Competitive Arsenate and Phosphate Adsorption on Ferrihydrite as Described by the CD-MUSIC Model

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ABSTRACT: The solubility and bioavailability of arsenic in the environment are to a large extent governed by adsorption reactions with iron (hydr)oxides, the extent of which is affected by competitive interactions with other ions, for example, phosphate. Here, batch experiments were performed with ferrihydrite suspensions to determine the adsorption of arsenate [As(V)] and phosphate (PO₄) at different As(V)−PO₄ ratios. A surface complexation model based on the Charge Distribution MUltisite Ion Complexation (CD-MUSIC) concept (the "Ferrihydrite CD-MUSIC model") was developed to describe these interactions in a way consistent with results from spectroscopic studies. For this purpose, several previously published data sets on As(V) and PO₄ adsorption in ferrihydrite suspensions were reviewed, including a number of systems containing other major ions (CO₃²⁻ and Ca²⁺), and new surface complexation constants were derived. During model development, it was found that the inclusion of ternary complexes was not needed to describe the observed Ca²⁺−PO₄ interactions. For both As(V) and PO₄, the resulting model predicts the presence of corner-sharing bidentate complexes as well as monodentate complexes, with the latter being important particularly at low pH. The experimental results showed that As(V) and PO₄ displayed similar adsorption patterns in the single-ion systems studied, which were conducted using a constant anion-to-Fe ratio of 0.2. Even so, As(V) was preferentially adsorbed over PO₄ in competitive systems, particularly at low As(V)-to-PO₄ ratios when the K_d values for As(V) were up to 2.1 times as high as those for PO₄. The model, which described these patterns very well, suggests that adsorbed As(V) consists of a larger fraction of bidentate complexes than in the case of PO₄. This causes a flatter adsorption isotherm for As(V), which leads to a stronger As(V) adsorption as the As(V)-to-Fe ratio decreases, compared to that for PO₄.

KEYWORDS: ferrihydrite, phosphate, arsenate, surface complexation modeling, CD-MUSIC, competitive binding

INTRODUCTION

Iron (hydr)oxides have long been known for their high reactivity toward the environmentally important arsenate [As(V)] and orthophosphate (PO₄) oxyanions. Ferrihydrite, in particular, is an excellent adsorbent due in part to its very high specific surface area (SSA). In freshly prepared suspensions of 2-line ferrihydrite, the SSA can range from 500 to 800 m² g⁻¹. Other factors leading to the high reactivity toward As(V) and PO₄ include a relatively high point of zero charge at around 8.1 and a high concentration of singly coordinated oxygens on the surface, resulting from a structure where relatively symmetrical iron(III) octahedra and tetrahedra, where the two latter structures are depleted from the surface.

In single-ion systems, that is, laboratory systems in which only one oxyanion is allowed to react with pure ferrihydrite or goethite, As(V) and PO₄ are adsorbed to about the same extent across a wide range of pH values, which can create the...
impression that they are adsorbed in an identical fashion. However, in early works, it was observed that when both As(V) and PO₄ are present in the same suspensions, preferential adsorption of As(V) is observed.⁹ Similar observations were made also more recently.⁹⁻¹¹ Despite the potential importance of this effect for correctly simulating, for example, levels of dissolved As(V) in the environment, so far there have been relatively few attempts in describing the preferential adsorption of As(V) on ferrihydrite in a quantitative manner that allows existing models, for example, surface complexation models (SCMs), to account for this.

Any differences in the binding strength of As(V) and PO₄ are probably related to differences in coordination at the surface. As concerns As(V), most results from extended X-ray absorption fine-structure (EXAFS) spectroscopy show As(V) to predominantly form corner-sharing (Cc) surface complexes on ferrihydrite and goethite, in which As(V) binds to two adjacent iron(III) octahedra.¹¹⁻¹⁶ This also agrees with molecular orbital (MO) calculations, applying density functional theory (DFT), which suggest that this coordination geometry is the most thermodynamically stable.¹⁷ However, the presence of edge-sharing (Ec) complexes has also been reported in a few publications.¹⁸⁻¹⁹ Moreover, monodentate complexes have been identified by attenuated total reflection (ATR)⁻Fourier transform infrared (FTIR) spectroscopy.²⁰⁻²² If present at relatively low concentrations, such complexes are difficult to identify with EXAFS spectroscopy due to the weak second-shell Fe−As interactions of such complexes. Still, in a few EXAFS studies, there was evidence for the presence of monodentate complexes.²²⁻²³ For PO₄, the composition of surface complexes is more uncertain, in part due to the low molar mass of P, which makes EXAFS more difficult. However, Khare et al.²³ obtained X-ray absorption near-edge structure (XANES) evidence for a predominance of bidentate complexes on ferrihydrite at pH = 6. The presence of corner-sharing bidentate complexes on ferrihydrite between pH 3 and 8 has been shown by atomic pair distribution function analysis.²⁴ Ari and Sparks²⁵ used ATR−FTIR spectroscopy to conclude that nonprotonated bidentate complexes were likely dominant at pH > 7.5, whereas the data at pH < 7.5 could be described by different combinations of monodentate and bidentate complexes. On the other hand, Persson et al.²⁶ obtained FTIR spectra suggesting a predominance of monodentate complexes on goethite. Another study using ATR−FTIR suggested that PO₄ adsorption on iron (hydr)oxides can occur via a range of different mechanisms (monodentate/bidentate binding) that depend on the crystal faces present in the individual oxide preparation.²⁷

