CrossMark

ORIGINAL PAPER

Computational study of Th^{4+} and Np^{4+} hydration and hydrolysis of Th^{4+} from first principles

Davi H. T. Amador[1] · **Julio R. Sambrano**[2] · **Ricardo Gargano**[3] ·
Luiz Guilherme M. de Macedo[1,3]

Abstract The aqueous solvation of Th and Np in the IV oxidation state was examined using cluster models generated by Monte Carlo simulations and density functional theory embedded within the COSMO continuum model to approximate the effect of bulk water. Our results suggest that the coordination number (CN) for both Th(IV) and NP(IV) should be 9, in accordance to some experimental and theoretical results from the literature. The structural values for average oxygen–metal distances are within 0.01 Å compared to experimental data, and also within the experimental error. The calculated ΔG^0_{Sol} are in very good agreement with experimental reported values, with deviations at CN = 9 lower than 1% for both Th(IV) and Np(IV). The hydrolysis constants are also in very good agreement with experimental values. Finally, our methodology has the advantage of using a GGA functional (BP86) that not only makes the calculations more affordable computationally than hybrid functional or ab initio molecular dynamics simulations (Car-Parrinello) calculations, but also opens the perspective to use resolution of identity (RI) calculations for more extended systems.

✉ Luiz Guilherme M. de Macedo
lgm@ufpa.br

[1] Faculdade de Biotecnologia, Instituto de Ciências Biológicas, Universidade Federal do Pará (UFPA), Belém, PA 66075-110, Brazil

[2] Departamento de Matemática, Universidade Estadual Paulista (UNESP), PO Box 473, Bauru, SP 17030-360, Brazil

[3] Instituto de Física, Universidade de Brasília (UnB), PO Box 04455, Brasília, DF 70919-970, Brazil

Introduction

Despite the environmental [1], political and energetic [2] importance of actinides, the basic characteristics, such as ionization potential and thermodynamic properties for several ions, of many actinides are still unknown, due mainly to experimental difficulties related to their high radioactivity and instability. Furthermore, their chemical behavior is quite complex since they have a large number of oxidation states, and by the appearance of valence 5f orbitals, which are more extended and less shielded by the outer 6s and 6p, making them more prone to participate in bonding than 4f orbitals [3].

It is important to note that understanding the behavior of actinides in aqueous solution is important to the separation and long-term storage of nuclear waste. In particular, studies are still needed on actinides (IV) such as Neptunium and Thorium [4, 5]: Np is considered to be the most problematic actinide [6] due to its high solubility and mobility, whereas the main interest in Th lies in its potential as a source of nuclear fuel [7].

The experimental study of the aqueous chemistry of Th(IV) and Np(IV) requires knowledge of their hydrolysis, which is very complex for Th(IV) due to colloid or polymeric species even at low concentrations [8–10] , and for Np [11, 12] due to complex redox, solubility and sorption behavior to hydrologic processes. Since both Np(IV) and Th(IV) are strongly hydrated due to their high charge to ionic radius ratio, elucidation of their aqueous hydration environment is necessary to understand their aqueous chemistry.

Nevertheless, there is huge experimental uncertainty regarding the number of water molecules present in the first hydration shell (i.e., the coordination number) for Th(IV) and Np(IV), and also for the hydrolysis constants of Th(IV): the coordination numbers (CN) of Np(IV) and Th(IV) have been studied by X-ray experiments, and were estimated to be 8–11 for Th(IV) [13–16] and 8–12 for Np(IV) [11–18], while theoretical calculations suggest 9–10 [19–21] for Th(IV) and 8–9 [22, 23] for Np(IV). In turn, the hydrolysis constants for Th(IV) varies significantly in the literature [9], sometimes more than three orders of magnitude, and, to the best of our knowledge, there is no relativistic density functional calculations for hydrolysis constants of Th(IV).

First principles theoretical calculations are an alternative means of obtaining structural, thermodynamic and chemical properties of actinide ions in the condensed phase [24–26]. In this work, we investigate the structural properties of the hydration shell and thermodynamics of solvated Np(IV) and Th(IV) ions by first principles in order to address preferred CN, molecular structure, binding energies and Gibbs free energies of solvation. The aim was to obtain results at affordable computational costs using a GGA functional, pseudopotentials, cluster-continuum models and metropolis algorithm to generate initial structures.

Computational details

It was necessary to obtain good starting geometries for the clusters before performing the quantum chemical calculations, and these geometries were obtained through Monte Carlo (MC) simulations. The MC simulations were performed using standard procedures [27] for the Metropolis sampling technique in the isothermal-isobaric NpT ensemble. All simulations were performed using the program DICE [28]. In both simulations, the Th^{4+} and Np^{4+} ions were surrounded by 1000 water molecules at a pressure of 1 atm and temperature of 298 K. After a long equilibration of 1×10^8 steps, the MC simulations were performed with 2×10^8 steps.

