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General Quantum-Mechanical Study on the Hydrolysis Equilibria for a Tetravalent Aquaion: The Extreme Case of the Po(IV) in Water

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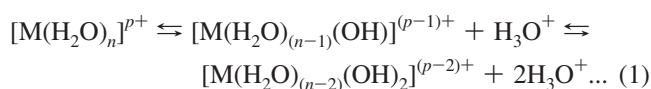
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A systematic study of the different hydrolyzed species derived from the hydrated Po(IV) in water, $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{(4-m)+}$ for $1 \leq m \leq 4$, and $4 \leq m + n \leq 9$, has been carried out by means of quantum mechanical computations. The effects of outer solvation shells have been included using a polarizable continuum dielectric model. For a fixed number of hydroxyl groups, the preferred hydration number for the Po(IV) can be determined in terms of Gibbs energy. It is shown that the hydration number (n) systematically decreases with the increase in the number of hydroxyl groups (m) in such a way the total coordination number ($n + m$) becomes smaller, being 9 in the aquocomplex and 4 in the neutral hydroxo-complex. Free energies for the hydrolysis processes involving Po(IV) complexes and a different number of hydroxyl groups have been computed, revealing the strong tendency toward hydrolysis exhibited by these complexes. The predominant species of Po(IV) in aqueous solutions are ruled by a dynamical equilibrium involving aggregates containing in the first coordination shell OH^- groups and water molecules. Although there is not experimental information to check the theoretical predictions, theoretical computations in solution seem to suggest that the most likely clusters are $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_2]^{2+}$ and $[\text{Po}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$. The geometry of the different clusters is ruled by the trend of hydroxyl groups to be mutually orthogonal and to promote a strong perturbation of the water molecule in *trans*-position by lengthening the Po–H₂O distances and tilting the corresponding bond angle. A general thermodynamic cycle is defined to compute the Gibbs free energy associated to the formation of the different hydrolyzed forms in solution. From it, the estimates of $\text{p}K_a$ values associated to the different protolytic equilibria are provided and discussed. Comparison of the relative values of $\text{p}K_a$ along a hydrolysis series with the experimental values for other tetravalent cations supports its consistency.

1. Introduction

Highly charged metal cations are generally involved in a series of consecutive proton transfers or hydrolysis processes in aqueous solutions



These hydrolysis processes occur when the polarization and partial charge transfer suffered by the first hydration shell water molecules make them acid enough to promote a proton transfer to second-shell water molecules. These deprotonation processes can become complex since they can be followed by the formation of polymeric species, dehydration, and subsequent precipitation processes.¹

Tetravalent metal aquaions, $[\text{M}(\text{H}_2\text{O})_n]^{4+}$, are species with a strong tendency to suffer hydrolysis processes² and thus they are generally strong acids in aqueous solutions.¹ There are some evidence of possible equilibria among $[\text{Ti}(\text{H}_2\text{O})_n]^{4+}$ and $[\text{Ti}(\text{OH})_m]^{4-m}$ ($m = 1-4$) in the pH interval $[-0.3, 4.8]$, the relative abundance of each species depending on the medium acidity.^{3,4} Although no real evidence for the TiO^{2+} unit in

aqueous solutions have been found, it seems that under certain acid conditions, this species could exist.⁵ The formation of polymeric Ti(IV) species and insoluble oxides has also been reported.^{1,6} $\text{p}K_a$'s values for the formation of monomeric Zr(IV) and Hf(IV) hydrolyzed species have been estimated to be within the range -0.3 to 17 . However, polymerization processes take place to a significant extent and polymeric species are then predominant in aqueous solutions.¹ VO^{2+} dominates the solution chemistry of V(IV) at acid media, but it undergoes hydrolysis process above $\text{pH} = 4$ and between $\text{pH} = 9-10$ polymeric species are formed.¹ Actinide(IV) ions have high charge/radius ratios and have strong tendency to suffer hydrolysis processes^{7,8} although on some occasions aquaions of these species can be stabilized in highly acidic media.^{6,9,10} Hydrolysis reactions are significant for all the actinide ions at pH values found in natural waters.² The study of trivalent and tetravalent actinide cations in solution introduces additional experimental difficulties given that some of these cations have high radioactivity and radiolysis processes in solution are present as well. For these reasons, the experimental evidence on the microscopic details of the structure of the resulting species and their hydrolysis processes are hard to find. Computational chemistry appears as an appropriate tool to investigate in a sequential and systematic way the hydrolysis process, particularly in cases where experimental determination is difficult for several physicochemical, medical, or environmental reasons, such as toxicity, low availability, absence of appropriate experimental methods, and so forth. The main

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difficulties associated with the understanding of hydrolysis processes are not only due to the inherent properties of the ion but also with the medium conditions required to stabilize it.¹¹ Then, particular attention must be paid to the ion-induced hydrolysis phenomena in aqueous solutions. Formation of hydrolyzed forms can drastically modify the migration, diffusive, and chemical behavior of these ions in solution. For instance, it was observed that the rate constants for water exchange in hydrolyzed complexes are several orders of magnitude higher than those corresponding to aquaions of the same ion.¹

Among the tetravalent cations, the Po(IV) solution chemistry is the most unknown due to its extremely high toxicity and low availability. Scientific interest in Po is focused on two main areas: its application as tracer of environmental processes and its impact on human health through radiation exposure and poisoning.¹² No detailed physicochemical description about its solution chemistry has been developed. In this sense, its theoretical study is particularly challenging and could represent a first guide to undertake experimental determinations. On the basis of the body of knowledge on the solution chemistry of other highly charged (trivalent and tetravalent) cations, a global study of aqueous solutions containing Po(IV) needs the detailed modelization of the following phenomena: hydration, hydrolysis, polymerization, and complexation. In a previous work,^{13,14} we dealt with the hydration carrying out a computational study of fundamental aspects of the Po(IV) aquaion properties in aqueous solutions such as hydration number, free energy of solvation and the nature of the Po–H₂O bonding, establishing the adequate methodology for this type of studies. The MPW1PW91 density functional was found to provide an appropriate description of the system. We concluded that the hydration number of Po(IV) is ruled by a dynamic equilibrium involving the octa- and ennea-hydrates with a solvation free energy of -1480 ± 70 kcal/mol. It was found that the covalent component of the Po–H₂O bonding was based on the interaction between the 6p orbitals of polonium ion and the lone pairs of water molecules with the role of the 6s orbital of polonium ion being negligible.

In this paper, we examine the structure and chemical equilibria of the predominant monomeric chemical species of Po(IV) in aqueous solutions on the basis of a combined discrete-continuum model. In this approach, the Po(IV) ion and a set of ligands (H₂O and OH[−]) defining its first coordination shell are explicitly treated quantum-mechanically while the bulk solvent is modeled by a dielectric continuum. A global scheme to establish the interrelation between hydrolysis degree and total hydration is developed.

