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Permalink https://escholarship.org/uc/item/4ws2542v

Journal The Journal of Physical Chemistry B, 120(29)

ISSN 1520-6106

Authors

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Publication Date 2016-07-28

DOI 10.1021/acs.jpcb.6b05452

Peer reviewed



Solvation of the Ca₂UO₂(CO₃)₃ Complex in Seawater from Classical Molecular Dynamics

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Supporting Information

ABSTRACT: Uranium from the sea provides a long-time supply guarantee of nuclear fuels for centuries to come, and the neutral $Ca_2UO_2(CO_3)_3$ complex has been shown to be the dominant species of uranium in seawater. However, the solvation and structure of the $Ca_2UO_2(CO_3)_3$ complex in seawater have been unclear. Herein we simulate the $Ca_2UO_2(CO_3)_3$ complex in a model seawater solution via classical molecular dynamics. We find that Na⁺ and Cl⁻ ions interact very differently with the neutral $Ca_2UO_2(CO_3)_3$ complex in seawater. Especially, one Na⁺ ion is closely associated with the $Ca_2UO_2(CO_3)_3$ complex, thereby effectively making the complex have a +1 charge, while Cl⁻ ions are much farther away. Hence, this work reveals the important role of Na⁺ ions in affecting the solvation of the $Ca_2UO_2(CO_3)_3$ complex in seawater, which has implications in designing ligands to attract the $Ca_2UO_2(CO_3)_3$ complex to the sorbent.



1. INTRODUCTION

Geological deposits of nuclear fuel resources are limited, but the large mass of seawater contains about 4.5 billion metric tons of uranium that have been considered as a long-term supply of nuclear fuels, even though the concentration of uranyl in seawater is very low (at 3.2 ppb).¹ The potentially promising future of uranium from the sea has inspired researchers to find methods to extract uranium from seawater.

Functionalized polymers with the amidoxime-type ligand were used to sequester uranyl in the 1970s and 1980s.² This effort continued into the 1990s, 2000s, and today.³⁻¹¹ Moreover, many fundamental studies have been carried out to understand the speciation of uranium in seawater and the competition from vanadium.¹²⁻¹⁵

In aqueous solution, U(VI) forms two strong bonds with oxygen atoms, resulting in the formation of the uranyl cation $UO_2^{2^{+},16}$ A number of investigations reported a strong complexation of $UO_2^{2^{+}}$ by carbonate due to its considerable concentration in natural seawater, to form $[UO_2(CO_3)_3]^{4^{-}}$ of high stability constants.^{17–21} Over the past two decades, a consensus has been reached that $[UO_2(CO_3)_3]^{4^{-}}$ forms cation-balanced complexes in seawater. In 1996, Bernhard et al. reported the aqueous complex $Ca_2UO_2(CO_3)_3$ via time-resolved laser-induced fluorescence spectroscopy (TRLFS),^{22,23} which was further explored by Kelly et al. via extended X-ray absorption fine structure (EXAFS) measurements.²⁴ Most recently, Rao et al. examined the thermodynamics of uranium in seawater and the complexation between Ca/Mg and $[UO_2(CO_3)_3]^{4^{-},25}$ They concluded that in

seawater pH (~8.2) Ca₂UO₂(CO₃)₃ accounts for 58% of the total uranium in the solution while $[CaUO_2(CO_3)_3]^{2-}$ and $[MgUO_2(CO_3)_3]^{2-}$ account for 18% each and $[UO_2(CO_3)_3]^{4-}$ accounts for only 6%.²⁵ In addition, the stability constant for the speciation of calcium is larger than that for magnesium.²⁵

Researchers have also studied the characteristics of the uranyl ion via molecular dynamics (MD) simulations^{26–28} and firstprinciples calculations.^{21,29,30} Kerisit et al. examined structural properties of the various aqueous species and in particular of the bidendate binding configuration by Ca²⁺ in Ca₂UO₂(CO₃)₃ via classical MD simulation.²⁶ Hofer et al. examined the structure and dynamics of $[UO_2(CO_3)_3]^{4-}$ in water using quantum mechanical charge field molecular dynamics (QMCF-MD).²⁸ Most recently, Priest et al. analyzed the solvation of Ca₂UO₂(CO₃)₃ in water via first-principles MD,³¹ while Hofer et al. studied it using QMCF-MD.²⁷

These previous simulations offered us insights into the structure of the calcium–uranyl–carbonate species in pure water. However, in seawater, there are large concentrations of salt ions such as Na^+ and Cl^- whose impact on the solvation of $Ca_2UO_2(CO_3)_3$ has not been addressed before in simulation. This knowledge would be useful in designing polymer sorbents to be deployed in seawater. In fact, a recent marine testing of a polymer fiber sorbent after 56-day seawater exposure showed that a significant amount of Na^+ ions was retained in the

 Received:
 May 31, 2016

 Revised:
 July 2, 2016

 Published:
 July 5, 2016

sorbent.³² Thus, it is of great importance to illuminate the impact of salt on the solvation of $Ca_2UO_2(CO_3)_3$ in seawater.

