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Understanding Arsenate Reaction Kinetics with Ferric Hydroxides

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Abstract

Understanding arsenic reactions with ferric hydroxides is important in understanding arsenic transport in the environment and in designing systems for removing arsenic from potable water. Many experimental studies have shown that the kinetics of arsenic adsorption on ferric hydroxides is biphasic, where a fraction of the arsenic adsorption occurs on a time scale of seconds while full equilibrium may require weeks to attain. This research employed density functional theory modeling in order to understand the mechanisms contributing to biphasic arsenic adsorption kinetics. The reaction energies and activation barriers for three modes of arsenate adsorption to ferric hydroxides were calculated. Gibbs free energies of reaction depended on the net charge of the complexes, which is a function of the system pH value. Physical adsorption of arsenate to ferric hydroxide proceeded with no activation barrier, with Gibbs free energies of reaction ranging from -21 to -58 kJ/mol. The highest Gibbs free energies of reaction for physical adsorption resulted from negative charge assisted hydrogen bonding between H atoms on the ferric hydroxide and O atoms in arsenate. The conversion of physically adsorbed arsenate into monodentate surface complexes had Gibbs free energies of activation ranging from 62 to 73 kJ/mol, and Gibbs free energies of reaction ranging from -23 to -38 kJ/mol. The conversion of monodentate surface complexes to bidentate, binuclear complexes had Gibbs free energies of activation ranging from 79 to 112 kJ/mol, and Gibbs free energies of reaction ranging from -11 to -55 kJ/mol. For release of arsenate from uncharged bidentate complexes, energies of activation as high as 167 kJ/mol were encountered. Increasingly negative charges on the complexes lowered the activation barriers for desorption of arsenate, and in complexes with -2 charges, the highest activation barrier was 65 kJ/mol. This study shows that the slow kinetics associated with arsenic adsorption and desorption can be attributed to the high Gibbs free energies of activation for forming and breaking bonds with the ferric hydroxide.

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SUPPORTING INFORMATION

Illustrations showing Hirshfeld⁵¹ atomic charges for uncharged binding site, uncharged monodentate complex, uncharged bidentate complex, transition state structures for forming the -1 charged monodentate complex and uncharged bidentate complex and table of ΔG_{f}^0 values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

INTRODUCTION

Arsenic is often present in contaminated groundwater due to weathering of rocks, industrial waste discharges and agricultural use of arsenical herbicides and pesticides.¹ Both arsenic(V) and arsenic(III) are strongly adsorbed by iron oxide minerals, and by amorphous ferric hydroxide coatings on soils and sediments.^{2–14} The strong adsorption of arsenic to ferric hydroxide is a significant natural attenuation mechanism for arsenic contamination in groundwater, and has also been exploited for removing arsenic from drinking water.¹⁵

Previous studies have shown that the adsorption mechanism involves the formation of inner-sphere complexes via ligand exchange with OH^- or OH_2 groups on ferric hydroxide.^{2,6,16} Investigators have used x-ray absorption fine structure (EXAFS) spectroscopy results along with structures derived from molecular modeling to infer the type of chemisorption complexes that form.^{17,18} Several investigators have reported that arsenate (HAsO_4^{2-}) forms both mono- and bidentate complexes with goethite ($\alpha\text{-FeOOH}$).^{12,13,19} In addition, Fendorf et al. reported that arsenate may form three types of complexes, monodentate, bidentate binuclear, and bidentate mononuclear with ferric hydroxides.¹⁴ The type of complex that formed was found to be dependent on the surface loading, with the bidentate complexes dominating at high surface loadings.^{13,14} Other investigators have concluded that monodentate complexes are unstable¹⁸, and that previously reported evidence for monodentate complexes can be attributed to a misinterpretation of the EXAFS results.¹⁶

The kinetics for adsorption and desorption of arsenate on ferric hydroxides affects the transport of arsenic in groundwater and also affects arsenic removal from drinking water using iron oxide-based adsorbents. Many studies have investigated the kinetics of arsenate adsorption to iron and aluminum oxides and have observed biphasic kinetics consisting of a fast adsorbing fraction and a slowly adsorbing fraction.^{19–22} The fast adsorbing fraction reacts on a time scale of less than 1 minute¹⁹, while the slow adsorbing fraction requires more than 162 hours to reach equilibrium.^{20,23} This phenomenon has been attributed to slow diffusional mass transport^{4,20,24}, heterogeneous adsorption sites²¹, the formation of surface precipitates²⁵, the rearrangement of surface complexes²⁶, and conversion of monodentate to bidentate complexes.¹⁹ Using a kinetic model developed for anion adsorption²⁷, Zhang and Stanforth concluded that slow adsorption was not due to diffusion, but rather to heterogeneity in surface site binding energy or to other rate controlling reactions.²¹

