

Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite–water interface

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Abstract

The surface properties of a well-crystallized synthetic goethite have been studied by acid–base potentiometric titrations, electrophoresis, and phosphate and arsenate adsorption isotherms at different pH and electrolyte concentrations. The PZC and IEP of the studied goethite were 9.3 ± 0.1 and 9.3 ± 0.2 , respectively. Phosphate and arsenate adsorption decrease as the pH increases in either 0.1 or 0.01 M KNO_3 solutions. Phosphate adsorption is more sensitive to changes in pH and ionic strength than that of arsenate. The combined effects of pH and ionic strength result in higher phosphate adsorption in acidic media at most ionic strengths, but result in lower phosphate adsorption in basic media and low ionic strengths. The CD-MUSIC model yields rather good fit of the experimental data. For phosphate it was necessary to postulate the presence of three inner-sphere surface complexes (monodentate nonprotonated, bidentate nonprotonated, and bidentate protonated). In contrast, arsenate could be well described by postulating only the presence of the two bidentate species. A small improvement of the arsenate adsorption data could be achieved by assuming the presence of a monodentate protonated species. Model predictions are in agreement with spectroscopic evidence, which suggest, especially for the case of arsenate, that mainly bidentate inner-sphere complexes are formed at the goethite–water interface.

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1. Introduction

Phosphorus and arsenic are of major concern in environmental chemistry. Phosphorus is essential for plant growth in soils and is the nutrient that usually limits algal growth and eutrophication in surface water bodies [1]. Arsenic, on the other hand, is a toxic element that may be present at high levels in groundwater [2].

Phosphorus and arsenic are both Group 5A elements and thus they form species that have similar chemical properties. For example, phosphate is the species analogous to arsenate, and both have very similar structures and affinities for

proton ions [3]. However, there may be also very important differences between phosphate and arsenate, since their biogeochemical behavior is completely different. In fact, whereas phosphate is a macronutrient constituent of most biological tissues, arsenate is a toxic substance even at very low concentrations.

It is well known that both phosphate and arsenate have a relatively strong affinity for mineral surfaces [3–5]. They strongly adsorb at the surfaces of metal (hydr)oxides, especially iron and aluminum (hydr)oxides, which are important constituent of soils and sediments and key solids for the control of the transport and bioavailability of many anions. The affinity of phosphate and arsenate for (hydr)oxide surfaces depends on one hand on the anions' complexing capacity, which allows binding to surface groups by ligand exchange reactions, and on the other hand on attractive or repulsive

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electrostatic interactions with the charged (hydr)oxide surfaces [6].

The adsorption of phosphate and arsenate on different (hydr)oxides has been compared in many articles. Most of the articles deal with adsorption on goethite (α -FeOOH), which has become a model solid for adsorption studies. This is because goethite is one of the most common and stable crystalline iron (hydr)oxides in natural environments and is also a solid that can be prepared in a very reproducible way with particles of controlled size and geometry. Whereas in some articles it is reported that arsenate adsorbs more strongly than phosphate, in some others the opposite behavior is observed. Gao and Mucci, for example, studied the adsorption of phosphate and arsenate on goethite in 0.7 M NaCl solutions and pH range 3–10 [7]. They found that the adsorption decreases as the pH increases in both cases. They also reported that although the affinity of both anions for the surface is high, that of arsenate is higher. No data for lower ionic strength were presented in the mentioned article. Hongshao and Stanforth [8], on the other hand, studied adsorption on goethite in 0.001 M NaCl solutions at pH 2.45 and 5.15. They found similar adsorption behavior at low anion concentrations and slightly higher adsorption of arsenate at high concentrations. Manning and Goldberg compared the adsorption on goethite at different pH in 0.1 M NaCl solutions [5]. They found very similar behaviors, but in this case the affinity of arsenate for the surface seemed to be slightly lower than that of phosphate, especially in neutral or alkaline media. This is in agreement with results previously reported by Hingston et al. [9], who found a higher adsorption of phosphate than arsenate on goethite in 0.1 M NaCl at different pH. Hiemstra and Van Riemsdijk [4,10] reported and modeled the adsorption of phosphate on goethite and compared model predictions with experimental data published by Hingston et al. [9]. Their results indicate that in 0.1 M NaCl solutions the affinity of arsenate for goethite was lower than that of phosphate. Lumsdon et al. suggested that arsenate may interact more strongly with a solid surface because it is larger in size than phosphate [11].

