Solvation of the vanadate ion in seawater conditions from molecular dynamics simulations

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Abstract

One of the current challenges present in uranium extraction from seawater is the competitive sorption of vanadium. But compared with uranium, much less is known about the solvation and speciation of the vanadate ion in seawater. Herein, we utilize both first principles molecular dynamics and classical molecular dynamics simulations to provide a microscopic insight into the solvation of the HVO_4^{2-} ion in pure water and in seawater. In pure water, we found that the dianion state is the most probable structure. But in a simulated seawater with 0.55 M NaCl, the NaHVO_4^- ion is most probable, followed by the neutral Na_2HVO_4 ; averaging over 100-nanosecond trajectory, the coordination number of Na^+ ions around V was found to be 1.5 within a radius of 4.0 Å. We found that the NaHVO_4^- ion can exist in two interchangeable states: a bidentate state where the Na^+ ion interacts directly with two vanadate oxo groups; a monodentate where the Na^+ ion interacts with only one vanadate oxo group. From this monodentate state, the Na^+ ion can further dissociate away with a free-energy barrier of 2.5 kcal/mol. Our work therefore demonstrates that Na^+ ions are closely associated with the vanadate species in seawater.

1. Introduction

When terrestrial nuclear resources become scarce and expensive due to increasing demand from more nuclear reactors, uranium recovery from seawater is needed. An estimated 4.5 billion metric tons of uranium in seawater theorizes an auspicious source of nuclear energy for many millennia [1-2]. Experimental screening methods have shown that the most promising method for uranium extraction from seawater entails an amidoxime-grafted polymer [3-4]. These poly(amidoxime) adsorbent material can be prepared with methods such as radiation-induced graft polymerization [5] and atom-transfer radical polymerization [6-7]. Although promising, these poly(amidoxime) sorbents attract more vanadium (V) than uranium from seawater [8-9]. Hence, one prevalent challenge of developing advanced sorbents for uranium from seawater is to enhance U/V selectivity while increasing the U uptake at the same time.

Vanadium exists in seawater at 1.7-2.3 ppb [10] with a predominate oxidation state of 5+ as a vanadate anion, [11] while uranium is found at 3.3 ppb as a uranyl ion [1]. The speciation of vanadate (V) in solution can involve complex equilibria between various mono- and oligonuclear clusters, critically depending on concentration and pH [12]. In seawater pH of 8.2, V(V) is present in equilibrium with two oxyanion forms of the orthovanadate, H_2VO_4^- and HVO_4^{2-} . Although a number of recent studies have shed important light on speciation of uranyl in different aqueous environments,[13-16] [17] little is known about speciation of vanadium species in seawater [12, 18-21]. Equilibrium complexation of HVO_4^{2-} has been previously determined from speciation calculations using free ion concentrations modeled for seawater and calculated stability constants at the appropriate ionic strength [20].

From the perspective of molecular simulations, Buhl et al. have investigated water effects on the ^{51}V NMR chemical shifts of H_2VO_4^- with Car-Parrinello molecular dynamics (CPMD) [22]. They found that the aqueous environment induced a conformational change on the two VOH moieties from C_2 symmetry to C_s symmetry and an exchange of water molecules between the first solvation sphere of H_2VO_4^- and the solution. Recent work with coupled cluster theory examined coordination number and prominent binding modes of water and other ligands to vanadyl (VO_2^+) [19]. From a single-crystal structure, Rao and coworkers have found a unique binding mode of vanadium to amidoxime-type ligand, where the V-O bonds are sequentially displaced by two amidoximate oxygens [23]. In addition, the oxovanadium (IV) and dioxovanadium (V) complexation with an amidoximate ligand has been studied computationally [18-19].

To our knowledge, the solvation of the HVO_4^{2-} ion, a major species of V(V) in seawater, has not been studied from a computational perspective, especially under the realistic solvation conditions. In this paper, our goal is to understand solvation of the HVO_4^{2-} ion in seawater from molecular dynamics simulations. We use both density functional theory molecular dynamics (DFT-MD) and classical molecular dynamics (CMD) simulations. Starting with Na_2HVO_4 , we first pry into dissociation of sodium ions. Next, we investigate how Na^+ ions interact with the vanadate ion. Furthermore, we calculate the potential of mean force of dissociating Na^+ from vanadate.