Studies investigating the release of arsenate from ferric hydroxides have used a variety of extractants, including phosphate or high pH solutions, to displace adsorbed arsenate.^{20,28,29} Fuller et al. reported that after raising the pH from 8 to 9, the system required ~100 hours to come within 5% of the equilibrium adsorption amount at pH=9, indicating a very slow release of adsorbed arsenate.²⁰ O'Reilly et al. reported that at a pH value of 6, a 6 mM phosphate solution was able to displace 35% of the adsorbed arsenate in a 24-hour period.²⁸ However, after the initial rapid release, the rate of release slowed dramatically, and after more than 150 days, approximately 40% of the adsorbed arsenic remained on the goethite. A general finding in these desorption studies is that only a small fraction of adsorbed arsenate is released using a competing adsorbate, such as phosphate or hydroxide ions. This has led

investigators to speculate that a fraction of arsenate adsorption to iron oxides may be irreversible.²³

The objective of this study was to investigate the reactions involved in arsenate adsorption and desorption from ferric hydroxides. Towards that end, density functional theory (DFT) simulations were used to calculate the energy changes and activation barriers associated with physical and chemical adsorption of arsenate to ferric hydroxides. The reaction energies calculated here are useful in interpreting a wide range of experimental results.

MATERIALS AND METHODS

DFT simulations were performed to determine the Gibbs free energy changes and Gibbs free energy activation barriers for arsenate adsorption to ferric hydroxides. Energies for physical adsorption, and for formation of mono- and bidentate surface complexes were calculated. Ferric hydroxides were simulated using clusters similar to those used in several previous studies.^{17,18,30} As illustrated in Figure S1 in the supporting information, the clusters consisted of two iron atoms in octahedral coordination with 10 oxygen atoms, with the general formula $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_7$. Clusters with different numbers of protons were also used in order to simulate binding sites with positive or negative charges.

DFT calculations were performed using the DMol3^{31,32} package in the Accelrys Materials Studio³³ modeling suite using a personal computer. All simulations were unrestricted spin, all electron calculations using double-numeric with polarization (DNP) basis sets³⁴, and the gradient corrected VWN-BP functionals^{35–37} for exchange and correlation. Implicit solvation was incorporated into all aqueous phase simulations using the COSMO-ibs³⁸ polarizable continuum solvation model. COSMO-ibs is based on the conductor like screening model³⁹ and can account for solute induced polarization of the solvent. In contrast to other widely used polarizable continuum models, COSMO-ibs can be used during geometry optimization of the solute, since it does not have the high computational costs and convergence problems of the widely implemented PCM model and its variants^{39,40,41,42} when performing geometry optimizations. In addition to the implicit solvation, all simulations also included one explicit water molecule in order to allow for hydrogen bonding and better outlying charge correction for negatively charged species.⁴³ Previous investigators have reported that inclusion of a single water molecule nearly always leads to better energies for charged species, but inclusion of multiple water molecules may yield results with considerably greater errors than those with no explicit water molecules⁴³.

The geometry of the binding sites were optimized without any geometry constraints. In order to simulate the binding sites being part of a larger ferric hydroxide structure, simulations that included bound arsenic species employed geometry constraints that fixed the positions of the six peripheral oxygen atoms that were not part of the binding reaction, as illustrated in Figure S1. This was necessary in order to avoid gross distortions of the dioctahedral geometry seen in previous investigations performed using similar ferric hydroxide clusters.⁴⁴ Frequency calculations were performed on geometry optimized structures without any constraints in order to determine zero point vibrational energies and thermal corrections. Transition state searches were performed using linear and quadratic

synchronous transit (LST/QST) methods⁴⁵ and refined using conjugate gradient energy minimization.⁴⁶ Transition states were confirmed by frequency analyses verifying that the single negative frequency corresponded to the normal mode along the reaction coordinate.