In MC simulations, molecules interact via Lennard-Jones (LJ) potential. The LJ parameters [20, 29, 30] were kept fixed, and are presented in Table 1. Since the interaction coefficients for Np(IV) and U(IV) are similar [9], and they have also similar hydration behavior [22, 31], we adopted in the simulation the U(IV)'s LJ parameters for Np(IV).

All calculations at DFT level were performed with the TURBOMOLE v6.3 program package [32] with the BP86 [33–35] exchange-correlation functional due to its good unscaled frequencies [36] and computational performance compared to hybrid functionals. The m5 grid quadrature was employed for the numerical XC term, and entropy calculations were carried out for $T = 198.15$ K and $p = 0.1$ MPa. All molecular structures were optimized without any constraints, and

Table 1 Intermolecular parameters for Lennard-Jones (LJ) intermolecular potential used in Monte Carlo (MC) simulation for water molecules and ions Th^{4+} and Np^{4+}

Specie	Atoms	q_I	ε_I	σ_I
H_2O	O	-0.8476[a]	-0.8476[a]	3.165[a]
	H	0.4238[a]	0.000	0.000
	H	0.4238[a]	0.000	0.000
Th^{4+}	Th	+4[b]	0.080[b]	2.000[b]
Np^{4+}	Np	+4[c]	0.17392181[c]	3.500[c]

[a] From Berendsen, Grigera and Straatsma [29]

[b] From Yang, Tsushima and Suzuki [20]

[c] From Li, Song and Mertz Jr [30]

frequency calculations were performed numerically to ensure that structures were local minima and to obtain thermochemical corrections. For Th and Np, the small core scalar relativistic ecp-60-mwb pseudo potentials and their corresponding ecp-60-mwb-gencont basis set were employed [37–39], whereas for O and H, the def-TZVP [40] basis set was used. The spin-orbit (SO) effects were neglected in all calculations as recent studies showed SO to be negligible [41, 42], and all binding energies were corrected by counterpoise scheme [43] although the BSSE of these systems were reported as small [23, 44].

The atomic radii employed at COSMO PCM calculations for thorium (IV) [45] and neptunium (IV) [46] were 114 and 128 pm, respectively. For O and H, the recommended values [47, 48] of r of 172 and 130 pm were used.

It is known that dielectric continuum models alone will not give accurate predictions of solvation free energies of charged species due to strong solute–solvent interactions [49, 50]. In order to overcome this limitation, part of the solvent was treated explicitly by the thermodynamic cluster cycle [51–53] depicted in Fig. 1. In this cluster cycle, a cluster of n water molecules reacts with the ionic solute.

The quantum chemical calculations for hydration (solvation) also followed the strategy proposed by Wiebke et al [44], and is presented in Fig. 2. First, gas phase molecular optimizations, frequency and gas phase binding energies D_0 of $[M^{IV}(H_2O)_h]^{4+}$ considering $h = 9$ and 10, and M = Th and Np were performed from geometries obtained from the MC step.
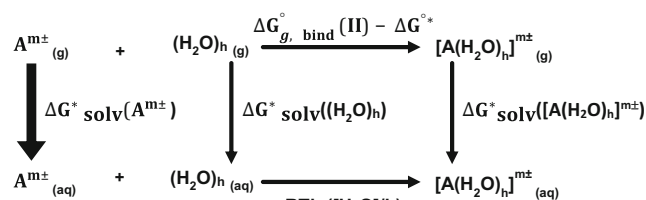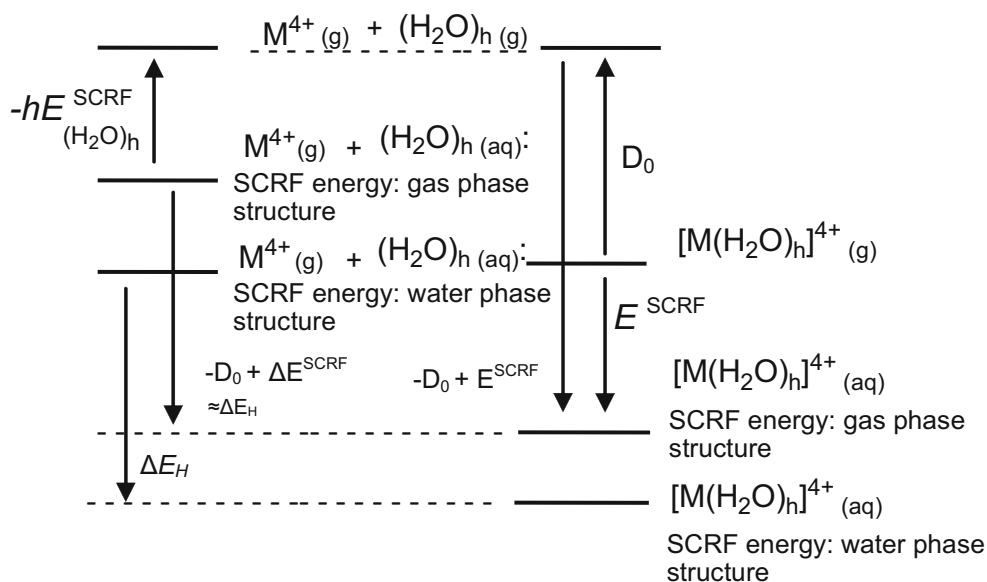

