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Computational chemistry study of zirconium monomers in low acid concentration aqueous solutions

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Abstract. Zirconium and hafnium have to be separated prior to their use in nuclear energy reactors. Therefore, a lot of research has been done on the solvent extraction of zirconium. However, most of this research involved screening studies that focused on finding suitable solvent extraction processes, rather than attempting to gain insights into the extraction mechanisms. An important part of understanding extraction mechanisms is knowing which zirconium species are present in aqueous solutions since these are the species with which extractants react. In this study, we used density functional theory based molecular dynamics calculations to model zirconium monomers in low acid concentration solutions. Specifically, we modelled aqua and hydroxo zirconium complexes using an explicit solvent approach. By calculating radial distribution functions for each of these zirconium complexes, using either 10, 20, 30, 40 or 50 explicit solvent water molecules, we were able to determine that at least about 30 solvent water molecules are needed to model the first two solvation spheres of a zirconium ion during an explicit solvent approach. We anticipate that this work will be useful for further explicit solvent based computational chemistry studies on the solvent extraction mechanisms of zirconium and hafnium.

1. Introduction

During the production of nuclear energy, uranium undergoes nuclear fission and in the process produces thermal neutrons [1]. These liberated thermal neutrons radiate between uranium atoms, which are held in so-called fuel rods inside a nuclear reactor, causing further fission of other uranium and sustaining the nuclear reaction [1]. The heat given off by this nuclear reaction causes water, which is also present in the nuclear reactor, to rise as steam. This rising steam causes turbines to rotate and produce electrical energy.

Zirconium and hafnium have important applications in nuclear energy reactors. Since zirconium is transparent to thermal neutrons, it is used to make the casing of the uranium fuel rods [2]. Conversely, hafnium absorbs thermal neutrons and is therefore sometimes used to make control rods which are used to moderate nuclear reactions [2]. Since zirconium and hafnium have opposing thermal neutron capturing properties, these two metals have to be separated prior to their use in nuclear energy reactors. A promising candidate technology for the separation of these two metals is solvent extraction [3].

A lot of research has been published on the solvent extraction of zirconium and hafnium [3]. When poring over this published research it becomes apparent that most of it was done by adopting an experimental screening approach. This approach involved choosing an extractant on the basis of novelty. Then doing a sequence of solvent extraction experiments in which the extractant's concentration was varied in a stepwise manner. Although this approach can lead to the discovery of

suitable extractants for the solvent extraction of zirconium, it seldom yields insights into the mechanisms that underpin how these extractants extract zirconium. An important part of understanding these mechanisms is knowing exactly which zirconium species are present in an aqueous solvent since these are the species with which extractants react. Besides for understanding the extraction mechanisms, knowing exactly which zirconium species are present in an aqueous solution could also be applied to the selection, or design, of extractants for zirconium.

Although the aqueous speciation of zirconium is not fully understood, it has been experimentally established that in low acid concentration aqueous solutions zirconium can be present as either a monomer, dimer or tetramer [4]. In this study, we used computational chemistry to model the zirconium monomer in such aqueous solutions. In principle, it is possible that monomeric zirconium exists as an aqua or hydroxo complex in such aqueous solutions, and therefore we focused on both cases. Specifically, we modelled aqueous zirconium complexes surrounded by water molecules; an approach is known as explicit solvent modelling [5]. Given these systems, we did density functional theory based molecular dynamics (MD) calculations in order to calculate so-called radial distribution functions (RDF). In simple terms, these RDF indicate how oxygen and hydrogen atoms are spatially arranged around a zirconium ion.

We calculated the RDF for systems that contained added either 10, 20, 30, 40 or 50 explicit water solvent molecules. Using these RDF we determined how many water molecules are necessary to model the solvation sphere around a zirconium complex when using an explicit solvent approach. Following this, we made predictions regarding the structures of aqua and hydroxo zirconium complexes. These predictions include coordination numbers of the zirconium complexes and the extent to which the aqua and hydroxo ligands undergo protonation or deprotonation. We anticipate that this work will serve as a foothold for future computational chemistry studies on the solvent extraction of zirconium; especially studies that also use an explicit solvent approach.

2. Method

All the modelling presented in this paper was done within the paradigm of density functional theory, using the DMol [6] code [6,7] as implemented in Biovia's Materials Studio 2018 computational chemistry software package. Specifically, we used the PBE functional [8]. As for the basis set, the DMol^3 code implements numerical basis sets. In this study, we used the DNP basis set, which is an unrestricted basis set in which each core orbital is represented by a single primitive, while each valence orbital is represented by two primatives plus a third primitive. This third primitive is a p function for hydrogen, and a d function for all other elements. Zirconium's core electrons were represented by a relativistic core potential.

