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Aqueous chemistry of Ce(IV): estimations using actinide analogues

Rémi Marsac[a]*, Florent Réal[b], Nidhu Lal Banik[c], Mathieu Pédrot[a], Olivier Pourret[d], Valérie Vallet[b]

[a]Géosciences Rennes UMR 6118, Université Rennes 1, CNRS, 35042 Rennes cedex, France

[b]Univ. Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers Atomes et Molécules, F-59000 Lille, France

[c]JRC-KARLSRUHE, G.II.6 - Nuclear Safeguards and Forensics, European Commission, P.O.Box 2340, D-76125 Karlsruhe, Germany

[d]HydrISE, UniLaSalle, 60026 Beauvais cedex, France

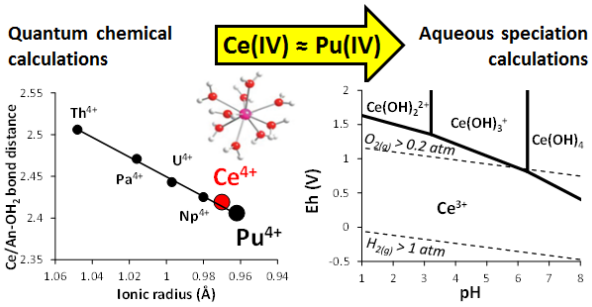
*Corresponding author : Géosciences Rennes UMR 6118, Université Rennes 1, CNRS, 35042 Rennes cedex, France. E-mail address: remi.marsac@univ-rennes1.fr (R. Marsac).

Abstract

Prediction of Cerium (Ce) aqueous speciation is relevant in many research fields. Indeed, Ce compounds are used for many industrial applications, which may require the control of Ce aqueous chemistry for their synthesis. Aquatic geochemistry of Ce is also of interest. Due to growing industrial use and its release to the environment, Ce is now considered as emerging contaminant. Cerium is also used as a proxy of (paleo)redox conditions due to the Ce(IV)/Ce(III) redox transition. Finally, Ce(IV) is often presented as a relevant analogue of tetravalent actinides (An(IV)). In the present study, quantum chemical calculations were conducted to highlight similarities between the structure of Ce(IV) and tetravalent actinides (An(IV); An = Th, Pa, U, Np, Pu) aqua-ions, especially Pu(IV). Current knowledge of An(IV) hydrolysis, solubility and colloid formation in water were briefly reviewed but important discrepancies observed with available data for Ce(IV). Therefore, new estimation of the hydrolysis constants of Ce(IV) and solubility of Ce(IV)-(hydr)oxides are proposed, by analogy with Pu(IV). By plotting pH-Eh (Pourbaix) diagrams, we showed that the pH values corresponding to the onset of Ce(IV) species formation (i.e. Ce(IV)-(hydr)oxide or dissolved Ce(IV)) agreed with various experimental results. Although, further experimental studies are required to obtain a more accurate thermodynamic database, the present work might yet help to predict more accurately Ce chemical behavior in aqueous solution.

Keywords: Cerium, actinide, tetravalent, hydrolysis, solubility, speciation, aqua-ions, quantum chemical calculation.

TOC



Quantum chemical calculations and a comparison of Cerium(IV)/Actinide(IV) justify the estimation of Cerium(IV) aqueous speciation using Plutonium(IV) as analogue.

Introduction

The solution chemistry of actinide (An) ions in aquatic systems relevant for the disposal of nuclear wastes is influenced by hydrolysis reactions and complexation with inorganic and organic anions.[1] Actinides can be found in various oxidation states in aqueous solution, which commonly range from +III to +VI depending on the An (i.e., Th, U, Np, Pu). Change in oxidation state has drastic consequences on An aqueous chemistry, solubility and sorption to natural organic and inorganic particles and colloids, which, in turn, affect their mobility in natural systems.[2–9] Only Th(IV) exists in aqueous solution. U(IV) and U(VI) prevail in reducing and oxidizing conditions, respectively, the stability field of U(V) (found in moderately reducing conditions) being rather narrow.[10] Np(IV) and Np(V) are the prevalent oxidation states of Np but Np(VI) can form in oxidizing alkaline solutions.[8,11,12] Pu can be found in oxidation states ranging from +III to +VI in environmentally relevant conditions.[3,7,13] For all these An elements, the tetravalent oxidation state is pertinent in near-neutral pH values expected to be found in nature. Because of their high electric charge, tetravalent actinide ions have a strong tendency toward hydrolysis in aqueous solution and undergo polynucleation or further lead to colloid formation.[14] Therefore, many studies were dedicated to An(IV) hydrolysis, solubility and colloids formation.[15–19] The chemical behavior of An(IV) was found highly consistent across the series, as commonly observed for f-elements (lanthanides (Ln) (4f) and An (5f)) in the same oxidation state, and are thus often considered as chemical analogues (e.g.[20–25]).