2. Methodology

Optimizations of $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ ($n = 0-8$, $m = 1-4$) clusters in gas phase and in solution were performed with the Gaussian03 program.¹⁵ As shown in the previous work on the Po(IV) hydration,¹³ the MPW1PW91 functional together with the Dunning aug-cc-pVDZ¹⁶ basis sets for O and H and the relativistic small core pseudopotential (60 core electrons) developed by Dolg and co-workers¹⁷ for Po was shown to supply an appropriate quantum mechanical level of calculation. The basis set superposition error to the formation energy of the cluster was not considered due to its small contribution in all cases. The BSSE values were computed for the formation energy of the $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ clusters, $\Delta E_{\text{cluster}}$, from which the $\Delta G_{\text{cluster}}$ will be computed and used in eq 2. At the computational level here employed the BSSE on $\Delta E_{\text{cluster}}$ is less than a 0.4% for all clusters. (See Table S1 in Supporting Information). Clusters that were characterized as minima in gas phase (no

negative frequencies) were taken as starting points for the optimizations in solution via the polarizable continuum model (PCM) in the integral equation formalism (IEFPCM) implementation.¹⁸⁻²¹ For some of the larger clusters ($[\text{Po}(\text{H}_2\text{O})_8(\text{OH})]^{3+}$, $[\text{Po}(\text{H}_2\text{O})_7(\text{OH})_2]^{2+}$, $[\text{Po}(\text{H}_2\text{O})_6(\text{OH})_2]^{2+}$, and $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_3]^{+}$) and some of those containing four OH[−] ligands ($[\text{Po}(\text{H}_2\text{O})_3(\text{OH})_4]$ and $[\text{Po}(\text{H}_2\text{O})_2(\text{OH})_4]$), it was not possible to find minima structures in gas phase. These clusters were only optimized in solution.

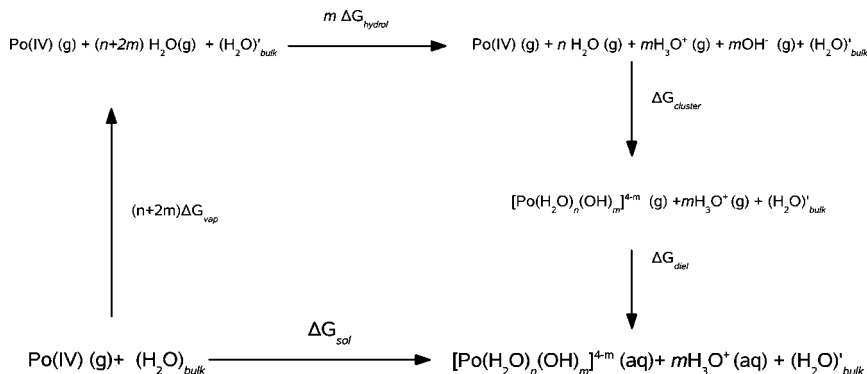
The continuum-discrete model used in this study takes into account a cavity containing the solute and its first hydration shell and the surrounding dielectric continuum.^{22,23} The static dielectric permittivity of liquid water at 25 °C ($\epsilon = 78.39$) was used for the dielectric medium. The geometries were fully reoptimized using this model to seek their structures in aqueous solution. Thus, solvent effects were taken into account on both energies and geometries. Cavities were built on the basis of a set of interlocking spheres centered on the different atoms for which the following radii were employed: 1.82 (O), 1.44 (H), and 2.82 Å (Po).^{24,25} These radii result from multiplying the van der Waals radius (1.52 (O), 1.20 (H), and 2.35 Å (Po)) by a standard factor of 1.2 in order to take into account the fact that atomic bond or lone pair centers of the solvent molecules are normally located slightly further away from the solute atom positions.²⁶

As shown in a number of previous studies on monatomic cation hydration, the explicit consideration of solvent molecules to describe the first hydration shell is necessary to converge to reliable values of solvation free energies.^{22,27,28} Inclusion of the second or outer solvation shells is not used generally due to the rapid increase of computational effort, as well as methodological concerns associated to the proper inclusion of statistical contributions in the quantum mechanical computations.²⁸⁻³⁰ An intermediate strategy is the consideration of a partial second hydration shell, such as the total hydration number remains constant.^{31,32} Although this strategy has been useful at the quantum mechanical level to describe the energetics of water exchange mechanism in the first hydration shell,^{33,34} the strong asymmetry included in the solvation model precludes an adequate balance of the discrete and continuum solvation contributions.^{29,30,35,36}

We can define a Gibbs energy in solution, ΔG_{sol} , for a given hydrated/hydrolyzed form of Po(IV) within the semicontinuum model^{37,29,38} following the thermodynamical cycle shown in Scheme 1, where $(\text{H}_2\text{O})_{\text{bulk}}$ means the pure water solvent and $(\text{H}_2\text{O})'_{\text{bulk}}$ denotes the release of the appropriate number of water molecules from the bulk needed to define a given Po(IV) cluster. It is worth underlying that the thermodynamic cycle (Scheme 1) is more complex than expected for the case of a $[\text{ML}_n]^{q+}$ cluster in solution. It comes from the need for dealing with two formal ligands coordinated to the central ion when one of the ligands (OH[−]) comes from the hydrolysis of the other (H₂O). This requires the following relationship for the formation of the $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{(4-m)+}$ cluster in aqueous solution

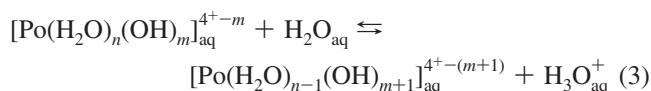
$$\Delta G_{\text{sol}} = (n + 2m)\Delta G_{\text{vap}} + m\Delta G_{\text{hydrol}} + \Delta G_{\text{cluster}} + \Delta G_{\text{diel}} \quad (2)$$

where $(n + 2m)\Delta G_{\text{vap}}$ is the free energy needed to evaporate $(n + 2m)$ water molecules from the liquid pure solvent to the gas phase; $m\Delta G_{\text{hydrol}}$ is the free energy associated to the autoprotolysis of $2m$ water molecules into OH[−] and H₃O⁺ fragments; $\Delta G_{\text{cluster}}$ is the free energy of formation of the cluster; ΔG_{diel} is the solvation free energy associated to the process of including

SCHEME 1: Thermodynamical Cycle That Shows the Solvation Process of $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ Clusters ($n = 0-9$ and $m = 0-4$)


the aquaion and the H_3O^+ in a dielectric continuum. It is decomposed into three contributions $\Delta G_{\text{cav}} + \Delta G_{\text{disp-rep}} + \Delta G_{\text{cont}}$ where ΔG_{cav} is the free energy needed to create the cavity, $\Delta G_{\text{disp-rep}}$ is a term which collects the solute-continuum dispersion and repulsion contributions and ΔG_{cont} is the solvation energy corresponding to the long-range interactions of the hydrated cluster embedded in a cavity inside a polarizable continuum. A temperature of 298 K was assumed for the thermodynamic cycle. Although no parameters are currently available for the polonium contribution to the dispersion and repulsion terms, this contribution should be negligible given that the dispersion-repulsion term of the aggregate is largely dominated by the first solvation shell where water molecules and hydroxyl ligands roughly enclose the polonium cation.