Further insight into the likely mechanisms governing the interaction between As(V) and PO₄ can come from applying SCMs. Over the years, a number of models have been used for describing ion adsorption onto ferrihydrite. Examples include the generalized two-layer model and versions thereof,²⁸⁻³⁰ the extended triple-layer model (ETLM),²⁹ the Charge Distribution Multisite Ion Complexation (CD-MUSIC) model.³⁰⁻³¹ As shown in many papers, these SCMs can describe the data of single-ion systems well. The challenge is to describe also competitive systems, with two or more interacting ions in the same system, in a consistent manner, which is commonly the case in the environment. It can be argued that if SCMs are to be used to infer anything about adsorption mechanisms, they should be shown to work not only for single-ion systems but also for various types of multicomponent systems.

Many attempts have been made to test SCMs in binary systems, with mixed results. One example is the work of Kanematsu et al.,³² who used the ETLM to simulate As(V) adsorption to goethite in the presence of PO₄ or Ca²⁺. Although As(V) was well described in single-ion systems, and also worked well to describe As(V) in binary systems with PO₄, the effect of Ca²⁺, causing an enhanced As(V) adsorption, could not be correctly captured by the model. Furthermore, almost all SCMs, including the previous version of our own CD-MUSIC model for ferrihydrite,³³ fail when applying them to the binary PO₄−CO₃ systems of Mendez and Hiemstra.³⁴ Recently, Hiemstra and Zhao³¹ moved forward with an updated Ferrihydrite CD-MUSIC model that divides the singly coordinated =FeOH sites into two groups, one that is able to form ³Cc complexes and one that can form ²Ec complexes, whereas both groups can form monodentate complexes. This model was used to investigate PO₄ adsorption as affected by the presence of Ca²⁺, Mg²⁺, and CO₃²⁻.³⁴⁻³⁶ It was concluded not only that a model in which PO₄ was bound as a mixture of monodentate and bidentate complexes worked well to describe these interactions but also that ternary Ca−PO₄−Fh and Mg−PO₄−Fh (Fh is ferrihydrite) complexes needed to be accounted for in the modeling. As this model has shown to be able to handle competitive interactions in a better way than previous models, it serves as a starting point for the modeling exercise in the current paper.

Although the competition between As(V) and PO₄ on ferrihydrite has been studied previously,²³⁻³⁶ these data were obtained only over a relatively limited range of conditions and were often incomplete, for example, no PO₄ data for single-ion systems were collected in the two latter studies, which makes it difficult to properly evaluate As(V)−PO₄ competition with SCMs. The current work supplies data for the competitive interactions of As(V) and PO₄ on ferrihydrite over a wider range of conditions by varying the As/P ratio in the system. The Ferrihydrite CD-MUSIC model is then optimized for single-ion systems of As(V), PO₄, Ca²⁺, and CO₃²⁻, considering also the model performance in binary systems. Model parameters were optimized in an iterative process where the goal was to arrive at a consistent model able to describe ion adsorption across a wide range of conditions. The resulting model was then applied to simulate the interactions in competitive systems consisting of As(V), PO₄, and ferrihydrite. The overall aim of this work was to assess the extent of preferential As(V) adsorption over PO₄ and to obtain clues on the mechanisms involved. As shown later, the model suggests that the observed fractionation effect is due to the higher proportion of monodentate complexes in the case of PO₄. Moreover, our model suggests that it is not necessary to account for ternary complexes to describe the interaction between PO₄ and Ca²⁺ on ferrihydrite.

## MATERIALS AND METHODS

**Ferrihydrite Synthesis.** The procedure for the synthesis of ferrihydrite suspensions has been detailed earlier.³³⁻³⁷ Briefly, 2-line ferrihydrite was synthesized with a method similar to the one described by Schwertmann and Cornell,³⁸ in which a solution containing 36 mM Fe(NO₃)₃ and 12 mM NaNO₃ was brought to pH 8.0 after dropwise addition of 4 M NaOH, after which the suspension was aged for 18 h. Before the start of the batch experiments, the suspension was brought back to pH 4.6
using 1 M HNO₃ and then shaken vigorously on a magnetic stirrer for at least 15 min to remove excess CO₂. Fe(III) oxide formed by this procedure has been confirmed to consist of 2-line ferrihydrite, and the SSA has been estimated to be 611 m² g⁻¹.¹¹

