Study of Hydration and Hydrolysis of Pu(IV) by the Density Functional Method

M. K. GANUSOVA[1], E. A. IVANOVA-SHOR[1,2], A. M. SHOR[2], V. A. NASLUZOV[2], and A. I. RUBAYLO[1,2]

[1]*Institute of Biophysics, Siberian Branch, Russian Academy of Sciences,
Krasnoyarsk, Russia*

E-mail: shor-elena@rambler.ru

[2]*Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences,
Krasnoyarsk, Russia*

Abstract

The structure and the first step of hydrolysis of hydrated Pu(IV) ion in aqueous medium were studied using relativistic density functional theory and the polarizable continuum model (PCM). According to calculations, the Pu(IV) ion was mainly coordinated with eight water molecules. The calculated distance Pu–O of 238–241 pm was in good agreement with the experimental value ((239±2) pm). It was demonstrated that for the correct replication of constants $\log K_1^0$ of the first hydrolysis step, it was important to use scaling multipliers adequate to the charge of the hydrated complex when constructing the density that included the solvated complex in PCM model. The calculated values of $\log K_1^0$ of $-1.1...-0.2$ were close to the experimentally defined range ($-0.6-0.6$). The correct replication of hydrolysis constants allowed considering the calculated range of the hydratation free energies of the Pu(IV) ion of 6070–6157 kJ/mol as a reasonable prediction of experimental values.

Key words: density functional method, plutonium (IV) complexes, the polarizable continuum model, hydrolysis constants, hydration free energy model, hydrolysis constants, hydration free energy

INTRODUCTION

The study of the behaviour of actinoide ions in aqueous medium provides information required for understanding processes of migration of actinoide compounds into soil aquifers, what is directly related to the problem of separation, storage, and radioactive waste disposal [1, 2]. The utilization issue is most acute for plutonium that is a major component of nuclear fuel due to its large reserves and a long half-life. The Pu(IV) oxidation state prevails under oxygen shortage conditions that are realized in deep ocean and ground water [3]. Plutonium ion in aqueous medium is found as a solvated complex, therefore, knowledge of features of the chemical structure and the chemical behaviour of $[Pu(H_2O)_n]^{4+}$ aqua ion acts as a starting point for an explanation of its further more complex conversions.

The structure of the first coordination shell of hydrated Pu^{4+} ion has been experimentally explored by mainly Extended X-Ray Absorption Fine Structure (EXAFS) [4–6]. The first coordination shell in all experiments consisted of 8 or 9 water molecules; herewith, the average Pu–O distance was (239±2) pm. Theoretical quantum mechanical (QM) calculations carried out in the framework of the model of continuous environment polarized the polarizable continuum model (PCM) [7, 8] or using a molecular dynamics (MD) method [8] are in good agreement with experimental results and char-

acterize $[Pu(H_2O)_8]^{4+}$ species as the most stable hydrated complex. The calculated average Pu−O distances vary in a 239−241 pm range.

It has been demonstrated in [10] that a satisfactory replication of both structural features of hydrate complexes and free hydration energies ΔG_{solv} of metal ions within the PCM solvent model should be included in the QM model of the system under study up to two hydration shells of solvated ions. Even the introduction of the second hydrate shell into a solvated cluster cannot guarantee a significant increase in the accuracy of calculated energy characteristics. This problem can be solved using molecular cavities, the size of which generally decreases with increasing the charge of a solvated system. The simplest method to decrease the size of a molecular cavity is to use scaling multipliers S depending on the charge of the system under study [12]. Multipliers S or radiuses R, from which a molecular cavity is constructed, are traditionally obtained by replication of experimental values of solvation free energies ΔG_{solv} in theoretical calculations using the PCM model [13]. Unfortunately, there are no data for experimental values of ΔG_{solv} for actinoide An(IV) ions. At the same time, there is a broad set of experimental data including free energies of hydrolysis ΔG_{hydr} and hydrolysis constants of mononuclear $[An(H_2O)_n]^{4+}$ complexes. Tetravalent actinoide ions demonstrate a high tendency to hydrolysis that may begin already in acid medium (pH $\leq$ 2) with the formation of monohydroxide $[An(OH)]^{3+}$ at the first step of hydrolysis [2]. According to the equation of the reaction

