone) is only valid at ionic strengths less than 10 or 1 mM, while the SIT formula is usually a good approximation for aqueous solutions with ionic strength up to 4 mol kg$^{-1}$ [2]. The use of $\epsilon_{ij}$ empirical coefficients certainly partly compensates systematic errors (of $D$ in the SIT formula), which might very well explain why the numerical values for $\epsilon_{ij}$ are correlated with the size and the charges of the ions (Fig. 2).

Unknown $\epsilon_{ij}$ numerical values can be estimated by analogy with ions of same charge and similar sizes [3,4]. In that case it was proposed to increase the $\epsilon_{ij}$ uncertainties by $\pm 0.05$ kg mol$^{-1}$ [4]. Moreover, we observed a reasonable linear correlation between interaction coefficients and the charge/radius ratios (Fig. 2(a)). For this correlation we used the formal charge of the cation (or the complex), which is indeed the charge seen by the ($\text{ClO}_4^-$) counter-anion at large distance. Unfortunately this assumption does not hold for high ionic strengths, the only conditions where the $\epsilon_{ij}$ term cannot be neglected. Indeed some data for
AnO$_2^{3-4}$ cations are not in the middle of the correlation cloud, indicating that the relevant phenomenological charge might be higher (than the formal one). Conversely, the corresponding points are moved to the other side of this correlation plot (not represented on the figure), when using the atomic charge (Section 2.3) of An (in AnO$_2^{3-4}$, for this reason, we also plotted other correlations without using the charges (Fig. 2(b) and (c))).

2.3. Quantum calculations

In our hydrolysis correlation study, we used the formal charges of An$^{3+}$ (3) and An$^{4+}$ (4), while we used the atomic charge of An(X) in AnO$_2^{3-4}$ (X = 5 or 6). This latter was deduced from quantum (DFT) calculations performed at the same calculation levels (ECP and basis sets) as in our recent previous works [17,20], from which we extracted NPA atomic charges [21,22]. Note that in Gaussian98 and 03, these NPA charges are calculated with the NBO software, which is known to consider the UO$_2^{2+}$ 6d orbitals as Rydberg orbitals, despite the final result gives the 7s5f6d electronic configuration. This overestimates the U atomic charge by 0.50 electron. For this reason we recalculated the NPA charge assuming the 6d to be valence orbitals for all theoxy actinide cations.

For the ligands (alone) closed-shell ab initio calculations were performed at the MP2/6-311+g(2df,2p) level; open-shell calculations are not needed, as checked at the B3LYP/6-31+g(d,p) level. All the quantum calculations were done with the Gaussian98 and 03 suites of programs [23,24].

$\Delta_\text{pK}$, the ab initio energy, was calculated for the protonation reaction corresponding to the p$\text{K}_\text{a}$ equilibrium (Fig. 3). p$\text{K}_\text{a}$ represents pH$_{1/2}$; similarly, when adding

![Image of empirical correlations for estimating SIT ion pair coefficients.](image)

![Image of protonation reactions of RO$_2^{3-4}$ ligands in the gas phase and in aqueous solutions. The p$\text{K}_\text{a}$ (in pure liquid water at 25 °C) are converted to kJ mol$^{-1}$ (\(\Delta\text{G} = -RT\text{pK}_\text{a}\)) and compared to the energy of the corresponding reaction ab initio calculated (with neither matrix nor temperature correction), where the protonation is on an O (black points) or S (white points) atom.](image)
the entropic contribution to $\Delta_r E$, it represents $P_{H_{2}O}$, the $H^+$ partial pressure: the hydration energy of $H^+$ is related to the slope in the $\Delta_r E$ plot as a function of $pK_a$ (Fig. 3), while the intercept rather reflects the hydration energy change between the reactants and products. Since the slope is much greater than 1, the $E$ scale had to be contracted, which means that the final correlation is quite poor. Slope $\neq 1$ also means it is not equivalent to use $pK_a$ or $\Delta_r E$ for our estimates of complexing constants: $pK_a$ appeared to be better correlated with measured complexing constants. Furthermore $pK_a$ represents a marginal value of $\Delta_r E$, which already is a marginal part of the DFT calculated electronic energy: the experimental $pK_a$ values are more reliable for our purpose and more accurate than the $\Delta_r E$ ones obtained from quantum calculations in the gas phase.

3. Results and discussions

3.1. Comparing the affinities of hard anions for $H^+$ and $\text{AnO}_2^{2+}$

We first examined U(VI) aqueous complexation and hydrolysis data, since a sufficiently large set of complexing constants is available. Positive $\log K_1^c$ vs $pK_a$ correlations are observed, and even linear correlations appear to fit the data reasonably well. The plot appeared to be less scattered when restricted to the consistent set of data selected by the NEA-TDB reviews (Fig. 4); we finally used these (NEA-TDB) consistent sets of data for the figures and numerical correlations given in the present paper with the following exceptions. For An(VI) we did not use the NEA-TDB $\text{PuO}_2\text{CO}_3(\text{aq})$ formation constant based on only (log $K_1^c = 13.8_{-0.6}^{+0.8}$ [26] and $9.3 \pm 0.5$ [27]) two experimental determinations that are not consistent (within uncertainties). The latter