Since the systems that we modelled consisted of multiple molecules, interatomic dispersion interactions had to be accounted for. We did this using the Grimme DFT-D scheme [9]. In addition to modelling the solvent environment around the zirconium complexes explicitly, we used an implicit solvent model to model the solvent environment around the entire solute-explicit solvent cluster. For this purpose we used the COSMO implicit solvent model [10], with a dielectric constant of 78.54, to represent a water solvent environment. The reason why we added this implicit solvent model was to stabilize the cluster's charge.

Regarding the MD calculations, we calculated NVT trajectories using a time step of 1.0 fs. The temperature was controlled at 298 K using the Nose-Hoover thermostat [11,12]. We equilibrated each system by doing 1000 step geometry optimization calculations, followed by 2 ps MD calculations. After this equilibration procedure, we did 3 ps MD calculations and used the resulting trajectories to create RDF.

We created the RDF by writing a Python script. Given a trajectory, this script samples the coordinates from every configuration in the trajectory. These sampled coordinates are then used to create a histogram of either Zr-O or Zr-H distances, using a bin width of 0.01 Å. The histogram is normalized and used as the RDF for the system whose trajectory was subjected to the script.

3. Results and discussion

We began by doing geometry optimization calculations on $Zr(H_2O)_8^{4+}$ and $Zr(OH)_8^{4-}$. For these calculations, we used an implicit solvent model without adding explicit solvent molecules. Both structures converged to eight coordinate complexes. Thus, when using a purely implicit solvent model hydroxo zirconate was predicted to exist as an eight coordinate structure. However, as will be shown later, when explicit solvent molecules were present, hydroxo zirconate was predicted to be either a six or seven coordinate structure, depending on how many explicit solvent molecules were present. This observation highlights the fact that different approaches to modelling the solvent environment can result in markedly different predictions.

Using the geometrically optimized $Zr(H_2O)_8^{4+}$ and $Zr(OH)_8^{4-}$ complexes, we created new structures by placing either 10, 20, 30, 40 or 50 additional water molecules around each of these complexes. This resulted in ten new systems which contained varying amounts of explicit solvent molecules; five of these structures had a charge of 4+, while the other five had a charge of 4-. Since the 4+ systems each had 8 H_2O ligands to begin with, these systems ended up with either 18, 28, 38, 48 or 58 total water molecules after adding explicit water molecules. Similarly, the 4- systems ended up with a total of either 18, 28, 38, 48 or 58 oxygen atoms. These ten systems were equilibrated, before doing further MD calculations to create Zr-O and Zr-H RDF for each systems. Figure 1 shows a representative example of what these structures looked like after equilibration.
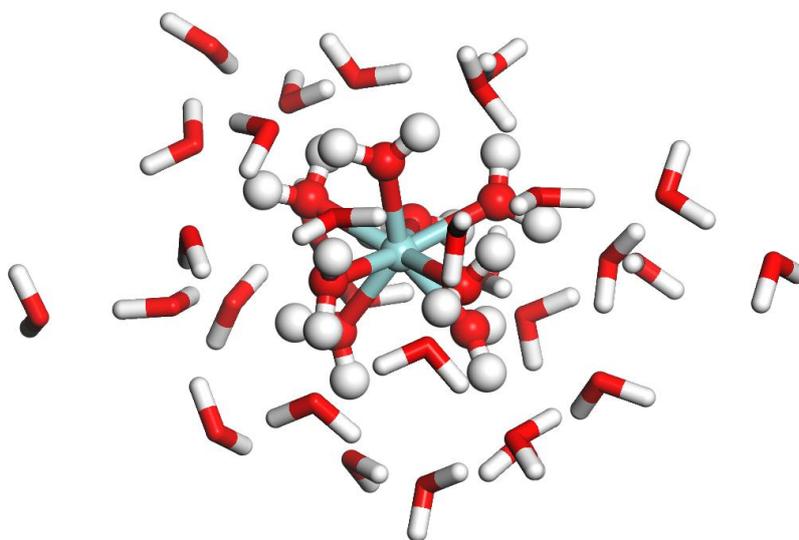

Figure 1. The equilibrated structure of $Zr(H_2O)_8^{4+}$ in the presence of 30 explicit solvent water molecules. Zirconium, oxygen and hydrogen atoms are shown in teal, red and white.