$$An^{4+} + H_2O \rightarrow [An(OH)]^{3+} + H^+$$
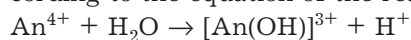
the first hydrolysis constant $\log K_1^0$ is defined by the solvation free energies ΔG_{solv} of An^{4+} ion and its monohydroxide [14]. This allows using experimentally defined constants $\log K_1^0$ as the first reference quantities to calculate ΔG_{solv} of An^{4+} ion. Herewith, multipliers S that define the size of molecular cavities of solvated ions with $+3e$ and $+4e$ charges are the sole parameters that can vary during the fitting procedure.

According to the data in [14], the value of $\log K_1^0 = 0.6$ is most reliable for Pu(IV) complexes. However, the refined data point out at the negative (approximately −0.6) and zero value of $\log K_1^0$ [15, 16]. Despite practical importance, there is a shortage of works devoted to quantum mechanical calculations of hydrolysis constants of An^{4+} ions. At the same time, successful calculations of $\log K_1^0$ can act as a reliability indicator of calculating the values of hydration free energies. The sole attempt was made to calculate $\log K_1^0$ values using MD method in case of Pu(IV) complexes [9]. The calculated value (−0.17) reproduces recently obtained experimental data with a good accuracy [15].

The paper studies hydratation and hydrolysis of Pu^{4+} ion using the density functional (DF) method. The study is focused on structural and electronic features of hydrated complexes formed, and their stability, and also an opportunity of correct calculations of the free hydration Gibbs energy ΔG_{solv} and the hydrolysis constant $\log K_1^0$. The work objectives included demonstration on an example of hydrate Pu(IV) complexes of the importance of using adequate parameters of solvation models that meet the charge state of solvated complexes for successful description of energy characteristics of highly charged metal cations in aqueous medium.

EXPERIMENTAL

All-electron scalar relativistic QM calculations were carried out within density functional LCGTO-FF [17] realised in PARAGAUSS software package [18] using exchange-correlation functional BP86 [19, 20]. To represent the Kohn−Sham orbitals the following basis sets of Gaussian type were used (including scalar relativistic corrections for Pu): $(24s19p16d11f) \rightarrow [10s7p7d4f]$ for Pu [21], $(9s5p1d) \rightarrow [5s4p1d]$ for O[22−24] and $(6s1p) \rightarrow [4s1p]$ for H [22−24]. All calculations were performed without considering spin orbital interactions, since it does not affect the fidelity of reproduction of electronic properties of basic states in actinoide systems with open shells in the DF method [25]. All the studied Pu(IV) complexes had the quintet configuration in the ground state. Charge distribution is assessed by the Baider method [26] using the Baider program [27].

All geometrical complex parameters both in the gas phase and aqueous solution were completely optimised. When calculating solvent effects the electrostatic contribution into the sol-

vation energy is taken into account using option C PCM of PCM model realised in program package ParaGaus [28]. A solvent was presented in this model as a conducting medium [29]. The work used the scheme of construction of FIXPVA molecular cavity that provides continuous and smooth potential energy surface [30]. This cavity was constructed from atomic spheres with van der Waals radii R_{vdW} obtained in the work by Bondi [31]. Atomic radii of neutral or weakly charged ($+1e$) systems were multiplied by the scaling multiplier $S(0) = 1.125$. Multipliers $S(3) = 1.030$ and $S(4) = 1.000$, respectively, were used for Pu(IV) complexes with $+3e$ and $+4e$ charges. Multiplier selection was carried out using the developed procedure for fitting of the calculated constants for hydrolysis of Pu(IV) complexes to experimental data in accordance with the reaction

$[Pu(H_2O)_n]^{4+} \rightarrow [Pu(OH)(H_2O)_{n-1}]^{3+} + H^+$

Free energies of complexes in the gas phase were calculated by the addition of the energy zero-point vibrations to the electronic energy of the system, and also the thermodynamic contribution assessed from analysis of normal mod vibrations. Free energies of reactions in aqueous medium were calculated using thermodynamic cycles [32]. The obtained free energies of

reactions were corrected by bringing all particles participating in reactions to the standard state of 1 M (1 mol/L) at a temperature of 298.15 K. In the gas phase, the correction for each particle was $RT\ln (24.46)$ kJ/mol, for water molecules in an aqueous solution $- RT\ln (55.34)$ kJ/mol [10]. The electron binding energies in the gas phase were calculated considering the superposition error of basic sets by the counterbalance method [33] on equilibrium geometries of gas-phase complexes.