Fig. 4. Proton and other cation affinities for ligands. $K_1^c$ is the standard formation constant of the $\text{ML}^{2+}$ complex, and $K_a$ is the protonation constant of the $L^{3-}$ ligand written on the figure (Table 1). Since all the ($\log K_{1,x} = a_x + b_x pK_a$) lines are virtually parallel for all the ($X$) oxidation states (a). We also used the same ($b_x = 0.62 \pm 0.16$) slope in $\log K_{1,x-an} = ((0.62 \pm 0.16) pK_a$) regressions for the $\text{RO}_2^{2-}$ ligands, and shifted the curves by $a_x$ (b): $a_x - a_\text{VI} = (\log K_{1,\text{x,VI}} - \log K_{1,\text{VI}}) = \log K_{1,\text{VI}}$ (Eq. (5)), where $K_{1,\text{VI}}$ is the constant for the $\text{AnO}_2\text{RO}_2^{2-}$ exchange equilibrium (Eq. (6a)) for $M^{3+} = \text{An}^{3+}$, $\text{An}^{4+}$ or $\text{An}^{5+}$. For An at the oxidation state $X$.$a_x = -0.62 + 0.62 pK_a$ can be used as a definition of a quantitative scale for the (up to now qualitative) $\text{An}^{n+} > \text{AnO}_2^{2+} = \text{An}^{n+} > \text{AnO}_2^{2+}$ series (y axis of (c)). It is compared (black filled symbols) with the hydrolysis constant ($K_a$) scale on the $x$ axis of (c)), and $z_{\text{An}}$, the An atomic charge (blue open symbols corresponding to the top scale). $z_{\text{O}}$, the atomic charge of O in $\text{RO}_2^{2-}$ is not specially correlated with its $pK_a$ (d). The $x$-axes are the same for (a), (b) and (d); the names of the ligands are only written on (a).
value (that we published ourselves) is closer to the U(VI) and Np(VI) ones (Table 1) [2,4], but it is rather a maximum possible value corresponding to the detection limit of our solubility measurements. For this reason, we also do not rely on the 9.5 ± 0.5 similar value more recently updated by the NEA-TDB review [16].

The PO₄³⁻ tri-anion is out of the correlation, while the F⁻ mono anion could probably be included into the correlation, but HO⁻ cannot (Fig. 4). When restricting the correlations to L• = RO₂⁻ potentially bidentate oxygen-donor ligands, virtually the same log K⁺ value is observed for a given ligand with AnO₂⁻ for An = U, Np, Pu or Am: the variations along this series are only slightly higher than experimental uncertainties. log K⁺₁,VI = (2.0 ± 0.3) + (0.665 ± 0.085) pKa is obtained for these (AnO₂⁻) cations. Adding not critically reviewed (log K⁺₁,VI) values gives similar regression coefficients with increased uncertainties, namely (2.6 ± 0.8) instead of (2.0 ± 0.3), and (0.58 ± 0.08) instead of (0.665 ± 0.085).

3.2. AnO₂RO₃⁻/MRO₂⁻⁻ exchanges for M⁻⁻ = An⁵⁺, An⁶⁺ or AnO₂⁻

Similar log K⁺₁ vs pKa correlations and observations (as for AnO₂⁻, Section 3.1) are made for the An³⁺ and AnO₂⁻, cations, while there are too few data for M⁴⁺.

For the M³⁺/CO₂⁻ systems, we used our own complexing constants (Table 1) [28], AmHCO₃⁻ is an outlier, in part due to the stabilisation of H₂CO₃ as CO₂⁻(aq): the measured pKₐ (of the HCO₃⁻/CO₂⁻(aq) couple) is not the relevant parameter for our correlations. For L⁻⁻ = RO₂⁻⁻ we found K⁺₁ values in the order An⁴⁺ > AnO₂²⁻ ≈ An⁵⁺ > AnO₂⁻, a classical order for the reactivity of actinide cations toward hard anions. However, AnO₂²⁻ > An³⁺ is often written (instead of AnO₂⁻ ≈ An³⁺). Here the available data for An³⁺ appear to be within the correlation lines of AnO₂⁻. The atomic charge of U in UO₂⁻ is 2.8 electron, which compares with the charge of Am³⁺. Nevertheless, using atomic charges in the correlations gave poorer results (see below and Fig. 4(c)). We obtained log K⁺₁,III ≈ 2.2 ± 0.55 pKa for An³⁺ and log K⁺₁,IV ≈ −0.7 + 0.54 pKa for AnO₂⁻.

There are too few data for a statistical evaluation of all the uncertainties. Nevertheless, it seems that b⁺, the slopes (of every log K⁺ vs pKa correlations) are the same within uncertainties. Indeed a reasonable fit is obtained when fixing b⁺ = b₁ = 0.665, namely log K⁺₁,X = (aX + 0.665 pKₐ) for all the oxidation states. We finally fitted the slope (and aX) on all the data, and obtained log K⁺₁,X = (aX + (0.616 ± 0.055) pKₐ) with a₁ = 2.253 ± 0.075, a₁V = 5.444 ± 0.249, aV = −1.236 ± 0.489 and a₁V = 2.408 ± 0.453 fitted

