Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 375 (2003) 204–212

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Ab initio study on the structures of Th(IV) hydrate and its hydrolysis products in aqueous solution

Satoru Tsushima [a,b,*], Tianxiao Yang [a,c], Yuji Mochizuki [d,e], Yasuharu Okamoto [f]

[a] Department of Quantum Engineering and Systems Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan
[b] Department of Nuclear Engineering, Nagoya University, Furocho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
[c] Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA
[d] CCSE, Japan Atomic Energy Research Institute, Higashi-ueno 6-9-3, Taito-ku, Tokyo 110-0015, Japan
[e] Advancesoft, Incubation Project (FSIS), CCR, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8904, Japan
[f] Fundamental Research Laboratories, NEC Corporation, Miyukigaoka 34, Tsukuba, Ibaraki 305-8501, Japan

Received 24 February 2003; in final form 10 May 2003

Abstract

Ab initio calculations have been performed to study the structures of thorium(IV) hydrate and its hydrolysis products in aqueous solution. The conductor-like polarizable continuum model (CPCM) has been used to perform geometry optimization calculations in aqueous solution. The calculated results demonstrate that the molecule geometries obtained in solvent are generally consistent with the experiments. The coordination number of thorium(IV) hydrolysis products has been investigated. The effect of the relativistic effective core potential (RECP) on the structures is also discussed.

1. Introduction

The accurate description of solvation phenomena presents a significant challenge to theoretical chemistry. Two typical approaches are used to incorporate the solvent effects. One is the so-called supermolecular approach or the discrete model, where explicit solvent molecules are added and treated at the same level of theory as that used for the solute. However, this supermolecular approach does come with a substantial increase in computational expense. Another approach is the polarizable continuum model (PCM), where the solvent is described by dielectric polarizable continuum. Recently, an increasing interest has been devoted to solvent effects on the geometry and energy of the actinide complexes [1,2]. The rapid development of both quantum chemistry theory and computer makes the computation of actinide complexes in aqueous solution possible.

Previously, we have studied the structures of thorium(IV) hydrate in gas phase by means of the

---

[*] Corresponding author. Fax: +81-52-789-3785.
E-mail address: s-tsushima@nucl.nagoya-u.ac.jp (S. Tsushima).

0009-2614/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0009-2614(03)00806-6

B3LYP/6-31G* level of calculation [3]. We made geometry optimization in vacuo, and the energy calculation was based on the gas-phase optimized geometries. The solvent effects were described through the polarizable continuum model (PCM) of Tomasi et al. [4] because the PCM model offers a balanced and theoretically sound treatment of all solute–solvent interactions at a very reasonable computational cost. It was approved to be an appropriate method to compute the energy of thorium(IV) aquo ions. We found that the most stable hydration number of Th^{4+} ion is 9 or 10, which has a good agreement with the experiments [5–9]. However, the optimized Th–O bond distance of $[Th(H_2O)_9]^{4+}$ (2.54–2.55 Å), is 0.06–0.10 Å longer than the experimental Th–O bond distance [6–11]. The Th–O bond distance of $[Th(H_2O)_{10}]^{4+}$ (2.54–2.68 Å), is 0.06–0.20 Å longer than the experiments.

This Letter focuses on the solvent effects on the structures of thorium(IV) hydrate by means of ab initio quantum chemical calculation performed in aqueous solution. We discuss the effects of relativistic effective core potential (RECP) of thorium on the calculated properties. The coordination states of thorium(IV) hydrolysis products $Th(OH)_n(H_2O)_{9-n}^{4-n}$ $(n = 1, 2, 3, 4)$ and $Th(OH)_n(H_2O)_{10-n}^{4-n}$ $(n = 1, 2, 3, 4)$ both in vacuo and in aqueous phase are also investigated.

2. Computational methods

In previous study [3], the Stuttgart large core RECP of Küchle et al. [12] was used for thorium, where 78 electrons are in the core and 12 outermost electrons are treated explicitly. In this work, small core RECP of Küchle et al. [13] is employed to investigate the effects of RECP on the structures and energies. The Stuttgart small core RECP includes 30 valence electrons and 60 core electrons. The computations in vacuo show that the small core RECP does not improve the molecular geometries. Therefore, in the following ab inito calculations of thorium(IV) hydrate in solution, the large core RECP is used.

Solvent effects were evaluated using the Gaussian 98 implementation of the conductor-like polarizable continuum model (CPCM) [14]. The CPCM model uses the united atom topological model (UTAM), and the solute cavity is built as an envelope of spheres centered on atoms or atomic groups with appropriate radii. Due to the geometry convergence difficulty using the CPCM model in solution, the solvent effects of thorium(IV) hydrolysis products are described by adding a full second hydration shell explicitly.