Arsenate and phosphate adsorption on goethite has been also studied by infrared spectroscopy and extended X-ray absorption fine structure spectroscopy. The studies suggest that these anions can form several surface complexes with goethite surface sites. Tejedor-Tejedor and Anderson [12] reported that phosphate forms three kinds of complexes: a monodentate nonprotonated complex and two bidentate complexes, one protonated and one nonprotonated. Slightly different were the conclusions of Persson et al. [13], who stated that three monodentate complexes of phosphate are formed at the surface of goethite, differing only in their degree of protonation (nonprotonated, monoprotonated, and biprotonated complexes). For arsenate, similar kinds of surface complexes were proposed at the surfaces of goethite or other iron (hydr)oxides [3,14–16]. Fendorf et al. [15] and Waychunas et al. [16] concluded that arsenate forms mainly

bidentate complexes, but some monodentate complexes may form at very low coverages.

The competitive adsorption of phosphate and arsenate on goethite has also been reported in most of the previous cited articles. The general finding is that both anions do compete for the solid surface [3–5,7], competing for the same kind of surface sites. It has also been proposed that some surface groups appear to be uniquely specific for arsenate or phosphate [17].

Although many studies have been carried out so far, most of the comparative adsorption experiments were performed at constant ionic strength, and the nature of phosphate and arsenate adsorption at different electrolyte concentrations is poorly known. Given the environmental importance of the anions in either low-ionic-strength media (such as rivers, lakes, and groundwaters) or high-ionic-strength media (such as seawater or saline groundwaters), studying the effects of ionic strength on adsorption results important.

The aim of this article is to compare the adsorption of phosphate and arsenate on goethite at different pH and electrolyte concentrations. The study was carried out by measuring adsorption isotherms under different conditions and by performing electrophoretic mobility measurements. The CD-MUSIC model [10] is used to interpret the experimental data.

2. Experimental

2.1. Goethite synthesis and structural characterization

Goethite was synthesized following a procedure similar to that described by Atkinson et al. [18]. Briefly, 800 ml of a 5 M NaOH solution were slowly added (dropwise) to 4 L of a 0.1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution under continuous stirring and N_2 bubbling. The obtained dispersion was then aged for 72 h at 60 °C, cooled at room temperature, and dialyzed until the conductivity was lower than 10 $\mu\text{S}/\text{cm}$. After that, the dispersion was freeze-dried in order to obtain a dry powder.

Powder X-ray diffraction was measured with a Phillips PW1710 diffractometer between 10° and 70° 2θ using $\text{CuK}\alpha$ radiation. Transmission electron microscopy was performed using a Philips CM-12 microscope. FTIR spectra were obtained with a FTIR Nexus 470 spectrophotometer. The BET surface area was measured by N_2 adsorption with a Micromeritics ASAP 2000 V3.03 instrument.

2.2. Surface charge and anion adsorption

The surface properties of the synthesized goethite were studied by acid–base potentiometric titrations, phosphate and arsenate adsorption isotherms, and electrophoretic mobilities. All studies were performed using KNO_3 as supporting electrolyte.