| Table 1 | Formation constants used to draw Fig. 4: pKₐ of RO₂⁻⁻ ligands and corresponding K⁺₁ formation constants with cations of f-block elements [2–4,16] |
|---------|-------------|-------------|-------------|-------------|-------------|
| RO₂⁻⁻   | pKₐ b       | log K⁺₁,III c | log K⁺₁,IV c | log K⁺₁,IV c | log K⁺₁,IV c |
| S₂O₃⁻⁻  | 1.59        | 6.6 ± 0.8 a  | 6.58 (U)    | 3.54 (U)    | 2.8 (U)     |
| SO₄⁻⁻   | 1.98        | 3.85 (Am)   | 6.85 (Np)   | 0.44 (Np)   | 3.28 (Np)   |
| HPO₄⁻⁻   | 2.72        | 9.5 ± 2.3 a  | 2.95 (Np)   | 7.24 (U)    | 6.2 (Np)    |
| SO₄⁻⁻   | 2.22        | 9.5 ± 2.3 a  | 6.6 (U)     | 6.6 (U)     |
| CO₃⁻⁻   | 10.32       | 7.7 ± 0.3 (Am) | 11.1 ± 3.2 a | 4.96 (Np) | 9.67 (U) |
|         |             | 7.8 ± 0.2 (Eu) | 5.12 (Pu)  | 5.1 (Am)   | 9.32 (Np)   |
| a⁺       | 2.2         | 5.8 ± 0.4   | −0.7        | 2.0 ± 0.3   | 0.665 ± 0.085 |
| b⁺       | 0.55        | 0.51 ± 0.2  | 0.54        | 0.665 ± 0.085 |
| aX       | 2.25 ± 0.075 | 5.44 ± 0.240 | −1.236 ± 0.480 | 2.408 ± 0.453 |
| log K⁺₁,X | −0.1 ± 0.5  | 3.04 ± 0.5 | −3.6 ± 0.5 | 0 |
| log K⁺₁,V | −1.7        | 4.81        | −6.2        | 0          |

a Value estimated in the present work.
b pKₐ of the RO₂⁻⁻ ligand.
c K⁺₁ is the standard constant of equilibrium M⁺⁺ + RO₂⁻⁻ ↔ MRO₂⁻⁻ for M⁺⁺ = An⁺⁺ (X = 3 or 4) or AnO₂⁻⁻ (X = 5 or 6) from published data (see text) [2–4,7].
d a and b, the coefficients of the log K⁺₁,X = (a + b pKₐ) linear regression are fitted for a given oxidation state, X.
e while aX is the (fitted) intercept of a similar regression, but with the same (0.62 ± 0.16) slope for all the oxidation states: log K⁺₁,X = aX = (0.62 ± 0.16) pKₐ. |
values, where uncertainties are 1.96σ (the maximum errors on log $K_{i,X}^*$ was $+0.9$ for UO$_2$CO$_3$ and $-0.8$ for AnCO$_3^+$. Since there are not enough data for a meaningful statistical analysis, we finally increased the uncertainties: log $K_{i,X}^*$ = $a_X$ = $(0.62 \pm 0.16) pK_a^*$ (Fig. 4(b)). The standard deviation of the fit is 0.5 (it represents less than 3 kJ mol$^{-1}$), a value only a little higher than that of many direct experimental determinations in aqueous solutions, and of the order of magnitude of the variations of the log $K_i^*$ values among the series of the analogous cations considered here. However, when a slope is fitted for each oxidation state, a small systematic deviation can be inferred, namely the slopes when a slope is fitted for each oxidation state, a small less than 3 kJ mol$^{-1}$.

The standard deviation of the fit is 0.5 (it represents
correctly to their $pK_a^*$ values, but not specially to $z_n$, the atomic charge of $O$ (Fig. 4(d)). We also attempted to force $b = 1$ in the fits, but without success: the correlations cannot simply be interpreted with Eq. (4).

Similarly, hydrolysis equilibria were compared using $K_{X/VI}$ (Eq. (8)), the constant of a hydrolysis competition equilibrium (Eq. (7)) between actinide ions at oxidation states $X$ and $+6$: log $K_{III/VI}$ = −1.7, log $K_{IV/VI}$ = 4.81 and log $K_{V/VI}$ = −6.2 for Np [4]. These results give nearly the same An$^{4+}$ >> AnO$_2^{2+}$ > An$^{3+}$ >> AnO$_2^-$ qualitative scale (Fig. 4(c)), and the log $K_{X/VI}$ = $(0.36 + 0.60)\log K_{X/VI}$ linear correlation.