The geometry optimizations are made without any symmetric constraints. The basis set superposition error (BSSE) corrections are not taken into account in the present study. The spin–orbit effects are not included. All the calculations use the Gaussian 98 package of programs [15].

3. Calculated results and discussion

3.1. Molecular geometries of $[Th(H_2O)_n]^{4+}$ complexes

Previously published data of experimental study on thorium(IV) hydrates reported that the hydration number of thorium(IV) ion is between 8 and 12, and the Th–O(water) bond distance is between 2.45 and 2.50 Å (Table 1). The structures of thorium(IV) hydrate and hydration number of Th^{4+} ion have been discussed by theoretical calculations in previous study by our group [3], where solvent effects were estimated by single-point energy calculations using the gas-phase geometry without performing a full geometry optimization in solvent. Our previous ab initio quantum chemistry study showed that the primary hydration number of Th^{4+} ion is 9 or 10. However, the calculated Th–O bond distances of $[Th(H_2O)_9]^{4+}$ in vacuo are 2.54–2.55 Å, which is 0.06–0.10 Å longer than the experiments. The Th–O bond distance difference between $[Th(H_2O)_{10}]^{4+}$ and the experiments is 0.06–0.20 Å.

We suppose that the discrepancy with the experiments comes from two reasons. The first reason is that the calculations employed the large core RECP for thorium, where only 12 outer valence shell electrons are treated explicitly, and the small size basis sets 6-31G* are used for oxygen and hydrogen atoms. The second possible source of the

Table 1
Hydration numbers and Th–O bond distances of Th^{4+} ion obtained from literatures

Hydration numbers	Th–O (Å)	Technique	Reference
8	2.49	X-ray Scattering	[10]
9	Not available	Proton MR	[5]
9–11	2.45 ± 0.01	EXAFS	[6]
10	2.45	EXAFS	[7]
10	2.47		[8]
10–12	2.45 ± 0.01	XAFS	[9]
11	2.50	X-ray	[11]

discrepancy is that the geometry optimization did not include the surrounding solvent effects explicitly. In aqueous solution, the water molecules in the first shell form strong hydrogen bonds with the water molecules in the second shell due to the strong polarization of highly charged Th^{4+} ion. In order to consider the strong hydrogen bonds between the first and the second hydration shells, one more computational demand is to explicitly include a full second hydration shell or optimize the structures in solution.

3.1.1. The effects of the relativistic effective core potential on the structures of thorium(IV) hydrate

The effects of the RECP on the geometries and energies of thorium(IV) hydrate, $[Th(H_2O)_9]^{4+}$ and $[Th(H_2O)_{10}]^{4+}$, are investigated by comparing the results using the large core RECP with those using the small core RECP. Density functional theory (DFT) calculations are too difficult when small core RECP is used. Therefore, the Hartree–Fock (HF) method is applied. The computations are made at both the HF/6-311G** and the HF/6-311+G* levels. The calculated results are shown in Tables 2 and 3.

By comparing the geometries of $Th(H_2O)_9^{4+}$ in vacuo, it is found that the Th–O bond distances at the HF/6-311+G* level using the small core RECP have an improvement of 0.003–0.007 Å than that at the HF/6-31G* level using the large core RECP. It is concluded that the small core RECP for thorium does not largely improve the geometries. It is noteworthy to find that the B3LYP/6-31G* level applied in our previous study give the shortest Th–O bond distance in vacuo.

The optimization of $Th(H_2O)_{10}^{4+}$ complex lead to the same conclusion. At the HF/6-311G** level in vacuo, the Th–O bond distance keeps unvaried even when small core RECP is used. Compared to the Th–O bond distances optimized at the

Table 2
Calculated bond distance Th–O in Angstrom (Å) for complex $[Th(H_2O)_9]^{4+}$ at the different levels of theory (LC: large core RECP; SC: small core RECP)

	Gas phase					Aqueous phase	
	B3LYP LC 6-31G*	B3LYP LC 6-311G**	HF LC 6-311G**	HF SC 6-311G**	HF SC 6-311+G*	B3LYP LC 6-31G*	HF LC 6-31G*
Th–O	2.575	2.583	2.601	2.602	2.597	2.476	2.500
	2.575	2.583	2.601	2.602	2.597	2.476	2.500
	2.575	2.583	2.601	2.602	2.597	2.476	2.500
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
	2.531	2.534	2.551	2.550	2.545	2.471	2.492
SCF energy (Hartree)	−722.368446	−722.697159	−718.663384	−1089.474897	−1089.394991		