**Batch Experiments.** All reacted suspensions contained a background electrolyte of 0.01 M NaNO₃. In one set of experiments carried out by Carin Sjöstedt at the Swedish University of Agricultural Sciences, As(V) adsorption as a function of pH was studied by mixing an amount of ferrihydrite stock suspension with NaNO₃ in a 40 mL polypropylene centrifuge bottle to which a certain volume of stock solution (18 mM Na₂HAsO₄) was added to produce the desired concentration (Table S3 and Figure S3f). Different additions of 0.01 M HNO₃ or 0.01 M NaOH were used to produce a range of pH values between pH 3 and 9. In another set of experiments conducted by the main author, the competition between As(V) and PO₄ was studied in a similar way using a fixed ferrihydrite concentration (as 1 mM Fe). Five different combinations of As(V) and/or PO₄ were used, that is, (i) 200 μmol L⁻¹ As(V); (ii) 200 μmol L⁻¹ PO₄; (iii) 100 μmol L⁻¹ As(V) + 100 μmol L⁻¹ PO₄; (iv) 160 μmol L⁻¹ As(V) + 40 μmol L⁻¹ PO₄; and (v) 40 μmol L⁻¹ As(V) + 160 μmol L⁻¹, using stock solutions of 6 mM Na₂HAsO₄ and 6 mM NaH₂PO₄. To ensure maximum consistency between the series, the whole set of experiments was carried out with the same ferrihydrite batch and at the same time (1–2 July 2021). In all experiments, the suspensions were shaken on an end-over-end shaker at 22 °C for 24 h prior to centrifugation and filtration using 0.2 μm single-use Acrodisc PF filters (Pall Corporation, Ann Arbor, MI, USA). The pH was measured on unfiltered samples using a Radiometer PHM93 pH meter equipped with a combination electrode (Radiometer Analytical SAS, Lyon, France). The filtered samples were acidified to 1% HNO₃ before determination of As and P with inductively coupled plasma–optical emission spectrometry using a Thermo iCAP 6300 instrument (Thermo Fisher Scientific, Waltham, MA, USA). No unexpected or unusually high safety hazards were encountered during these experiments.

**Ferrihydrite CD-MUSIC Model.** The version of the CD-MUSIC model used here employs the same division of sites between singly and triply coordinated groups as the model by Hiemstra and Zhao,³¹ that is, with site densities of 5.8 and 1.4 sites nm⁻², respectively (Table 1). The singly coordinated sites are divided into two groups, one able to form edge-sharing and the other able to form corner-sharing bidentate complexes, here referred to as FeOeH and FeOeH. These have site densities of 3.0 and 2.8 sites nm⁻², respectively. Moreover, within each group, there are subgroups of high-affinity sites, referred to as FeOeH(h) and FeOeH(h), which both have a site density of 0.058 sites nm⁻². The latter assignment differs from that by Mendez and Hiemstra,³²,³³ who only considered FeOeH(h) having a site density of 0.32 sites nm⁻². All singly coordinated sites (i.e., both FeOeH and FeOeH, the sum of which is simply referred to as FeOeH) are able to bind monodentate complexes. The triply coordinated FeO sites do not form inner-sphere surface complexes in the model but may form outer-sphere complexes with an equal affinity to that of the FeOeH sites.

Furthermore, the model uses equations that relate the molar weight and the Stern layer capacitances C₁ and C₂, to the SSA, reflecting the nanoparticle dimensions of ferrihydrite assuming a spherical geometry⁴⁹ (see the Supporting Information). Hence, the model used in this paper simulates the acid–base characteristics of Fh in an identical manner as in the cited papers, and therefore, the same equilibrium constants for proton binding and ion-pair formation were used (see Table S1, Supporting Information).

**Model Application.** The Ferrihydrite CD-MUSIC model was optimized for As(V), PO₄, Ca²⁺, and CO₃²⁻ using data from single-ion systems. For this purpose, the available literature was screened for published data that fulfilled the following criteria: (i) 2-line Fh should have been used in the experiments. If this was not confirmed in the study, the synthesis process should at least have been well described and consistent with the formation of 2-line Fh. (ii) The data should indicate an SSA of at least 500 m² g⁻¹. Lower SSAs often result from drying/freeze-drying the Fh product, leading to aggregation. Because the aggregated Fh may disaggregate to an unknown extent during equilibration, this leads to difficulties with the data interpretation. (iii) An equilibration time of >2 h should be used as the observed adsorption may depend on this parameter.¹³¹ Finally, (iv) only “adsorption edge” data were included, in which the adsorption was studied as a function of pH. Moreover, because the Fh synthesis conditions may vary, the SSA may vary slightly and can be treated as an adjustable parameter to fit PO₄ or As(V) adsorption data at high surface coverage.¹⁹ In the current study, the same SSAs were used as those in the recent applications of the CD-MUSIC model for Fh, and some additional SSAs were adjusted from the default value of 611 m² g⁻¹ to improve the fit at high surface coverage (for values cf. Tables S2–S5).