Lanthanides are naturally occurring trace elements in the environment. In contrast to its lanthanide neighbors, which predominate in +III oxidation state, Ce(III) can be oxidized to Ce(IV) under oxidizing conditions. Preferential removal of Ce(IV) than Ce(III) from aqueous solution by natural particles can lead to the development of a so-called Ce anomaly (implicitly, by comparison

with the behavior of its lanthanide neighbors La(III) and Pr(III)). The presence (under oxidizing conditions) or the absence (under more reducing conditions) of a Ce anomaly in natural samples is widely used as a proxy of (paleo)redox conditions.[26–29] Since Ce is also used for many applications,[30–34] it is now considered as emerging contaminant that could affect ecosystems, due to its release to the environment.[30] Ce(IV) is often presented as a relevant analogue of An(IV).[22,24,25] As Ce is not radioactive, experimental studies can be more easily conducted with Ce(IV) than with An(IV), which could improve our scientific knowledge on An(IV) environmental chemistry. Therefore, prediction of Ce aqueous speciation is of great interest for different research fields.

However, by contrast with An(IV), there is much less information regarding Ce(IV) aqueous chemistry. In fact, the present situation is such that it might be more appropriate to use An(IV) to shed light on Ce(IV) aqueous chemistry than the contrary. For instance, thermodynamic constants selected by Baes and Mesmer[35] are often used to predict Ce(IV) hydrolysis and solubility in water. This database only contains formation constants for $CeOH^{3+}_{(aq)}$ and $Ce(OH)_2{}^{2+}_{(aq)}$, and is obviously incomplete because at least the electrically neutral $Ce(OH)_{4(aq)}$ species should be in equilibrium with Ce(IV)-(hydr)oxides at neutral and/or alkaline pH. Omission of such species inevitably leads to drastic underestimation of Ce(IV) solubility. Hayes et al.[36] used hydrolysis constants of Ce(IV) more recently determined by Bilal and Müller[37] to plot a pH-Eh predominance diagram. According to these results, under ambient conditions (air; P_{O_2} = 0.2 atm), Ce(IV) should prevail at pH above ~4.5. This result contrasts with Th(IV) and lanthanide adsorption studies on $MnO_{2(s)}$ which is known to rapidly oxidize Ce(III) to Ce(IV). Almost complete and pH-independent uptake of Th(IV) by $MnO_{2(s)}$ is observed for $3 < pH < 11$.[38] By contrast, although more efficiently removed from the solution by $MnO_{2(s)}$ than its lanthanide neighbors, only partial

uptake of Ce (initially +III) by $MnO_{2(s)}$ is observed under ambient air and it increases from pH = 4 to pH = 6-7.[29,39] This suggests that, at 4 < pH < 6-7, although Ce(IV) is associated with the solid phase (precipitated or adsorbed on $MnO_{2(s)}$), Ce(III) prevails in solution,[40] as also observed in previous studies dealing with Pu uptake by clays in moderately reducing conditions (where the Pu(IV)/Pu(III) redox couple was involved).[41,42] Therefore, Ce(IV) hydrolysis constants determined by Bilal and Müller[37] appear to be questionable.

In this study, we briefly summarized current knowledge about An(IV) aqua-ions structure, hydrolysis, solubility and colloids formation in water, in the absence of complexing ligands. Quantum chemical calculations were conducted to highlight similarities between the structure of Ce(IV) and Th/U/Np/Pu(IV) aqua-ions. Because available hydrolysis constants and solubility data for Ce(IV) were found partly inconsistent with those of Th/U/Np/Pu(IV), new estimated thermodynamic constants for Ce(IV) were proposed.

Materials and methods

Quantum chemical calculations

The quantum chemical methodology used to discuss the structure and relative free energies of Ce(IV) hydrates with 10, 9 and 8 water molecules $[Ce(H_2O)_{10}]^{4+}$, $[Ce(H_2O)_9]^{4+}\cdot H_2O$, and $[Ce(H_2O)_8]^{4+}\cdot(H_2O)_2$ is similar to that of our previous study on early tetravalent An species.[43] A small-core relativistic effective core potential[44] of the Stuttgart-Cologne group was employed for the cerium atom along with the corresponding segmented basis set.[45] Augmented correlation-consistent polarization valence triple-ζ (aug-cc-pVTZ) basis sets were used for oxygen,[46] and hydrogen atoms.[47] The geometries were optimized without symmetry constraints at

the restricted MP2 level using the parallel resolution of the identity approximation,[48,49] with the appropriate atomic auxiliary basis functions.[50,51] Harmonic frequency calculations were computed numerically at the optimized geometry, not only to confirm that the optima found correspond to energy minima, but also to compute the vibrational partition functions at 298.15 K and 0.1 MPa, which are necessary to calculate the enthalpic and entropic contributions to the gas-phase energies. The contribution of hydration to the free energies of all isomers was estimated by single-point COSMO calculations with a dielectric constant of 78.9.[52] To comply with the relatively low level of theory (HF or DFT with small basis sets) at which the COSMO model has been parameterized,[53] a B3LYP based density and small def2-SVP basis sets[54] on all atoms are used to compute free energies of solvation. All calculations were performed with the Turbomole 7.1 quantum chemistry package.[55] A comparison of the nature of the cerium-water bond with that of the other tetravalent actinide elements was performed using the quantum theory of atoms in molecules (QTAIM) approach, implemented in the AIMAll package,[56] that analyzes the appropriate wave function extended files (wfx) obtained with Gaussian09.[57]

Geochemical speciation code and thermodynamic database

PHREEQC (version 2)[58] is a computer code that can perform speciation and saturation-index calculations in water. PHREEQC was used to calculate species distribution plots. Predominance (pH-Eh) diagrams were obtained using PhreePlot,[59] which contains an embedded version of PHREEQC. The specific ion interaction theory (SIT[60]) was used to extrapolate thermodynamic constants at various ionic strengths. In the present work, thermodynamic constants for An aqueous speciation and solubility and SIT parameters were taken from the NEA

thermodynamic database[2]. The metastability of ClO_4^-, sometimes used as background anion, is avoided in the models by defining perchlorate as a master species.