Table 3
Calculated bond distance Th–O in Angstrom (Å) for complex $[Th(H_2O)_{10}]^{4+}$ at the different levels of theory (LC: large core RECP; SC: small core RECP)

	Gas phase					Aqueous phase	
	B3LYP LC 6-31G*	B3LYP LC 6-311G**	HF LC 6-311G**	HF SC 6-311G**	HF SC 6-311+G*	B3LYP LC 6-31G*	HF LC 6-31G*
Th–O	2.683	2.690	2.693	2.690	2.689	2.572	2.596
	2.542	2.548	2.573	2.573	2.562	2.497	2.519
	2.587	2.593	2.611	2.610	2.605	2.502	2.525
	2.542	2.548	2.572	2.573	2.562	2.497	2.519
	2.587	2.593	2.611	2.610	2.605	2.502	2.525
	2.683	2.690	2.693	2.690	2.689	2.572	2.596
	2.542	2.548	2.573	2.573	2.562	2.497	2.519
	2.587	2.593	2.611	2.610	2.605	2.502	2.525
	2.542	2.548	2.572	2.573	2.562	2.497	2.519
	2.587	2.593	2.611	2.610	2.605	2.502	2.525
SCF energy (Hartree)	−798.837824	−799.204791	−794.765905	−1165.577913	−1165.489769		

HF/6-31G* level using the large core RECP, the HF/6-311+G* level using small core RECP has an improvement of 0.003–0.009 Å.

From the preceding results, it can be concluded that the geometry optimizations with small core RECP for thorium does not improve the structure of thorium(IV) hydrates though it drastically increases the computational cost. In addition, adding diffuse functions on the oxygen and hydrogen atoms shows very minor Th–O bond distance change, demonstrating that the diffuse function on O and H has no significant influence on the geometries of thorium(IV) hydrate. Because we mainly concern about the relative energies of different thorium(IV) hydrate, we suppose that the impact of the RECP and the basis sets on the energies of these complexes is identical. Thus, we apply the Stuttgart large core RECP for thorium and is basis sets 6-31G* for oxygen and hydrogen in the following computations in solvent.

3.1.2. Solvent effects on the structures of thorium(IV) hydrates

We optimized thorium(IV) hydrates, $[Th(H_2O)_9]^{4+}$ and $[Th(H_2O)_{10}]^{4+}$, in solvent at the HF/6-31G* and B3LYP/6-31G* levels with the large core RECP using the CPCM model. The optimized structural parameters are given in Tables 2 and 3. The optimized structure $[Th(H_2O)_9]^{4+}$ has D_{3h} symmetry. The Th–O bond distances have been greatly improved from 2.550–2.602 Å to 2.492–2.500 Å at the HF/6-31G* level and from 2.531–2.575 Å to 2.471–2.476 Å at the B3LYP/6-31G* level. The optimized structure $[Th(H_2O)_{10}]^{4+}$ has approximate staggered D_{4d} symmetry. The Th–O bond distances have been improved 0.052–0.096 Å at the HF/61G* level, and 0.045–0.111 Å at the B3LYP/6-31G* level. The Th–O bond distance of 2.47 Å for $[Th(H_2O)_9]^{4+}$ optimized in aqueous solution at the B3LYP/6-31G* level has good agreement with the experimental bond distance of 2.45–2.50 Å (Table 1). In point of bond distance, $[Th(H_2O)_9]^{4+}$ has better agreement with experiments than $[Th(H_2O)_{10}]^{4+}$ does.

Furthermore, the molecular energies are calculated in solvent. $[Th(H_2O)_8(H_2O)_1]^{4+}$, $[Th(H_2O)_9(H_2O)_1]^{4+}$, $[Th(H_2O)_9(H_2O)_3]^{4+}$, and $[Th(H_2O)_{10}(H_2O)_2]^{4+}$ are optimized in aqueous phase at the B3LYP/6-31G* level using the CPCM model. The calculated bond distances and the energies are given in Table 4. It shows that $[Th(H_2O)_9]^{4+}$ is 8.78 kcal/mol more stable than $[Th(H_2O)_8(H_2O)_1]^{4+}$. $[Th(H_2O)_{10}]^{4+}$ is 0.23 kcal/mol more stable than $[Th(H_2O)_9(H_2O)_1]^{4+}$, and is 12.35 kcal/mol more stable than $[Th(H_2O)_8(H_2O)_2]^{4+}$. $[Th(H_2O)_9(H_2O)_3]^{4+}$ is 1.68 kcal/mol more stable than $[Th(H_2O)_{10}(H_2O)_2]^{4+}$. The energy difference between $[Th(H_2O)_{10}]^{4+}$/$[Th(H_2O)_9(H_2O)_1]^{4+}$, and [Th(H$_2$