2. Computational methods

2.1. DFT-MD

First-principles molecular dynamic simulations based on density functional theory (DFT-MD) and Born–Oppenheimer approximation were carried out using Vienna Ab-initio simulation package (VASP) with plane wave basis and periodic boundary conditions [24-25]. The Kohn-Sham equations are solved with the all-electron projected augmented wave (PAW) method [26-27]. We have chosen the Perdew-Burke-Ernzerhof (PBE) functional of the generalized-gradient approximation (GGA) for electron exchange and correlation [28]. PBE is one of the most versatile GGA functionals, which provides a balance description for diverse molecules and materials, instead of being designed for a special class of molecules or interactions. The MD calculations were carried out at 298 K in a canonical NVT ensemble for a periodic cubic box that contains one Na_2HVO_4 complex in a fixed number of water molecules: we examined two concentrations with 50 and 100 water molecules. The temperature was kept constant via Nose-Hoover thermostat. A Verlet algorithm was used to integrate Newton’s equation of motion with a time step of 1 femtosecond. After equilibration at 298 K for 15 ps, another 15 ps of production run was followed. Graphical visualization and analysis of the liquid structure packing of the vanadate complex was examined with VMD [29].

2.2. Force field parameters

Generalized Amber force field (GAFF) format was used for the HVO_4^{2-} anion based on Gaussian09 calculations at the B3LYP level of theory with the 6-31G(d) basis sets for O and H and the LANL2DZ effective-core potential for V. Restrained electrostatic potential (RESP) charges were obtained from fitting into the electrostatic potential from Gaussian09 calculations. The van der Waals parameter for V was taken from the UFF while those for O and H from

AMBER [30]. Bond stretching, bond bending, and dihedral angle parameters were from fitting the potential energy curves from Gaussian09 scanning. All the force field parameters were provided in the supplementary materials (Fig. S1-S2; Table S1-S4). To validate these parameters, gas-phase bond lengths and angles of HVO_4^{2-} optimized with Gaussian09 at the B3LYP level and with AMBER using the determined force field parameters were compared in Table S5 of the supplementary materials. One can see an overall excellent agreement.

2.3. Classical MD

To investigate Na_2HVO_4 in water, both fresh and seawater were used: the fresh water model contains 1500 water molecules, while the seawater model contains additional 15 Na^+ and Cl^- ions, to mimic the salinity of seawater at 0.54 M NaCl. The TIP3P model was used for water, while the vdW parameters for Na^+ and Cl^- ions are the same as used previously [31]. Before an unconstrained production run, a sequence of constrained steps was employed to keep the sodium's localized around the vanadate complex: first, a simple minimization step with 2000 optimization steps; second, a NVT heating run from 0 K to 300 K for 100 ps with a 1fs time; next, a 10 ns NPT equilibration step for optimal volume and density. After an equilibration run, a 100 ns unconstrained production run was performed. For the production run, the temperature was kept constant using the Nose-Hover thermostat at 300 K, and the geometry of the water molecules was held fix with the SHAKE algorithm.

2.4. Umbrella Sampling

The potential of mean force (PMF) simulation via umbrella sampling was performed to obtain the free-energy profile of NaHVO_4^- dissociation into HVO_4^{2-} and Na^+ . A bias potential of 40 kcal/mol along the reaction coordinate (the Na-V distance, $r_{\text{Na-V}}$) drove the system from an initial NaHVO_4^- thermodynamic state to a final HVO_4^{2-} (product). Starting at $r_{\text{Na-V}}=3.0$ Å the system took intermediate steps of 0.1 Å that was covered by a series of windows performed at 10 ns time frame to a final 6.0 Å. All windows were then stitched together with the Weighted Histogram Analysis Method (WHAM) to generate the PMF.