The present work seeks to simulate $Ca_2UO_2(CO_3)_3$ in seawater via classical MD simulation, by including Na⁺ and Cl⁻ ions explicitly in our model. In section 2, we explain the force field parameters and the simulation details. In section 3, we show our simulation results and focus the discussion on the interaction and distribution of Na⁺ and Cl⁻ ions around the $Ca_2UO_2(CO_3)_3$ complex. We conclude in section 4 that the Na⁺ and Cl⁻ ions interact very differently with the uranyl complex.

2. COMPUTATIONAL METHODS

2.1. Force Field Parameters. Our simulation used parameters from Guilbaud and Wipff for the UO22+ cation that were fitted to the hydration energies of uranyl in aqueous solution^{33,34} with the TIP3P water, a rigid three-site model similar to SPC/E.35 Kerisit et al. chose the SPC/E model for water in their simulation of the uranyl complex in water.²⁶ Here we selected the SPC/E model for consistency with Kerisit et al. Several different potential models for the carbonate ion exist, either as ions in solution or in the vicinity of carbonate mineral surfaces.^{36,37} We adjusted the force constant for the carbonate (O-C-O) angles so that the overall structure of the tricarbonate complex was reproduced well in the uranyl equatorial plane.³⁸ The ion parameters based on the SPC/E water model were used for $Ca^{2+,39}$ Na^{+,40} and Cl^{-,40} The potential parameters for modeling the interactions between Ca²⁺ and water as well as between Ca²⁺ and carbonate were of the Buckingham potential form from de Leeuw and Park.³⁹ For all other types of atom-atom van der Waals interactions, the Lorentz–Berthelot combination rules $[\varepsilon_{ii} = (\varepsilon_{ii}\varepsilon_{ii})^{1/2}$ and $\sigma_{ii} =$ $(\sigma_{ii} + \sigma_{ii})/2$ were used for the Lennard-Jones parameters between different types of atoms. All the parameters used in this work were tabulated in detail in the Supporting Information.

2.2. Molecular Dynamics Simulation. Two systems were considered in our MD simulations: (1) $Ca_2UO_2(CO_3)_3$ in pure water and (2) $Ca_2UO_2(CO_3)_3$ in seawater. The simulation cells contained 1000 water molecules at zero applied pressure in the NPT ensemble (constant number of particles, constant pressure, and constant temperature) using the LAMMPS package.⁴¹ For the initial configuration of the first system, we placed an initial structure of the uranium complex, as shown in Figure 1, into a periodic water box. For the initial configuration of the second system, 10 Na⁺ and 10 Cl⁻ ions were randomly placed in the first system to create the simulated seawater with a concentration of Na⁺ 10.7 g/kg.⁴² The volume of the box was $\sim 31 \times 31 \times 31 \text{ Å}^3$ with 3D periodic boundary conditions, and



Figure 1. Structure of the $Ca_2UO_2(CO_3)_3$ complex in water.

the cutoff was set as 12 Å for all nonbonded interactions. The long-range electrostatic interaction was calculated by means of Ewald summation with a 12 Å cutoff for the real space forces.⁴³ The Ewald sum parameters were chosen to achieve a relative error smaller than 10^{-6} for the electrostatic energy. The initial structure of each system was first minimized with 1000 steps of the steepest descent method, and then, the system was heated up from 100 to 300 K for 100 ps with a time step of 1 fs. Then, the system was equilibrated for 50 ns at 300 K, followed by a 50 ns production run from which the trajectory was sampled every 10 ps for analysis; the temperature was kept constant via the use of the Nosé–Hoover thermostat,⁴⁴ and the geometry of the water molecules was held fixed using the SHAKE algorithm.⁴⁵

To evaluate the long-time scale dynamics of the system, we ran a 600 ns simulation via the GPU-accelerated AMBER 14.0 package,⁴⁶ using the same parameters and setup as in the CPU-based LAMMPS MD simulation described in the preceding paragraph.