RESULTS AND DISCUSSION

Hydrated Pu(IV) complexes

Structure and charges. Equilibrium structures of hydrated Pu(IV) complexes with 8 and 9 water molecules in the first coordination shell are presented in Fig. 1. Optimisation of complexes was initially carried out with limitations by symmetry imposed on them (see Fig. 1): D_{4h} (square prism) and D_{4d} (square prism) for 8-coordinated $[Pu(H_2O)_8]^{4+}$ complexes; D_{3h} (triangular prism with three additional water molecules in the equatorial plane of the complex) and C_{2v} (square antiprism with an additional water molecule is placed above the up-
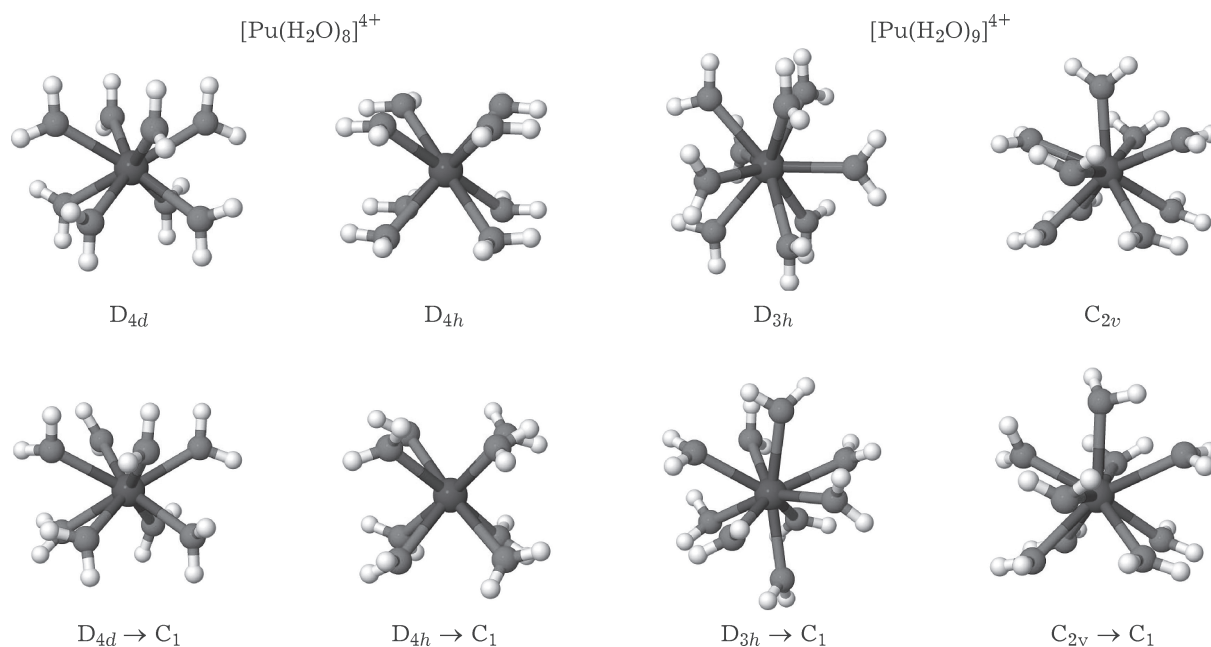

$[Pu(H_2O)_8]^{4+}$

D$_{4d}$ D$_{4h}$ D$_{3h}$ C$_{2v}$

$[Pu(H_2O)_9]^{4+}$

D$_{4d}$ → C$_1$ D$_{4h}$ → C$_1$ D$_{3h}$ → C$_1$ C$_{2v}$ → C$_1$

Fig. 1. Optimised structures of hydrated $[Pu(H_2O)n]^{4+}$ complexes ($n = 8$, 9) considering constraints on symmetry (top row) and after the removal of symmetry constraints (bottom row).