The selected data sets are described in the Supporting Information in Tables S2 (PO₄), S3 [As(V)], S4 (Ca²⁺), and S5 (CO₃²⁻). For PO₄, 18 adsorption edges from eight studies were included. All were studies from the Wageningen and Uppsala research groups, including data from two MSc theses, which have been shown earlier.³³ For AsO₄, 30 adsorption edges from eight studies were processed during model fitting. However, one data point (“outlier”) from the data set of Dixit and Hering³⁶ was excluded from optimization as it affected the optimized model to an unreasonable extent (Figure 2 and Table S3). For Ca²⁺ and CO₃²⁻, fewer studies met the criteria; for Ca²⁺, there were four studies with 25 adsorption edges; and for CO₃²⁻, only two studies with 5 adsorption edges. The surface complexations constants were obtained by model fitting, which was carried out with the Visual MINTEQ 4.0-PEST coupling³⁴,³⁵ using % adsorbed as the fitting variable and by maximizing the correlation coefficient R, which is a goodness-of-fit parameter reported by PEST.¹⁵ The aqueous speciation was modeled using the standard thermodynamic database of Visual MINTEQ (Table S6).³⁶ The Davies equation was used for activity corrections, except for systems with ionic strengths ≥0.5 mol L⁻¹, for which specific ion-interaction theory (SIT) was used.⁴⁶ In the

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**Table 1. Sites in the Ferrihydrite CD-MUSIC Model**

<table>
<thead>
<tr>
<th>site</th>
<th>site density (sites nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOeH</td>
<td>2.942</td>
</tr>
<tr>
<td>FeOeH(h)</td>
<td>0.058</td>
</tr>
<tr>
<td>FeOeH</td>
<td>2.742</td>
</tr>
<tr>
<td>FeOeH(h)</td>
<td>0.058</td>
</tr>
<tr>
<td>FeO</td>
<td>1.4</td>
</tr>
</tbody>
</table>
modeling, we used the MO/DFT-calculated charge distribution (CD) factors of Huisman and co-workers as a starting point, but where relevant, these were adjusted for a better fit, while keeping to the guidelines defined by Rietra et al. They observed Fe(III) phosphate precipitation in the mmol range. Hence, for the single-ion systems of Antelo et al.,7,48 to which PO4 or As(V) had been added, much improved model predictions of the adsorption isotherms were obtained when assuming that the SSA was variable. To derive such a model, the SSA was fitted for the PO4 adsorption isotherms determined at pH 4.5, 7, 8, and 9.48 Based on the resulting SSA values (250, 300, 350, and 400 m2 g−1), respectively, a second-order polynomial was derived to predict the variation of SSA with pH:

$$\text{SSA (m}^2\text{g}^{-1}) = 6.243 \times (\text{pH})^2 - 50.52 \times \text{pH} + 350.6$$

(1)

This equation was applied to all model predictions of Antelo et al.’s7,48 data on PO4 and As(V) adsorption in single-ion and binary systems as shown in this paper.

In the modeling, it was assumed that the formation of Fe(III) phosphate and arsenate minerals (e.g., strengite and scorodite) was insignificant. Although their solubility products were exceeded in some data sets, the results did not suggest any involvement of such a mineral phase. Recently, Wang et al. used P K-edge XANES spectroscopy to study PO4 sorption mechanisms in similar batch experiments with ferrihydrite. They observed Fe(III) phosphate precipitation in the mmol

### Table 2. Best-Fit Results for Surface Complexation Reactions in the Ferrihydrite CD-MUSIC Model

<table>
<thead>
<tr>
<th>ion, model</th>
<th>no. of data points</th>
<th>surface complex</th>
<th>no. of H+ in the reaction</th>
<th>(\Delta z^0, \Delta z^1 )</th>
<th>(\log K^\infty)</th>
<th>same for high</th>
<th>PEST (R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsO43−</td>
<td>317</td>
<td>(\equiv\text{FeOAsO}_2\text{OH})1/2−</td>
<td>2</td>
<td>(0.4, −0.4)</td>
<td>29.01 ± 0.14</td>
<td>y</td>
<td>0.990</td>
</tr>
<tr>
<td>Ca2+</td>
<td>215</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO32−</td>
<td>70</td>
<td>(\equiv\text{FeO}_2\text{CO})−</td>
<td>2</td>
<td>(0.5, −0.5)</td>
<td>21.60 ± 0.06</td>
<td>y</td>
<td>0.961</td>
</tr>
<tr>
<td>PO43−</td>
<td>235</td>
<td>(\equiv\text{FePO}_2\text{OH})1/2−</td>
<td>3</td>
<td>(0.4, −0.4)</td>
<td>30.32 ± 0.08</td>
<td>y</td>
<td>0.995</td>
</tr>
</tbody>
</table>

a The stoichiometry of H+ in the surface complexation reaction using \(\equiv\text{FeOH}\)1/2 as the surface component. b The charge of charge in the 0 and 1 planes, respectively (CD factors).  