The results for the Zr-O RDF are shown in figure 2. For each of the ten systems, we integrated the first two Zr-O RDF peaks and multiplied the integral by the total number of oxygen atoms in the system. This gave us the average number of oxygen atoms that corresponds to each peak. For instance, the first peaks for the 4+ systems, which are all centred at 2.3 Å, each corresponds to an average of 8 oxygen atoms. After considering the Zr-H RDF, which is discussed later, we interpreted these oxygen atoms as belonging to aqua ligands that are coordinated to the zirconium centres. The results of these kinds of integrations of the Zr-O RDF are shown in figure 3.

When considering figures 2 and 3, it seems that in addition to any aqua or hydroxo ligands coordinated to zirconium, at least about 30 water molecules were necessary to model the first and second solvation spheres of a zirconium ion. This is clearly apparent when considering the left side of Figure 3. As the number of water molecules in the 4+ systems increased, so too did the number of oxygen atoms corresponding to the second Zr-O RDF peak. However, the number of oxygen atoms corresponding to this second peak seems to plateau for systems that contained 38, 48 or 58 water

molecules. This suggests that for the structures that contained 18 or 28 water molecules, the second solvation sphere had not been "filled up".
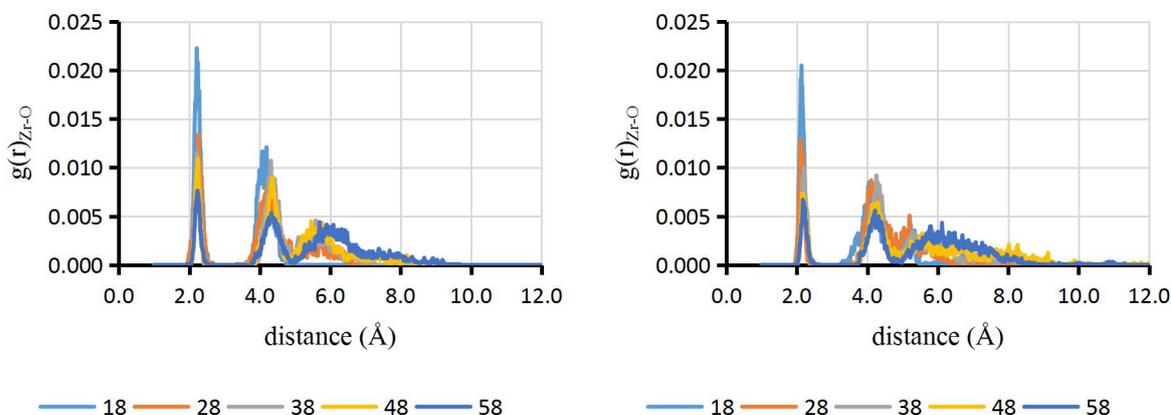

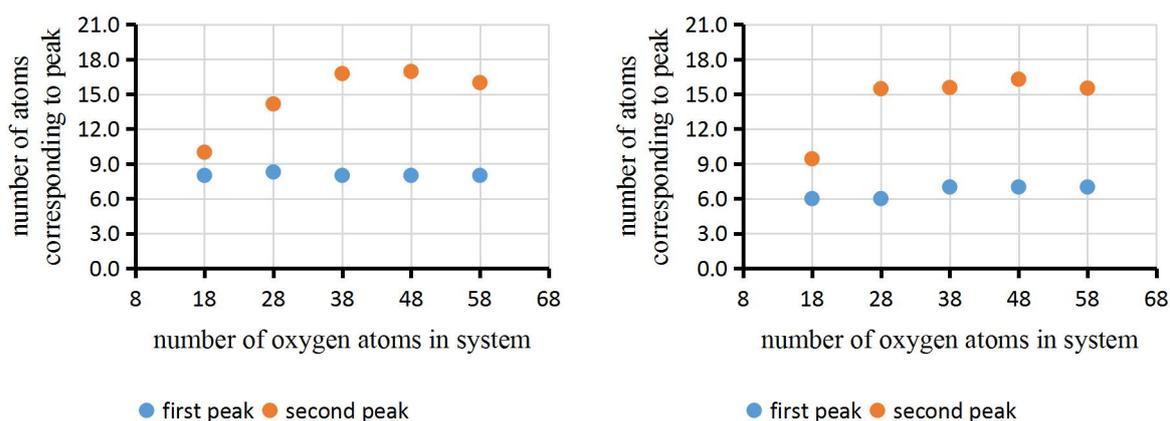**Figure 2.** Zr–O RDF for each of the 4+ (left) and 4- (right) systems.