Results and discussion

Tetravalent actinides and cerium aqua-ions

Figure 1a plots the mean An–OH_2 bond distances of tetravalent actinide aqua ions determined by L_3-edge extended X-ray absorption fine structure (EXAFS) versus their ionic radii for coordination number of eight.[43,61] In a previous work, a linear relationship with a slope of about one was observed for the ions from Th^{4+} to Pu^{4+}.[43] Because the An–OH_2 bond distances for the ions up to Pu^{4+} follow closely this line, and hence the actinide contraction, it was assumed that there is no major change in these ions' hydration number. To obtain detailed information on the preferred coordination structure for An^{4+} ions in solution quantum chemical calculations were performed on the decahydrates $[An(H_2O)_{10}]^{4+}$, $[An(H_2O)_9]^{4+}\cdot H_2O$, and $[An(H_2O)_8]^{4+}\cdot(H_2O)_2$ (see Fig. 1b; Table S1 and S2).[43] Calculation of relative free energies (Table S2) showed that the nine-coordinate isomer, having distorted tricapped trigonal prismatic first shell geometry, was the most stable species for all ions from Th^{4+} to Pu^{4+}. Although overestimated (see discussion in Vallet et al.[62]), calculated An–OH_2 bond distances follow a linear relationship with the ionic radii, as observed by EXAFS.

With an ionic radius of 0.97 Å, Ce^{4+} is expected to be an analogue of either Np^{4+} (0.98 Å) or Pu^{4+} (0.96 Å).[61] Available EXAFS data somehow disagree with this hypothesis (Figure 1a),[63] Ce^{4+}–OH_2 bond distance (= 2.42 Å) being larger than that of Np^{4+} and Pu^{4+}, but comparable to Pa^{4+}–/U^{4+}–OH_2 bond distance (Fig. 1a; see also Table S3 of reference 43). In fact, standard redox potential of Ce^{4+}/Ce^{3+} ($E_{Ce^{4+}/Ce^{3+}}$) is larger than that of O_2/H_2O,[36,37] hence Ce^{4+} is not

thermodynamically stable in water at acidic pH. As observed by Sham,[63] the solution contained a mixture of Ce^{4+} and Ce^{3+} and the Ce^{4+}–OH_2 bond distance was only estimated, hence subjected to relatively large uncertainty. By contrast, present quantum chemical calculations confirm that, for aqua-ions, (i) Ce^{4+} coordination number is 9 like in the early An^{4+}, (ii) relative free energies for the ten- and eight-coordinate isomers of Ce^{4+} are comparable to that of Np^{4+} and Pu^{4+} (Table S2) and (iii) bond distance follow Np^{4+}–OH_2 < Ce^{4+}–OH_2 < Pu^{4+}–OH_2 (Figure 1a). The topological analysis of the electron charge density at the Ce/An^{4+}–OH_2 bond critical points, presented in Table S3, reveal that the values of all bonding indicators, the density ρ, its Laplacian $\nabla^2\rho$, the energy density H_b, and the bonding index D(M,L) of Ce superimpose with that of Np and Pu. This further supports the strong resemblance of Ce with Np and Pu, and suggests that, as in tetravalent actinide aqua ion, Ce(IV)-water bonds can be described as electrostatic. Furthermore, the difference from the formal atomic valence f population in $[Ce(H_2O)_9,(H_2O)]^{4+}$ are very similar to that of the Pu(IV) homologue. The valence d orbitals are however, slightly more populated, simply reflecting the fact the 5d states/orbitals are more energetically accessible in Ce(IV) than the 6d ones in the heavy actinide (Np or Pu) homologues. To stress further the similarity between Ce(IV) and Pu(IV) ions, it is worthy to mention a previous theoretical study, where the objective was to find a surrogate for the Pu(IV) ion in HNO_3/TBP solution when it is complexed by nitrate ions, i.e $Pu(NO_3)_6^{2-}$ and $Pu(NO_3)_4(TBP)_2$.[24] It was found that the Ce(IV) complexes have comparable behaviors in term of structures, charge distribution and stabilities to those of Pu(IV), and that Ce(IV) is *a priori* a better surrogate for Pu(IV) for experimental studies than Th(IV) or U(IV). This conclusion is in line with the observed applicability of cerium dioxide CeO_2 as a surrogate for plutonium dioxide PuO_2 steaming from their structural similarities and comparable redox behavior.[64–67]