Gibbs free energy changes for the adsorption reactions were calculated using published literature values for the dissolved species and DFT calculated values for the complexes and binding sites. Standard Gibbs free energies of formation (ΔG_f^0) for the binding sites and arsenic complexes were determined from the DFT calculated formation energies (ΔG_f^{DFT}) by adjusting the vacuum scale to the standard thermodynamic and electrochemical energy scales. For uncharged structures, the ΔG_f^{DFT} values were converted to standard Gibbs free energies of formation (ΔG_f^0) by subtracting ΔG_f^{DFT} energies calculated for the elements in their natural state at 25°C and 1 atm. Energies for charged structures were adjusted to the electrochemical scale by adding 417 kJ/mol for the standard hydrogen electrode (SHE) reaction (ΔG_{SHE}^0) to the ΔG_f^{DFT} for all species with a -1 charge, and subtracting ΔG_{SHE}^0 for all species with a $+1$ charge.⁴⁷ The standard Gibbs free energies of formation (ΔG_f^0) used in all calculations are listed Table S1 in the supporting information. Based on previous research investigating similar systems, the ΔG_f^0 values calculated for the binding sites and surface complexes are conservatively expected to be accurate to within ± 20 kJ/mol.^{48,49} However, errors in calculating standard Gibbs free energies of reaction (ΔG_r^0) and Gibbs free energies of activation (E_a) are likely to be much smaller, since bias in the calculations would largely cancel because only differences in energy between similar structures are used to calculate these values. All energy values reported in the manuscript are Gibbs free energies.

RESULTS AND DISCUSSION

The ferric hydroxide clusters used in modeling the complexation reactions had charges of -1 ($\text{Fe}_2\text{O}_{10}\text{H}_{13}^{1-}$), 0 ($\text{Fe}_2\text{O}_{10}\text{H}_{14}$) or $+1$ ($\text{Fe}_2\text{O}_{10}\text{H}_{15}^{1+}$). The ΔG_f^0 for each cluster was used to calculate the speciation of the clusters as a function of the pH, as shown in Figure 1. The calculated pK_{a1} value for $\text{Fe}_2\text{O}_{10}\text{H}_{15}^{1+}$ was 7.78 and the pK_{a2} was 10.1. These values are close to experimental measurements for ferric hydroxide minerals, and yield a pH_{pznpc} (point zero net proton charge) value of 8.94, which is intermediate between the pH_{pznpc} for hematite (8.5) and goethite (9.4).⁵⁰ The similar pH_{pznpc} of the ferric hydroxide clusters to that for real ferric hydroxides indicates that the clusters bind H^+ ions similarly to real adsorbents. Figure S2 in the Supporting Information shows the Hirshfeld⁵¹ charges on each atom in the uncharged binding site.

Standard Gibbs free energies of reaction between arsenate and the ferric hydroxide clusters were calculated for physically adsorbed arsenate, a monodentate complex, and a bidentate, binuclear complex. The energies of for systems where arsenate does not interact with the ferric hydroxide cluster were calculated by energy minimization of systems where the nearest O atom of the arsenate species was fixed 20 Å away from the Fe atom of the binding site. Next, energies for physically adsorbed arsenate were calculated by energy minimization of the systems after removing the 20 Å fixed-distance constraint.

At neutral pH, the most prevalent arsenate species is HAsO_4^{2-} and the most prevalent binding site is $\text{Fe}_2\text{O}_{10}\text{H}_{15}^+$. Figure 2 illustrates HAsO_4^{2-} physically adsorbed to the binding site, which resulted in a net charge of -1 on the reaction product ($\text{Fe}_2\text{O}_{10}\text{H}_{15}-\text{HAsO}_4^-$). The overall Gibbs free energy change for this reaction was $\Delta G_r^0 = -58 \text{ kJ/mol}$. This is a highly exergonic value for physical adsorption, and likely resulted from the negative charge assisted hydrogen bonds (CAHB) formed between the two reactants. Negative CAHB are known to form between carboxylate and alkoxide ions and water⁵², and have been recently implicated as being responsible for the strong adsorption of carboxylate anions to organic matter in soils and sediments.⁵³ Figure 2 shows that there were three negative CAHBs formed upon physical adsorption of HAsO_4^{2-} to the binding site. The hydrogen bonding is indicated by electron withdrawal from the two O atoms in HAsO_4^{2-} . The Hirshfeld⁵¹ charges on the two unprotonated O atoms in the isolated HAsO_4^{2-} molecule increased from -0.627 to -0.46 and -0.43 , after forming the CAHBs. For reactions involving H_2AsO_4^- and $\text{Fe}_2\text{O}_{10}\text{H}_{15}^+$ to form a neutrally charged, physisorbed reaction product ($\text{Fe}_2\text{O}_{10}\text{H}_{15} - \text{H}_2\text{AsO}_4$), the physical adsorption energy reduced to $\Delta G_r^0 = -21 \text{ kJ/mol}$. Reaction of H_2AsO_4^- with a neutral binding site to form $\text{Fe}_2\text{O}_{10}\text{H}_{14}-\text{H}_2\text{AsO}_4^-$ had a similar adsorption energy of $\Delta G_r^0 = -20 \text{ kJ/mol}$.