Figure 3. The number of oxygen atoms corresponding to the first and second Zr-O RDF peaks of the 4+ (left) and 4- (right) systems.

A similar argument can be made for the right side of figure 3 when considering the number of oxygen atoms corresponding to the first Zr-O RDF peak. For systems that contained 10 or 20 additional water molecules, the first peaks corresponded to an average of 6.0 oxygen atoms each. Conversely, for systems that contained more explicit solvent water molecules, the first peaks corresponded to an average of 7.0 oxygen atoms each. Therefore, it seems that the number of explicit solvent molecules influenced how the first and second solvation spheres of the zirconium ion were predicted to be.

Since its clear that 30 explicit solvent molecules were necessary to model a zirconium ion's first two solvation spheres, the rest of the discussion will focus only on the two systems that contained 30 explicit solvent molecules. However, the arguments that follow can also be made for the systems that contained 40 or 50 explicit solvent molecules.

We now discuss the Zr-H RDF, which is shown in figure 4, and the number of hydrogen atoms corresponding to the first two Zr-H RDF peaks, shown in figure 5. For the 4+ system, the first Zr-H RDF peak corresponds to 16.0 hydrogen atoms. Given that this system's first Zr-O RDF corresponds to 8.0 oxygen atoms, it seems that for the 4+ system zirconium's first solvation sphere consisted of eight water molecules. Furthermore, when considering the relative positions of these Zr-O (2.3 Å) and Zr-H (3.0 Å) RDF peaks, it becomes clear that these eight water molecules were aligned in such a way

that their oxygen ends pointed towards the zirconium centre. This interpretation is consistent with the notion that these water molecules were coordinated to the zirconium centre.
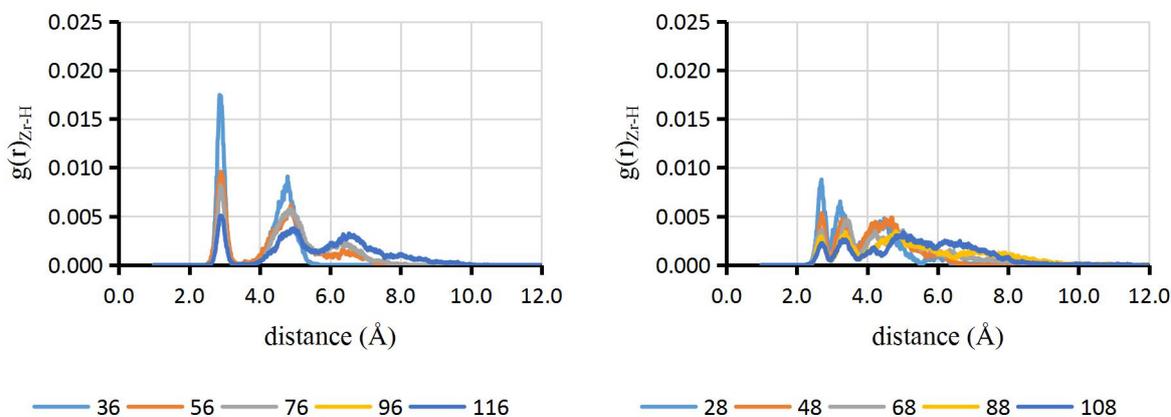