Fig. 1 Thermodynamic cluster cycle for the calculation of ΔG_{Sol} ($A^{m\pm}$)

Fig. 2 Computational strategy to obtain the Gibbs free energy on hydration for Th^{4+} and Np^{4+} (adapted from [44])

Hydration energies ΔE_{H} and Gibbs free energies of hydration were approximated by single-point energies for constrained gas phase structures within COSMO [54] self-consistent reaction field (SCRF).

Equation 1 [55] (see also the thermodynamic cycle in Fig. 3),

$$\Delta\Delta G^{*}_{x,hydrat,\,aq} = \Delta G^{0}_{x,hydrat,g} + \Delta\Delta G^{*}_{solv} + \Delta G^{0\rightarrow *} \quad (1)$$

where

$$\Delta\Delta G^{*}_{solv} = \Delta G^{*}_{solv}\left(\left[M(OH)(H_2O)_h\right]^{3+}\right)$$
$$+ \Delta G^{*}solv(H^{+}) - \Delta G^{*}solv\left(\left[M(H_2O)_h\right]^{4+}\right) \quad (2)$$

, used to obtain the hydrolysis constants, represents how the free energy of the xth reaction step, $\Delta\Delta G^{*}_{x,hydrat,\,aq}$, can be written as the sum of the gas phase deprotonation energy ($\Delta G^{0}_{x,hydrat,g}$), the differential solvation free energy ($\Delta\Delta G^{*}_{solv}$) and the standard state correction[55, 56] term ($\Delta G\ 0 \rightarrow *$), where the $\Delta G\ 0 \rightarrow *$ value for 9-fold coordination [57] is −12.43 kJ mol^{-1}.
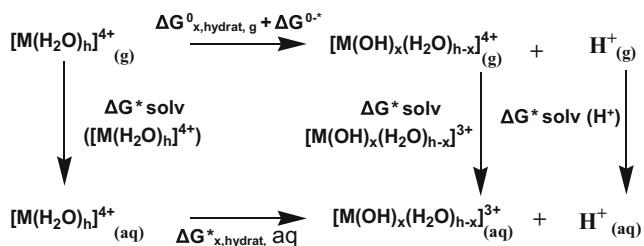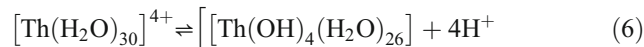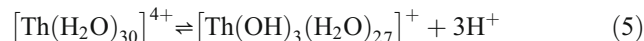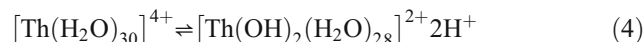

Fig. 3 Thermodynamic cycle used for calculation of Log(K) for Th^{4+} hydrolysis

Since the Gibbs free energy for the hydrolysis reactions [9] for Th(IV),

$$\left[Th(H_2O)_{30}\right]^{4+} \rightleftharpoons \left[Th(OH)(H_2O)_{29}\right]^{3+} + H^{+} \quad (3)$$

$$\left[Th(H_2O)_{30}\right]^{4+} \rightleftharpoons \left[Th(OH)_2(H_2O)_{28}\right]^{2+}2H^{+} \quad (4)$$

$$\left[Th(H_2O)_{30}\right]^{4+} \rightleftharpoons \left[Th(OH)_3(H_2O)_{27}\right]^{+} + 3H^{+} \quad (5)$$

$$\left[Th(H_2O)_{30}\right]^{4+} \rightleftharpoons \left[\left[Th(OH)_4(H_2O)_{26}\right] + 4H^{+} \quad (6)$$

were calculated using the thermodynamic cycle [55] presented in Fig. 3, so a relevant question about the solvated proton presented in these four reactions shows up. The protons on equations 3–6 are in fact solvated ions, which could be a $H_5O_2^{+}$ (Zundel complex ion [58]), or H_3O^{+}. The solvation energies for $H_5O_2^{+}$ and H_3O^{+} differ by 43 kJ mol^{-1}, so we decided to use the experimental value [59] of 265.9 kcal mol^{-1} for the proton free energy of solvation.