3. Results and discussion

3.1. DFT-MD analysis of Na_2HVO_4 in water

To investigate the most stable vanadate structure, we simulated the interaction of vanadate in water with DFT-MD using the Na_2HVO_4 salt as the initial state. Fig. 1 shows a molecular model of Na_2HVO_4 : a tetrahedral structure that is charge balanced with two sodium ions within close proximity of vanadate's oxygens. Two types of vanadate oxygens exist: a protonated V-OH group and three unprotonated V-O groups. To study the solvation of sodium ions, we monitored the interaction of sodium ions to vanadium. In the 50-ps DFT-MD simulation, the dissolution of one sodium ion was observed. In the case of a simulation cell of 50 water molecules, the dissociating sodium departure is at about 6 ps (Fig. 2a), while in the case of 100 water molecules, the dissociation of the sodium is around 8 ps (Fig. 2b). One can also see that during the 50-ps time frame, one sodium ion remains associated with the vanadate anion as NaHVO_4^- . Limited by the accessible timescale of our DFT-MD simulation, we could not examine the dissolution of the remaining sodium ion from the brute-force DFT-MD simulation.

So we turn to classical MD which allows us to simulate Na_2HVO_4 in both pure water and seawater for a much longer time scale.

Fig. 1. A snapshot of Na_2HVO_4 used as the initial state in the simulation.

Fig. 2. V-Na1 and V-Na2 distances as a function of time, starting with Na_2HVO_4 (Fig. 1) in water, from DFT-MD: (a) in a simulation cell of 50 water molecules; (b) in a simulation cell of 100 water molecules.

3.2. Classical molecular dynamics of Na_2HVO_4 in pure water and seawater

To further follow the dissolution of the two sodium ions, we first explore the coordination number (CN) of sodium ions around the vanadate in a 100-ns time frame. In pure water (Fig. 3a), we found that both sodium ions can dissociate away and spend most of their time away from the HVO_4^{2-} anion (CN=0), while one sodium ion often associates with the HVO_4^{2-} anion (CN=1) and occasionally two sodium ions associate with the HVO_4^{2-} anion at the same time (CN=2). In seawater conditions (Fig. 3b), we found that both sodium ions can dissociate away from the HVO_4^{2-} anion (CN=0), but the most probable CN is between 1 and 2; sometimes there are three and even four sodium ions around the HVO_4^{2-} anion.

Fig. 3. Change of coordination number of Na^+ ions around V with time from 100-ns classical molecular dynamics simulations: (a) in pure water; (b) in NaCl solution.

Averaging over the 100-ns trajectories in Fig. 3, we obtained the radial distribution function (RDF) of sodium ions around V (Fig. 4). In both pure water and seawater, two peaks can be seen at 2.95 Å and 3.55 Å. These peaks represent two interacting sites around the vanadate complex. The snapshots in Fig. 5 show that the 2.95-Å site corresponds to a state where Na^+ interacting with two oxo groups (Na-O_V distances at about 2.42 and 2.54 Å), while the 3.55-Å site corresponds to a state where Na^+ interacting with one oxo group (Na-O_V distance at about 2.30 Å). Furthermore, CN from the integrated RDF shows that there is 0.3 Na^+ within a 4.0-Å radius around V in pure water, while there are 1.5 Na^+ around V in seawater.

Fig. 4. Radial distribution function (black) and coordination number (blue) of Na^+ ions around V averaged over 50-ns trajectories of classical molecular dynamics simulations: (a) in pure water; (b) in seawater.

Fig. 5. Snapshots of two states of NaHVO_4^- in pure water, corresponding to the two peaks in radial distribution function of Na around V in Fig. 4a: (a) $r_{\text{V-Na}} = 2.95 \text{ \AA}$; (b) $r_{\text{V-Na}} = 3.55 \text{ \AA}$. Na, yellow; V, gray; O, red; H, white.

3.3. Salt effect on hydrogen bonding

The CN of sodium ions around the vanadate anion is closely related to the hydrogen-bond network. So we explored the hydrogen bond lifetime of the vanadate anion in pure water and in seawater. To define the hydrogen bonds between water and the vanadate, we used geometrical criteria of the O-H...O distance within $3.0 \text{ \AA}$ and angles greater than 135° . From Fig. 6, one can see that a longer lifetime of hydrogen bonds around the vanadate anion is observed in pure water than in seawater. So the existence of a high concentration of NaCl disrupts the hydrogen-bond network around the vanadate anion, thereby accelerating the hydrogen-bond dynamics. This is consistent with our finding that 1.5 sodium ions are closely associated with the vanadate anion as shown in the RDF plot (Fig. 4b).