Acid–base potentiometric titrations were performed using a fully automated system consisting in a Crison GLP 22

pH meter, a Crison BU2S burette, and a Radiometer GH2401 combined glass electrode. The pH meter and the burette were connected to a PC that controlled the whole titration experiments. Standard Crison buffer solutions (pH 4.00, 7.02, and 9.26) were used to calibrate the electrode. Standard 0.1 M HNO₃ and KOH solutions were used as titrants. For titrations, a 14 g/L goethite suspension was prepared suspending dry goethite in 50 ml of 0.005, 0.02, or 0.1 M KNO₃ solution. The pH of the dispersion was then changed with HNO₃ to a value near 4 under continuous N₂ bubbling. Under this condition, the suspension was bubbled overnight in order to remove CO₂ [19]. After that, the suspension was titrated with KOH until pH around 10 and backtitrated with HNO₃ until pH around 4 in order to check reversibility. After each titrant addition, whose volume was calculated in order to have around 12 data points per pH unit, the electrode reading and drift were monitored until the drift was lower than 0.2 mV/min for 45 s. This took about 3 min. After that, a new titrant addition was performed. Reversibility of the titration curve was checked by backtitrating the dispersion with HNO₃. The adsorption of protons as a function of pH was calculated as the difference between total amounts of H⁺ or OH⁻ added to the suspension and those required to bring a blank solution of the same KNO₃ concentration to the same pH. Proton adsorption values were directly converted into surface charge density values using the BET surface area of the solid and Faraday's constant.

Phosphate and arsenate adsorption was measured with batch adsorption experiments, which allowed to measure adsorption isotherms at different pH and ionic strengths. For each data point, a phosphate or arsenate solution of the desired initial concentration was prepared at the desired pH and ionic strength. The solution was then added to a goethite dispersion of the same pH and ionic strength, and stirred with a magnetic bar. Any change in pH after the mixing was corrected by adding HNO₃ or KOH solutions. After 15–18 h, the pH was registered, the suspension filtered, the supernatant analyzed for either phosphate or arsenate, and the adsorbed amount calculated. With this procedure adsorption isotherms were obtained at pH 4.5, 7.0, 8.5, and 10.0 for phosphate and 4.5, 7.0, 9.0, and 10.0 for arsenate. The electrolyte concentrations investigated were 0.1 and 0.01 M, KNO₃ being the electrolyte. Phosphate concentration was quantified following the method proposed by Murphy and Riley [20]. Arsenate concentration was quantified according to the molybdene blue method [21]. In both cases, a JASCO V-530 UV-vis spectrophotometer was used, equipped with a 1-cm quartz cell. The detection limit for phosphate and arsenate was around 1 μM. Each data point is the result of one individual measurement.

Electrophoretic mobilities were measured with a Malvern Zetamaster 5002 instrument. Dispersions of 0.015 g/L goethite were prepared in 0.01 M KNO₃ and pH between 3 and 10. The dispersions were equilibrated for 15–18 h before the measurements. Special care was taken to avoid CO₂ contamination, keeping the dispersions in a N₂ atmosphere.

The effects of phosphate and arsenate on the electrophoretic mobility of goethite were also investigated by working with dispersions that contained 0.01 M KNO₃ and either phosphate or arsenate at different concentrations. Electrophoretic mobility data were converted to zeta potentials using the Smoluchowsky equation. Each data point is the average of two different measurements.

All chemicals were of Merck p.a. quality. The water used in the experiments was double-distilled and CO₂-free. Polycarbonate flasks were used in order to avoid silicate contamination, and the temperature was maintained at 25 ± 1 °C in all the experiments.

3. Results and discussion

X-ray diffraction data revealed that the synthesized solid was a well-crystallized pure goethite. No evidence of other iron (hydr)oxides phases was detected with this technique. Transmission electron microscopy, on the other hand, showed that goethite particles have a typical acicular shape [22]. The solid was polydisperse, with particle lengths ranging between 400 and 1000 nm and widths between 30 and 65 nm. This shape indicates that the prevailing surface is that corresponding to the 110 face, whereas the 021 face is present at the top ends of the crystals [23].

The FTIR spectrum was also typical of goethite. It showed a characteristic absorption band at around 3160 cm⁻¹ due to the bulk OH stretch; an 892 cm⁻¹ band and a 795 cm⁻¹ band due to OH bends; and a 637 cm⁻¹ band and a 408 cm⁻¹ band due to Fe–O stretches [22,24]. No evidence of carbonate contamination was detected by FTIR.