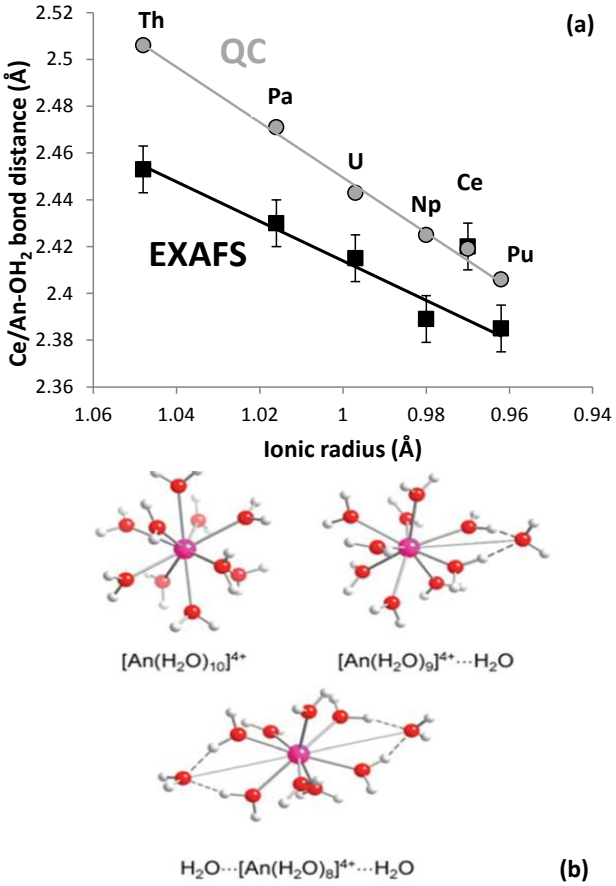


Figure 1. (a) Mean An–OH_2 or Ce–OH_2 bond distance determined by L_3-edge extended X-ray absorption fine structure (EXAFS) or by quantum chemical calculations (QC; for $[An/Ce(H_2O)_9]^{4+}\cdot H_2O$) versus An/Ce(IV) ionic radii (b) (U)-MP2 gas-phase optimized isomeric 10-, 9-, and 8-coordinated clusters, $[An(H_2O)_{10}]^{4+}$, $[An(H_2O)_9]^{4+}\cdot H_2O$, and $[An(H_2O)_8]^{4+}\cdot(H_2O)_2$.[43]

Solubility of Actinide(IV)- and Cerium(IV)-(hydr)oxides

Solubility products K_{sp}^{0} (at infinite dilution) of amorphous An(IV) precipitates ($An(OH)_{4(am)}$ or $AnO{\cdot}xH_2O_{(am)}$) and crystalline dioxides $AnO_{2(cr)}$ globally refer to the dissolution equilibrium:[14]

$$An(OH)_{4(s)} \rightleftharpoons An^{4+} + 4\ OH^{-} \quad (1)$$

A relationships between log K_{sp}^{0} of $An(OH)_{4(am)}$ or $AnO_{2(cr)}$ and the ionic radii of An^{4+} was evidenced.[18] Baes and Mesmer[35] determined log K_{sp}^{0} of $CeO_{2(cr)}$ from data given in the NBS tables,[68] which we find in excellent agreement with An(IV) (Figure 2a).

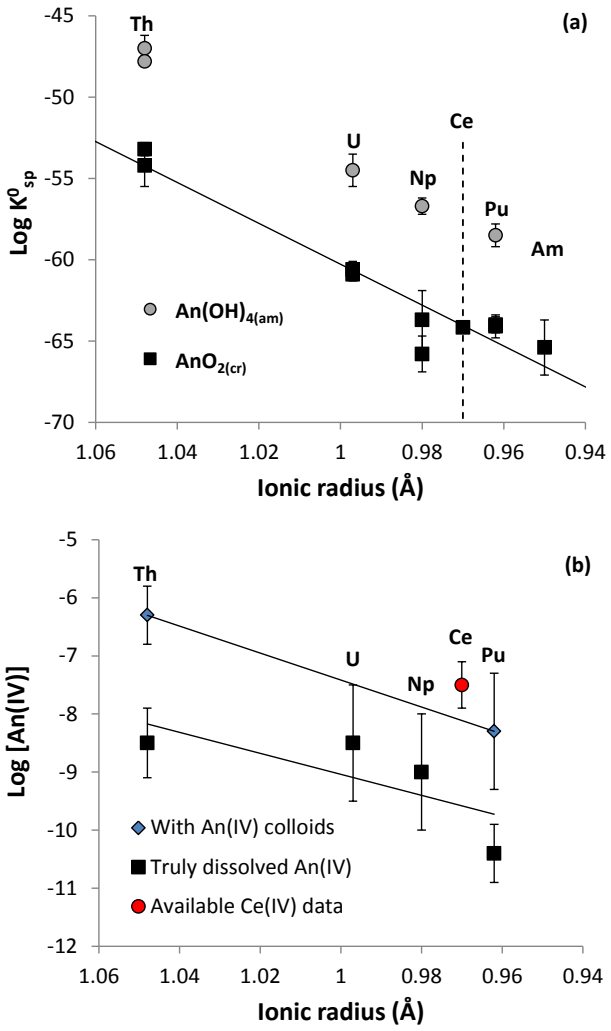
As previously demonstrated, the thermodynamically stable crystalline dioxides $AnO_{2(cr)}$ may be the solubility limiting solid phase at very low pH or elevated temperature.[14,18,19] However, experimental solubility data in neutral and alkaline solutions at room temperature are 6–7 orders of magnitude higher than the low values of less than 10^{-15} mol L^{-1} calculated from the known thermodynamic data. In fact, they correspond to solubility data obtained for $An(OH)_{4(am)}$. It was concluded that hydration of the surface of crystalline $AnO_{2(cr)}$ results in an amorphous solubility limiting surface layer.[14,18] By analogy with An(IV), Ce(IV) solubility might be strongly underestimated in near neutral to alkaline solutions when using log K_{sp}^{0} of $CeO_{2(cr)}$. It might be more realistic to consider $Ce(OH)_{4(am)}$ as the solubility limiting phase.