Figure 1. pH-dependent As(V) and PO4 adsorption to ferrihydrite; \(I = 0.01 \text{ M NaNO}_3, \text{Fe} = 1 \text{ mM}, \text{total P} + \text{As} = 0.2 \text{ mM. Left: arsenate adsorption at different molar As/P ratios. Right: phosphate adsorption at different P/As molar ratios.}"

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range (for PO₄) in combination with low pH values. All data treated in the current study were in the sub-mmol L⁻¹ range except for a few data points of Hiemstra and Zhao,³¹ for which the pH was very high (>10.5), making Fe(III) phosphate precipitation unlikely. For As(V), the situation is less clear. For some of the treated data sets, As(V) was in the mmol L⁻¹ range (Figure S3), but since As(V) sorption could be described by a consistent set of adsorption parameters across all data sets, we consider that the formation of Fe(III) arsenate phases is unlikely/not significant.

Furthermore, for the binary systems of Ca²⁺−PO₄ and Ca²⁺−As(V) with Fh, the possible precipitation of amorphous Ca₃(PO₄)₂ × nH₂O (ACP) or Ca₃(AsO₄)₂ × nH₂O (ACA) phases was considered. For ACP, a log Kₛ of −27.94 was inferred from a study with filter materials used for wastewater treatment.⁴⁹ In the Fh systems analyzed in the current study, a high solubility is likely due to the shorter equilibration time. We chose a log Kₛ of −27 and −27.5 for the data of Antelo et al.⁷ and Mendez and Hiemstra,²⁵ respectively, judging from the shape of the adsorption edges at high pH. For similar reasons, a log Kₛ of −20.5 was selected for ACA, which is slightly higher than the literature value of −21.14.⁵⁰

### RESULTS AND DISCUSSION

**Batch Experiment Results.** Although As(V) and PO₄ were adsorbed equally strongly across the studied pH range in single-ion systems, significant fractionation of As(V) over PO₄ was observed in binary systems, particularly at the low As/P ratios (Figure 1). In single-ion systems at pH 5.8, the Kₛ value of PO₄ (defined by the ratio of adsorbed to dissolved PO₄) was slightly higher than the Kₛ value of As(V), that is, 27,800 and 25,800 L kg⁻¹, respectively. However, in binary systems at an As/P ratio of 4 and under similar pH conditions (5.6), the Kₛ value was 1.3 times higher for As(V) than it was for PO₄. When the As/P ratios decreased further to 1 and 0.25, the Kₛ values of As(V) were 1.5 and 2.1 times higher, respectively (the pH values were 5.8 and 5.9). This supports earlier studies in which similar fractionation behavior was observed, that is, that As(V) is preferentially adsorbed.⁸⁻⁻¹⁰,₃₆

![Figure 2](https://example.com/fig2.png)  **Figure 2.** Modeled vs observed adsorption of As(V), PO₄, Ca²⁺, and CO₃²⁻ of the single-ion data sets (Table S1) using the surface complexation constants from Table 2. The empty data point among the As(V) data was excluded from optimization (cf. text).

![Figure 3](https://example.com/fig3.png)  **Figure 3.** Modeled distribution of surface complexes as a function of pH for PO₄ (left) and for As(V) (right). Single-sorbate systems with PO₄ or As(V) = 200 μmol L⁻¹. Other conditions: I = 0.01 M NaNO₃, Fe = 1 mM, SSA = 611 m² g⁻¹, and T = 25 °C.
The studied data sets were highly consistent with regard to PO$_4$ binding, which resulted in excellent fits for the CD-MUSIC model (Table 2 and Figures 2 and S1). Consistent with Hiemstra and Zhao, bidentate complexes were allowed on corner-sharing sites but not on the edge-sharing sites. No EXAFS data exist that corroborate this assignment, but given the small size of the PO$_4$ tetrahedron, it seems unlikely that it is able to form a stable edge-sharing bidentate complex with one iron(III) octahedron as this would lead to a substantial decrease of the O−Fe−O angle. In all, five surface complexes were included in the model: the two bidentate complexes ($\text{FeO}$)$_2$POOH$^-_2$ and ($\text{FeO}$)$_2$PO$_2$$^-_2$ and the three monodentate complexes $\text{FeOPO(OH)}_2^{1/2^-_2}$, $\text{FeOPO}_2\text{OH}^{1/2^-_2}$, and $\text{FeOPO}_3^{1/2^-_2}$. The model is fairly similar to the one earlier proposed by Hiemstra and Zhao, although the CD values of the monodentate complexes were adjusted slightly upward to improve the fit for the binary PO$_4$−Ca$^{2+}$ and PO$_4$−CO$_3$$^{2-}$ systems. As Figure 3 shows, the optimized model implies that a large part of the adsorbed PO$_4$ occurs as monodentate complexes, particularly at low pH when more than 50% of the adsorbed PO$_4$ is predicted to be monodentate. This percentage is predicted to increase in binary systems with Ca$^{2+}$ and to decrease in systems with As(V) or CO$_3$$^{2-}$ mainly because of the higher negative surface charge associated with the monodentate complexes. Also, as will be discussed below, the chosen PO$_4$ model was able to produce reasonably good predictions for the binary systems investigated, both for the Ca$^{2+}$−PO$_4$ systems (Figures 4 and S8) and for the PO$_4$−CO$_3$$^{2-}$ systems (Figures 5 and S10).