2.3. Quantum Chemistry Calculation. To validate the force field, quantum chemistry calculations were performed via the Gaussian 09 suite of programs.⁴⁷ The geometry of the complex was fully optimized with the B3LYP functional.^{48,49} The LANL2DZ basis set, which uses effective-core potentials to describe the inner core orbitals, was employed for uranium,⁵⁰ while for the remaining atoms 6-31G(d) was applied.⁵¹ During geometry optimizations, no symmetry or geometry constraint was imposed. Frequency calculations performed at the same theoretical level indicated that the structure obtained corresponds to energetic minima without imaginary frequency.

3. RESULTS AND DISCUSSION

The most important structural feature of the $Ca_2UO_2(CO_3)_3$ species is the binding between the two Ca^{2+} ions and the $[UO_2(CO_3)_3]^{4-}$ ion (Figure 1). The three carbonate groups bind to the uranyl group on the equatorial plane in a bidentate mode, and the two calcium ions are in the plane of the carbonate ions and bound to two oxygen atoms from two neighboring carbonate groups, consistent with the crystal structure of the naturally occurring mineral Liebigite $[Ca_2(UO_2)(CO_3)_3 \cdot 11H_2O]^{52}$ and fitting of the EXAFS data.^{22,24} Before we simulate this complex in seawater (section 3.3), we first validate our force field (section 3.1) and compare our simulation in pure water with previous simulations and experiments (section 3.2).

3.1. Validation of the Force Field. To validate our force field, we compared our force field parameters (MM) and the quantum mechanical (QM) calculations for Ca²⁺ and carbonate interaction: the Ca-O distance (2.14 Å) from our force field is close to that of QM calculation (2.13 Å) (Figure 2a). To further validate our parameters, the potential energy surface of the $Ca_2UO_2(CO_3)_3$ in a water cluster was scanned as a function of the U-Ca distance for both our force-field parameters and the B3LYP method (Figure 2b). One can see that the two curves agree quite well, though the difference becomes more apparent at larger U-Ca distances. The discrepancy may be due to the fact that we used the formal charge +2 for the Ca²⁺ ion and ignored charge transfer and polarization between Ca²⁺ and $[CaUO_2(CO_3)_3]^{2-}$ in the force-field curve, while they are included in the B3LYP curve. This deficiency of the force field approach is expected to be less an issue for the Na⁺ ion due to its smaller formal charge.

3.2. The Structure of the $Ca_2UO_2(CO_3)_3$ Complex in Pure Water. To further test our force-field parameters, we



Figure 2. Comparison between Gaussian (B3LYP) and LAMMPS (force field, MM): (a) Ca^{2+} and carbonate interaction; (b) the potential energy surface of the $Ca_2UO_2(CO_3)_3$ in a water cluster as a function of the U–Ca distance. Color code: U, yellow; C, gray; O, red; H, white.

Table 1. Comparison of Key Distances (in Å) for the $Ca_2UO_2(CO_3)_3$ Complex in Water among the Present Molecular-Mechanical MD Simulation (MM-MD-1) with Previous MM-MD (MM-MD-2), DFT-MD, QMCF-MD Simulations, and EXAFS Data

method	U–O _{eq}	U-O _{ax}	U-O _{dis}	U–Ca	U–C	ref
MM-MD-1	2.45	1.85	3.95	4.05	2.85	p.w.
MM-MD-2	2.43	1.83	3.97	4.00	2.88	26
DFT-MD	2.45 ± 0.12	1.85 ± 0.04	4.15 ± 0.14	4.07 ± 0.15	2.85 ± 0.10	31
QMCF-MD	2.47	1.73		4.04	2.93	27
EXAFS-1	2.45 ± 0.01	1.78 ± 0.01	4.11 ± 0.07	4.02 ± 0.02	2.89 ± 0.01	12
EXAFS-2	2.44 ± 0.07	1.81 ± 0.03	4.22 ± 0.04	3.94 ± 0.09	2.90 ± 0.02	22