Actinide(IV) solubility determined in neutral and alkaline solutions by ultracentrifugation (e.g. 5×10^{5}g during 1h)[19] or ultrafiltration (typically 10 kDa)[15] refer to "truly dissolved" An(IV) ($[An(IV)]_{aq}$) and can be ascribed to the following solubility equilibrium:

$$An(OH)_{4(s)} \rightleftharpoons An(OH)_{4(aq)} \quad (2)$$

Figure 2b shows that experimental values of log $[An(IV)]_{aq}$ tend to decrease with the An(IV) ionic radii. When no or insufficient phase separation is applied, the measured Th(IV) and Pu(IV) concentrations in the aqueous phase are generally ~2.5 orders of magnitude larger.[15,19] This was attributed to the formation of small An(IV) eigencolloids. Their size was estimated to be in the range 1.5–2 nm, whereas $An(OH)_{4(am)}$ particles would be 2–5 nm large.[15] Experimentally determined apparent Th(IV) and Pu(IV) solubilities in neutral and alkaline solutions in presence of eigencolloids ($[An(IV)]_{coll}$) are plotted in Figure 2b. A similar trend is found for log $[An(IV)]_{coll}$ and log $[An(IV)]_{aq}$ versus ionic radii. Although data are missing for U and Np, this result further highlights the coherence across the An(IV) series.

Recently, the solubility of nanocrystalline cerium dioxide ($CeO_{2(cr,nano)}$) was determined.[69] At pH > 6, log [Ce(IV)] = -7.5 ± 0.4 (1σ) was found. This result is highly contrasting with log $[An(IV)]_{aq}$ (Fig. 2b). However, the authors performed phase separation by ultracentrifugation during 4 h at 4×10^4g. By analogy with An(IV), if we assume that Ce(IV) eigencolloids might form, this set-up might be inappropriate to remove such colloids. This hypothesis is supported by the fact that log [Ce(IV)] measured by Plakhova et al.[69] is in excellent agreement with log $[An(IV)]_{coll}$ (Fig. 2b).



223

224 **Figure 2.** (a) Solubility products of $An(OH)_{4(am)}$ and $AnO_{2(cr)}$ as a function of ionic radius.[18] Available data for $CeO_{2(cr)}$
225 are also included.[35] (b) Measured log [An(IV)] versus ionic radii at neutral to alkaline pH in equilibrium with
226 $An(OH)_{4(am)}$ after ultrafiltration or ultracentrifugation ("truly dissolved An(IV)") and with insufficient or without
227 phase separation ("with An(IV) colloids").[14] Value of log [Ce(IV)] determined by Plakhova et al.[69] at pH > 6 is shown
228 for comparison.

229

Hydrolysis and polynuclear species of Actinide(IV) and Cerium(IV)

Actinide(IV) hydrolysis reactions can be written as follows:

$$An^{4+} + n\ H_2O \rightleftharpoons An(OH)_n^{(4-n)} + n\ H^+; \qquad \beta_{An,n} \qquad (3)$$

Where $\beta_{An,n}$ is the corresponding hydrolysis constant (at infinite dilution) and $1 \leq n \leq 4$. There is no evidence for the formation of $An(OH)_{5\ (aq)}^-$. As reviewed by Neck et al.[14] values of log $\beta_{An,n}$ are consistent in the An(IV) series, and increase from Th(IV) to Pu(IV). An(IV) also tend to form polynuclear species, observed for pH-[An(IV)] values approaching the solubility limit of An(IV) with respect to $An(OH)_{4(am)}$. Polynuclear species formation can be described as follows:

$$x\ An^{4+} + y\ H_2O \rightleftharpoons An_x(OH)_y^{(4x-y)} + y\ H^+; \qquad \beta_{An,x,y} \qquad (4)$$

In the case of Th(IV), dimers to hexamers ($2 \leq x \leq 6$) could be identified and corresponding formation constants could be determined because of its single oxidation state in water.[70] Due to its complex redox chemistry, an extremely large diversity of polynuclear Pu species was observed, including polymers of mixed valence states (Pu(IV) with Pu(III) or Pu(V)).[71] Unfortunately, corresponding formation constants could not be determined. Recent studies suggested that the selected hydrolysis constants of Np(IV) and Pu(IV) by the NEA might be overestimated by approximately one log unit (see e.g. reference 72 and references therein) because they might implicitly include polynuclear Np/Pu(IV) species as well as larger Np/Pu(IV) polymers (small colloids) that are hardly removed from the solution. Nevertheless, only the selected hydrolysis constants of Np(IV) and Pu(IV) by the NEA will be discussed below because recently proposed sets of hydrolysis constants are incomplete and polynuclear species formation constants are missing, which does not allow predicting Np/Pu(IV) solubility.