**Model Optimization: Phosphate.** The studied data sets were highly consistent with regard to PO$_4$ binding, which resulted in excellent fits for the CD-MUSIC model (Table 2 and Figures 2 and S1). Consistent with Hiemstra and Zhao, bidentate complexes were allowed on corner-sharing sites but not on the edge-sharing sites. No EXAFS data exist that corroborate this assignment, but given the small size of the PO$_4$ tetrahedron, it seems unlikely that it is able to form a stable edge-sharing bidentate complex with one iron(III) octahedron as this would lead to a substantial decrease of the O−Fe−O angle. In all, five surface complexes were included in the model: the two bidentate complexes ($\text{FeO}$)$_2$POOH$^-_2$ and ($\text{FeO}$)$_2$PO$_2$$^-_2$ and the three monodentate complexes $\text{FeOPO(OH)}_2^{1/2^-_2}$, $\text{FeOPO}_2\text{OH}^{1/2^-_2}$, and $\text{FeOPO}_3^{1/2^-_2}$. The model is fairly similar to the one earlier proposed by Hiemstra and Zhao, although the CD values of the monodentate complexes were adjusted slightly upward to improve the fit for the binary PO$_4$−Ca$^{2+}$ and PO$_4$−CO$_3$$^{2-}$ systems. As Figure 3 shows, the optimized model implies that a large part of the adsorbed PO$_4$ occurs as monodentate complexes, particularly at low pH when more than 50% of the adsorbed PO$_4$ is predicted to be monodentate. This percentage is predicted to increase in binary systems with Ca$^{2+}$ and to decrease in systems with As(V) or CO$_3$$^{2-}$ mainly because of the higher negative surface charge associated with the monodentate complexes. Also, as will be discussed below, the chosen PO$_4$ model was able to produce reasonably good predictions for the binary systems investigated, both for the Ca$^{2+}$−PO$_4$ systems (Figures 4 and S8) and for the PO$_4$−CO$_3$$^{2-}$ systems (Figures 5 and S10).

**Model Optimization: Arsenate.** Parameter values of the final selected model and its model fits for single-ion systems are shown in Table 2 and Figure S4, respectively, while the fit quality is shown in Figure 2. A number of different models, having different sets of parameter values, were able to provide reasonable fits to the single-ion arsenate adsorption data. In all these models, corner-sharing bidentate complexes accounted for the majority of the adsorbed As(V), in agreement with most EXAFS evidence, with monodentate complex(es) being of some additional significance at low pH. One possible modeling approach is to include only the two corner-sharing ($\text{FeO}$)$_2$AsOOH$^-_2$ and ($\text{FeO}$)$_2$AsO$_2$$^-_2$ complexes, with
Model-predicted As(V) sorption agreed well with the observations for the data set of Antelo et al., when using the presence of Ca\(^{2+}\), leading to a promoting effect although not perfect (Figure 4). Ca\(^{2+}\) on As(V) has also been shown for goethite, it seemed clear that an additional complex was needed. In agreement with Hiemstra and Zhao, a second, monoprotonated, monodentate complex, was included. In the model with a variable SSA, when using a fixed SSA, the model was much poorer, similar to what was found for PO\(_4\) (Figure S4), while the overestimated As(V) adsorption (Figure S9). In some of the binary Ca−As(V) data provided by Antelo et al. (Figure 4) as too little enhancement of As(V) adsorption was predicted in the presence of Ca\(^{2+}\) (data not shown). As a promoting effect of Ca\(^{2+}\) on As(V) has also been shown for goethite, it seemed clear that an additional complex was needed. In agreement with Hiemstra and Zhao, a second, monoprotonated, monodentate complex, \(\text{FeOAsO}_2\text{OH}^{11/2-}\), was included. Although present at a relatively small concentration in single-ion systems (Figure 3), its significance increased in the presence of Ca\(^{2+}\), leading to a promoting effect, although the fit was not perfect (Figure 4).

For the two data sets that were excluded from optimization due to an insufficient equilibration time, the model overestimated As(V) adsorption (Figure S4), while the model-predicted As(V) sorption agreed well with the observations for the data set of Antelo et al., when using the model with a variable SSA. When using a fixed SSA, the model fit was much poorer, similar to what was found for PO\(_4\) (data not shown).