Table 4
Calculated bond distances in Angstrom (Å) and the energies for the various complexes of $Th(H_2O)_n^{4+}$

N			Th–O	E(SCF + CPCM) (Hartree)	ΔE (kcal/mol)
9	$Th(H_2O)_8(H_2O)_1$	C_{2v}	2.427, 2.419, 2.448, 2.425, 2.464, 2.440, 2.439, 2.438,	−723.419741	8.78
	$Th(H_2O)_9$	D_{3h}	2.471(6), 2.476(3)	−723.433728	0.0
10	$Th(H_2O)_{10}$	$\approx D_{4d}$	2.572(2), 2.497(4), 2.502(4)	−799.878894	0.0
	$Th(H_2O)_9(H_2O)_1$	C_1	2.480, 2.484, 2.436, 2.496, 2.467, 2.491, 2.484, 2.481, 2.441, 4.052	−799.878417	0.23
	$Th(H_2O)_8(H_2O)_2$	D_{2d}	2.456(4), 2.426(4), 4.096(2)	−799.859217	12.35
12	$Th(H_2O)_9(H_2O)_3$	C_1	2.463, 2.483, 2.498, 2.502, 2.477, 2.475, 2.467, 2.458, 2.464, 4.266, 4.245, 4.210	−952.766226	0.0
	$Th(H_2O)_{10}(H_2O)_2$	C_1	2.591, 2.527, 2.492, 2.527, 2.490, 2.574, 2.488, 2.521, 2.488, 2.522, 4.262(2)	−952.763556	1.68

All geometry optimizations were done without symmetric constraints at the B3LYP level in solvent.

$O)_9(H_2O)_3]^{4+}$/$[Th(H_2O)_{10}(H_2O)_2]^{4+}$ is very minor. This result is concordant with the result in the gas phase [3]. This confirms our previous conclusion that the first hydration number of Th^{4+} ion is 9 or 10. It demonstrates that though the surrounding effects should be included in the geometry optimization to obtain molecular structures in better agreement with solid state and solution experimental structures, the energetics of these systems can be appropriately calculated in gas phase optimized structures after inclusion of the bulk solvent effects by the PCM model. This conclusion is identical to what Cosentino et al. [16] found on lanthanide ions.

According to our previous molecular dynamics simulations of thorium(IV) hydrate, each water molecule of the first hydration shell binds two water molecules in the second hydration shell [17]. Thus, we further evaluate the solvent effects by adding a full second hydration shell around the Th^{4+} ion. Totally 27 water molecules is explicitly included in the calculated model, $[Th(H_2O)_9(H_2O)_{18}]^{4+}$. Eighteen water molecules bond to the hydrogens of the first hydration shell water molecules, and form a second hydration shell. The second shell waters are embedded in the plane of H_2O of the first hydration shell. The computations are performed at the B3LYP/6-31G* level without any symmetric constraints. The optimized structure is shown in Fig. 1. The structure is confirmed to be the energy minimum via analytic vibrational frequency calculation because no imaginary frequency presents. It is interesting to find that the first shell water molecules show approximate symmetric bonds to the central Th atom. The Th–O_I bond length is around 2.500 Å, which is 0.04–0.05 Å shorter than the Th–O bond lengths obtained without including the second hydration shell at the same level of theory. It demonstrates that the geometry of the inner solvation sphere is significantly affected by the external second sphere in $[Th(H_2O)_9(H_2O)_{18}]^{4+}$ cluster, and a complete second coordination sphere stabilizes the inner sphere. This effect is identical to other cation hydrates after adding a complete second hydration shell [18,19].

The optimized structure reveals asymmetric Th–O_{II} bond lengths in the second hydration sphere. Each water molecule of three equatorial plane H_2O molecules binds two H_2O molecules in the same Th–O_{II} bond length of 4.70 Å. Each water molecule of six axial tricapped H_2O molecules binds two molecules in different Th–O_{II} bond lengths of 4.45 and 5.00 Å.