The BET surface area of the studied goethite resulted to be 70.8 m²/g.

3.1. Potentiometric titrations

Titration of goethite dispersions at all the electrolyte concentrations investigated was reversible; i.e., there was coincidence in the titration curves when data obtained by titrating with HNO₃ and NaOH were compared. Hysteresis in the curves is normal for samples contaminated with carbonate [25]. Fig. 1 shows the experimental surface charge vs pH curves at different electrolyte concentrations. The point of zero charge (PZC) of the sample is 9.3 ± 0.1, as revealed by the crossing point of the curves. This PZC is in close agreement with previously reported values for goethite. Lumsdon and Evans, for example, informed a PZC of 9.1 [26], Filius et al. reported values between 9.2 and 9.3 [27], and Villalobos and Leckie measured PZC between 9.0 and 9.2 [28]. Lower PZC values (between 7.5 and 9) were also informed for goethite, but it has been suggested that these low values are usually a consequence of the presence of some carbonate or other anion contaminating the solid [26,29]. Theoretical surface charge vs pH curves are also shown in Fig. 1. They will be discussed in the section modeling.

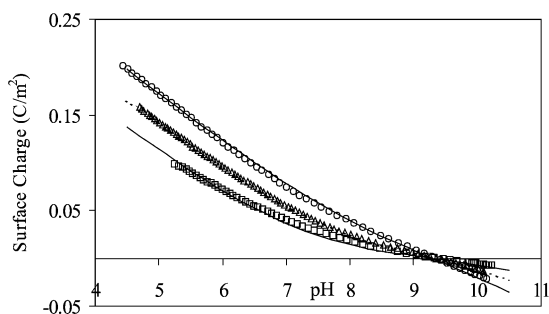


Fig. 1. Goethite surface charge as a function of pH at different KNO_3 concentrations. Symbols, experimental points; lines, model predictions. KNO_3 concentration: circles, 0.1 M; triangles, 0.02 M; squares, 0.005 M.

3.2. Phosphate and arsenate adsorption experiments

Fig. 2 shows the adsorption isotherms of phosphate and arsenate in 0.1 M electrolyte at different pH values. In both cases the adsorption increases as the pH decreases. This effect is well known for phosphate and arsenate on goethite [4,9,10,17,30]. At pH 10 the adsorption is similar in both cases, but the effects of decreasing pH are less important for arsenate, which adsorbs a 20% less than phosphate at pH 4.5. Model predictions are also drawn in Fig. 2. They will be discussed in section modeling.

The effect of pH on adsorption isotherms of phosphate and arsenate in 0.01 M electrolyte were similar to those in 0.1 M, i.e., the adsorption increased by decreasing pH, and the effects of changing pH were less important for arsenate than for phosphate. Since the general trends of these isotherms were very similar to those shown in Fig. 2, it is not necessary to draw an analogous figure. We prefer to present the data at low ionic strength by comparing them with those obtained at high ionic strength. This is done in Fig. 3. The left hand side of the figure shows the effects of changing ionic strength on phosphate adsorption isotherms at different pH. The right hand side of the figure does the same comparison for arsenate. At pH 4.5 there is no salt effect on the adsorption of phosphate. However, at pH 7, 8.5, and 10 the effects are evident, and a decrease in the

adsorption by decreasing the electrolyte concentration can be noticed. The behavior is somewhat different for arsenate: there is very little or no salt effect on the adsorption of this anion at any pH.