Results and discussion

Initially, we considered primary coordination numbers as 8, 9 and 10 for Np(IV) and 9 and 10 for Th(IV) based on results obtained from theoretical studies [19–23]. Since we could not find a structure free of negative frequencies for $[Np(OH_2)_8]^{4+}$, we focused the first hydration shell with CN = 9,10. Structural data obtained from DFT minimizations that gave best concordance to experimental data are presented in Table 2. The inclusion of water dielectric through COSMO lowers the average BP86/ecp-60mwb/def-TZVP bond lengths from 2.54 to 2.47 Å for Th(IV), and from 2.47 to 2.39 Å for Np(IV). Both results in the first solvation shell for < rm-O > average distances are within 0.01 Å compared to experimental data, and

Table 2 Average BP86/ecp-60mwb/def-TZVP $< r_m$-O $>$ bond lengths (in Å) for $[Th(H_2O)_9]^{4+}$ and $[Th(OH)(H_2O)_8]^{3+}$ in comparison with experimental values

Complex	$< r_m$-O$>$	BP86/ ecp-60mwb def-TZVP (gas phase)	BP86/ ecp-60mwb def-TZVP (COSMO)	Experimental
$[Th(H_2O)_9]^{4+}$	Th-O	2.54	2.47	2.46 ± 0.02[a]
$[Np(H_2O)_9]^{4+}$	Np-O	2.47	2.39	2.40 ± 0.01[b]

[a] From Moll et al. [14], and Neck and Kim [9]

[b] From Neck and Kim [9]

also within the experimental error. This seems to indicate a preference for a 9 coordinate environment for both Np(IV) and Th(IV). Our findings are in agreement with experimental [60] and previous theoretical results from Tsushima and Yang [61], but are in contrast with the conclusions drawn by Clark and co-workers [23], who found a thermodynamic preference for the 8-coordination species.

The (negative) zero point energy (ZPE)-corrected gas phase dissociation energies for reaction $[M(OH_2)_{h(g)}]^{4+} \rightarrow M_{(g)}^{4+} + (OH_2)_{h(g)}$ (see also Fig. 4a) were calculated according to the thermodynamic cycle of Fig. 1, and the computational scheme of Fig. 2. As expected, the dissociation energies are of the same order of magnitude of corresponding values [44, 57] for actinide(III), and more negative (Table 3). The dissociation energy shows a smooth increase when one moves from Th(IV) to Np(IV): for h = 9, the D_0 increases by 239.48 kJ mol^{-1} while for h = 10 the increase is 246.59 kJ mol^{-1}. The D_0 difference for Th(IV) when the CN increases from 9 to 10 increases by 132 kJ mol^{-1}, while the corresponding value for Np(IV) increases by 139.77 kJ mol^{-1}. The solvent contribution ΔE^{SCRF} increases almost by one order of magnitude less when one moves from Th(IV) to Np(IV) with values for h = 9 and 10 of 27.24 kJ mol^{-1} and 17.15 kJ mol^{-1}, respectively. The interesting point is that the ΔE^{SCRF} decreases as one moves from h = 9 to h = 10 for Th(IV) by 2.38 kJ mol^{-1}, and the corresponding value for Np(IV) also decreases by 12.47 kJ mol^{-1}. So, the major contribution for free energy of solvation should come from the binding energy.

Now it seems convenient to make some comments about the limitations of the cluster continuum model: within this model, it is possible to include incorrect orientations of water molecules near the dielectric boundary, as well imprecise evaluation of entropic effects of hydrogen bounded complexes. These problems were minimized in this work by including the first (and second solvation shells for the calculation of hydrolysis constants) by MC methods, and by using hydrogen-bonded complexes of similar size in both sides of the thermodynamic cycle [51], respectively.

The calculated Gibbs free energies of solvation are listed in Table 4. The values were calculated according to equations,

$$\Delta G^0_{Solv} = \Delta H^0_H - T\Delta S^0_H \approx \Delta E_H - T\Delta S^0 \qquad (7)$$

and

$$\Delta E_H \approx - \quad D_0 + \quad \Delta E^{SCRF}$$
$$\approx -D_0 + E^{SCRF}\left([A(H_2O)_h]^{4+}\right) - E^{SCRF}\left((H_2O)_h\right). \qquad (8)$$

We had to approximate ΔH by ΔE since $An_{(g)}^{4+}H^0$ data is neither available from experiment or could not be obtained from quantum chemical calculations. The ΔG^0 Solv show better accordance for h = 9 when compared to experimental data [62–64]. Since ΔG^0 Solv decreases with CN, we also would expect that a Np(IV)'s hypothetical value for h = 8—we could not find a structure free of small negative frequencies for h = 8—would be close to that reported by Clark et al. [23]. The differences at CN = 9 are lower than 1%: they are 24 and