### 3.3. Estimating the stabilities of $An^{(IV)}RO_2^{2+}$ complexes

We now want to estimate missing complexing constants for U(IV), namely with the SO$_2^{2-}$ and S$_2O_2^{2-}$ anions. For this we could not use the same type of correlations as those observed for UO$_2^{2+}$ and the other cations (Section 3.2), because reliable formation constant has been published for only one type of 1:1 An(IV) complexes, namely for the MSO$_2^{2+}$ complexes: log $K_{IV}^*$ = 6.58 (USO$_2^{2+}$) [2], 6.85 (NpSO$_2^{2+}$) [4], 6.89 (PuSO$_2^{2+}$) [4] and 7.04 (ZrSO$_2^{2+}$) [15]. When using this single datum and the $(0.62 \pm 0.16)$ slope value estimated above, the $(\log K_{IV}^* = ((5.6 \pm 0.2) + (0.62 \pm 0.16) pK_a^*)$ line is drawn, from which log $K_{IV}^*$ = $(12.0 \pm 1.9)$, $(10.1 \pm 1.4)$, $(6.8 \pm 0.5)$ and $(6.6 \pm 0.5)$ are calculated for the An(IV) complexes of CO$_2^{2-}$, SO$_2^{2-}$, SO$_4^{2-}$ and S$_2$O$_2^{2-}$, respectively. The value of $a_{IV}^*$ = 5.6 ± 0.2 was chosen to fit the 6.58 (USO$_2^{2+}$), 6.85 (NpSO$_2^{2+}$) and 6.89 (PuSO$_2^{2+}$) data by giving less weight to USO$_2^{2+}$, because the +4 oxidation state is more difficult to stabilise for uranium, even if more experimental studies of U(IV) are available. However, the log $K_{IV}^*$ (=6.6 ± 0.5) MSO$_2^{2+}$ value is close to the MSO$_2^{2+}$ fixed point (of the correlation). Therefore it does not depend sensitively on the value estimated for the slope (of the log $K_{IV}^*$ vs $pK_a^*$ linear correlation). Consequently the uncertainties are relatively small for (the log $K_{IV}^*$ estimate of) M$_2$SO$_2^{2+}$. Conversely the biggest uncertainty is for MCO$_2^{2+}$ the most stable complex, since CO$_2^{2-}$ appeared to be the most reactive RO$_2^{2-}$ ligand we studied: it is one of the endpoints of the correlation lines. For this reason, we estimated an upper bound for the value of log $K_{IV}^*$ from experimental data: we re-interpreted available published experimental solubilities of actinides(IV) by using the same methodology as in Refs. [4,5,29]. We obtained formation constants consistent with the original interpretation (by the authors of Ref. [9]). However, for consistency we added the known stabilities of An(CO$_3$)$_i^{3-2i}$ ($i = 4$ and $5$), and we tested many possible complexes for which we also estimated maximum possible stabilities (Table 2) for sensibility analysis; our purpose was essentially to estimate a value for AnCO$_3^+$. As expected from pH vs log [CO$_3^{2-}$] predominance diagrams [7,26,28], the most restrictive conditions were found for published solubilities of An(IV) measured at low pH and high CO$_2$ partial pressure, namely in Refs. [9,30]. In both cases we obtained virtually the same values: log $K_{1,IV}^{*} \leq 11.1$ or 11.5 for the ThCO$_3^{2+}$ complex. Using this value (and the sulfate data), log $K_{IV}^*$ = $(5.8 + 0.51 pK_a^*)$ is calculated, from which log $K_{IV}^*$ = 11.1, 9.5, 6.8 and 6.6 are calculated for the An(IV) complexes CO$_3^{2-}$, SO$_2^{2-}$, SO$_4^{2-}$ and S$_2$O$_2^{2-}$, respectively. These values are within the uncertainties of the previous estimates above. The AnCO$_3^{2+}$ value of 11.1 is identical as, or slightly smaller (by 0.9 ± 1.9) than the central value (12.0 ± 1.9) of the above estimate, and the same trend was observed for AnCO$_3^+$: it was overestimated by 0.8 log$_{10}$ unit when using the
same slope (0.62) for all oxidation states. This correlation predicts under-stabilisation of the AnCO$_3^{1-2}$ complexes (X = 3 or 4) as compared to the An$_2$CO$_3^{3-6}$ systems (X = 5 or 6); it might be attributed to the planar structure of CO$_3^{2-}$, which offers a better fit to the geometry of the coordinating equatorial plane of the AnO$_2^{4-}$ actinyl cations. Unfortunately, such an explanation would also hold for the SO$_4^{2-}$ (quasi-) planar ligand (Fig. 5), which is not specially confirmed (Fig. 4). For consistency with our estimate, log $K_{1,IV}^{+}$ ≤ 11.1, we prefer the last correlation log $K_{1,IV}^{+} = (5.8 + 0.51 \ pK_a^+)$, where we increased the uncertainties to encompass the previous log $K_{1,IV}^+ = ((5.6 \pm 0.2) + (0.62 \pm 0.16) \ pK_a^+)$ correlation: log $K_{1,IV}^+ = ((5.8 \pm 0.4) + (0.51 \pm 0.27) \ pK_a^+)$ from which we obtain log $K_{1,IV}^{+}$ ≤ 11.1 ± 3.2 for AnCO$_2^{+}$, 9.5 ± 2.3 for AnSO$_2^{+}$, 9.5 ± 2.3 for AnHPO$_2^{+}$ and 6.6 ± 0.8 for AnS$_2$O$_3^{+}$, where uncertainties are increased take into account the lack of experimental data.

The $\log K_{1,IV}^+$ value estimated for AnS$_2$O$_3^{+}$ is quite similar to those for the AnSO$_2^{+}$ complexes: 6.58 (USO$_2^{2+}$), 6.85 (NpSO$_2^{2+}$) and 6.89 (PuSO$_2^{2+}$). This is consistent with the molecular structures of these ligands: SO$_4^{2-}$ and S$_2$O$_3^{2-}$ both have a tetrahedral structure (Fig. 5) — an O atom (of SO$_4^{2-}$) being replaced by an S atom (in S$_2$O$_3^{2-}$) and similar pK$_a$ values. SO$_4^{2-}$ has a different structure, a higher pK$_a$, and a higher estimated value of the complexion constant. Unfortunately, it does not seem easy to draw any simple explanation just from $z_O$, the atomic charge of the free ligand in vacuum (Fig. 4(d)).