investigated the $Ca_2UO_2(CO_3)_3$ complex in pure water, since there are quite a few previous experimental and computational studies that we can compare our work with. Table 1 compares the key distances in the $Ca_2UO_2(CO_3)_3$ complex among the present classical MD work (MM-MD-1), classical MD from Kerisit et al. (MM-MD-2),²⁶ DFT-MD from Priest et al.,³¹ quantum mechanical charge field MD (QMCF-MD) from Tirlor and Hofer,²⁷ and two EXAFS studies from Kelley et al.¹² (EXAFS-1) and Bernhard et al.²² (EXAFS-2). One can see that the general agreement among the different MD simulations is quite good for U-Oeq, U-Ca, and U-C distances. Although both MM-MD simulations underestimate the U-O_{dis} distance in comparison with DFT-MD and the experiments, our U-O_{dis} distance (3.95 Å) is consistent with that from Kerisit et al. (3.97 Å). Thus, this could be a deficiency of the force-field parameters that need to be improved further. Since this distance is not essential in comparison with the other distances, we consider our current force field parameters good enough for our purpose of exploring the solvation of the $Ca_2UO_2(CO_3)_3$ complex in water.

Figure 3 shows radial distribution functions (RDFs) of oxygen atoms from the water molecules around the two Ca^{2+} ions both separately and together. One can see that the solvation shell around Ca1 has an average Ca–O distance of 2.35 Å and the integrated RDF gives a coordination number of five. On the other hand, Ca2 has four water molecules in the solvation shell with an average Ca–O distance of 2.25 Å. Thus, together, the average coordination number of the two Ca²⁺ ions is 4.5 in terms of water molecules. This asymmetry between the two Ca²⁺ ions is consistent with the previous DFT-MD simulation.³¹

3.3. The Structure of the $Ca_2UO_2(CO_3)_3$ Complex in Seawater. The force field validation and the comparison with



Figure 3. Radial distribution function (left axis; black) and its integration (coordination number, CN; right axis; blue) of water oxygen atoms around Ca1 and Ca2 separately (top two panels) and together (bottom panel).

previous simulations and experiments of the $Ca_2UO_2(CO_3)_3$ complex in pure water discussed above gave us confidence in the force field parameters in our simulation. Now we apply these parameters to simulate the $Ca_2UO_2(CO_3)_3$ complex in seawater which has not been done before. To model the seawater, here we focus on Na⁺ and Cl⁻ ions which are the most abundant in the seawater. To mimic seawater salinity,⁴² we added 10 Na and 10 Cl ions in our 1000-water simulation box that contains one $Ca_2UO_2(CO_3)_3$ complex.

3.3.1. Na^+ and Cl^- lons around the $Ca_2UO_2(CO_3)_3$ Complex. We first examine the stability of the complex in seawater. We found that in our simulation time frame (100 ns) the structure of the $Ca_2UO_2(CO_3)_3$ complex is stable in the saline water, as evidenced by the sharp peak at about 4.05 Å in the RDF of Ca around U (Figure 4). Thus, we have further



Figure 4. Radial distribution functions (left axis) and coordination numbers (CN; right axis) of Ca^{2+} (black), Na^+ (red), and Cl^- (blue) around U.

confirmed the stability of the $Ca_2UO_2(CO_3)_3$ complex in seawater. Figure 4 also shows the RDFs of Na⁺ and Cl⁻ ions around the $Ca_2UO_2(CO_3)_3$ complex. One can see that the distributions of Na⁺ and Cl⁻ ions are not the same: Some Na⁺ ion is close to the $Ca_2UO_2(CO_3)_3$ complex with a mean Na–U distance of about 5.25 Å. In contrast, the Cl⁻ ion is much further away from U and the closest average U–Cl distance is about 11 Å. The coordination number of Na around U suggests that there is one Na⁺ ion that is very close to U (within 6.0 Å). To locate the close-by Na⁺ ion, we analyzed some snapshots of the trajectory. Figure 5 shows such a typical snapshot. One can see that the Na⁺ ion interacts with the complex indirectly through a water bridge (top arrow in Figure 5) to one of the two axial O atoms of the uranyl group. This interaction is also shown schematically in Figure 6a.



Figure 5. Snapshot of the $Ca_2UO_2(CO_3)_3$ complex in seawater, showing only water molecules directly interacting with the two Ca^{2+} ions and the Na⁺ ion. Arrows indicate the bridging water molecules.

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Figure 6. Schematics of (a) how the Na⁺ ion interacts with the uranyl group and (b) how the Na⁺ ion interacts with one Ca²⁺ ion of the Ca₂UO₂(CO₃)₃ complex.