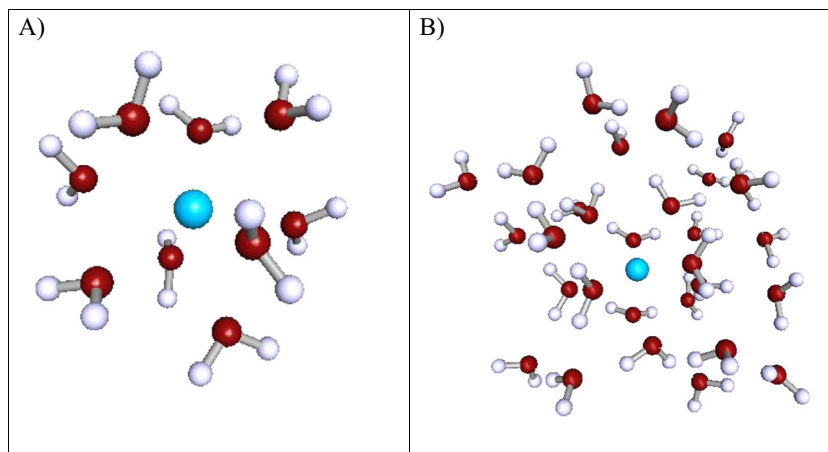**Fig. 4** Representative BP86/ecp-60mwb/def-TZVP optimized geometries for the 1st and 2nd solvation shell structures **a** $[M(H_2O)_9]^{4+}$ (M = Th or Np) and **b** $[Th(H_2O)_{30}]^{4+}$

Table 3 Zero point energy (ZPE)-corrected negative gas phase binding energies ($-D_0$) and differences in self-consistent reaction field (SCRF) stabilization energies ΔE^{SCRF} between $[A(H_2O)_h]^{4+}$ and $(H_2O)_h$ (in kJ mol^{-1})

Ion	$-D_0$		ΔE^{SCRF}	
	$h = 9$	$h = 10$	$h = 9$	$h = 10$
Th^{4+}	−3098.81	−3231.47	−2629.22	−2526.84
Np^{4+}	−3338.29	−3478.06	−2656.46	−2543.99

58 kJ mol^{-1} for Th(IV) and Np(IV), respectively. Regarding the question about the coordination numbers: from Tables 2 and 4, the value for both Th(IV) and Np(IV) that is both reasonable and consistent vis-à-vis experimental results is 9.

The hydrolysis constants for Th(IV) are difficult to determine experimentally since they vary with the ionic strength (I), and also because several species appear even at low pH, resulting in complex interconnected equilibria [9]. In general, these constants are obtained [65] in a semi-empirical way and extrapolated to I = 0. On the other hand, accurate theoretical equilibrium constants are also a *tour de force* to be obtained, since a change of only ~5 kJ mol^{-1} (approximately 1.2 kcal mol^{-1}) in ΔG changes logK by a unit. So it is sensible to expect that an error of 2–3 logarithm units is a very good result due to all the approximations involved in the calculations.

The calculated hydrolysis constants are presented in Table 5, as well corresponding experimental [10, 66–69] available data for I = 0. The calculations followed the thermodynamic cycle presented in Fig. 3 (see also Fig. 4b), and results show very good agreement, except for reaction 4, where the constant deviates 3 logarithm units. In addition to the complex equilibria, the hydrolysis constants are also dependent from temperature, concentration and counter ions presented in solution [9]. Concerning the theoretical calculations, even the third solvation shell could be important. Probably, the deviation can be credited mainly to the formation of polymeric species [8], but more research should be done in order to obtain a satisfactory explanation.

Finally, this methodology uses only a GGA functional in all first principles calculations. This opens the perspective to

Table 5 Calculated hydrolysis constants (log K) for $[Th(H_2O)_{30}]^{4+}$ reactions for formation of hydroxide complexes using reactions 3–6 (see text for details) at 298.15 K in comparison to experimental data with I = 0

Reaction number	Log K (BP/def-TZVP)	Log K (experimental)
3	−2.62	−2.3 ± 0.1[a]
		−2.1 ± 0.2[b]
		−3.0 ± 0.2[c]
		−3.1 ± 0.3[d]
4	−9.89	−5.8 ± 0.2[c]
		−6.6 ± 0.2[b]
5	−8.30	−9.3 ± 0.4[d]
		−11.4[b]
6	−17.26	−15.9 ± 0.3[c]
		−13.6 ± 0.4[d]
		−17.0 ± 0.5[b]

[a] From Brown, Ellis and Sylva [66]

[b] From Ekberg et al. [10]

[c] From Baes and Mesmer, and Baes; Meyer; Roberts [67, 68]

[d] From Grenthe and Lagermann [69]

use RI techniques [70] to include a third hydration shell to obtain better hydrolysis constants, or to include polymeric species and formation of colloidal nanoparticles with actinide (IV) systems. The errors associated to RI are usually small [71], and could be minimized by error cancellation when one performs the energy differences into the thermodynamic cycles, and further investigation is ongoing in this direction.