per base of the prism) for 9-coordinated $[Pu(H_2O)_9]^{4+}$ complexes. The spatial arrangement of the ligands in $[Pu(H_2O)_8]^{4+}$ and $[Pu(H_2O)_9]^{4+}$ complexes correspond to the energetically most preferable configurations of multinuclear metal complexes with terminal ligands [34]. Table 1 presents the data on the major structural feature of complexes considered that is the average Pu−O distance. A 8-coordinated complex with aqua ligands that form the inhibited configuration (D_{4d} complex) is characterised by the shortest Pu−O distance of 237 pm and the best agreement with experimental data (239 pm). The screened configuration of aqua ligands in a D_{4h} complex contributes to a greater mutual repulsion of water molecules in the first coordination shell, which is reflected in an increase in a Pu−O distance to 245 pm. In case of a 9-coordinated $[Pu(H_2O)_9]^{4+}$ complexes, the calculated Pu−O distances exceed the experimental value by 3 (D_{3h}) and 9 (C_{2v}) pm, respectively. Moreover, the D_{3h} complex with a higher symmetry is characterized by a shorter Pu−O distance. Note that the average Pu−O distance for the D_{3h} complex is lower by 3 pm compared to that for the 8-coordinated D_{4h} complex.

The further optimisation of hydrated Pu(IV) complexes in an aqueous solution is carried out without any limitations by symmetry using equilibrium geometries of symmetrical complexes as initial structures. The resulting structures of $[Pu(H_2O)_8]^{4+}$ ($D_{4d} \rightarrow C_1$ and $D_{4h} \rightarrow C_1$) and

TABLE 1

Structural parameters of $[Pu(H_2O)_n]^{4+}$ complexes (n = 8, 9) in an aqueous environment, pm

n	Complexes	Pu−O distance, pm		
		This paper	Other calculations[a]	Experiment[b]
8	D_{4h}	245	239 [7, 8], 241 [9]	239 [4−6]
8	$D_{4h} \rightarrow C_1$	241		
8	D_{4d}	237		
8	$D_{4d} \rightarrow C_1$	238		
9	C_{2v}	248	240 [8], 247 [9]	
9	$C_{2v} \rightarrow C_1$	246		
9	D_{3h}	242		
9	$D_{3h} \rightarrow C_1$	242		

[a] Complex optimisation in C_1 symmetry.

[b] Coordination number (n) is not determined unequivocally.

$[Pu(H_2O)_9]^{4+}$ ($C_{2v} \rightarrow C_1$) complexes resemble in general terms their symmetric precursors (see Fig. 1). On the contrary, a 9-coordinated $D_{3h} \rightarrow C_1$ complex completely loses the resemblance with a D_{3h} complex. Lifting restrictions leads to a slight increase in the average Pu−O distance by 1 pm for a $D_{4d} \rightarrow C_1$ complex ($[Pu(H_2O)_8]^{4+}$) and to a decrease in the Pu−O distance by 4 and 2 pm in $D_{4d} \rightarrow C_1$ complexes ($[Pu(H_2O)_8]^{4+}$) and $C_{2v} \rightarrow C_1$ ($[Pu(H_2O)_9]^{4+}$), respectively. The removal of symmetry in case of a $D_{3h} \rightarrow C_1$ complex does not affect the average Pu−O distance. Note that the Pu−O distance for all symmetrical complexes is increased with an increase in the coordination number of Pu(IV) *i. e.* with a greater repulsion of water molecules in the first coordination shell of Pu(IV).