Figure 4. Zr–H RDF for each of the 4+ (left) and 4- (right) systems.
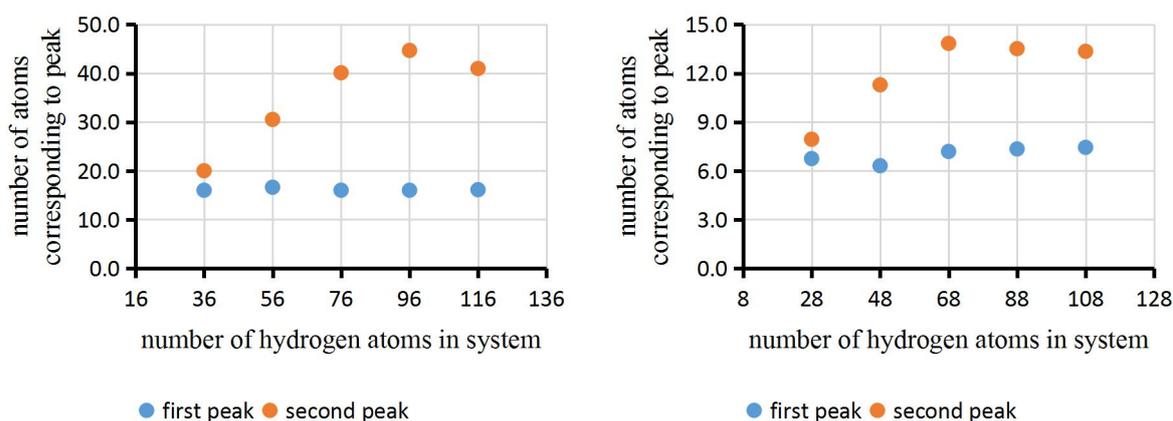

Figure 5. The number of hydrogen atoms corresponding to the first and second Zr-H RDF peaks of the 4+ (left) and 4- (right) systems.

When considering the second RDF peaks of the 4+ system, we see that the Zr-O RDF peak (4.5 Å) is closer to the zirconium centre than the Zr-H RDF peak (5.0 Å). This suggests that the water molecules in the second solvation sphere also had their oxygen ends pointed towards the zirconium centre. An explanation for this orientation is that hydrogen bonds were present between the hydrogen atoms in the first solvation sphere and oxygen atoms in the second solvation sphere.

Lastly, we discuss the right sides of figures 4 and 5. The first Zr-H RDF peak of the 4- system correspond to 7.19 hydrogen atoms, while the first Zr-O RDF peak corresponds to 7.0 oxygen atoms. Therefore, it seems that the first solvation sphere of the 4- system consisted of approximately 7 hydroxy groups. Similar to the 4+ system, the Zr-O RDF peak (2.2 Å) is closer to the zirconium centre than the Zr-H RDF peak (2.9 Å). This suggests that these hydroxo groups were coordinated to the zirconium centre. Observing that the average number of hydrogen atoms corresponding to the first Zr-H RDF is greater than 7.0, it seems that some of these hydroxo ligands were protonated for a portion of the 3 ps MD trajectory.

The second Zr-H RDF peak of the 4- system corresponds to 13.8 hydrogen atoms. To be clear, the 4- system's second Zr-H RDF peak is not analogous to the 4+ system's second Zr-H RDF peak. The 4+ system's second Zr-H RDF peak (5.0 Å) is centred further away from the zirconium centre than its first (2.3 Å) and second (4.5 Å) Zr-O RDF peaks. Conversely, the 4- system's second Zr-H RDF peak

(3.5 Å) is centred between its first (2.2 Å) and second (4.4 Å) Zr-O RDF peaks. A possible explanation for this may be that the water molecules in the system's second solvation sphere was orientated in such a way that hydrogen atoms in the second solvation sphere formed hydrogen bonds with oxygen atoms in the first solvation sphere.

Analysis of the third Zr-H peak may have granted further insights into the solvation environments of the 4- systems. However, the 4- systems that contained 10, 20 and 40 explicit solvent molecules all have a third Zr-H RDF peak that extends from about 4.0 to 6.0 Å. Conversely, the other two 4- systems have a third and fourth Zr-H RDF peak in this same interval. Given this inconsistency, we could not be sure that we had an adequate number of explicit solvent molecules to describe this feature of the solvent environment. Therefore, we make no attempt at analyzing the Zr-H RDF beyond the second peak.

4. Conclusions

In this study, we modelled the solvent environment around aqua and hydroxo zirconium complexes. Specifically, we used density functional theory based MD calculations to calculate Zr-O and Zr-H RDF for each of these complexes. Using these RDF we concluded that, in addition to aqua or hydroxo ligands, at least approximately 30 explicit solvent molecules are needed to describe the first two solvation spheres of a zirconium ion. Furthermore, we also predicted that aqua zirconium exists as an eight coordinate complex, while hydroxo zirconate exists as a seven-coordinate complex.

It is our intention that this work will serve as a foothold for future computational chemistry studies into the mechanisms that underpin the solvent extraction of zirconium. For instance, attempts at modelling other aqueous zirconium species, such as dimers or tetramers, should include at least approximately 30 explicit solvent molecules. Attempts at modelling the attack of extractants on zirconium species in aqueous solvents might also need at least 30 explicit solvent molecules.

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