The reaction free energies, ΔG_{react} , corresponding to the hydrolysis processes



can be calculated as the difference of the ΔG_{sol} of the species involved in the process

$$\Delta G_{\text{react}} = \Delta G_{\text{sol}[\text{Po}(\text{H}_2\text{O})_{n-1}(\text{OH})_{m+1}]^{4+-(m+1)}} + \Delta G_{\text{sol}\text{H}_3\text{O}^+} - \Delta G_{\text{sol}[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}} - \Delta G_{\text{sol}\text{H}_2\text{O}} \quad (4)$$

with n and m ranging from 4 to 9 and from 0 to 4, respectively.

$\text{p}K_{\text{a}}$ estimations are based on eq 4 and computed according to the expression

$$\text{p}K_{\text{a}} = \frac{\Delta G_{\text{react}}}{2.303RT} \quad (5)$$

During the last ten years an intense debate has been opened on the accuracy of the theoretical computation of the solvation free energies using semicontinuum (or discrete-continuum) solvation models, as well as the $\text{p}K_{\text{a}}$ values associated to the corresponding hydrolysis reactions.³⁹⁻⁴¹ As there are no experimental $\text{p}K_{\text{a}}$ data for the hydrolysis processes of Po(IV), in order to check the methodology here employed we have computed the two first hydrolysis constants for the Fe(III) aquaion. The $\text{p}K_{\text{a}}$ values obtained for the first and second hydrolysis reaction were 2.2 and 17.8. Martin et al.⁴² compute values of 1.2 and 13.5, whereas De Abreu et al.⁴³ report 2.9

and 8.3. Experimental values are 2.2 and 3.5.^{44,45} The comparison between experimental and theoretical results indicates the difficulty to obtain a quantitative agreement for the $\text{p}K_{\text{a}}$ values. However, comparisons on relative values, $\Delta \text{p}K_{\text{a}} = \text{p}K_{\text{a},i} - \text{p}K_{\text{a},i-1}$, along a series of successive hydrolysis processes gives quite reasonable agreement among the experimental cases of the Th(IV) and U(IV) aquaions and the theoretical case of the Po(IV) computed in this work. (See Figure 5 and its discussion in the main text).

3. Results and Discussion

3.1. Structural Properties. Table 1 collects Po–O distances for $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4+-m}$ ($n = 0-8$, $m = 1-4$) clusters optimized in gas phase and in solution. The structures of the clusters optimized in solution are shown in Figure 1. For the sake of completeness, previous results^{13,14} for $[\text{Po}(\text{H}_2\text{O})_n]^{4+}$ ($n = 4-9$) aquaions were also included (Table 2 and Figure 1).

A comparison of aquaions and hydrolyzed species shows that structures with the same number of ligands adopt similar arrangements, although some differences can be identified. The most significant difference is that water molecules in trans positions with respect to OH^- ligands are located at longer distances from the polonium ion than the other water molecules in the cluster (see for example, the water molecule at 2.59 Å in cluster (5,1)). It has long been recognized that a given ligand can have a significant influence upon other metal–ligand bonds making them more labile, particularly those in a trans position. The trans-effect,^{46,47} is a well-known kinetic and structural effects in coordination compounds that is related to reaction processes involving trans ligands and their associated structural changes in the reactants, usually implying a lengthening and loosening of the trans-bond. Results of Table 1 show that in the case of hydroxo complexes, an elongation of the metal–water bond located in trans with respect to a hydroxyl ligand is appearing. Then, we could refer to this geometrical feature as a structural trans-effect. In some of the cases studied, there is an additional structural feature: the water molecule in trans to the OH^- ligand is deviated from the direction described by the Po–O(OH) vector by 30–60°. Figure 2 shows in a schematic way this deviation (angle between the OH^- group and the water molecule in a trans position). When the number of OH^- ligands in the cluster increases, these effects are more difficult to identify because other contributions, such as electrostatic repulsions, increase significantly. Therefore, they must be taken into account to explain the final rearrangements, which reflect a compromise among several factors. However, the lengthening of the Po–O(H_2O) distances of the water molecules in trans position

TABLE 1: Po–O distances (Å) of the $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ Clusters in Solution ($n = 0-8$ and $m = 1-4$) Optimized at MPW1PW91 Level Using a Semicontinuum Model

n, m	Po–O(H_2O) gas	Po–O(OH^-) gas	Po–O(H_2O) sol	Po–O(OH^-) sol
3,1	2.22, 2.25, 2.30	1.96	2.17, 2.21, 2.23	1.96
2,2	2.34×2	1.98, 1.99	2.30×2	1.99, 2.00
1,3	2.56	$2.02 \times 2, 2.03$	2.47	$2.03 \times 2, 2.04$
0,4		$2.05 \times 2, 2.09$		$2.05 \times 2, 2.12$
		2.18		2.17
4,1	2.27, 2.31×2	1.97	$2.23, 2.26 \times 3$	1.98
	2.32			
3,2	2.36, 2.37, 2.60	1.99, 2.00	$2.32 \times 2, 2.50$	2.00, 2.02
2,3	2.58×2	2.03, 2.04, 2.05	2.53×2	$2.04, 2.06 \times 2$
1,4	2.76	$2.05 \times 2, 2.13$	2.74	2.05, 2.07
		2.19		2.14, 2.18
5,1	2.27, 2.30, 2.35	1.99	$2.26 \times 2, 2.31 \times 2$	2.00
	2.36, 2.59		2.50	
4,2	2.33, 2.41	2.01, 2.02	2.31, 2.37	2.03×2
	2.59, 2.65		2.54, 2.56	
3,3	2.62×3	2.05×3	$2.57, 2.59 \times 2$	2.06×3
2,4			2.76, 2.80	2.08×2
				2.14, 2.20
6,1	2.35, 2.36, 2.37	2.00	2.30, 2.31, 2.34	2.01
	2.39, 2.45, 2.63		2.36, 2.39, 2.56	
5,2	$2.36 \times 2, 2.65,$	2.02, 2.03	$2.35 \times 2, 2.59$	2.04, 2.05
	2.70, 2.80		2.60, 2.61	
4,3	2.63, 2.64	2.05, 2.06	$2.60, 2.61 \times 2$	2.06, 2.07
	2.67, 2.95	2.07	2.90	2.08
3,4			2.73, 2.76	2.08, 2.09
			3.07	2.17, 2.20
7,1	$2.36, 2.38 \times 2,$	2.01	$2.34 \times 2, 2.36 \times 2$	2.04
	$2.41 \times 2, 2.63,$		2.37, 2.56	
	2.71		2.59	
6,2			2.37, 2.45	2.05, 2.06
			2.50, 2.54	
			2.62, 2.79	
5,3			$2.60, 2.70,$	$2.06 \times 2, 2.08$
			2.72, 2.87	
			2.97	
8,1			2.30, 2.33	2.06
			2.36, 2.38,	
			2.52, 2.58	
			2.64, 2.65	
7,2			$2.36 \times 2, 2.61$	2.06, 2.07
			$2.66 \times 2, 2.73$	
			2.76	

to OH^- groups persists regardless the hydrolysis degree of the aggregate (see Table 1 for details).