According to our calculations, the 8-coordinated $D_{4d} \rightarrow C_1$ complex demonstrates the best agreement of the calculated Pu−O distance (238 pm) with the value obtained according to the EXAFS method [4−6]. At the same time, the Pu−O distance in the $D_{4h} \rightarrow C_1$ complex exceeds the experimental value only by 2 pm. This excess for 9-coordinated complexes reaches 3−7 pm (see Table 1). Our results are consistent with the data obtained in previous calculations of hydrate Pu(IV) complexes by the DF method [7, 8]. In work [7], the calculated Pu−O distance for the $[Pu(H_2O)_8]^{4+}$ complex is 239 pm. The author of [8] studied 8- and 9-coordinated complexes that included the second coordination shell of water molecules. A good agreement of Pu−O distances with experimental data was obtained for both $[Pu(H_2O)_8(H_2O)_{22}]^{4+}$ and $[Pu(H_2O)_9(H_2O)_{21}]^{4+}$ complexes and is 239 and 240 pm, respectively. Note that hydrated Pu(IV) clusters in the latter work were optimised only in the gas phase and solvation effect was assessed without over optimisation of clusters in aqueous medium. Modelling of Pu(IV) hydratation by the molecular dynamics (MD) method was carried out in work [9]. It was found that that the stable number of water molecules around Pu(IV) ion with the average Pu−O distance of 241 pm was equal to eight. At the same time, a 9-coordinated complex proved to be unstable.

Our calculations demonstrate a decrease in the charge of Pu(IV) in hydrated complexes from the formal ion charge of $+4e$ to $+2.47e$ − $2.50e$ (Table 2), which is due to the transfer of

TABLE 2
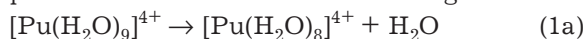
Charge distribution in hydrated Pu(IV) complexes
and their monohydroxides calculated by the Bader method

n	$[Pu(H_2O)_n]^{4+}$		$[Pu(OH)(H_2O)_{n-1}]^{3+}$	
	Pu	H_2O^a	PuOH	H_2O^a
8	2.50	0.19	2.13	0.12
9	2.47	0.17	2.09	0.12

^a Average value.

a part of electron density from water molecules. Note that the charge quantity for Pu(IV) ion is slightly decreased with an increase in the coordination number from 8 to 9. Donation of electron density to Pu(IV) ion leads to the formation of positively charged water molecules. Moreover, with an increase in the coordination number of Pu(IV), the charge on water molecules is decreased from $+0.19e$ to $+0.17e$. Thus, the total electron density donated to Pu(IV) ion increases with an increase in the coordination number. At the same time, the average charge for one molecule is decreased, which can be explained by a greater Pu–O distance in $[Pu(H_2O)_9]^{4+}$ complexes. The latter, in turn, is driven by a greater repulsion between water molecules inside the first coordination shell in comparison with $[Pu(H_2O)_8]^{4+}$ complexes.

Energy characteristics. The relative stability of aqueous Pu(IV) complexes was calculated as the free energy ΔG_{diss} of reactions for complexes with different numbers of ligands:
$$[Pu(H_2O)_9]^{4+} \rightarrow [Pu(H_2O)_8]^{4+} + H_2O \quad (1a)$$
and for isomers of the same complex:
$$[Pu(H_2O)_8]^{4+} \rightarrow [Pu(H_2O)_8]^{4+} \quad (1b)$$

With the aim of assessing the effect of the imposed symmetry limitations, the relative stability ΔG_{diss} of symmetric and non-symmetric complexes has been studied. The ΔG_{diss} energy has been calculated relatively to 8-coordinated complexes: D_{4d} (for symmetric systems) and $D_{4d} \rightarrow C_1$ (for non-symmetric) (Table 3).

The stability range of symmetric complexes is 109 kJ/mol. The 8-coordinated D_{4d} complex is the most stable hydrated Pu(IV) complex. The energy of the D_{4h} complex is higher by 21 kJ/mol compared to the energy of the D_{4d} complex. Stabilities of nine-coordinated C_{2v} and D_{3h} complexes are lower by 85 and 109 kJ/mol, respectively. Among non-symmetric complexes, the $D_{4h} \rightarrow C_1$ complex is lowest by energy.