Bilal and Müller[37] determined Ce(IV) hydrolysis constants by cyclic voltammetric measurement in aqueous $HClO_4$ solutions ($[Ce]_{tot} = 1.25\times10^{-4}$ mol L^{-1}), which are compared with that of Np(IV) and Pu(IV) in Figure 3a. Although a large diversity of polynuclear Ce (including mixed Ce(IV)-Ce(III)) species have been suggested (e.g. Ce(IV)-dimer)[70], corresponding set of formation constants might be incomplete and questionable.[35] Bilal and Müller[37] did not account for the formation of polynuclear Ce(IV) species. Cerium(IV) hydrolysis constants might implicitly include such species and, therefore, should be somehow comparable to the selected hydrolysis constants of Np(IV) and Pu(IV) by the NEA. Values of log $\beta_{Ce,1}$ and log $\beta_{Ce,2}$ are quite similar to that of Np(IV) and Pu(IV), which supports the idea that these elements can be considered as analogues. However, relatively large deviation is observed for the third and a huge one for the fourth hydrolysis constants: $\beta_{Ce,3}$ (≈ -1.5) and $\beta_{Ce,4}$ (≈ -4.4) values are, respectively, 0.8 and 4.4 orders of magnitude larger on average than the corresponding constants for Pu (-2.3 and -8.5, respectively). Note that these differences would be larger if Pu(IV) hydrolysis constants were overestimated.[72] This result is highly contrasting with complexation data with other hard Lewis bases (e.g. OH^-, F^-, CO_3^{2-}, Cl^-)[73]. For instance, formation constants of $AnF^{3+}_{(aq)}$, $AnF_2^{2+}{}_{(aq)}$, $AnF_3^{+}{}_{(aq)}$ and $AnF_{4(aq)}$ are comparable to those of Ce(IV) (Fig. S1).[74,75] In fact, Bilal and Müller[37] determined log $\beta_{Ce,4}$ less than 0.5 pH unit below the onset of $Ce(OH)_{4(am)}$ precipitation (determined visually). We suspect that log $\beta_{Ce,3}$ value determined by Bilal and Müller[37] might have been affected by the formation of small Ce(IV) colloids, and that log $\beta_{Ce,4}$ very likely refers to the reaction $Ce^{4+} + 4\ OH^- \rightleftharpoons Ce(OH)_{4(am,fresh)}$, where $Ce(OH)_{4(am,fresh)}$ is a freshly precipitated amorphous (colloidal) Ce(IV) hydroxide. The consequence on Ce(IV) and Pu(IV) aqueous speciation is shown in Figure 3b,c ($[NaClO_4]$ = 0.1 mol L^{-1}). Successive Ce(IV) hydrolysis are predicted to occur within a narrow pH-range, and $Ce(OH)_{4(aq)}$ prevails at pH > 3 (Figure 3b). By contrast, $Pu(OH)_{4(aq)}$ prevails only at pH > 6 (Figure 3c).

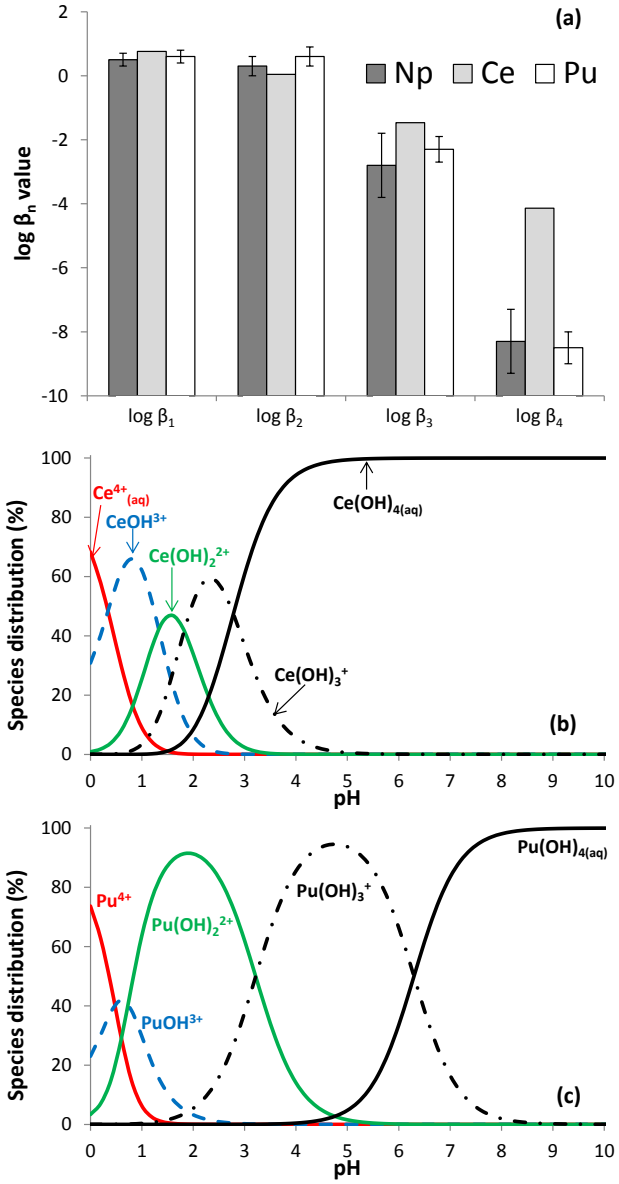


Figure 3. (a) Comparison between hydrolysis constants of Np(IV),[2] Pu(IV),[2] and Ce(IV).[37] Predicted speciation of (b) Ce(IV) and (c) Pu(IV) versus pH ([$NaClO_4$] = 0.1 mol L^{-1}) using the hydrolysis constants given in Table 1.[2,37]

Estimated speciation of Ce

As previously observed for trivalent actinides (Am and Cm) and relevant trivalent lanthanide analogues (Nd and Eu), the hydrolysis constants are indistinguishable within the given uncertainties.[20] The same should be observed between Ce(IV) and Pu(IV) given their similarities.