3.3.2. The Interaction of the Na⁺ lon with Ca in $Ca_2UO_2(CO_3)_3$. The snapshot in Figure 5 also suggests that the close-by Na⁺ ion is closer to the Ca2 ion than Ca1. This interaction is also mediated via hydrogen bonding through two water molecules (indicated by the two arrows in Figure 5) and schematically in Figure 6b. In other words, the solvation environments around the two Ca²⁺ ions of the Ca₂UO₂(CO₃)₃ complex in seawater are not the same. To further examine this finding, we plot the RDFs of Na⁺ ions around the two Ca²⁺ ions separately (Figure 7). Indeed, one can see that the mean



Figure 7. Radial distribution functions (left axis; solid lines) and the coordination numbers (CN; right axis; dotted line) of Na around Ca1 (blue) and Ca2 (red).

distance between Ca2 and Na is much shorter than that between Ca1 and Na. The coordination number of Na around Ca2 is two within a sphere of 7.5 Å.

To analyze the impact of the Na⁺ ions on the solvation of the $Ca_2UO_2(CO_3)_3$ complex, we show the RDFs of Ca around U in both pure water (Figure 8a) and seawater (Figure 8b). One can see that the distribution of Ca1 around U is similar to that of Ca2 in pure water, with an average U–Ca distance of 4.05 Å. However, the distribution of Ca1 around U is narrower and higher than that of Ca2 in seawater; the distance between U and Ca1 at 4.05 Å is shorter than that between U and Ca2 at 4.25 Å. In other words, the closer interaction between Ca2 and Na (Figures 5 and 7) in seawater makes the interaction between Ca2 and U weaker. Hence, the presence of Na⁺ ions makes the asymmetry in binding of the two Ca²⁺ ions in the complex even greater.

3.3.3. Switching of the Na⁺ lon between the Ca²⁺ lons in $Ca_2UO_2(CO_3)_3$. To find out the residence time of the Na⁺ ion around one Ca²⁺ ion, we ran a 600 ns GPU-accelerated MD



Figure 8. Radial distribution function of Ca1 (blue) and Ca2 (red) around U: (a) in pure water; (b) in seawater.

simulation (Figure 9). We found that the Na^+ ion can switch between Ca1 and Ca2 with a lifetime of about 300 ns. Thus,



Figure 9. Change of the Ca1–Na (blue) and Ca2–Na (red) distances with time during the 600 ns dynamics of the Ca₂UO₂(CO₃)₃ complex in seawater; the Na⁺ ion here refers to the close-by Na⁺ ion, as shown in Figure 5.

over a long time (microseconds or longer), the two Ca^{2+} ions would look the same to the close-by Na^+ ion. However, with time-resolved experimental techniques such as time-resolved EXAFS that can observe bond length changes on the ps time scale,⁵³ one would be able to see the difference between the Ca^{2+} ions.

3.4. Implications of Our Simulation Results. The present simulations of the $Ca_2UO_2(CO_3)_3$ complex in seawater have several interesting implications. First, our work shows that there is one Na⁺ ion close-by to the complex, so the whole complex can be viewed as a Na[Ca₂UO₂(CO₃)₃] cation of +1 charge. This indicates that a negatively charged sorbent could more effectively attract the complex for binding. Indeed, the amidoxime-grafted polymer sorbent is usually preconditioned with a strong base such as KOH before deployment, which

deprotonates the functional groups and renders them anionic.⁵⁴ Second, the close-by Na⁺ ion also makes the two Ca²⁺ ions very different in binding inside the complex. Especially, the Ca²⁺ ion closely interacting with the Na⁺ ion will become easier to break away from the whole complex. We are currently simulating this process for a future publication.

4. SUMMARY AND CONCLUSIONS

We have simulated the $Ca_2UO_2(CO_3)_3$ complex in seawater by classical molecular dynamics simulation. We found that the structure of the $Ca_2UO_2(CO_3)_3$ complex is very stable in the model seawater. A Na⁺ ion was found to be closely associated with the $Ca_2UO_2(CO_3)_3$ complex at a U–Na distance of 5.25 Å, while the Cl ion is at least 11 Å away from U. The Na⁺ ion interacts indirectly with one axial oxygen atom of the UO_2 group bridged by a water molecule. In addition, the Na⁺ ion interacts more closely with one Ca^{2+} ion than the other. The present simulations revealed the key role of common ions such as Na⁺ in impacting the solvation, structure, and apparent charge of the $Ca_2UO_2(CO_3)_3$ complex in seawater. This knowledge will be useful in understanding the chemistry of uranium recovery from the sea by sorbents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b05452.

The force field parameters (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the US-DOE Office of Nuclear Energy - Nuclear Energy University Programs (Grant No. DE-NE0008397). W.W. was supported by a scholarship from the China Scholar Council.

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