Once physical adsorption occurs, an arsenate species may displace an OH^- or OH_2 from the binding site to form a monodentate surface complex, as illustrated in Figure 3. The shortest Fe-As distance in the -1 charged monodentate complex of $3.36 \text{ \AA}$ is slightly shorter than EXAFS observation of $3.60 \text{ \AA}$ that has been attributed to monodentate complexes.¹⁴ However, the shortest Fe-As distance in the uncharged monodentate complex is $3.52 \text{ \AA}$ (shown in Figure S3 in the supporting information), indicating that the charge on the complex affects the bond distances. This effect should be taken into account when using EXAFS spectra to determine binding modes. Formation of the monodentate complexes required passing through activation energy barriers, the magnitude of which depended on the net charge of the complex. Conversion of an uncharged physisorbed complex to an uncharged monodentate complex via the reaction: $\text{Fe}_2\text{O}_{10}\text{H}_{15} - \text{H}_2\text{AsO}_4 \rightarrow \text{Fe}_2\text{AsO}_{13}\text{H}_{15} + \text{H}_2\text{O}$, had a transition state that was 73 kJ/mol higher in Gibbs free energy than the physisorbed complex, as illustrated by the energy for the monodentate transition state (TS Mono-) species in Figure 4. Although there was a high activation barrier, conversion of the physisorbed complex into the monodentate complex was energetically favorable, with a reaction energy of $\Delta G_r^0 = -38 \text{ kJ/mol}$, as indicated by the energy of the Mono- species in Figure 4. Once formed, the monodentate complex may convert into a bidentate, binuclear complex, as illustrated in Figure 5. The average Fe-As distance in the uncharged bidentate complex of $3.23 \text{ \AA}$ is close to the $3.25 \text{ \AA}$ observed for bidentate, binuclear complexes in previous spectroscopic studies.¹⁸

The transition state for formation of the uncharged bidentate complex (shown in Figure S4 in the supporting information) had an energy that was 112 kJ/mol higher than the uncharged monodentate complex, as illustrated by the energy of the bidentate transition state (TS Bi-)

species in Figure 4. The overall Gibbs energy change for converting the neutral monodentate complex into a neutral bidentate complex was $\Delta G_r^0 = -55 \text{ kJ/mol}$.

The energy changes and activation barriers associated with formation of complexes with a -1 net charge are illustrated in Figure 6. The most notable differences between the -1 and the neutrally charged systems are the relatively higher energies for the mono- and bidentate complexes in the -1 charged system. In the -1 charged system, formation of the mono- and bidentate complexes from the noninteracting species were 15 and 35 kJ/mol less energetically favorable than their neutrally charged counterparts. This finding is consistent with experimental observations of weaker adsorption with increasing pH that is observed for arsenate.⁹ In addition to weaker adsorption for the -1 charged complexes, the activation barriers for converting the physisorbed complex into the monodentate complex was only 62 kJ/mol, which is 10 kJ/mol smaller than the activation barrier for the uncharged complex. The transition state structure for formation of the -1 charged monodentate complex is shown in Figure S5 in the supporting information. The activation barrier associated with formation of the -1 charged bidentate complex was 100 kJ/mol, which is 12 kJ/mol smaller than the activation barrier for the uncharged complex.

The relative energies of the mono- and bidentate complexes were also affected by the net charge on the system. The -1 charged bidentate complex was only 36 kJ/mol lower in energy than the -1 charged monodentate complex, whereas in the neutral system, the bidentate complex was 55 kJ/mol lower in energy than the monodentate complex. For systems with a -2 net charge, the bidentate complex was only 11 kJ/mol lower in energy than the monodentate complex. This trend in relative favorability between the mono- and the bidentate complexes is consistent with several experimental observations showing increasing importance of the monodentate complexes with decreasing surface loadings.^{12–14} In these studies, the surface loadings of arsenate were controlled by the pH, and thus the lower surface loadings were the result of the higher pH values.^{13,14} Results from the DFT calculations suggest that the factor influencing the relative preponderance of different binding modes is the pH rather than the surface loading.