Conclusions

The study of basic thermodynamic properties is important to reproduce experimental data, and to produce reliable predictions as well. In this study, we investigated gas phase and condensed phase structures, binding energies, hydrolysis constants, structural parameters, and Gibbs free energies for Th(IV) and Np(IV) at $[M(OH_2)_h]^{4+}$ with values of h = 8 (Np), and 9, 10 (Th and Np) or 30 (Th) using mixed cluster continuum model at BP86/ecp-60mwb/def-TZVP level of theory with starting geometries generated through MC

Table 4 Calculated ΔG^0_{Solv} (in kJ mol^{-1}) for Th^{4+} e Np^{4+} with different CN numbers (h)

Ion	ΔG^0_{Solv} (theoretical, this work)		ΔG^0_{Solv} (theoretical)	ΔG^0_{Solv} (experimental)
	$h = 9$	$h = 10$		
Th^{4+}	−5836	−5873	−6100[a]	−5860[c]
Np^{4+}	−6108	−6133	−6494[a], 6069[b]	−6050[c]

[a] From David and Vokhmin [46]

[b] From Clark et al. [23], with h = 8

[c] From Bratsch and Lagowski [62], Marcus and Loewenschuss [63], and Chopin and Jensen [64]

methods. Our results suggest that, for both ions, the CN should be 9, and for solvation Gibbs free energy the first hydration shell is sufficient. There is very good agreement with available experimental structural data and Gibbs free energy of solvation. There is also good agreement regarding hydrolysis constants at I = 0.

Finally, this methodology opens a perspective to use RI techniques for future calculations with a third hydration shell, or to include polymeric species and formation of colloidal nanoparticles with actinide (IV) systems.