Model Optimization: Calcium. No spectroscopic evidence exists concerning the adsorption mechanism of Ca\(^{2+}\) on iron(III) (hydr)oxides. Similar to previous model approaches, we assumed that Ca\(^{2+}\) forms bidentate complexes on Fh. In their CD-MUSIC model approach, Mendez and Hiemstra recently assumed Ca\(^{2+}\) to form \((\text{FeO}+\text{H})\text{Ca}^{+}\) complexes with relatively high CD values (\(\Delta z_0 = 0.94, \Delta z_1 = 1.06\)) involving also high-affinity sites with a higher log \(K\) (5.13, as compared to 2.64 for the low-affinity sites). The predominance of \((\text{FeO}+\text{H})\text{Ca}^{+}\) is supported also by recent XANES evidence for goethite. The model of Mendez and Hiemstra described their data well but was not able to describe Ca\(^{2+}\)−PO\(_4\) binary systems without inclusion of a ternary Ca−PO\(_4\)−Fh complex. As there is no spectroscopic evidence for such a complex in the literature, we decided to investigate whether an alternative model could be formulated, without the need to consider ternary complexes. As a starting point, it was noted that the MO/DFT-calculated CD values of Mendez and Hiemstra were based on the assumption of sixfold coordination of Ca\(^{2+}\) (i.e., \(\text{CN} = 6\)). The coordination number (CN) of Ca\(^{2+}\) in, for example, water molecules and minerals may, however, be variable, that is, in the range of 6−8. A higher CN would lead to lower \(\Delta z_0\) of the surface complex. We found that by using \(\Delta z_0 = 0.6, \Delta z_1 = 1.4\) for the low-affinity sites, while assuming that a small number of high-affinity sites could bind Ca\(^{2+}\) in a sixfold coordination \((\Delta z_0 = 0.9, \Delta z_1 = 1.1)\), very good model fits were obtained for the single-ion systems including the isotherm obtained by Kinniburgh and Jackson (Table 2 and Figures 2, S5, and S6). This six-coordinated Ca\(^{2+}\) was assumed to bind to the \(\text{FeO}+\text{H}\) groups (i.e., as edge-sharing complexes), in agreement with the observation that six-coordinated Ca\(^{2+}\) is able to form such complexes on Fh. With our model, reasonable model predictions were obtained for binary Ca−PO\(_4\) systems without the need to include ternary complexes (Figure S9). In some of the binary Ca−PO\(_4\) systems considered, the observed Ca−PO\(_4\) interactions were very probably also affected by the precipitation of ACP, contributing to the Ca\(^{2+}\)-mediated increase in PO\(_4\) retention (Figures 4 and S8).

Model Optimization: Carbonate. The coordination of carbonate on hydrated ferricyanide was determined using ATR−FTIR spectroscopy and was found to involve a corner-sharing bidentate complex \((\text{FeO}+\text{H})\text{CO}^-\) as well as an outer-sphere complex. The latter was assumed to be CO\(_3\)\(^{2-}\).
electrostatically attracted to $\equiv\text{FeOH}^{1/2+}$ and to $\equiv\text{Fe}_2\text{OH}^{1/2+}$ groups. In both available data sets (Table S5), the ($\equiv\text{FeO}_3$)$_3\text{CO}^-$ complex was found to dominate. To fit these data, the CD values for this surface complex were adjusted from ($\Delta z_0 = 0.66$, $\Delta z_1 = -0.66$), as estimated from MO/DFT calculations,34 to ($\Delta z_0 = 0.5$, $\Delta z_1 = -0.5$), which provided a much better fit to the adsorption edges of Zachara et al.60 which were not considered by Mendez and Hiemstra.34 This difference could, to some extent, be ascribed to the uncertainty of using the correct template for MO/DFT modeling; by using these cases, the partial pressure of CO$_2$ was calculated to be much better. The authors also used a second bidentate complex that involved an interaction with Na$^+$, which improved the model fit particularly at high pH. However, also CD values of ($\Delta z_0 = 0.57$, $\Delta z_1 = -0.57$) produce clearly poorer fits to the data of Zachara et al.,34 although it can be remarked that there is considerable scatter in this data set. In the absence of additional high-quality data that better constrain the CD values, we chose to use the lower $\Delta z_0$ value as it is based on experimental data, although it should be considered uncertain.

The surface complexation constant of the outer-sphere complex could not be constrained satisfactorily from the single-ion data, and instead, the constant was estimated to be $\log K = 11.6$ based on the effect of CO$_3$ on PO$_4$ adsorption, cf. Table 2 and Figures 5 and S10. The model is slightly different from the one proposed by Mendez and Hiemstra,34 who used a monodentate complex instead of an outer-sphere complex. These authors also used a second bidentate complex that involved an interaction with Na$^+$, which improved the model fit particularly at high pH. However, the model chosen in the current paper provided a reasonable description of the CO$_3$– PO$_4$ interaction, except for a few data points at very high pH. Furthermore, in some systems to which high CO$_3$ concentrations had been added, the model performed less satisfactorily at relatively low pH (Figures 5 and S10). In all these cases, the partial pressure of CO$_3$ was calculated to be $>0.1$ atm, which might have caused partial CO$_3$ degassing during the pH measurement and thus a higher pH. Because of the reasonably good model fit, it was decided not to include a third surface complex that would increase the degrees of freedom of the model.

**Arsenate–Phosphate Interaction.** With the PO$_4$ and As(V) surface complexation reactions constrained from the single-ion data sets, and from the other binary systems mentioned above, the Ferrihydrite CD-MUSIC model was able to provide a very good description of the observed fractionation between As(V) and PO$_4$ at the Fh–water interface, as observed in this study (Figure 6). The model was also able to predict As(V) and PO$_4$ competitive adsorption reasonably well for the dataset obtained by Jain and Loepffer,9 while it underestimated As(V) adsorption as observed by Dixit and Hering (Figure S11).34 However, the latter results are difficult to properly evaluate as no data were reported for PO$_4$ adsorption.