Because the hydrolysis constants (i) are expected to follow Np(IV) < Ce(IV) < Pu(IV) and (ii) do not significantly differ between Np(IV) and Pu(IV) given the experimental uncertainties, we suggest to simply use the complete thermodynamic database of Pu(IV) to estimate Ce(IV) aqueous speciation. The advantage is that, for further estimations of Ce(IV) behavior in more complex solutions (e.g. in presence of carbonates[2] or natural organic matter[76]), the available database of Pu(IV) can be used for Ce(IV) without any additional corrections. Presently selected hydrolysis constants for Ce(III) and Ce(IV) are listed in Table 1. Although the Pu(IV) speciation model provided by the NEA might not be fully mechanistic (polynuclear species are missing, as discussed above)[72], it allows predicting overall Pu(IV) solubility quite accurately,[13,15] which is a sufficient information for the present purpose. Because the solubility data of Plakhova et al.[69] at pH < 6 refer to the half reaction $CeO_{2(cr,nano)} + 4\ H^+ + e^- \rightleftharpoons Ce^{3+} + 2\ H_2O$, the present estimations have no consequence on the interpretations of the latter authors, as verified by speciation calculations (not shown). In particular, the authors found log $K_{sp}^0(CeO_{2(cr,\ nano)})$ = -59.3 ± 0.3. This value is higher than for larger $CeO_{2(cr)}$ particles, which agree with Schindler equation[77] and corresponding analysis of Th(IV) and Pu(IV) data.[15]

Table 1. Comparison between hydrolysis constants of Ce(III) and Ce(IV) used previously[36,69] and in the present work (p.w.).

	log β[36,69]	log β (p.w.)
$Ce^{3+} + H_2O \leftrightarrows CeOH^{2+} + H^+$	−8.41 ± 0.08[78]	−8.41 ± 0.08[78]
$Ce^{3+} + 2\ H_2O \leftrightarrows Ce(OH)_2^+ + 2H^+$	−17.60 ± 0.24[78]	−17.60 ± 0.24[78]
$Ce^{3+} + 3\ H_2O \leftrightarrows Ce(OH)_{3(aq)} + 3H^+$	−27.23 ± 1.19[78]	−27.23 ± 1.19[78]
$Ce^{4+} + H_2O \leftrightarrows CeOH^{3+} + H^+$	0.764[37]	0.6 ± 0.2[2]
$Ce^{4+} + 2\ H_2O \leftrightarrows Ce(OH)_2^{2+} + 2H^+$	0.048[37]	0.6 ± 0.3[2]
$Ce^{4+} + 3\ H_2O \leftrightarrows Ce(OH)_3^+ + 3H^+$	−1.485[37]	−2.3 ± 0.4[2]
$Ce^{4+} + 4\ H_2O \leftrightarrows Ce(OH)_{4(aq)} + 4H^+$	−4.124[37]	−8.5 ± 0.5[2]