References

1. Walter C, Denecke MA (2013) Actinide colloids and particles of environmental concern. Chem Rev 113:995–1015
2. Brook BW, Bradshaw CJA (2014) Key role for nuclear energy in global biodiversity conservation. Conserv Biology 29:702–712
3. Cotton S (2006) Lanthanide and actinide chemistry. Wiley, London
4. Moulin C, Amekraz B, Hubert S, Moulin V (2001) Study of thorium hydrolysis species by electrospray-ionization mass spectrometry. Anal Chim Acta 441:269–279
5. Gorden AEV, McKee ML (2016) Computational study of reduction potentials of Th^{4+} compounds and hydrolysis of ThO(H$_2$O)$_n$, n = 1, 2,4. J Phys Chem A 120:8169–8183
6. Kaszuba JP, Runde WH (1999) The aqueous geochemistry of neptunium: dynamic control of solube concentrations with applications to nuclear wate disposal. Environ Sci Technol 33:4427–4433
7. Lombardi C, Luzzi L, Padovani E, Vettraino F (2008) Thoria and inert matrix fuels for a sustainable nuclear power. Progr Nucl Energy 50:944–953
8. Zanonato PL, Bernardo PD, Zhang Z, Gong Y, Tian G, Gibson JK, Rao L (2016) Hydrolysis of thorium(IV) at variable temperatures. Dalton Trans 45:12763–12771
9. Neck V, Kim JI (2001) Solubility and hydrolysis of tetravalent actinides. Radiochim Acta 89:1–16
10. Ekberg C, Albisson Y, Comarmond MJ, Brown PL (2000) Studies on the complexation behavior of thorium(IV) 1. Hydrolysis Equilibria. J Sol Chem 29:63–86
11. Antonio MR, Soderholm L, Williams CW, Blaudeau JP, Bursten BE (2001) Neptunium redox speciation. Radiochim Acta 89:17–25
12. Efurd DW, Runde W, Banar JC, Janecky DR, Kaszuba JP, Palmer PD, Roensch FR, Tait CD (1998) Neptunium and plutonium solubilities in a Yucca Mountain groundwater. Environ Sci Tech 32:3893–3900
13. Johansson G, Magini M, Ohtaki H (1991) Coordination around thorium (IV) in aqueous perchlorate, chloride and nitrate solutions. J Sol Chem 20:775–792
14. Moll H, Denecke MA, Jalilehvand F, Sandstrom M, Grenthe I (1999) Structure of the aqua ions and fluoride complexes of uranium (IV) and thorium (IV) in aqueous solution an EXAFS study. Inorg Chem 38:1795–1799
15. Sandstrom M, Persson I, Jalilehvand F, Lindquist-Reis P, Apangberg D, Hermasson K (2001) Hydration of some large and highly charged ions. J Synchroton Rad 8:657–659
16. Rothe J, Denecke MA, Neck V, Muller R, Kim JI (2002) XAFS investigation of the structure of aqueous thorium(IV) species, colloids, and solid thorium (IV) oxide/hydroxide. Inorg Chem 41:249–258
17. Allen PG, Bucher JJ, Shuh DK, Edelstein NM, Reich T (1997) Investigation of aquo and chloro complexes of UO$_2$$^{2+}$, NpO$_2$$^+$, Np^{4+} and Pu^{3+} by X-ray absorption fine structure spectroscopy. Inorg Chem 36:4676–4683
18. Reich T, Bernhard G, Geipel G, Funke H, Hennig C, Rossberg A, Watz W, Schell N, Nitsche H (2000) The Rossendorf beam line ROBL—a dedicated experimental station for XAFS measurements of actinides and other radionuclides. Radiochim Acta 88:633–637
19. Real F, Trumm M, Vallet V, Schimmelpfennig B, Masella M, Flament JP (2010) Quantum chemical and molecular dynamics study on the coordination of Th(IV) in aqueous solvent. J Phys Chem B 114:15913–15924
20. Yang T, Tsushima S, Suzuki A (2001) Quantum mechanical and molecular dynamical simulations on Thorium (IV) hydrates in aqueous solution. J Phys Chem A 105:10439–10445
21. Tsushima S, Yang T, Mochizuki Y, Okamoto Y (2003) Ab initio study on structures of Th(IV) hydrate and its hydrolysis products in aqueous solution. Chem Phys Lett 375:204–212
22. Tsushima S, Yang T (2005) Relativistic density functional theory study on the structure and bonding of U(IV) and Np(IV) hydrates. Chem Phys Lett 401:68–71
23. Clark AE, Samuels A, Wisuri K, Landstrom S, Saul T (2015) Sensitivity of solvation environment to oxidation state and position in the early actinide period. Inorg Chem 54:6215–6225
24. Wang D, van Gunsteren WF, Chai Z (2012) Recent advances in computational actinoid chemistry. Chem Soc Rev 41:5836–5865
25. Bühl M, Wipff G (2011) Insights into uranyl chemistry from molecular dynamics simulations. ChemPhysChem 12:3095–3105
26. Vallet V, Macak P, Wahlgren U (2006) Actinide chemistry in solution, quantum chemical methods and models. Theor Chem Acc 115:145–160
27. Allen MP, Tildesney DJ (1987) Computer simulation of liquids. Clarendon, Oxford
28. Coutinho K, Canuto S (2003) DICE: a Monte Carlo program for molecular liquid simulation, University of São Paulo, Brazil, version 2.9
29. Berendsen HJC, Grigera JR, Straatsma TP (1987) The missing term in effective pair potentials. J Phys Chem 91:6269–6271
30. Li P, Song F, Mertz KM Jr (2015) Parametrization of highly charged metalions using the 12-6-4 LJ type nonbonded model in explicit water. J Phys Chem B 119:883–895
31. Smirnov PR, Trostin VN (2012) Structural parameters of the nearest surrounding of tri- and tetravalent actinide ions in aqueous solutions of actinide salts. Russ J Gen Chem 82:1204–1213
32. Ahlrichs R, Bär M, Häser M, Horn H, Kömel C (1989) Electronic structure calculations on workstation computers: the program system TURBOMOLE. Chem Phys Lett 162:165–169
33. Vosko SH, Wilk L, Nusair M (1980) Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can J Phys 58:1200–1211
34. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100
35. Perdew JP (1986) Density-functional approximation for the correlation-energy of the inhomogenous electron gas. Phys Rev B 33:8822–8824
36. Neugebauer J, Hess BA (2003) Fundamental vibrational frequencies of small polyatomic molecules from density-functional

calculations and vibrational perturbation theory. J Chem Phys 118: 7215–7225

37. Cao X, Dolg M, Stoll H (2003) Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials. J Chem Phys 118:487–496

38. Cao X, Dolg M (2004) Segmented contraction scheme for small-core actinide pseudopotential basis sets. J Molec Struct (Theochem) 673:203–209

39. Kuechle W, Dolg M, Stoll H, Preuss H (1994) Energy adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide. J Chem Phys 100:7535–7542

40. Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted gaussian basis sets of triple zeta valence quality for atoms Li to Kr. J Chem Phys 100:5829–5835

41. Parmar P, Samuels A, Clark AR (2015) Applications of polarizable continuum models to determine accurate solution-phase thermochemical values across a broad range of cation charge—the case of U (III-VI). J Chem Theory Comput 11:55–63

42. Clavaguera-Sarrio C, Vallet V, Mayssau D, Marsden CJ (2004) Can density functional methods be used for open-shell actinide molecules? Comparison with multiconfigurational spin-orbit studies. J Chem Phys 121:5312–5320

43. Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol Phys 19:553–566

44. Wiebke J, Moritz A, Cao X, Dolg M (2007) Approaching actinide (+III) hydration from first principles. Phys Chem Chem Phys 9:459–465