Electronic origin of the trans-effect in dissociation processes of highly symmetric ditungsten complexes has been shown by means of the identification of delocalized molecular orbitals (MO) through three- and four-centers determining the trans-effect.⁴⁸ To get insight into the origin of the structural effect we have carried out a wave function analysis of the (5,1) and (6,1) hydrolyzed forms. Contrary to those found by Magistrato et al.,⁴⁸ there are no MOs involving Po–O(OH) and trans-Po–O(H_2O) bonds. Since covalent contributions did not seem to play a significant role, we centered our analysis on the electrostatic part. We replace the OH ligand in the (5,1) Po(IV) cluster by two point charges $-2e$ and $+1e$ at the O and H positions, respectively and a partial geometry optimization was carried out starting from the (5,1) Po(IV) geometry where the $(-2e)\text{--Po--O}(\text{H}_2\text{O})$ was forming a 180° bond angle. The geometrical relaxation leads to a slight lengthening of the bond and to a decrease of the bond angle. A simplified picture of the electrostatic interaction causing this effect may be given by recognizing that favorable dipole–dipole interaction can be reached by the dipole associated to the O--H^- ligand and the Po–O(H_2O) formal bond.

A close analysis of Figure 1 indicates that when two or more OH^- ligands are present in a cluster, the adopted arrangement

is such that hydroxyl ligands are not opposite to each other. Thus, clusters with two OH^- ligands, (structures (2,2), (3,2), (4,2), (5,2), (6,2) and (7,2) in Figure 1) have one OH^- group in an axial position and the other one in an equatorial position. When three OH^- ligands are present (structures (1,3), (2,3), (3,3), (4,3) and (5,3) in Figure 1) the common arrangement locates two OH^- groups within the equatorial region in a *cis*-position and the third OH^- ligand in the axial region. The preference of the *cis* isomer with respect to the *trans* one has already been found for other highly charged metal cation, as Fe(III).^{42,43} Two OH^- groups opposite to each other are found when clusters with four OH^- ligands (structures (0,4), (1,4), (2,4) and (3,4) in Figure 1) are investigated. This is because covalent bonding is the driving force of the final structures, and as it was shown in ref 13 the orbital interaction between 6p orbitals of the polonium ion and lone pairs of the oxygen of the ligands forces them to follow the spatial distribution defined by the polonium 6p orbitals. When two OH^- ligands interact with the same p orbital, Po–O distances of the OH^- ligands in *trans* are 0.07–0.08 Å longer than those for other OH^- groups, which do not share the Po p orbital. This elongation was also found in the case of the aquaions when the Po–O distances of the clusters containing three and four water molecules were compared.¹³

The structural description of the Po(IV) species is split into four different subsections according to the following criteria: surface clusters (those with four and five ligands); intermediate clusters (clusters with six and seven ligands); large hydrolyzed clusters (those with eight and nine ligands); and solvent effects on distances.

3.1.1. Clusters with Four and Five Ligands. In our previous work about polonium aquaion equilibria,^{13,14} we found that small ($n \leq 5$) $[\text{Po}(\text{H}_2\text{O})_n]^{4+}$ hydrates can be labeled as surface clusters, denoting that the ion is not completely buried in the center of the cluster by the solvent molecules. When the structure of hydrolyzed species are analyzed, a similar behavior is found. This way, a cluster with four ligands can be described as a structure where three ligands are in a plane that contains the ion in such a way that two of them are mutually opposed, defining their bond angle close to 180° , the third one is at 90° to the formers, and the fourth ligand is perpendicular to the plane (structures (4,0) to (0,4), first row in Figure 1). Clusters with five ligands present a common structure similar to a tetragonal pyramid where the ion and four ligands are almost coplanar and the fifth ligand is perpendicular to that plane (structures (5,0) to (1,4), second row in Figure 1). As already found in the case of aquaions, this type of ligand arrangements around the ion is determined by covalent interaction and support the importance of the orbital interaction in these complexes. This becomes particularly significant in the case of clusters with more than one OH^- ligand, where electrostatic repulsions would play a major role in determining the final arrangement.

3.1.2. Clusters with Six and Seven Ligands. Clusters with six ligands (structures (6,0) to (2,4), third row in Figure 1) adopt structures close to a distorted octahedron where a structural trans-effect, including water deviation from the Po–O(OH) vector previously mentioned, are easily recognized. The optimized structure for the $[\text{Po}(\text{H}_2\text{O})_2(\text{OH})_4]$ cluster was only obtained in solution because gas phase optimization procedure led to a cluster where one water molecule has migrated to the second solvation shell. We are aware of the fact that to a certain extent this migration process is restrained in solution by the cavity that is enclosing the cluster, an effect which is implicitly coupled to the electrostatic solute-continuum interactions.