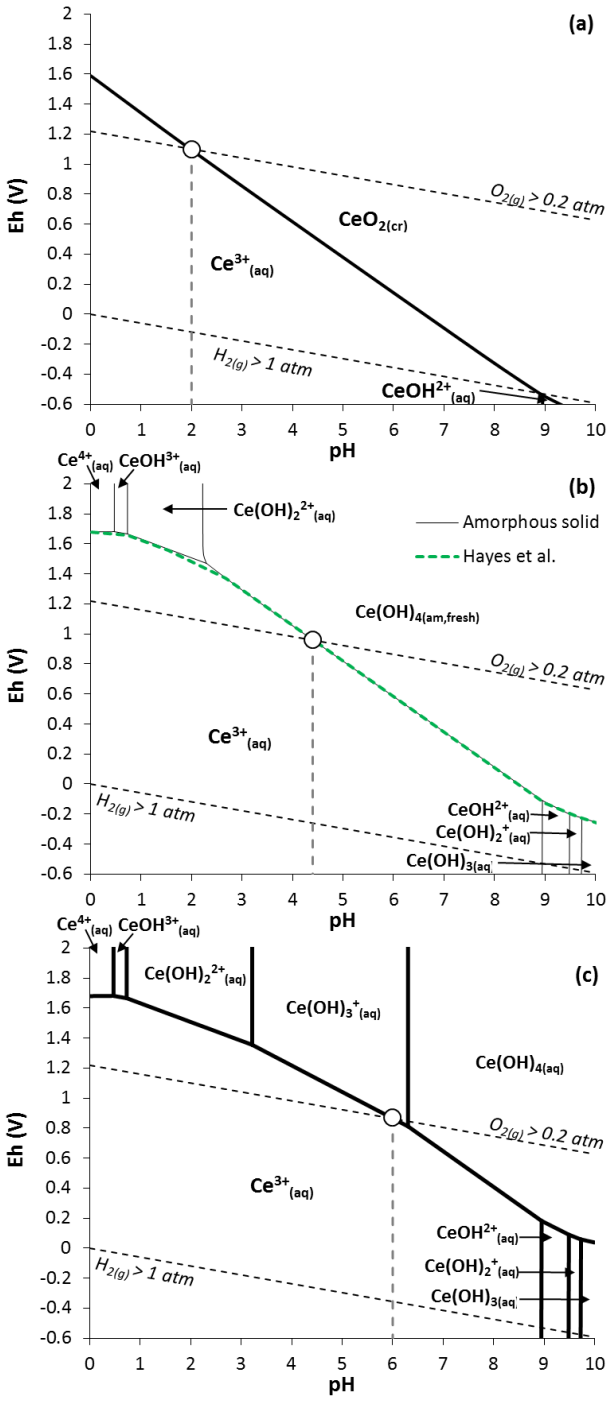


Figure 4. pH-Eh diagrams of Ce ([Ce] = 1.25×10^{-4} mol L^{-1}; [$NaClO_4$] = 0.1 mol L^{-1}) assuming (a) formation of $CeO_{2(cr)}$ (log K^0_{sp} = -64.16), (b) formation of $Ce(OH)_{4(am,fresh)}$ (log K^0_{sp} = -56.8) or (c) no formation of Ce(IV)-(hydr)oxide. In (b), the pH-Eh diagram calculated by Hayes et al.[36] is shown for comparison (only the Ce(IV)/Ce(III) redox transition is shown). White circles and vertical dotted lines show the pH value corresponding to the Ce(IV)/Ce(III) redox transition under ambient (air) atmosphere.

Three different pH-Eh diagrams of Ce are plotted in Figure 4 for [Ce] = 1.25×10^{-4} mol L^{-1} ([$NaClO_4$] = 0.1 mol L^{-1}; corresponding to the experimental conditions of Bilal and Müller[37]). When assuming the formation of $CeO_{2(cr)}$ (Fig. 4a), for P_{O2} = 0.2 atm (pH + pe = $-\log a_{H^+} - \log a_{e^-}$ = 20.6), Ce(III) prevails at low pH < 2 and rapidly disappears from the solution when pH further increases (not shown; log $[Ce(IV)]_{aq}$ = -16.6 at pH > 7 according to our calculations). Although redox conditions may differ from pH + pe = 20.6, this result is highly contrasting with previous Ce adsorption studies under ambient (air) conditions, where log $[Ce]_{aq}$ > -8 at pH = 6 in $MnO_{2(s)}$ aqueous suspensions, and where little Ce(III) oxidation to Ce(IV) by Fe(III)-(hydr)oxides occured.[29] Hence, $CeO_{2(cr)}$ is very likely not the solubility limiting phase in the latter study. Note that the present pH-Eh diagram (Fig. 4a) agrees very well with previous ones,[79] although Ce(IV) hydrolysis constants differ, because of the high stability of $CeO_{2(cr)}$.

The Ce(IV)/Ce(III) redox transition calculated by Hayes et al.[36] is shown as dotted line in Figure 4b. The latter authors used the hydrolysis constants reported by Bilal and Müller,[37] which we suspect to account for the precipitation of $Ce(OH)_{4(am,fresh)}$. By using Pu(IV) hydrolysis constants for Ce(IV), we found that both pH-Eh diagrams coincide when log K_{sp}^0 ≈ -56.8. This value agrees with log K_{sp}^0 = -57.6 ± 0.7, which could be estimated for $Ce(OH)_{4(am)}$ using the relationship between log K_{sp}^0 of $An(OH)_{4(am)}$ and An(IV) ionic radii (Fig. 2a). Figure 4c shows the pH-Eh diagram of dissolved Ce. This diagram applies only to Ce aqueous speciation, hence remaining true even when Ce precipitation and/or adsorption to another mineral occur.[7,80] When pH + pe = 20.6, Ce(III) prevails up to pH ≈ 6. This result is qualitatively consistent with the observation that Ce(III) prevails in solution under ambient conditions in $MnO_{2(s)}$ aqueous suspensions, while Ce(IV) is associated with the solid phase (precipitated or adsorbed onto $MnO_{2(s)}$).[27,29,39,40] These results further suggest that (i) previously determined hydrolysis

330 constants[37] were inaccurate and (ii) Pu(IV) might be a good analogue of Ce(IV).

331

332 Conclusions

333 In summary, we briefly reviewed most relevant mechanisms responsible for An(IV)
334 solubility in water and demonstrated the highly consistent behavior of Ce(IV) and An(IV) with
335 quantum chemical calculations, and more specifically the strong resemblance of Ce(IV) aqua ion
336 with the Np(IV) and Pu(IV) aqua ions. Because discrepancies were sometimes observed between
337 experimentally determined thermodynamic parameters of Ce(IV) and An(IV), we chose to simply
338 use the thermodynamic database of Pu(IV) to predict Ce(IV) speciation and solubility. The present
339 estimations are in good agreement with experimental studies of e.g. Ce adsorption to $MnO_{2(s)}$ and
340 Fe(III)-(hydr)oxides. However, the latter comparisons were only qualitative because of the lack of
341 experimental data on redox potentials in $MnO_{2(s)}$ or Fe(III)-(hydr)oxides aqueous
342 suspensions.[27,29,39] Although, further experimental (e.g. solubility or adsorption) studies are
343 required to verify the present assumptions and to obtain more accurate thermodynamic databases
344 for Ce(IV) and An(IV) (including mono- and polynuclear dissolved species), the present work
345 might yet help (i) to predict more accurately Ce speciation and its fate in environmental conditions
346 (ii) to use more accurately Ce as a proxy of (paleo)redox conditions (iii) to use Ce(IV) as analogue
347 for the study of An(IV) (geo)chemical behavior and (iv) to develop new cerium compounds
348 requiring the control of certain key processing factors.

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