45. Marcus Y (1988) Ionic radii in aqueous solutions. Chem Rev 88:1475–1498

46. David HF, Vokhmin V (2003) Thermodynamic properties of some tri- and tetravalent actinide aquo ions. New J Chem 27:1627–1632

47. Klamt A, Jonas V, Bürger T, Lohrenz JCW (1998) Refinement and parametrization of COSMO-RS. J Phys Chem A 102:5074–5085

48. Klamt A, Eckert F (2000) COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. Fluid Phase Equilib 172:43–72

49. Chipman CM, Chen F (2006) Cation electric field is related to hydration energy. J Chem Phys 124:144507-1– 144507-5

50. Camaioni DM, Dupuis M, Bentley J (2003) Theoretical characterization of oxoanion, XO_m^{n-}, solvation. J Phys Chem A 107:5778–5788

51. Bryantsev VS, Diallo MS, Goddard WA III (2008) Calculation of solvation free energies of charged solutes using mixed cluster/continuum models. J Phys Chem B 112:9709–9719

52. Zhan C-G, Dixon DA (2004) Hydration of the fluorine anion: structures and absolute hydration free energy from first principles electronic structure calculations. J Phys Chem A 108:2020–2029

53. Mejias JA, Lago SJ (2000) Calculation of the absolute hydration enthalpy and free energy of H^+ and OH^-. J Chem Phys 113:7306–7316

54. Klamt A, Schürmann G (1993) COSMO: a new approach to dielectric screening in solvets with explicit expressions for the screening energy and its gradient. J Chem Soc Perkin Trans 2:799–805

55. Bryantsev VS, Diallo MS, Goddard WA III (2009) Computational study of copper(II) complexation and hydrolysis in aqueous solutions using mixed cluster/continuum models. J Phys Chem A 113:9559–9567

56. Kelly CP, Cramer CJ, Truhlar DG (2006) Aqueous solvation free energies of ions and ion-water clusters based on an accurate value for the absolute aqueous solvation free energy of the proton. J Phys Chem B 110:16066–16081

57. Heinz N, Zhang J, Dolg M (2014) Actinoid III hydration—first principle Gibbs energies of hydration using high level correlation methods. J Chem Theor Comput 10:5593–5598

58. Asthagari D, Pratt LR, Kress JD (2005) Ab initio molecular dynamics and quasichemical study of H^+. Proc Natl Acad Sci USA 102:6704–6708

59. Camaioni DM, Schwerdtfeger CA (2005) Comment on "Accurate experimental values for the free energies of hydration of H+, OH-, and H3O+". J Phys Chem A 109:10795–10797

60. Antonio R, Soderholm L, Williams CW, Blaudeau JP, Bursten BE (2001) Neptunium redox speciation. Radiochim Acta 89:17–25

61. Tsushima S, Yang T (2005) Relativistic density functional theory on the structure and bonding of U(IV) and Np(IV) hydrates. Chem Phys Lett 401:68–71

62. Bratsch SG, Lagowski JJ (1986) Actinide thermodynamic predictions. 3. Thermodynamics of compounds and aquo-ions of the 2+, 3+, and 4+ oxidation states and standard electrode potentials at 298, 15 K. J Phys Chem 90:307–312

63. Marcus Y, Loewenschuss A (1986) Standard thermodynamic functions of the gaseous actinyl ions MOn + 2 and for their hydration. J Chem Soc Faraday Trans 82:2873–2886

64. Chopin GR, Jensen MP (2010) Actinides in solution: complexation and kinetics. In: Morss LR, Edelstein NM, Fuger J (eds) The chemistry of the actinide and transactinide elements, 4th edn, Chapter 23, Springer, Dordrecht, pp 2524–2621

65. Rossotti FJC, Rossotti H (1961) The determination of stability constants and other equilibrium constants in solution, McGraw-Hill, London

66. Brown PL, Ellis J, Sylva RN (1983) The hydrolysis of metal ions. Part 5. Thorium (IV). J Chem Soc Dalton Trans 1983:31–34

67. Baes CF, Meyer NJ, Roberts CE (1965) The hydrolysis of thorium (IV) at 0 and 95°. Inorg Chem 4:518–527

68. Baes CF, Mesmer RE (1976) The hydrolysis of cations. Wiley-Interscience, New York

69. Grenthe I, Lagermann B (1991) Studies on metal carbonate equilibria. 23. Complex Formation in the Th(IV)-H_2O-CO_2(g) System. Acta Chem Scand 45:231–238

70. Sierka M, Hogekamp A, Ahlrichs R (2003) Fast evaluation of the coulomb potential for electron densities using multipole accelerated Resolution of Identity approximation. J Chem Phys 118:9136–9148

71. Weingend F, Kattannek M, Ahlrichs R (2009) Approximated electron repulsion integrals: Cholesky decomposition versus resolution of identity methods. J Chem Phys 130:164106-1–164106-8