3.4. Uranium geochemistry

In non-complexing aqueous solutions, the solubility of uranium is controlled by uraninite (UO$_2$(s)) in reducing conditions, and by schoepite (UO$_3$(s)) in oxidizing and neutral conditions, as illustrated in Fig. 6(a) for 1 μM [U]. Besides these minerals, aqueous U(VI) species are predominant in a large $E$–pH domain, while aqueous U(IV) is stable only in reducing conditions, and is mostly hydrolysed.

On adding carbonate ions at a typical concentration of underground waters, aqueous U(VI) carbonate complexes prevail between pH 4 and 12 (Fig. 6(b)), UO$_3$(s) is totally dissolved, and the UO$_2$(s) stability domain is reduced. We have ignored the reduction of the carbonate ions, since this reaction is usually very slow. Nevertheless, no carbonate complex of U(IV) appears on the Pourbaix diagrams. These complexes would dominate at higher carbonate concentrations than those studied here. Rai and Ryan have already proposed that carbonate complexation of actinide(IV) ions in environmental conditions can be neglected [8].

Among the main sulfur species, SO$_3^{2-}$ prevails over a large ($E$–pH) domain in oxidizing to slightly reducing equilibrium conditions. For high pH values, this domain even extends to reducing conditions (Fig. 1). H$_2$S, HS$^-$ and S$^{2-}$ prevail in reducing conditions, but their
complexing properties are not significant for the (hard) cations of the f-block elements. UO$_2$SO$_4$(aq) is the only predominating sulfur species in our typical underground water conditions (Fig. 6 (c)), even when introducing the 1:1 complexing constants estimated above (Section 3.3, Table 1) for US$_2$O$_2$$_{2+}$ and USO$_2$$_{2+}$. The RO$_2$/C$_{02}$ ligands are protonated in acidic conditions, which decreases their concentrations: the corresponding 1:1 complexing equilibria are actually the $M_zM^+HRO_{2}/C_{02}#MRO_zM/C_{02}^2+H^+$ (4a) exchange equilibria. Despite this concurrency between protonation and complexation, several complexes with the 1:1 stoichiometry are stable. Conversely, the existence of AnCO$_3$$_{2+}$ complexes has never been demonstrated, since the competition (between carbonate complexation and hydrolysis) is less favourable for An(IV) as compared to the actinides in the other oxidation states (Fig. 4(a)). The RO$_2^-$ concentration can also dramatically decrease as a result of redox reactions: CO$_2^-$ and SO$_2^-$ (= RO$_2^-$) are reduced in equilibrium chemical conditions, where U(IV) is stable. However, these reduction reactions are very slow: we have neglected them for the carbonate ions (Fig. 6). Similarly, the coexistence of S(VI) and S(–II) species is often observed, indicating that equilibrium conditions are not always achieved for S natural aqueous systems. The achievement of the U(IV)/U(VI) equilibrium can also last for a few weeks. Note that all these slow reduction reactions can be explained by the need to break strong (covalent) bonds of O(–II) with C, S(VI) or U(VI). Such kinetics is often handled by assuming that slow reactions are blocked, while equilibrium conditions are achieved for other equilibria. Therefore U(IV) might be complexed by sulfate and by reduced intermediary S species as well: we plotted two simulation diagrams corresponding to different kinetic assumptions that would stabilise sulfoxo-anion complexes (Fig. 7). In both cases, $E$, the redox potential, is at the limit of the H$_2$S$_2$O$_5$$^{-2}$ and H$_2$SO$_4$$^{-2}$ domains as plotted in Fig. 1(a) and line A in Fig. 6(c). In such redox conditions uranium aqueous species are stable at the +6 oxidation state. For this reason, the sulfate complexes of U(IV) are not seen on the Pourbaix’ diagram (Fig. 6(c)): the sulfate ions are reduced in equilibrium conditions, where U(IV) aqueous species are dominating i.e. the S(VI)/S(–II) frontier (line B in Fig. 6(c)) is at higher
is now the dominating S aqueous species (Fig. 1). US$_2$O$_3^{2+}$ is the major U(IV) species, and up to a few percent of USO$_3^{2+}$ is formed at pH less than 3.0 (Fig. 7(b)).

Even if sulfoxy-anions complexes of U(IV) are certainly not stable in equilibrium conditions, these simulations indicate that they might be formed as kinetic intermediates typically in the course of uraninite and pyrite oxidative dissolutions, or the interaction of aqueous uranium (including U(VI)) with pyrite surfaces [31,32]. Of course, this statement needs experimental confirmation, specially in less acidic to basic conditions, where higher and mixed An(RO$_2$)$_j$(OH)$_{4-j}$ complexes may form. Furthermore, at pH > 3, U(OH)$_3$(aq) is the dominant species in equilibrium reducing conditions, and the formation of S-containing complexes is less favourable, specially in the usual pH conditions of equilibrated natural underground-waters.