Although the general trends in the adsorption of phosphate and arsenate are rather similar, it is clear that phosphate adsorption is more dependent on pH and electrolyte concentration than arsenate adsorption. There are not many data in the literature to compare with the ones presented in Figs. 2 and 3. As indicated in the Introduction, most of the previous studies about phosphate and arsenate adsorption on goethite investigated mainly the effects of pH, and very scarce information exists about the effects of ionic strength. Moreover, in most of the mentioned publications, only one anion concentration was used in the adsorption experiments, and no isotherms, where the adsorption behavior was investigated in an ample range of adsorbate concentrations, were reported. Barrow et al. [31] presented one of the most complete data set on phosphate adsorption on goethite (PZC = 8.3) at different pH and NaCl concentrations. At pH 3 the adsorption showed a small salt effect, the adsorption increasing by decreasing NaCl concentration in the order 1.0, 0.1, and 0.01 M. At pH 6 the salt effect was stronger and the salt dependency was reversed: the adsorption increased by increasing NaCl concentration. At pH 9, the salt effect was even larger. As at pH 6, the adsorption increased with increasing NaCl concentration [31]. These data were modeled by Hiemstra and Van Riemsdijk with the CD-MUSIC model [10]. The model could successfully predict the unfavorable effect of increasing electrolyte concentration at pH 3 on adsorption and the reverse effect at pH > 5. The model also predicted no effect of the electrolyte concentration at pH 4.5. More recently, Geelhoed et al. [32] presented another data set for phosphate adsorption in KNO_3 that has the same trends as those informed by Barrow et al. [31]. All these data are in very good agreement with those presented in Fig. 3. No data about adsorption isotherms of arsenate at different pH and electrolyte concentration seems to be appeared in the literature for a single goethite, thus no comparison can be made with data in this article.

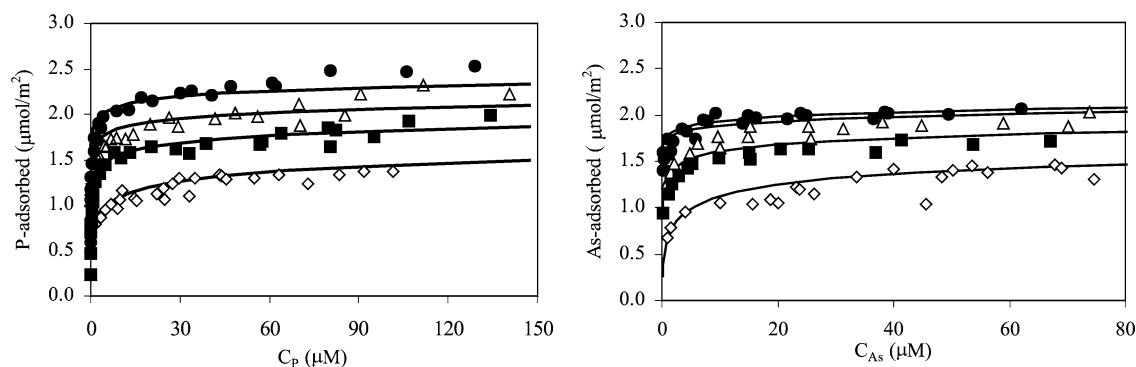


Fig. 2. Phosphate (left) and arsenate (right) adsorption on goethite in 0.1 M KNO_3 . Symbols, experimental points; lines, model predictions. pH: circles, 4.5; triangles, 7.0; squares, 8.5 for phosphates and 9.0 for arsenate; diamonds, 10.0.