However, the energy of the next by stability $D_{4d} \rightarrow C_1$ complex exceeds it only by 12 kJ/mol, which does not allow unequivocally speaking of the most-favoured configuration of the $[Pu(H_2O)_8]^{4+}$ complex. The removal of symmetry limitations in case of nine-coordinated complexes significantly increases the stability of the $D_{3d} \rightarrow C_1$ complex: it is less stable only by 29 and 41 kJ/mol in comparison with the reference $D_{4d} \rightarrow C_1$ complex and $D_{4h} \rightarrow C_1$ complex, respectively. Since the $D_{3h} \rightarrow C_1$ complex is sole that does not resembles its symmetric precursor (D_{3h} complex, see Fig. 1), it could be argued that the configuration of the $[Pu(H_2O)_9]^{4+}$ complex in D_{3h} symmetry is unstable. Optimisation without considering symmetry does not significantly increase the stability of the $C_{2v} \rightarrow C_1$ complex in comparison with the C_{2v} complex. As a result, it becomes least stable, and its energy is 61 kJ/mol lower than that of the reference $D_{4d} \rightarrow C_1$ complex. Note that generally there is no the expected correlation between the Pu–O distance and stability of the hydrated Pu(IV) complex. Perhaps, two factors play a role

TABLE 3

Hydration free energies ΔG_{solv} of Pu^{4+} ion and the relative stability ΔG_{diss} of hydrated $[Pu(H_2O)_n]^{4+}$ complexes ($n = 8, 9$) in an aqueous environment, kJ/mol

n^a	Complexes	$\Delta G_{diss}{}^b$	$\Delta G_{solv}{}^c$
	This paper		
8	D_{4d}	0	N/d
8	D_{4h}	21	N/d
9	C_{2v}	85	N/d
9	D_{3h}	109	N/d
8	$D_{4d} \rightarrow C_1$	0	−6146
8	$D_{4h} \rightarrow C_1$	−12	−6157 (−5974)
9	$C_{2v} \rightarrow C_1$	61	−6070
9	$D_{3h} \rightarrow C_1$	29	−6102 (−5934)
	Other calculations [8]		
8	C_1	0	−6173
9	C_1	52	−6121

Note. N/d – not determined.

^aCoordination number.

^bPositive values of ΔG_{diss} characterize the lower stability of the hydrated complex.

^cThe solvation free energy (ΔG_{solv}) calculated using the standard scaling multiplier *S*(0) is indicated in brackets.

in this case: the interaction between Pu(IV) ion with water molecules and mutual repulsion of water molecules.

The data presented by us about relative stabilities of 8- and 9-coordinated hydrated Pu(IV) complexes are consistent with calculations by the DF method for $[Pu(H_2O)_8(H_2O)_{22}]^{4+}$ and $[Pu(H_2O)_9(H_2O)_{21}]^{4+}$ complexes [8]. Optimisation of the both complexes in the gas phase followed by the use of the DF method indicates that the 8-coordinated complex is least stable surpassing the rest for energy by 52 kJ/mol (see Table 3). Modelling with the use of the MD method [9] also predicts the higher stability of the $[Pu(H_2O)_8]^{4+}$ complex, though its advantage over the nine-coordinated complex in this case does not exceed 6 kJ/mol.

The free hydration energies of Pu(IV) ion (ΔG_{solv}) are calculated using the cluster thermodynamic cycle [10] that corresponds to the reaction equation

$$Pu^{4+} + (H_2O)_n \rightarrow [Pu(H_2O)_n]^{4+} \qquad (2)$$

with water clusters $(H_2O)_8$ and $(H_2O)_9$ as reactants. As demonstrated in [11], the free hydration energy for U(IV) ion calculated using the PCM model depends on the size of the cavity, in which a hydrate cluster of actinoide An(IV) ion is placed. The use of various parameters that define the size of the molecular cavity for complexes consisting of one hydrate shell leads to the scatter of the calculated ΔG_{solv} values in about 400 kJ/mol. The addition of the second coordination shell reduces this range to ~180 kJ/mol [11]. The accuracy of theoretically obtained ΔG_{solv} values is usually verified by comparison with experimental values. There are no experimental ΔG_{solv} values in case of   ion. Consequently, the data for QM calculations are often compared with ΔG_{solv} values obtained using empiric models [8]. The both models are based on different sets of parameters and significantly differ in the ΔG_{solv} value for Pu(IV) ion under study: -6444 kJ/mol [35] and -6105 [36]. At the same time, the values calculated by us of free hydration energies of Pu(IV) are well consistent (with deviation of less than 1 %) with the data of [36]. Remember that $S(3)$ and $S(4)$ multipliers were used for construction of molecular cavities, the former depended on the charge of the hydrated ion (Pu^{4+} and $[PuOH]^{3+}$)and obtained by adjustment of the