The electrostatic interactions between solute and solvent play an important role in the geometry optimization in aqueous solution. In order to get accurate geometries by quantum chemistry calculation, it is prerequisite to include the surrounding solvent effects by using the polarizable continuum model or by explicitly adding a complete second hydration shell.

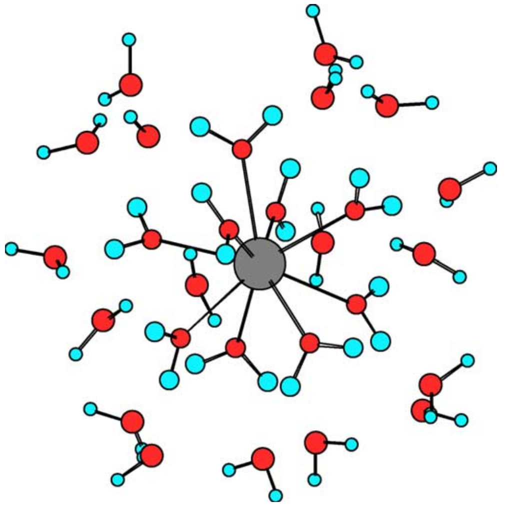

Fig. 1. Optimized structure of $[Th(H_2O)_9(H_2O)_{18}]^{4+}$.

3.2. The coordination states of thorium(IV) hydrolysis products

The actinide (IV) ions have high charge-to-radius ratio and form hydrolysis products even in acidic solutions as low as pH 0 [20]. Hydrolysis reactions are significant for all of the actinide ions at pH values found in natural waters. Actinide hydrolysis yields soluble hydroxide or oxide complexes, as well as precipitates of hydroxides, oxides, or basis salts. Th(IV) hydrolysis reactions have been investigated by a number of experimental researchers [21–23], and many of these studies indicated stepwise hydrolysis reactions to yield monomeric products of formula $Th(OH)_n^{4-n}$ with $n = 1, 2, 3$, and 4, in addition to a number of polymeric species. $Th(OH)^{3+}$ and $Th(OH)_4^0$ are important species in dilute solutions [23]. The study on the coordination number of thorium(IV) hydrolysis products using quantum chemical calculation is of great interest. Our computation focuses on the monomeric species.

One, two, three and four protons are removed from the optimized structures of $Th(H_2O)_9^{4+}$ and $Th(H_2O)_{10}^{4+}$, respectively. The structures of $Th(OH)(H_2O)_8^{3+}$, $Th(OH)_2(H_2O)_7^{2+}$, $Th(OH)_3(H_2O)_6^{+}$, $Th(OH)_4(H_2O)_5^0$, $Th(OH)(H_2O)_9^{3+}$, $Th(OH)_2(H_2O)_8^{2+}$, $Th(OH)_3(H_2O)_7^{+}$, and $Th(OH)_4(H_2O)_6^0$ are optimized at the B3LYP/6-31G* level in vacuo. The calculated structures show that the Th–OH bond lengths are shorter than the Th–OH_2 bond lengths, and removal of the first three protons does not change the coordination state of the complex. But the shortening of the deprotonated Th–OH bonds causes the remaining Th–OH_2 bonds to lengthen.

Upon removal of the fourth proton from $Th(H_2O)_9^{4+}$, one H_2O molecule leaves the first hydration shell at the Th–OH_2 bond length of 3.59 Å, leading $[Th(OH)_4(H_2O)_4]^0 \cdot (H_2O)$ to be the energy minimum. On the other hand, upon removal of four protons from $Th(H_2O)_{10}^{4+}$, two H_2O molecules leave the first hydration shell and enter the second shell at the Th–OH_2 bond lengths of 3.97 and 3.99 Å, leading $[Th(OH)_4(H_2O)_4]^0 \cdot 2(H_2O)$ to be the energy minimum. In both cases, four hydroxyl li-