### 3.5. Hydrolysis of actinide ions

We now consider where protactinium should be placed in the above correlations. There is little experimental published information on Pa aqueous chemistry. We first used the available information on its aqueous species in non-complexing (acidic) solutions and its hydrolysis. Although Pa is known to be an f-block element [17], Pa(V) aqueous chemistry is closer to that of d elements (in the same — the 5th column of the periodic table) than to the chemistry of AnO$_2^+$ trans-protactinian actinide cations. Here is a strong indication that PaO$_2^+$ is not the dominating aqueous Pa species.

Jaussaud et al. recently reviewed previous measurements of the Pa(V) hydrolysis constants [33–35]. They are essentially based on liquid—liquid extraction measurements, for which they pointed out many experimental difficulties: side reactions of the organic chemicals, sorption of Pa(V) on vessels and unwanted side reactions. Surprisingly most of the published studies are only based on measurements at trace concentrations of Pa(V), while sorption reactions are classically made negligible by using (non-radioactive) chemical analogues at macro-concentrations. The hydrolysis behaviour of Nb(V) seems similar to that proposed for Pa(V): we calculated the hydrolysis constants of Nb(V) by interpreting the aqueous solubility of Nb$_2$O$_5$ (Table 3) [25]. We re-interpreted the (Pa) experimental measurements at 25 °C by giving more weight to the data for which systematic errors seemed the lowest according to Jaussaud’s observations and comments: the measurements at high ionic strength and low (TTA = thenoyltrifluoroacetone) extractant concentrations. This essentially confirmed the original interpretation.
Table 3

<table>
<thead>
<tr>
<th>I (M)</th>
<th>log *K_{1,m}^a</th>
<th>log *K_{2,m}^a</th>
<th>log *K_{3,m}^a</th>
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<tr>
<td>3</td>
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<td>−5.8 ± 0.3b</td>
<td>[33−35]</td>
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<td>−1.75 ± 0.91</td>
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<td>−6.9 ± 0.6b</td>
<td>[33−35]</td>
</tr>
<tr>
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<td>−1.50 ± 0.56</td>
<td>&lt; −0.98b</td>
</tr>
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<td>−1.6 ± 0.2</td>
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<td>[33,35]</td>
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<td>−1.499</td>
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<td>[33]a</td>
</tr>
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<td>[33−35]</td>
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<td>−4.95 ± 0.2</td>
</tr>
<tr>
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<td>−7.03 ± 0.15b</td>
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</tr>
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<td>−7.15 ± 0.4b</td>
<td>[34]</td>
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<tr>
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<td>−0.04 ± 0.36c</td>
<td>−1.44 ± 0.71</td>
<td>&lt; −3.6c</td>
</tr>
</tbody>
</table>

One value is also tabulated for Nb(V).

a Graphically interpreted in the present work, and (last line) extrapolated to I = 0. See Fig. 8.
b Inconsistent value: since the measurements were performed at pH < 4, it is not possible to fit (from them) a log K_i value less than about -4.
c There is no clear experimental evidence of the corresponding reaction.
d Nb(V) value fitted from solubility data [36], and here tabulated for comparison.
e K_{i,m} is the constant of equilibrium PaO.

The half-point reaction) have been re-interpreted (Table 3) from the experimental data (and extrapolated to I = 0 with the SIT formula) of Ref. [30] in 0.1 (open symbols) to 3 (filled symbols of the same colour) mol L⁻¹ NaClO₄ aqueous solutions for the successive formations of species of charges 2 (dark blue diamonds), 1 (brown circles) and 0 (green squares). The intermediate colours are for 1 and 0.5 mol L⁻¹. For higher [TTA] values (not represented), a systematic deviation is observed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The formation of PaO₃⁺⁺⁺ (equivalently written PaO(OH)₃ or Pa(OH)₅). The formation of PaO₃⁺⁺⁺ is not proposed in the original interpretation of the authors, and indeed needs confirmation. Finally, the most reliable published Pa(V) standard hydrolysis constant is certainly log *K_{2} = −(1.26 ± 0.15) [34], a value consistent with our re-interpretation (−1.44 ± 0.71) (Fig. 8 and Table 3), and with the Nb(V) value of (−1.65 ± 0.2). We also propose log *K_{1} = −(0.04 ± 0.36) and log *K_{3} < −3.6, giving no credit to the (−7.15 ± 0.4) [34] and (−7.03 ± 0.15) [33,35] published interpretations from the same experimental data, because the corresponding hydrolysis species could not be detected in the experimental conditions used in this work (pH ≤ 4 corresponding to a maximum value of about 10⁻⁷⁺⁺⁺ = 0.1% for the concentration of the hydrolysis species to be compared with the 10⁻⁰.⁷¹ uncertainty in the measurements of log *K_{2}, even though they might provide a reasonable value: the Nb(V) value of −4.95 ± 0.2 might also be used as a rough estimate. These *K_i constants are actually the hydrolysis constant of PaO₃⁺⁺⁺, but the existence of this species has not clearly been demonstrated, and for this reason only the second stepwise experimental determination (∗K_2) seems reliable, while the first one (∗K_1) needs confirmation. The −log *K_2 value is only a little larger than that of −log *K_1: the two first hydrolyses of Pa(V) would be nearly simultaneous. This is also observed for the other actinide aqueous species.