calculated values of the free energy of hydrolysis ΔG_{hydr} to experimental data. Table 3 also presents ΔG_{solv} data for a number of Pu(IV) complexes calculated using the standard multiplier $S(0) = 1.125$, the value of which does not depend on the studied system charge. The ΔG_{solv} energies obtained in the latter case are lower (by modulus) on $168-183$ kJ/mol, *i. e.* differ by 3 % from the calculation results using $S(3)$ and $S(4)$ multipliers. This deviation may seem insignificant and call into question the need of using scaling multipliers that depend on the charge of the solvated ion. However, it will be demonstrated further that this is not the case and their use is a determining factor when calculating ΔG_{hydr} values, the absolute quantity of which is three orders lower compared to the ΔG value (Table 4).

The free hydration energies of Pu(IV) ion calculated in this paper are in good agreement with calculated ΔG_{solv} values presented in the paper by Clark [8] (see Table 3). This latter simulated hydrated $[Pu(H_2O)_{30}]^{4+}$ complexes with two hydrate shells. The effect of the S multiplier for the calculated ΔG_{solv} values is lower in this case. However, this effect is declining due to increasing costs for the search of lowest energy clusters.

Plutonium (IV) monohydroxide

Structure. Hydrated monohydroxide $[Pu(OH)]^{3+}$ complexes are obtained from the most stable 8- and 9-coordinated Pu(IV) complexes $D_{4h} \rightarrow C_1$ and $D_{3h} \rightarrow C_1$, respectively (Fig. 2) by separation of one proton from aqua land followed by optimisation of the complex. Proton separation does not result in a change of the coordination num-
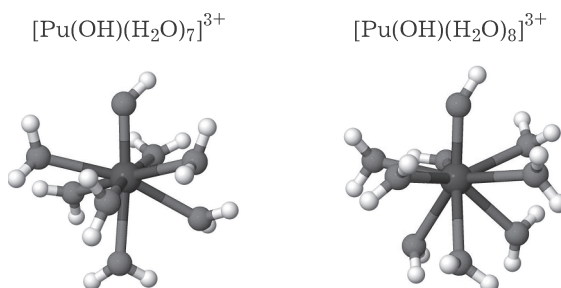
$[Pu(OH)(H_2O)_7]^{3+}$ $[Pu(OH)(H_2O)_8]^{3+}$

Fig. 2. Optimised structures of hydrated $[Pu(OH)(H_2O)_{n-1}]^{3+}$ complexes ($n = 8, 9$).

TABLE 4

Structural parameters of $[Pu(OH)(H_2O)_{n-1}]^{3+}$ complexes ($n = 8, 9$) in an aqueous environment, free energies of hydrolysis ΔG_{hydr} and Pu(IV) hydrolysis constants $\log K_1^0$

n^a	Bond length, pm		$\Delta G_{hydr}{}^c$,	$\log K_1^{0\ c}$
	$Pu-OH_2{}^b$	$Pu-OH$	kJ/mol	
8	245	205	6.3 (−73.1)	−1.1 (12.8)
9	250	204	1.4 (−81.7)	−0.2 (14.3)

^aCoordination number.

^bAverage value.

^cThe values calculated using the standard scaling multiplier $S(0)$ are indicated in brackets.

ber of Pu(IV) ion; however, the length of the formed Pu−OH bond is much lower (204−205 pm) than the distance from plutonium ion to aqua ligands (see Table 4). The formation of $[Pu(OH)(H_2O)_7]^{3+}$ and $[Pu(OH)(H_2O)_8]^{3+}$ monohydroxides is characterised by an increase in the Pu−O distance by 4−8 pm compared to the corresponding Pu(IV) hydrates. The Pu−O distance (250 pm) in case of the $[Pu(OH)(H_2O)_8]^{3+}$ complex is close to experimental values typical for Pu(III) hydrates (249 pm) [4].