A key to understanding why the model predicts As(V) to be preferentially adsorbed in binary systems with both As(V) and PO$_4$ is provided by Figure 3. Although As(V) and PO$_4$ seem to form very similar surface complexes on Fh, the proportion of bidentate complexes is higher for As(V) than it is for PO$_4$. Because a bidentate complex occupies two $\equiv\text{FeOH}$ sites and a monodentate only one, it follows that site saturation is reached more quickly for As(V) than it is for PO$_4$, and consequently, the slope of the isotherm is smaller for As(V), see example in Figure S12. As a consequence, when decreasing the As(V)–PO$_4$ ratio, As(V) adsorption will become relatively more efficient. In fact, the surface complexation constants of Table 2 actually imply a stronger As(V) adsorption than PO$_4$ adsorption at low anion–to–Fe ratios. A less important but contributing factor is that the formation of bidentate complexes affects the one-layer charge less than monodentate complexes at the same pH. Therefore, the adsorption of As(V) leads to less negative charge being accumulated in the one layer, at least if pH $> 4$. Under the conditions of the experiment, the Ferrihydrite CD-MUSIC model predicts the surface to have a net negative charge at pH $> \sim 3.3$ due to the adsorption of As(V) and PO$_4$. Hence, adsorbed As(V) can be accommodated somewhat more easily at pH $> 4$ in the competitive system. Similar reasons explain why (i) PO$_4$ is more sensitive to ionic strength variations, as was shown by Antelo et al.,62 and (ii) PO$_4$ adsorption is enhanced more strongly by an adsorbing cation such as Ca$^{2+}$, as seen in Figure 4.

To the best of our knowledge, other published models are not currently able to predict the As(V)–PO$_4$ interactions observed in this study. For example, the generalized two-layer model of Dzombak and Morel31 does not predict any preferential As(V) adsorption at all in binary systems. Our previous version of the CD-MUSIC model for ferrihydrite33 does predict preferential As(V) adsorption but to a smaller extent than in the current study and does not adequately describe competitive interactions with Ca$^{2+}$ and CO$_3$$^{2-}$. The CD-MUSIC model of Hiemstra and co-workers,1 which served as an inspiration to the current model, does a better job in predicting competitive interactions with Ca$^{2+}$ and CO$_3$$^{2-}$ but predicts too strong As(V) adsorption at low pH under all conditions and thus incorrect fractionation behavior. Hence, the model version presented in the paper should offer an improved performance concerning As(V) and PO$_4$ adsorption in multicomponent, competitive systems under variable conditions (pH, ionic strength, and concentration levels).

**CONCLUSIONS**

In competitive systems with Fh, As(V) adsorbs more strongly than PO$_4$ when the two ions occur together, particularly at low As(V)–PO$_4$ ratios despite the fact that the adsorption of both appear to be equally strong when they occur in single-ion systems at high surface coverage. The observed fractionation is attributed mainly to the larger proportion of bidentate complexes for As(V), which leads to a flatter isotherm near site saturation; hence, As(V) adsorption is actually stronger than PO$_4$ at low anion-to-Fe ratios. The higher negative charge of monodentate complexes also contributes to the observed fractionation. Although the main trends are known since earlier, the data set provided in the current paper, as well as the improved model descriptions of As(V) and PO$_4$ binding in single-ion or multicomponent systems, will improve our ability to predict these effects qualitatively, which is of importance, for example, for correctly simulating As(V) solubility in contaminated materials.

Furthermore, when optimizing the CD-MUSIC model, it was shown that there is no need to consider a ternary Ca$^{2+}$–PO$_4$ complex to properly describe the interactions between Ca$^{2+}$ and PO$_4$ in systems with ferrihydrite, as was recently suggested.33 By having a relatively low $\Delta z_0$ value for adsorbed Ca$^{2+}$, perhaps reflecting a high coordination number, or alternatively the presence of additional outer-sphere inter-
action mechanisms, the model adequately describes the promoting effect of Ca\(^{2+}\). The same was true for the interaction between Ca\(^{2+}\) and As(V). Of course, this does not mean that such ternary complexes do not exist. Rather, these observations lead us to conclude that in order to better constrain the Ferrihydrite CD-MUSIC model and other similar models, it would be highly desirable to more precisely understand the surface complexation mechanisms of Ca\(^{2+}\), alone and in systems with PO\(_4\), with spectroscopy and other methods.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00081.

Molar mass and Stern layer capacitances as a function of nanoparticle size; surface charging/ion-pair formation reactions used in the CD-MUSIC model; details on experimental conditions in single-ion systems; and additional figures of adsorption edges and isotherms in single-ion and competitive systems (PDF)

Adorption data (XLSX)

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**Notes**

The authors declare no competing financial interest.

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