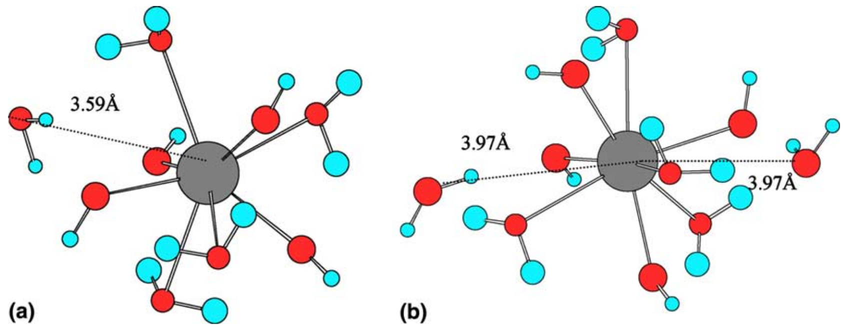

Fig. 2. Optimized structures of Th^{4+} hydroxyl complexe: (a) $Th(OH)_4(H_2O)_5^0$, the Th–OH bonds are 2.25, 2.29, 2.31, and 2.29 Å. Th–OH_2 bonds are 2.72, 2.72, 2.62, 2.73, and 3.59 Å. (b) $Th(OH)_4(H_2O)_6^0$, the Th–OH bonds are 2.27, 2.32, 2.26, and 2.32 Å. Th–OH_2 bonds are 2.77, 2.62, 2.77, 2.63, 3.97, and 3.99 Å.

gands (OH^-) are in *trans* position. The optimized structures upon deprotonation of $Th(H_2O)_9^{4+}$ and $Th(H_2O)_{10}^{4+}$ are given in Fig. 2.

According to Section 3.1, in order to get appropriate molecular geometries, it is prerequisite to include the surrounding effects in the geometry optimization computation. In order to confirm the above configurations are not artifact caused by neglecting the surrounding solvent effects, we further optimize the structures by including the surrounding solvent effects. Because of the optimization convergence difficulty by the CPCM model, we include the second shell of solvation by adding a complete second hydration shell. Totally 14 H_2O molecules around $Th(OH)_4(H_2O)_5^0$ is explicitly included. Energy minimization of the molecular cluster $[Th(OH)_4(H_2O)_5]^0 \cdot 14(H_2O)$ produces a 8-fold coordinate species $[Th(OH)_4(H_2O)_4]^0 \cdot 15(H_2O)$, where four H_2O molecules as well as four OH ligands directly bind to Th^{4+} cation in the first shell, and 15 H_2O molecules coordinate in the second shell. In the optimized structure, one H_2O molecule leaves the first hydration shell and enters the second hydration shell at the Th–O_{II} bond length of 4.68 Å (Fig. 3). This bond length is much longer than that of 3.59 Å when the second coordination sphere is not included. The complex $Th(OH)_4(H_2O)_4^0$ is stabilized by hydrogen bonds between the first and second hydration spheres. The structure $[Th(OH)_4(H_2O)_4]^0 \cdot 15(H_2O)$ is a true energy minimum because the vibrational frequency analysis gives no imaginary frequency. It confirms the previous conclusion obtained from the calculations without including the second coordination sphere that the coordination number of $Th(OH)_4(H_2O)_4^0$ is 8. The geometry optimization including a complete second hydration shell around $Th(OH)_4(H_2O)_6^0$ is not tried because it proves too costly to be implemented.

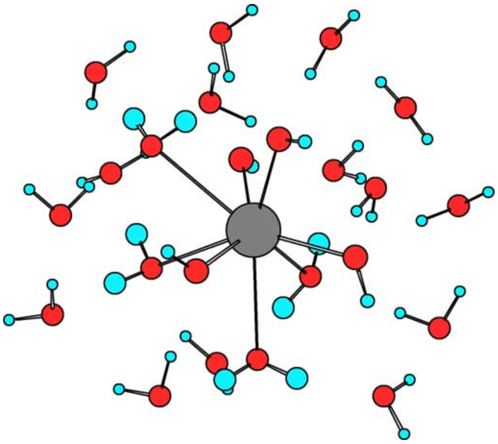

Fig. 3. Optimized structure of $Th(OH)_4(H_2O)_4^0 \cdot 15(H_2O)$. Th–$O_IH$ bonds are 2.26, 2.28, 2.30, and 2.32 Å. Th–O_IH_2 bonds are 2.71, 2.85, 2.73, and 2.82 Å.

Likewise, a complete second coordination sphere is also added around the species $Th(OH)(H_2O)_8^{3+}$, $Th(OH)_2(H_2O)_7^{2+}$, and $Th(OH)_3(H_2O)_6^{+}$, namely, totally 17, 16, 15 water molecules are included in the second coordination sphere, respectively. Geometry optimizations of the macroclusters $[Th(OH)(H_2O)_8]^{3+} \cdot 17(H_2O)$, $[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$, and $[Th(OH)_3(H_2O)_6]^{+} \cdot 15(H_2O)$ (Fig. 4) show that the primary coordination numbers of thorium(IV) hydrolysis products $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, and $Th(OH)_3^{+}$ are all 9. It argues that the removal of the first three protons does not change the coordination states of Th^{4+} ion. For $[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$, two configurations are calculated. Two hydroxo ligands (OH^-) are in *trans* and *cis* positions in the two isomers. The isomer *cis*-$[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$ with *cis* hydroxyl is 5.17 kcal/mol more stable than the isomer *trans*-$[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$ with *trans* hydroxyl. Attempts to optimize the geometry of *meta*-$[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$ where two OH^- ligands are in *meta* position failed.