An increase in the Pu−O distance found for hydrated $[Pu(OH)]^{3+}$ complexes correlates with a decrease in electron density transfer from water molecules to the monohydroxide compared to Pu(IV) complexes (see Table 2). The amount of electron density transferred to $[Pu(OH)]^{3+}$ ion from one water molecule is 0.12e, which contributes to a decrease in the positive charge in the monohydroxide by only ~0.89e, while in case of Pu(IV) ion, its charge is decreased on average by 1.52e.

Hydrolysis constants. The free energy of hydrolysis ΔG_{hydr} and the corresponding first hydrolysis constant ($\log K_1^0$) of Pu(IV) ion is calculated for the most stable hydrate complexes $D_{4h} \to C_1$ and $D_{3h} \to C_1$ in accordance with the reaction

$$[Pu(H_2O)_n]^{4+} \to [Pu(OH)(H_2O)_{n-1}]^{3+} + H^+ \quad (3)$$
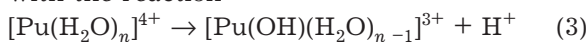
Experimental $\log K_1^0$ values vary from −0.6 to 0.6 [14−16], which corresponds to a change in the ΔG_{hydr} energy from 3.4 to −3.4 kJ/mol, respectively.

According to reaction (3), for the correct determination of the free ΔG_{hydr} energy, one needs to know the value of proton hydration free energy $\Delta G_{solv}(H^+)$. The recommended value is $\Delta G_{solv}(H^+) = -1112.5$ kJ/mol [37]. According to the calculations made by us using the thermodynamic cycle of the reaction

$$H^+ + (H_2O)_4 \to [H(H_2O)_4]^+ \quad (4)$$
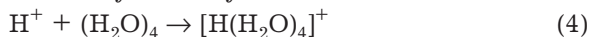
$\Delta G_{solv}(H^+) = -1108.8$ kJ/mol, which is in good agreement with the recommended value.

The calculated $\log K_1^0$ values are presented in Table 4. In accordance with the method used by us to simulate complexes solvation with +3e and +4e charges, $S(3)$ and $S(4)$ multipliers, respectively, are used. The values of $\log K_1^0$ for the both $[Pu(H_2O)_8]^{4+}$ and $[Pu(H_2O)_9]^{4+}$ complexes are negative, which is in agreement with MD calculation results presented in [9]. The calculated hydrolysis constant in case of $[Pu(H_2O)_9]^{4+}$ falls into experimentally defined borders. The calculated $\log K_1^0$ value for $[Pu(H_2O)_8]^{4+}$ is much lower than is somewhat lower than experimental lower bounds; however, it has a reasonable value and in this case. At the same time, the use of standard multiplier $S(0)$ results in significant (by an order of magnitude) reassessment of hydrolysis constants (see Table 4).

CONCLUSION

Ion hydratation and Pu(IV) hydrolysis were theoretically studied using the relativistic DF method and the polarizable continuum model (PCM). Hydrated Pu(IV) complexes represented a metal ion surrounded by 8 or 9 water molecules that formed its first coordination shell. The results presented in the paper demonstrate that an 8-coordinated complex in the form of prism and antiprism is the most energetically preferable configuration of Pu(IV) aqua ion in an aqueous solution. Nine-coordinated complexes are less stable, at least, by 29−41 kJ/mol.

This paper used for the first time scaling multipliers S, the values of which depended on the charge of the complex under study, in calculating energy characteristics of actinoides in aqueous medium. The values of scaling multipliers for hydrated Pu(IV) complexes with +3e and +4e charges were obtained by adjustment of the calculated values of the first hydrolysis constant to known experimental values.

It was demonstrated that the use of scaling multipliers dependent on the charge on complex defined the accuracy of calculations of the hydrolysis constant of Pu^{4+} ion. The fidelity of reproduction of experimental $\log K_1^0$ values suggests that the obtained values of scaling multipliers $S(3)$ and $S(4)$ are suitable for use in calculating free hydration energies of actinides, and the theoretically defined range of the free hydration energy of Pu(IV) of $-6070...-6157$ kJ/mol is a reasonable prediction of experimental values.

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