A linear regression correlates reasonably well log *K_1, the logarithm of the hydrolysis constant and z, the charge of the M⁺⁺⁺ cation for M⁺⁺⁺⁺ = Ru²⁺⁺⁺, Am³⁺⁺⁺, Pu⁴⁺⁺ (brown dotted line in Fig. 9(a)): −log *K_1 = (25.2₄ − 6.1₉z). Adding other An³⁺⁺⁺ and An⁴⁺⁺ cations gives virtually the same correlation (brown dotted line in Fig. 9(b)): −log *K_1 = (25.6₉ − 6.2₈z). The actinyl ions such as UO₂²⁺⁺⁺, and NpO₂⁺⁺⁺ are below this correlation line. This stabilisation of their hydrolysed species might be originated in an An−O₂⁻⁻ (intramolecular) charge transfer induced on approaching equatorial water...
molecules to $\text{UO}_2^{2+}$ [21], an inductive effects of $\text{O}_{\text{water}}$, which is expected to be more important for $\text{HO}^-$ equatorial ligands (where $\text{O}_{\text{eq}}$ is an O atom of an $\text{AnO}_2^{(X-4)+}$ actinyl cation, while $\text{O}_{\text{water}}$ is an O atom of a water equatorial ligand of the actinyl). Nevertheless, the actinyl cations are not far from the correlation lines: including $\text{UO}_2^{2+}$ and $\text{NpO}_2^+$ but excluding $\text{Ra}^{2+}$ (black lines in Fig. 9); $-\log \ k_i' \approx (24.43 - 6.01z)$, and adding other $\text{AnO}_2^{2+}$ and $\text{AnO}_2^+$: $-\log \ k_i' \approx (22.73 - 5.62z)$, while extrapolating (blue dashed lines in Fig. 9) the $\text{AnO}_2^{2+}$ and $\text{AnO}_2^+$ data give (blue dashed) lines (in Fig. 9) that are between the $\text{PaO}_3^{3+}$ and $\text{PaOOH}^2+$ data. Namely, $\text{PaO}_3^{3+}$ (aq) would be intermediate between the bare actinide hard cations ($\text{An}^{(X-3)+}, X = 3$ or 4), and the usual actinyl cations ($\text{AnO}_2^{(X-4)+}, X = 5$ or 6, $\text{An} = \text{U, Np, Pu or Am}$), whose polarization by equatorial ligands essentially results in the intramolecular charge transfer between $\text{An}$ and $\text{O}_{\text{eq}}$. Note that despite this polarization $\text{AnO}_2^{(X-4)+}$ is still a hard cation for the equatorial ligands — i.e. negligible charge transfer from the equatorial ligands — we may wonder whether assuming this concept of (equatorial) hardness/(intra-actinyl) softness is still relevant for such a behaviour. However, the $\text{AnO}_2^+/\text{AnO}_2^{2+} / \text{PaO}_3^{3+}$ set can as well be considered as a series of actinide oxo-cations on their own line (approximately the blue dashed one in Fig. 9). As a result of their polarizability, these oxo-cations are below the (brown dotted) line of the bare $\text{M}^{+}$ cations. This polarizability probably decreases $z_{\text{An}}$, the An atomic charge (in the oxo-cation) by inductive effect. This inductive effect would increase with $z_{\text{An}}$: this can explain the quite surprisingly low calculated atomic charges of U (in $\text{UO}_2^{2+}$) and Pa (in $\text{PaO}_3^{3+}$), which would therefore be at the origin of the more negative slope for the actinide oxo-cation line (as compared to that of the bare cations). However, this proposition needs confirmation, since the Pa(V) experimental results are neither very accurate, nor validated, and since physical explanations cannot be proven by only such empirical correlations: it is a limit of such correlations, rather than problems in the (very few) experimental data. According to this interpretation, two correlation lines are expected, one for the bare An$^{+}$ cations, and the other one for the $\text{AnO}_2^{(X-4)+}$ di-oxo-cations, while the $\text{PaO}_3^{3+}$ mono-oxo-cation would fall between these lines, as we actually observed.

The experimental hydrolysis data already indicated that $\text{PaOOH}^{2+}$ should be only a little less reactive than $\text{Pu}^{4+}$. Finally, it can still be under debate whether it is better to consider $\text{PaO}^{3+}$ or $\text{PaOOH}^{2+}$, or both, as the $\text{Pa(V)}$ aqueous species. Using atomic charges here gave unexpected correlations, as compared to the other chemical studies reviewed in the present paper. Nevertheless, it is not a convincing proof that $\text{PaO}^{3+}$ can be an important aqueous species (i.e. it is not a confirmation of the above estimate of its $-\log \ k'_1$ value).

Our DFT calculations give pictures confirming that $\text{PaOOH}^{2+}$ (aq) is a logical species, similar to $\text{UO}_2^{2+}$ (aq), while $\text{PaO}_3^{3+}$ (aq) is easily protonated. $\text{PaOOH}^{2+}$ is merely protonated $\text{PaO}_2^{+}$ [17]. However, our continuing DFT calculations for interpreting published EXAFS measurements clearly indicate that the $\text{PaO}_3^{3+}$ geometry exists in the $\text{Pa(V)}$ species formed in concentrated $\text{H}_2\text{SO}_4$ aqueous solutions, since none of the other tested model geometries reproduced the shortest experimental distance, including $\text{PaOOH}^{2+}$: it thus dissociates in complexing media, to give aqueous sulfate complexes of $\text{PaO}_{3+}$.