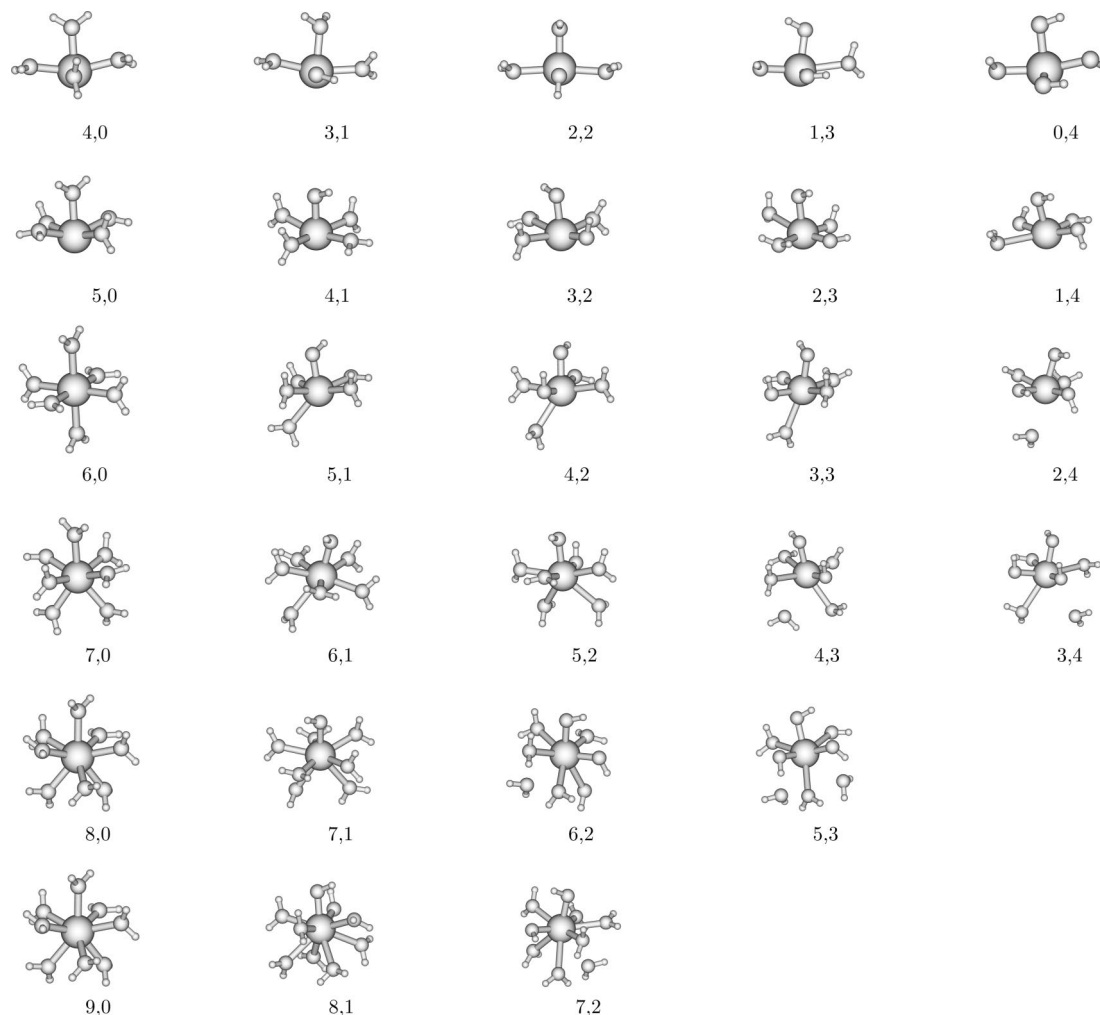


Figure 1. MPW1PW91 optimized structures in solution using a semicontinuum model for $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ clusters with $n = 0-9$ and $m = 0-4$.

TABLE 2: Po–O distances (Å) of the $[\text{Po}(\text{H}_2\text{O})_n]^{4+}$ Clusters in Solution ($n = 4-9$) Optimized at MPW1PW91 Level using a Semi-continuum model

n	Po–O(H_2O) gas	Po–O(H_2O) sol
4	2.17, 2.18, 2.26×2	2.09, 2.11, 2.18, 2.19
5	2.17, 2.28×4	2.10, 2.20×2 , 2.22×2
6	2.31	2.25
7	2.32×2 , 2.33, 2.36×2 , 2.38×2	2.26×2 , 2.27, 2.29, 2.30, 2.31, 2.32
8	2.38	2.32, 2.33×7
9	2.40×6 , 2.46×3	2.35×2 , 2.36×4 , 2.39×2 , 2.40

However, the fact that this structure is a well-characterized minimum when the continuum solvent effects are included allows us to perform a more complete study of Po(IV) hydrolysis in aqueous solutions.

Two types of structures can be identified in clusters with seven ligands. In the first type of structures, the hydroxyl occupies an axial position, four ligands and the ion are nearly coplanar, defining a plane, and two ligands are on the other side of this plane at around 145° to the first one. This structure is adopted by $[\text{Po}(\text{H}_2\text{O})_7]^{4+}$, $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_2]^{2+}$, $[\text{Po}(\text{H}_2\text{O})_4(\text{OH})_3]^+$ and $[\text{Po}(\text{H}_2\text{O})_3(\text{OH})_4]$ clusters (structures (7,0), (5,2), (4,3) and (3,4) in Figure 1). The second type of structures can be described as a distorted pentagonal bipyramid. This type of structure is adopted by the $[\text{Po}(\text{H}_2\text{O})_6(\text{OH})]^{3+}$ cluster (structure (6,1) in Figure 1). The $[\text{Po}(\text{H}_2\text{O})_3(\text{OH})_4]$ cluster was only

optimized in solution, since in gas phase it showed a behavior similar to that of the $[\text{Po}(\text{H}_2\text{O})_2(\text{OH})_4]$ cluster.

3.1.3. Clusters with Eight and Nine Ligands. Clusters with eight ligands (structures (8,0) to (5,3) fifth row in Figure 1) that contain four H_2O and four OH^- ligands did not show a minimum either in gas phase or in solution. $[\text{Po}(\text{H}_2\text{O})_6(\text{OH})_2]^{2+}$ and $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_3]^+$ clusters could only be optimized in solution. Although the structures of clusters with eight ligands are similar, some differences appear due to repulsive and steric interactions among them, especially in the case of the highly hydrolyzed forms. Similar results were obtained for clusters with nine ligands (structures (9,0) to (7,2), sixth row in Figure 1). Among these clusters, $[\text{Po}(\text{H}_2\text{O})_6(\text{OH})_3]^+$ and $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_4]$ aggregates are not minima either in gas phase or in solution whereas $[\text{Po}(\text{H}_2\text{O})_8(\text{OH})]^{3+}$ and $[\text{Po}(\text{H}_2\text{O})_7(\text{OH})_2]^{2+}$ clusters are minima only in solution.

The impossibility of optimizing large hydrolyzed clusters along with the energetic results presented in Section 3.2 shows a trend: when the Po(IV) hydrate suffers hydrolysis in aqueous solutions a decrease of the global coordination number is observed, as previously reported.⁴⁹ That is, an increase in the number of hydroxyl groups in the Po(IV) hydroxo complex implies a larger decrease in the number of first-shell water molecules. Tsushima has recently shown the same behavior for the case of Th(IV).⁵⁰

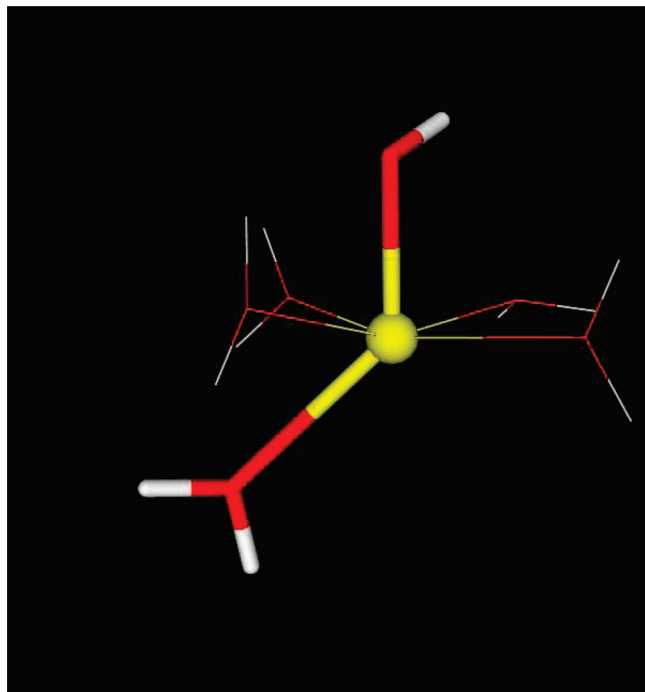


Figure 2. Schematic representation of the angle between the OH[−] group and the water molecule in a trans position.