In summary, the coordination numbers of thorium(IV) hydrolysis products $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, and $Th(OH)_3^{+}$ are all 9. The coordination number of thorium(IV) hydrolysis product $Th(OH)_4^0$ is 8. The hydrolysis product $Th(OH)_4^0$ has lower Th atomic charge and shorter Th–OH bond distance compared to the Th^{4+} hydrate. Thus, there is less attraction of water molecules in the former than in the latter. Through quantum chemistry calculations and the EXAFS measurements, Wahlgren et al. [24] found that in strong alkaline solutions, $UO_2(OH)_4^{2-}$ is the main component and the coordination number of U is 6 instead of 7 for the bare UO_2^{2+} ion. The results of Wahlgren et al. is in agreement with our results

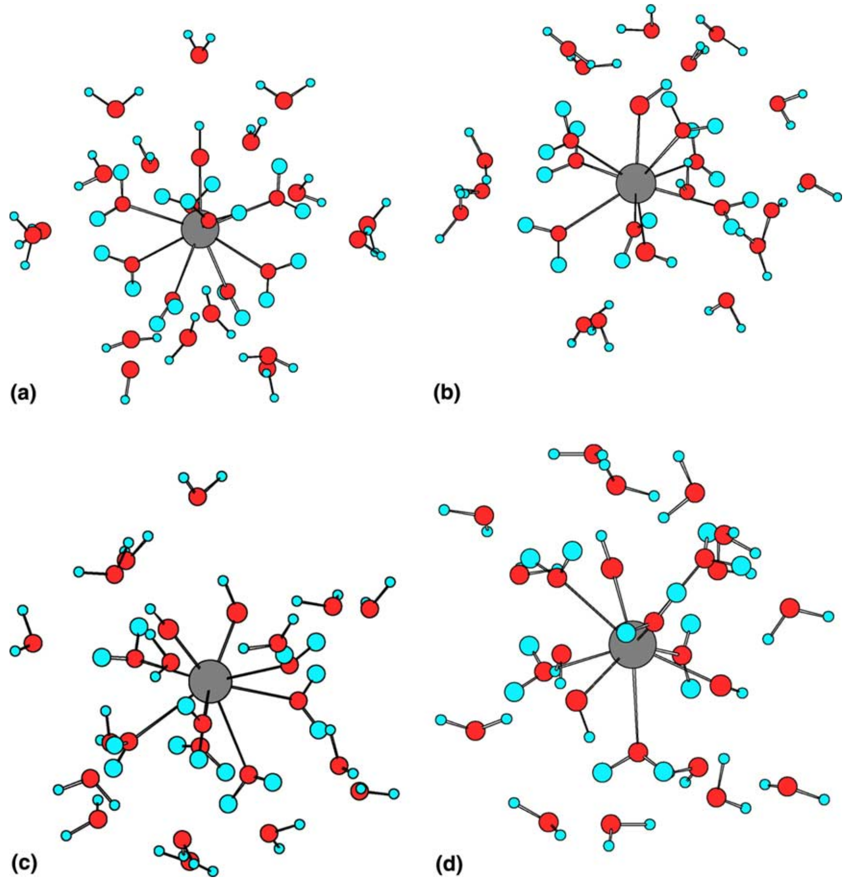

Fig. 4. Optimized structures of thorium hydroxyl complexes. (a) $[Th(OH)(H_2O)_8]^{3+} \cdot 17(H_2O)$, Th–$O_I$H bond is 2.13 Å, Th–$O_IH_2$ bonds are 2.59(2) and 2.58(6) Å. (b) *trans*-$[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$, Th–$O_I$H bonds are 2.24 and 2.26 Å, Th–O_IH_2 bonds are 2.65, 2.57, 2.60, 2.61, 2.59, 2.63 and 2.53 Å. (c) *cis*-$[Th(OH)_2(H_2O)_7]^{2+} \cdot 16(H_2O)$ is more stable than *trans*-one, Th–O_IH bonds are 2.21 and 2.24 Å, Th–O_IH_2 bonds are 2.61, 2.63(2), 2.60, 2.75, 2.64 and 2.67 Å. (d) $[Th(OH)_3(H_2O)_6]^{+} \cdot 15(H_2O)$, Th–$O_I$H bonds are 2.33, 2.33, and 2.34 Å, Th–O_IH_2 bonds are 2.62(2), 2.67, 2.72, 2.60 and 2.69 Å.

on thorium(IV) hydrate and its hydrolysis products.