Fig. 6. Hydrogen bond autocorrelation function, $C_{HB}(t)$, for water molecules hydrogen-bonded to HVO_4^{2-} in pure water (black) and in seawater (red).

The effects of adding NaCl on the solvation of the vanadate can be further inspected from the number of hydrogen bonds around each V-O group. Table 1 shows the average number of hydrogen bonds over the 100-ns trajectory. In pure water, the oxo groups (O1, O2, and O3) of vanadate (Fig. 1) are calculated to accept about three hydrogens from surrounding waters, whereas the $-OH$ group (O4) of vanadate accepts two. In seawater, the average number of hydrogen bonds decreases by about 0.3 to 0.4, as the sodium ions now compete with water molecules for the interaction with the vanadate anion.

Table 1

Average number of hydrogen bonds with the V-O groups of vanadate over 100-ns trajectory

V-O	In pure water	In seawater
V-O1	3.03 ± 0.68	2.74 ± 0.89
V-O2	3.06 ± 0.65	2.77 ± 0.86

V-O3	3.08 ± 0.63	2.83 ± 0.83
V-O4	2.24 ± 0.69	1.86 ± 0.89

3.4. Free-energy dissociation of NaHVO_4^-

The DFT-MD and CMD simulations above show the high probability of the vanadate anion with a sodium ion associated with it to form NaHVO_4^- . To examine the free-energy profile for this sodium ion to dissociate away from the vanadate, we used umbrella sampling with our CMD simulations to obtain the potential of mean force (PMF). Fig. 7 shows the free-energy profile of NaHVO_4^- dissociation to HVO_4^{2-} and Na^+ in pure water and in seawater. One can see that the sodium ion in NaHVO_4^- exists in two states, one with V-Na distance of 2.95 ± 0.15 Å and the other with V-Na distance of 3.5 ± 0.25 Å, as already shown in the RDF plot in Fig. 4 and in the snapshots in Fig. 5. The two states are separated by a small barrier of ~ 0.7 kcal/mol. From the 3.5-Å state, the sodium ion can then break away with a barrier of 2.2 kcal/mol in pure water and 2.5 kcal/mol in seawater; both barriers are small enough that we observed many crossings in our brute-force MD simulations at 300 K (Fig. 2). At the transition state (Fig. 8a), the snapshot shows that the Na-O_v distance is at about 2.63 Å and the Na^+ ion is surrounded by five water molecules. Fig. 7 also shows that the associated state (NaHVO_4^-) is more stable than the dissociated state (HVO_4^{2-} and Na^+). In addition, this stability is enhanced in seawater than in pure water. In the dissociated state, the snapshot shows that the Na^+ ion is now surrounded by six water molecules (Fig. 8b).

Fig. 7. Free-energy profile from the potential of mean force of NaHVO_4^- dissociation to HVO_4^{2-} and Na^+ in pure water and in seawater. Reaction coordinate is defined as the V-Na distance.

Fig. 8. Snapshots along the potential of mean force (PMF) of NaHVO_4^- dissociating into HVO_4^{2-} and Na^+ : (a) transition state (at a Na-V distance of ~ 4.25 Å in Fig. 7); (b) after dissociation (at a Na-V distance of ~ 5.75 Å in Fig. 7). Na, yellow; V, gray; O, red; H, white.

4. Conclusions

In summary, we have examined the solvation of the vanadate anion (HVO_4^{2-}) with molecular dynamics simulations. Starting with Na_2HVO_4 , DFT-MD showed that one Na^+ ion quickly dissociates away within a few ps, while the second Na^+ ion remains associated within the timescale of 50 ps. Classical MD simulations on the time scale of 100 ns showed that the fully dissociated state (HVO_4^{2-}) is most probable in pure water, while in seawater NaHVO_4^- is the most probable state. Relaxation of hydrogen bonds around the vanadate anion was found to be faster in seawater than in pure water due to the disruption of the hydrogen-bond network by the Na^+ ions. Potential of mean force for NaHVO_4^- dissociation into HVO_4^{2-} and Na^+ ion revealed a smaller barrier of ~ 2.5 kcal/mol. Our simulations show the importance of Na^+ ions in the solvation and speciation of vanadate in seawater; this knowledge will be useful for further understanding of the uranium/vanadium selectivity in ligand binding and design for seawater uranium recovery.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/>.

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