3.1.4. Po–O Distances and Solvent Effects. As expected, Po–O(OH) distances corresponding to the Po–hydroxyl bonds are shorter than Po–O(H₂O) distances corresponding to the Po–water bonds. Moreover, the Po–O(H₂O) distances are longer in the hydrolyzed forms than in the aquaions, especially those located in trans position respect to the OH[−] for which a lengthening of 0.3 Å in the Po–O distance is found. In addition to the analysis of distances of the Po(IV) complexes, inspection of Tables 1 and 2 allows us to examine the geometrical changes due to solvent effects. As expected, the changes induced by solvent effects are smaller than those induced by changes in the number or type of ligands in the first coordination shell. Roughly, whereas the former changes are in the order of tenths of angströms, the latter ones are in the order of hundredths of angströms. The analysis of Po–O(H₂O) distances in the different clusters shows a shortening of them in the range [0.04–0.1] Å when going from gas phase to solution. In contrast, Po–O(OH) distances lengthen by [0.01–0.03] Å when solvent effects are included. The smaller change caused by solvent effects on the Po–O(OH) distances than on the Po–O(H₂O) ones may be easily understood on the basis of the different strength of both types of bonds. The general shortening of the Po–O(H₂O) distances in solution is in agreement with previous results,^{23,29} where it was shown that two opposite solute–solvent effects are operating in the changes of metal–oxygen distances.

On the contrary, Po–O(OH) distances are not affected by the dielectric continuum. This different behavior of Po–O(H₂O) and Po–O(OH) distances with solvent effects could be general and appears in the case of other cations: preliminary results on Be(II), Mg(II), Te(IV), and Th(IV) hydroxo complexes support these findings.

3.2. Free Energies. Free energies in solution, ΔG_{sol} , computed as explained in the methodological section for the different Po(IV) clusters are shown in Figure 3. For the sake of comparison, the results computed for aquaions in the previous work,¹³ modified as explained in note⁵¹ were included in Figure

m $n+m$	0	1	2	3	4
4	-1375.91 ↓ -35.34	-1349.21 ↓ -24.30	-1298.29 ↓ -6.33	-1220.27 ↓ -1.21	-1114.44 ↓ +5.51
5	-1411.25 ↓ -21.08	-1373.51 ↓ -6.84	-1304.62 ↓ -3.58	-1221.48 ↓ +0.74	-1108.93 ↓ +2.21
6	-1432.33 ↓ -13.26	-1380.35 ↓ -5.79	-1308.20 ↓ -0.49	-1220.74 ↓ +7.33	-1106.72 ↓ +12.73
7	-1445.59 ↓ -8.24	-1386.14 ↓ -0.70	-1308.69 ↓ +9.07	-1213.41 ↓ +9.70	-1093.99
8	-1453.83 ↓ -0.92	-1386.24 ↓ +9.27	-1299.62 ↓ +9.20	-1203.71	
9	-1454.75	-1376.97	-1290.42		

Figure 3. Free solvation energies, ΔG_{sol} , in kcal/mol for $[\text{Po}(\text{H}_2\text{O})_n(\text{OH})_m]^{4-m}$ clusters ($n = 0-9$ and $m = 0-4$) computed using eq 2 for the thermodynamical cycle shown in Scheme 1.

3. The row indexes, $(n + m)$ give the total number of ligands bonded to Po(IV), whereas the column indexes (m) give the total number of OH[−] groups in the cluster. In a given row, moving from left to right, formally implies to increase the basicity of the medium as species more hydrolyzed are obtained. On the contrary, the degree of hydrolysis is constant on a column, the difference among species being the number of water molecules in the cluster. In this case, the stability results must be interpreted on the basis of a constant degree of acidity/basicity in the medium.

According to the model employed in the computation of ΔG_{sol} following Scheme 1, medium conditions, such as pH, are exactly the same for all the clusters regardless the number of OH[−] groups present in the aggregate. This assumption is valid on the basis of an infinite solvent bath that is able to buffer the H₃O⁺ species released during the hydrolysis process. In the semicontinuum computations used here, acidity/basicity of the medium is somehow fixed when a given cluster is immersed in the molecular cavity because we are assuming the existence of such molecular species in solution. Meaningful comparisons in Figure 3 can only be done among species in a given column since the differences arise only from the number of water molecules released from the infinite solvent bath to the cluster without any formal change in the chemical nature of the solute. However, this comparison cannot be extended to the species in the same row, since they exhibit different degree of hydrolysis, and consequently the magnitude ΔG_{sol} cannot be used as a criterion of preference of a given cluster. The chemical connection among species in the same row must be established through the series of protolysis processes represented by eq 3, and the relative stability among them discussed on terms of their associated energy reaction. As a matter of fact, such chemical equilibria can be employed to determine $\text{p}K_{\text{a}}$ values (see Section 3.3).

Column values show that in most cases, regardless of the hydrolysis degree, the differences among ΔG_{sol} values for the most stable clusters are small enough to allow equilibria between different species. This way, when the coordination ligands are water molecules the most stable clusters are those containing 8 and 9 water molecules (a cluster with 10 water molecules in the first hydration shell is not a minimum either in gas phase or in solution). In the case of clusters with one OH[−] ligand, the most stable species are those with 7 and 8 ligands, that is, $[\text{Po}(\text{H}_2\text{O})_7(\text{OH})]^{3+}$ and $[\text{Po}(\text{H}_2\text{O})_6(\text{OH})]^{3+}$ clusters; this implies

a decrease of one unit in the total coordination number of Po(IV). When two OH[−] ligands are considered, there is again a dehydration process because now the most stable clusters are those with 7 (5H₂O + 2OH[−]) and 6 (4H₂O + 2OH[−]) ligands. In the case of three OH[−] ligands, [Po(H₂O)₃(OH)₃]⁺ and [Po(H₂O)₂(OH)₃]⁺ species are the most stable ones in aqueous solution; this is again consistent with the observed trend. Finally, for the most hydrolyzed form (four OH[−] ligands), the cluster with the most negative ΔG_{sol} is the [Po(OH)₄] one, that is, the cluster with no water molecules. Therefore, it can be concluded that the higher the hydrolysis degree is, the smaller the number of ligands in the first hydration shell of the Po(IV) in aqueous solution is. Roughly, the total coordination number decreases one unit per hydroxyl group added to the cluster unit. These results run parallel to those obtained in the previous section where the optimization of larger hydrolyzed clusters ([Po(H₂O)₆(OH)₃]⁺, [Po(H₂O)₅(OH)₄], and [Po(H₂O)₄(OH)₄]) did not succeed in either gas phase or solution. This dehydration trend as the degree of hydrolysis increases has already been observed in other multivalent cations in aqueous solutions such as Al(III),^{52,53} Fe(III),^{43,53} or Th(IV).^{50,54} However, the small size of Po(IV) compared to other tetravalent ions magnifies this trend. This is significant because the deprotonation process related with the hydrolysis process rules out the existence of some clusters, especially larger hydrolyzed forms. This behavior may have important implications in different fields of Solution Chemistry, like Biochemistry or Homogeneous Catalysis, where some processes are indirectly conditioned by the coordination number of the metal ion in solution.⁵⁵