4. Conclusions

The quantum chemical calculations performed on thorium(IV) hydrate demonstrate that the polarizable dielectric continuum model (PCM) accounts for the effects of a bulk liquid environment, and generally describes the solvation energy reasonably in vacuo optimized structures, especially for the systems including the primary coordination sphere. However, in order to obtain molecular structures in better agreement with the solution experimental structures, the surrounding effects should be included in the geometry optimizations. The conductor-like polarizable dielectric continuum model (CPCM) calculation on thorium(IV) hydrate have got the structural parameters which are in good agreement with the experiments.

The first coordination number of Th^{4+} ion slightly decreases as the hydrolysis reaction proceeds. The coordination numbers of thorium(IV) hydrolysis products $Th(OH)^{3+}$, $Th(OH)_2^{2+}$ and $Th(OH)_3^{+}$ are all 9. $Th(OH)_4^{0}$ has coordination number 8.

Acknowledgements

The authors thank Technische Universität Dresden, Germany, for the generous allocation of computation time on SGI Origin 2000. We also thank Research Center for Computational Science of the Okazaki National Research Institutes, Japan, for the use of SGI2800 and the library program GAUSSIAN 98.

References

[1] V. Vallet, U. Wahlgren, Z. Szabo, I. Grenthe, Inorg. Chem. 41 (2002) 5626.

[2] V. Vallet, U. Wahlgren, B. Schimmelpfennig, H. Moll, Z. Szabo, I. Grenthe, Inorg. Chem. 40 (2001) 3516.

[3] T.X. Yang, S. Tsushima, A. Suzuki, J. Phys. Chem. A 105 (2001) 10439.

[4] J. Tomasi, M. Persico, Chem. Rev. 94 (1994) 2027.

[5] A. Fratiello, R.E. Lee, R.E. Schuster, Inorg. Chem. 9 (1970) 391.

[6] H. Moll, M.A. Denecke, F. Jalilehvand, M. Sandstrom, I. Grenthe, Inorg. Chem. 38 (1999) 1795.

[7] M. Sandstrom, I. Persson, F. Jalilehvand, P. Lindquist-Reis, D. Spangberg, K. Hermansson, J. Synchrotron Rad. 8 (2001) 657.

[8] R.D. Shannon, Acta Crystallogr., Sect. A 32 (1976) 751.

[9] J. Rothe, M.A. Denecke, V. Neck, R. Muller, J.I. Kim, Inorg. Chem. 41 (2002) 249.

[10] G. Johansson, M. Magini, H. Ohtaki, J. Solut. Chem. 20 (1991) 775.

[11] W.E. Bacon, G.H. Brown, J. Phy. Chem. 73 (1969) 4163.

[12] W. Küchle, M. Dolg, H. Stoll, H. Preuss, unpublished work.

[13] W. Küchle, M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 100 (1994) 7535.

[14] V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995.

[15] M.J. Frisch et al., GAUSSIAN 98 (Revision A 11), Gaussian, Pittsburgh PA, 2001.

[16] U. Cosentino, A. Villa, D. Pitea, J. Phys.Chem. B 104 (2000) 8001.

[17] T.X. Yang, S. Tsushima, A. Suzuki, Chem. Phys. Lett. 360 (2002) 534.

[18] C.C. Pye, W.W. Rudolph, J. Phys. Chem. A 102 (1998) 9933.

[19] J.M. Martinnez, R.R. Pappalardo, E.S. Marcos, B. Mennucci, J. Tomasi, J. Phys. Chem.B 106 (2002) 1118.

[20] J.J. Katz, G.T. Seaborg, L.R. Morss, The Chemistry of the Actinide Elements, second ed., vol. 2, 1986.

[21] C.F. Baes, R.E. Mesmer Jr., The Hydrolysis of Cations, Wiley-Interscience, New York, 1976.

[22] V. Neck, J.I. Kim, Radiochim. Acta 89 (2001) 1.

[23] D.L. Clark, D.E. Hobart, M.P. Neu, Chem. Rev. 95 (1995) 25.

[24] U. Wahlgren, H. Moll, I. Grenthe, B. Schimmelpfennig, L. Maron, V. Vallet, O. Gropen, J. Phys. Chem. A 103 (1999) 8257.