4. Concluding remarks on analogies

($\log k'_1$ vs $pK'_1$) correlations fit experimental data surprisingly well (Fig. 4(a)) for $\text{An(III to VI)}$ complexes, with the exception of Pa(V), with 5 anionic
potentially bidentate and oxygen-donor RO$_2^-$ ligands: CO$_3^{2-}$ > HPO$_4^{2-}$ = SO$_4^{2-}$ > SO$_2^{3-}$ ≥ S$_2$O$_5^{2-}$ in the order of their reactivities for the actinide cations. Furthermore, the correlations were found to be linear for each oxidation state, and the (0.62) slope of these H$^+$/An(X) correlations are approximately the same for all the oxidation states (X). This, of course, means that the An(X)/An(VI) correlations deduced are linear with slope 1: $a_x$, the intercept, is interpreted in terms of the half-reaction point, namely $10^{\text{pK}_{\text{aVI}}}=K_{1,X}/K_{1,VI} = K_{X/VI}$ (Eq. (5)) is the constant of the exchange equilibrium (Eq. (6a)), which takes (approximately) the same value (Table 1) for all the RO$_2^-$ ligands and for a given oxidation state. This provides $a_x$-based numerical values for the (up to now qualitative) scale An$^{4+}$ > AnO$_2^{2+}$ ≈ An$^{3+}$ > AnO$_2^{3+}$ (Fig. 4(c)). The $a_x$ values are also qualitatively correlated with $z$, the atomic charges of the An cations; but using $z$ instead of $a_x$ gives a poorer correlation (Fig. 4(c)). Note that measured energies of reactions, namely the hydrolysis constants of Pa(V), show clearly that it is not an analogue of the other An(V); quantum calculations give a chemical explanation of the destabilization of PaO$_3$ by hydration, typically resulting in clear apical H-bonded water molecules [17]. The two approaches are complementary: the experimental energies of reactions are more accurate, while quantum calculations provide geometries and other physical data that can be interpreted in terms of usual chemical concepts (atomic charges, bonds and their covalency...) for explaining the observed chemical reactivity.

All the correlations we used are totally empirical. They are probably the result of various effects, some of them more or less cancel out in the correlations, and they are probably all linked to $z$, the atomic charge of the cation. However, using $z$ gave poorer linear correlations than comparing only experimental equilibrium constants. For this reason it is certainly better to interpret the correlations with chemical concepts than with any unproven physical explanation. Nevertheless, intramolecular charge transfers are deducted from quantum calculations for (possibly protonated) actinyl cations. These charge transfers can be related to the slightly different trends observed between the hydrolysis behaviours for these three types of cations (An$^{4+}$, PaO$^{3+}$ and AnO$_2^{2-}$). This effect would be a little less important for PaO$_3$ than for the AnO$_2$ cations where there are more covalent bounds (which promote intramolecular charge transfer). Charge transfers might as well be at the origin of the over-stabilisation of the aqueous An(IV) hydroxides as compared to complexation. These predictions are restricted to similar complexes: the linear regression numbers cannot be extended to all types of complexes without validations. Indeed such approaches exist in literature, overestimating the stabilities of several hypothetical chemical species, whose existences have never been confirmed; such numbers are not considered in the NEA-TDB reviews [2–4].

We have in fact used several levels of analogy giving different rules of thumb (although some have similar mathematical equations), which might indicate that it is hopeless to develop more general empirical formulae. The strongest analogy is typically for M(X), the series of An and other cations with the same charge, geometry and oxidation state, X: they form soluble complexes and hydroxides with the same stoichiometries, and with stability constant values that hardly differ by more than the experimental uncertainties. For different (X) oxidation states, linear correlations were found with slope 1, which defines a second type of analogy: considering the AnO$_2^{2+}$/M$^\text{M}'$ exchange, a solution of activity AnO$_2^{2+}$ has the same reactivity (for the L$^2$ ligand) as a solution of activity [M$^\text{M}'$] $K_{X/VI}$. In a third type of analogy, the (b) slope of the linear correlation is no longer 1 (b ≠ 1), as found here for H$^+$/M$^\text{M}'$ exchanges (b is not correlated with $z_M$, so it is better not to consider the ($z_M$ H$^+$/M$^\text{M}'$ exchange); $K_{X/VI}'/K_{X/VI}$ as its equilibrium constant is no longer a relevant parameter for the analogy: analogue solutions should instead be based on the parameter $10^b = K_{X/VI}' = [(H^+L^{2-})/([M^{M'}][L^{2-}])]_1/2$, whose interpretation is less intuitive.

Similarly when comparing protonation energies in aqueous and gas phases, the slope of the energy correlation is determined by the ratio of the H$^+$ activity scales in both phases. It is far from 1 (Fig. 3), corresponding to differences in the orders of magnitude (of the energies of reactions) in each phase. The intercept is related to the balance of the hydration energies (it can be shifted by changing the reference state).

Finally the rules of thumb are often characterized by the value of the (fitted) slopes in linear correlations of equilibrium constants, or equivalently by the value of the corresponding exponent in ratios of activities, the ideal concentrations.

References