The evolution of ΔG_{sol} with the hydrolysis degree roughly can be understood in terms of two contributions. First, the increase in stability of the aggregate due to the ion-ligand interaction when water molecules are substituted by OH[−] groups. Second, the supermolecule (ion plus first solvation shell)-continuum interaction, which is dominated by the Born term, depends on the squared charge of the cluster.⁵⁶ Both contributions are opposite in a row. Absolute values collected in Figure 3 reflect the predominance of the charge term in the estimation of ΔG_{sol} .

Finally, it must be noted that the lack of experimental data for the Po(IV) aquaion and its different hydrolysis products precluded the direct validation of our results. However, the theoretical ΔG_{sol} value obtained for the Po(IV) aquaion is within the range of the experimental values reported for other tetravalent cations [−1380, −1800] kcal/mol.⁵⁷

The uncertainty associated to the theoretical procedure to estimate ΔG_{sol} by means of a semicontinuum method has been widely discussed in previous works for the case of metal cations.^{29,36,41,42,58} It may be quantified as a 5–7% of the absolute value for a highly charged metal cation.^{29,58} Nevertheless, when comparing ΔG_{sol} within a series, as it is the case in Figure 3, the uncertainty associated with the energy gap (for m constant, $\Delta\Delta G_{\text{sol}} = \Delta G_{\text{sol}}(n+m) - \Delta G_{\text{sol}}(n-1+m)$) decreases because there is a cancellation of common contributions. Thus, the relative values differing by ~10 kcal/mol cannot be easily discarded as possible structures involved in the equilibrium of species in solution. However, the global trend holds up when examining Figure 3, that is, the total coordination number ($n+m$) of the species involved in the equilibrium for a given hydrolysis degree (m) decreases when the number of hydroxyl groups increases in the complex.

3.3. Hydrolysis Processes and pK_a Estimations. In order to shed light on the tendency of Po(IV) complexes toward hydrolysis, the reaction free energy in solution of eq 4, ΔG_{react} ,

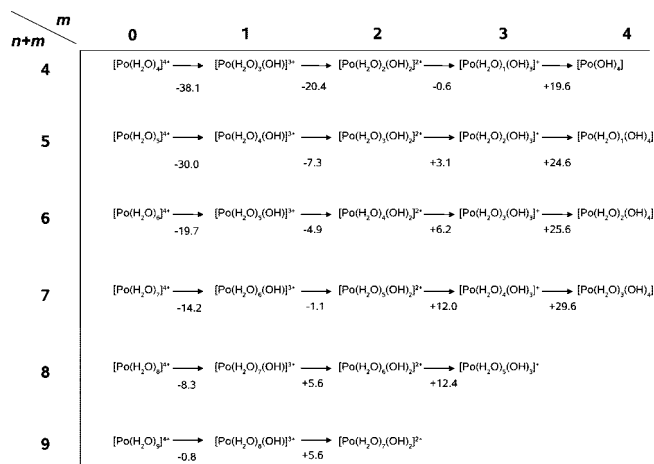


Figure 4. pK_a estimations calculated following eq 5 for all the possible consecutive processes started from the different aquaions.

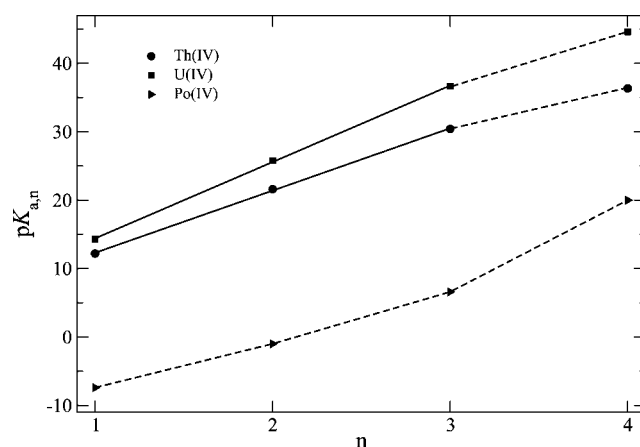


Figure 5. $pK_{a,n}$ values of successive hydrolysis processes $[M(H_2O)_n(OH)_m]^{(4-m)+} + H_2O \rightarrow [M(H_2O)_{(n-1)}(OH)_{m+1}]^{(3-m)+}$ (n for Th(IV), U(IV) (the three first pK_a are experimental and the fourth one semiempirically extrapolated)⁷⁰ and Po(IV) (pK_a 's theoretically estimated in this work).

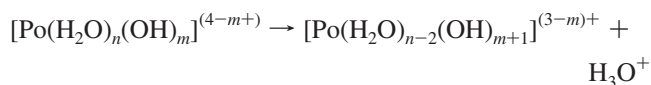
associated to the different equilibria collected in eq 3, and their associated pK_a defined by eq 5 have been computed.

As previously discussed for the case of the reliability of Gibbs free energies in solution of the different Po(IV) clusters, the computed pK_a values must be regarded rather as relative values than absolute ones. The more significant conclusions may be extracted from the examination of the trend along the series, which may supply a semiquantitative picture of the main equilibria in solution.

Figure 4 collects the pK_a estimations calculated following eq 5 for all the possible consecutive processes starting from the different aquaions. Analysis of Figure 4 indicates that the first protolysis reaction is clearly favorable ($\Delta G_{\text{react}} < 0$) for all reactions. Likewise, the same can be stated for the second protolysis reaction, but only up to a total coordination number of 7. The third step connecting species with two and three OH[−] groups is displaced to the most hydrolyzed species for the smallest cluster ($n+m=4$), whereas a real equilibrium is found in the case of the larger ones ($n+m=5, 6$) and those containing 7 and 8 ligands will be obtained only under very basic media conditions. The probability of the last protolysis process, that is, the one involving four OH[−] groups, is highly hampered according to our calculated pK_a values. A global prospection of Figure 4 reveals that larger aquaions establish their equilibria involving poorly

hydrolyzed complexes, whereas the smaller hydrated aquaions are involved in equilibria of polyhydrolyzed species ($m \leq 4$ and $n + m \leq 7$). This means that clusters with one, two, and three hydroxyl groups clearly define the hydrolysis range corresponding to the Po(IV) species more stable in aqueous solutions.