Although the bidentate complexes had lower energies than the monodentate complexes, in real systems, ligands adsorbed to neighboring sites may prevent conversion of mono- to bidentate complexation. Thus, there may be both mono- and bidentate complexes present at the same time. The low energies of both the mono- and bidentate complexes, as compared to the initial reactants, helps explain the kinetic hysteresis and the strong resistance to release of arsenate in competitive displacement experiments.^{20,28,29} The release of arsenate adsorbed via a bidentate complex would first require conversion into a monodentate complex. To convert an uncharged bidentate complex into an uncharged monodentate complex requires passing through an energy barrier of 167 kJ/mol, as illustrated by the energy difference between the Bi- and TS Bi- species in Figure 4. To convert an uncharged monodentate complex into H_2AsO_4^- physisorbed to $\text{Fe}_2\text{O}_3\text{H}_{15}^{1+}$ requires passing through an activation barrier of 110 kJ/mol, as illustrated in Figure 4. Thus, even for a ligand that strongly binds to ferric hydroxide, such as phosphate, the kinetics of the displacement process should be slow due to the high activation barriers. This may explain the observation

that 40% of the arsenate adsorbed on goethite could not be displaced by a 6 mM, pH=6 phosphate solution, even after 150 days.²⁸

As the charge on the bidentate complex decreased from 0 to -1, the barrier to convert the bidentate to the monodentate complex decreased from 167 to 134 kJ/mol, as illustrated in Figure 6. For a system with a -2 net charge, the activation barrier to go from bi- to monodentate decreases further to only 65 kJ/mol. This trend of decreasing activation barriers for conversion of bi- to monodentate complexes suggests that with increasing pH values (and concomitantly, increasingly negative charges on the surface complexes), the rate of arsenate release from ferric hydroxides should increase. This is consistent with past experimental observations. Fast rates of arsenic release from ferric hydroxides have been observed in ~1 M NaOH solutions when regenerating ferric-hydroxide based adsorbents.⁵⁴ In these studies, a large fraction of the adsorbed arsenate was released over a period of 2 to 3 hours. Although the rate of arsenate release was much slower than the adsorption rate, it was several orders of magnitude faster than release rates observed at a pH value of 9.²⁰

Understanding the mechanisms controlling the kinetics of arsenic adsorption is important for assessing the transport and fate of arsenic in the environment. The modeling data from this study can be used to better understand previously published experimental results. Because the physical adsorption reaction does not have an activation barrier, it should proceed rapidly. This is consistent with observations of a fast adsorbing fraction of arsenate on ferric hydroxides. The zero activation barrier is also consistent with the work of Grossl et al. who used a pressure jump relaxation technique to show that there was an adsorption reaction of arsenate on goethite with a time constant less than 50 ms.¹⁹ The high activation barriers for forming the mono- and bidentate complexes helps explain the slow approach to equilibrium for arsenic uptake by ferric oxides. This slow approach to equilibrium has often been attributed to mass transfer effects^{4,20} and surface precipitation phenomena.²⁵ The high activation barriers for formation of the mono- and bidentate complexes is consistent with the observations of Catelano et al. who reported that 25% of the arsenate adsorbed on hematite was not coherently adsorbed, and was likely bound in outer-sphere complexes.⁵⁵ The slow release of arsenate from ferric hydroxides has also been attributed to mass transfer effects,^{20,23} however, they can also be explained by the high activation barriers for the reactions required for arsenic desorption. The slow kinetics of these reactions must be taken into account in transport modeling.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The fraction of ferric hydroxide clusters with -1 , 0 and $+1$ charges as a function of pH.

Figure 2.

Physical adsorption complex resulting from adsorption of HAsO_4^{2-} on $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. Negative charge assisted hydrogen bonds (CAHB) are indicated by dashed lines showing the internuclear distances between atoms in units of Å. Atom key: As-purple; Fe-blue; O-red; H-white.

Figure 3. Monodentate complex with a net charge of -1 . Atom key: As-purple; Fe-blue; O-red; H-white.

Figure 4. Relative standard Gibbs free energies of formation for complexes with a net charge of zero. The zero of the energy scale is the sum of the Gibbs free energies for the isolated H_2AsO_4^- and $\text{Fe}_2\text{O}_{10}\text{H}_{15}^+$ species. Shown are energies for the physical adsorption complex (Phys), the transition state for forming the monodentate complex (TS Mono-), the monodentate complex (Mono-), the transition state for forming the bidentate complex (TS Bi-) and the bidentate complex (Bi-).

Figure 5. Bidentate complex with a net charge of 0. Atom key: As-purple; Fe-blue; O-red; H-white. Hirshfeld⁵¹ atomic charges for this structure are shown in Figure S6 in the supporting information.

Figure 6.

Relative standard Gibbs free energies of formation for complexes with a net charge of -1 . The zero of the energy scale is the sum of the Gibbs free energies for the isolated H_2AsO_4^- and $\text{Fe}_2\text{O}_{10}\text{H}_{14}$ species. Shown are energies for the physical adsorption complex (Phys), the transition state for forming the monodentate complex (TS Mono-), the monodentate complex (Mono-), the transition state for forming the bidentate complex (TS Bi-) and the bidentate complex (Bi-).