According to the relative stability of the different hydrolyzed forms, the decrease of the total coordination number with the degree of hydrolysis implies that some of the hydrolysis reaction couple a hydrolysis and a dehydration process, in such a way that the involved Po(IV) clusters do not belong to the same row of the Figure 4 as the process does not take place at a constant total coordination number ($n + m$). For instance



Considering the available experimental data^{1,10,59–69} for tetravalent cations and although the high charge on the ion gives rise to the formation of $[\text{M}(\text{OH})_m]^{4-m}$ species, two types of behavior according to hydrolysis phenomena can be identified. On one hand, heavy metal ions such as Th(IV), U(IV), Np(IV), or Pu(IV) can form stable aquaions under very acid conditions ($\text{pH} < 1$). On the other hand, ions like Ti(IV), Zr(IV), Hf(IV), or V(IV), suffer hydrolysis processes regardless of medium conditions, so that species only containing water molecules in the first hydration shell are not present in their aqueous solutions. Results collected in Figure 4 indicate that Po(IV) can be ascribed to the second group of these tetravalent cations, whose aquaion species are not stable enough in aqueous solutions and they suffer hydrolysis (c.f. $\text{p}K_a$ values connecting columns 0 and 1). The set of tetravalent actinide cations present experimental metal–oxygen distances within the range 2.4–2.5 Å.^{10,59–65} A first explanation, regardless electronic effects, is based on the ion size, measured through the metal–solvent distances.⁷⁰ In the Po(IV) case, the average Po–O distances estimated in ref 13 for the most likely aquaions are 2.33 and 2.37 Å for octa- and ennea-hydrates, respectively. For the rest of nonactinide tetravalent aquaions, the metal–oxygen distances are smaller than for the Po(IV) case.⁷⁰ This means shorter metal–oxygen distances when compared with the tetravalent cations which can be present as aquaions in strongly acid aqueous solutions; therefore more likely hydrolyzed forms must dominate aqueous solutions containing the Po(IV) metal cation.

Moriyama et al.⁷¹ have performed a systematic study of the hydrolysis constants of several tetravalent actinide ions. They develop a semiempirical method based on electrostatic and nonelectrostatic contributions and a set of experimentally determined hydrolysis constants to obtain a complete series of successive $\text{p}K_a$ values. Figure 5 shows the comparison of the four first $\text{p}K_a$ values for the Th(IV) and U(IV) in water with those computed for Po(IV) in this work. It is worth noting that the fourth $\text{p}K_a$ value for Th(IV) and U(IV) is not experimental but estimated from the semiempirical method proposed by Moriyama et al.⁷⁰ Although, we have shown the difficulties to obtain quantitative estimations of absolute $\text{p}K_a$ values for successive deprotonation equilibria of highly charged metal aquaions, the comparison of the $\Delta\text{p}K_a$ among Th(IV) and U(IV) experimental results and those here computed for Po(IV) is quite satisfactory. The trend is similar in all cases, and the relative changes are of the same order of magnitude. Likewise, the much higher values for Th(IV) and U(IV) supports the precedent

analysis on the higher trend to hydrolyze of Po(IV) than the tetravalent actinide ions.

4. Concluding Remarks

In this work, we carried out a systematic study of the hydrolyzed forms for the tetravalent metal aquaion, Po(IV), in aqueous solution on the basis of a semicontinuum model. A general scheme to deal with the reaction energies and relative stabilities among the species that can be formed has been established along the paper, allowing a global theoretical approach to the hydrolysis phenomena of highly charged metal cations in solution. It has been shown the strong tendency toward hydrolysis of Po(IV) hydrates in aqueous solutions particularly for the case of clusters with low hydration number.

The hydrolysis processes are intimately related with a decrease in the coordination number of Po(IV) in aqueous solutions: from 8–9 for the aquaion to 4 in the case of the most hydrolyzed species. Since the net charge of the complex decreases as hydrolysis proceeds to a certain extent, this is the expected behavior. Holokov and co-workers⁷² obtained similar results using a theoretical model allowing water hydrolysis and where the effect of the charge on the ion was studied. This dehydration trend indicates that the hydrolysis processes cannot be considered as isolated events, but rather they are part of a complete rearrangement of the closer environment of the ion and on some occasions involve also outer hydration shells, mainly the second one. The increase in the hydrolysis degree of a highly charged-metal hydroxo complex is coupled to a dehydration in such a way that the total coordination of the metal ion complex decreases.

From the structural point of view, the most remarkable fact is the structural trans-effect exerted by the OH^- group on the water molecules that lengthens their Po–O(H_2O) distances as much as 0.3 Å and modifies by 15–25° the corresponding bond angle. The electrostatic origin of this effect has been shown by replacing the hydroxyl group for a pure dipole charge distribution ($2q^-, q$). The optimization geometry for this new Po(IV) cluster induces the same type of geometrical distortion on the water molecule in trans with respect to the dipole charge distribution.

The combined examination of Figures 3 and 4 leads one to the conclusion that the predominant species of Po(IV) in aqueous solutions are ruled by a dynamical equilibrium involving aggregates containing one, two, and three OH^- groups. Equilibria involving $[\text{Po}(\text{H}_2\text{O})_5(\text{OH})_2]^{2+}$ and $[\text{Po}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$ species seems to be the most likely defined for the formally modeled medium conditions which would correspond to highly dilute and neutral aqueous solutions.

It is worth pointing out that the representative or predominant species of highly charged cations in aqueous solution cannot be established without accounting for medium conditions, being the combination of water/proton ratio and the highly charged core of the polonium ion responsible for the resulting ionic aqueous solution. According to our results, several species with different hydrolysis degrees and number of ligands can be present at the same time, especially, mono-, di-, and trihydroxyl aggregates, and their predominance being dependent on the medium conditions.

In this study, we have not taken into consideration the formation of polymeric products or the possibility of a double deprotonation on the same water molecules that means the formation of Po=O bonds. Nonetheless, the existence of these species should not be ruled out because the formation of monoxo or polyoxo tetravalent species has been reported elsewhere.^{1,5}

Polyoxo species can be stabilized using the semicontinuum model here used. However, it is necessary to consider specific interactions beyond the first hydration shell where a competition between the specific ligand (H_2O or OH^-)—solvent and solvent—solvent interactions are accounted for to study properly their existence in aqueous solutions. This competition may be well described by ab initio molecular dynamics simulations where all the species in the system are treated at the same level of computation.^{52,73} In this respect, the study of the hydrolysis processes using quantum molecular dynamics simulations must certainly shed light on the chemistry of the Po(IV) in aqueous solutions. Efforts in such direction are currently ongoing in our group.

Theoretical study on metal aqua ions in solution during the last two decades have largely contributed to model and understand their physicochemical behavior on the assumption that they were the predominant species in solution. However, the assumed chemical conditions represents a narrow range with respect to all the conditions that could adopt the condensed medium. To extend the range a careful analysis of the hydrolysis processes must be included. This represents a challenge for the Theoretical Chemistry in the next years.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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