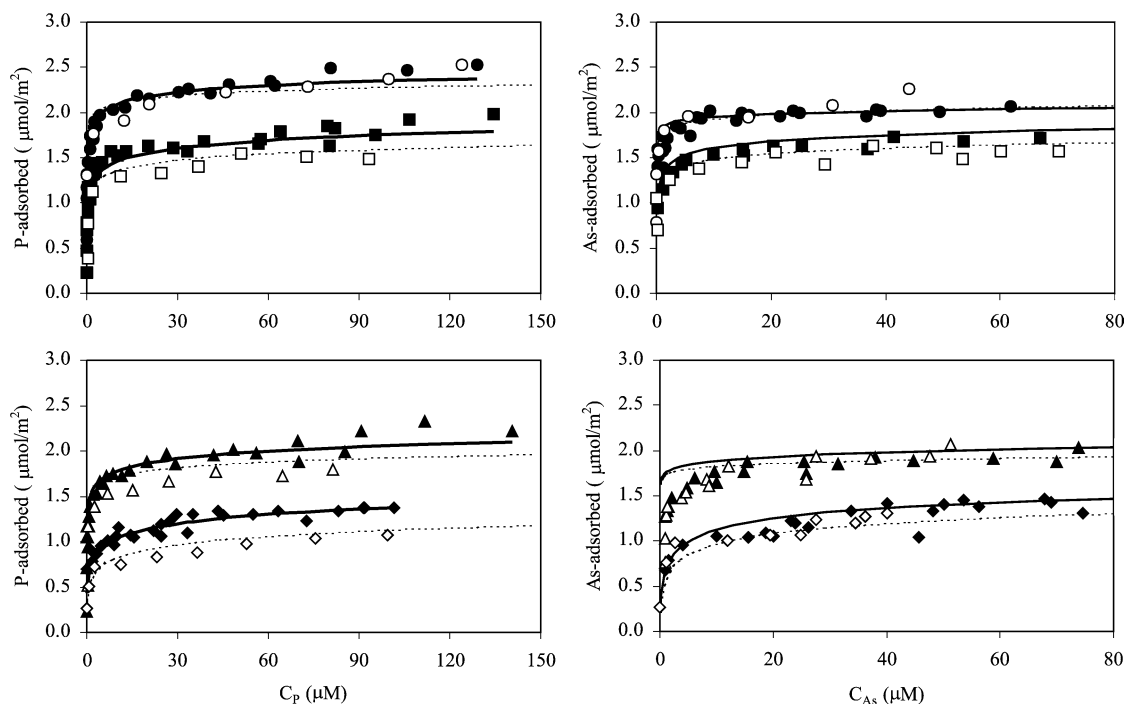


Fig. 3. Phosphate (left) and arsenate (right) adsorption on goethite in 0.1 and 0.01 M KNO_3 . Symbols, experimental points; lines, model predictions. pH: circles, 4.5; triangles, 7.0; squares, 8.5 for phosphate and 9.0 for arsenate; diamonds, 10.0. Solid lines and solid symbols correspond to 0.1 M KNO_3 . Dotted lines and open symbols correspond to 0.01 M KNO_3 .

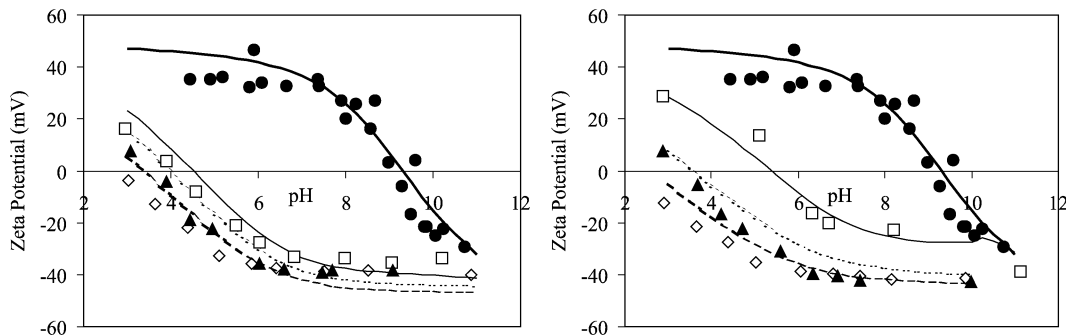


Fig. 4. Electrophoretic mobility of goethite in absence and presence of phosphate or arsenate in 0.01 M KNO_3 solutions. Symbols, experimental points; lines, model predictions. Left, phosphate concentration: solid circles and thick solid line, 0 M; squares and solid line, 1×10^{-5} M; triangles and dotted line, 1×10^{-4} M; diamonds and dashed line, 1×10^{-3} M. Right, arsenate concentration: solid circles and thick solid line, 0 M; squares and solid line, 1×10^{-6} M; triangles and dotted line, 1×10^{-4} M; diamonds and dashed line, 1×10^{-3} M.

The effects of the supporting electrolyte concentration are usually analyzed in terms of the type of complexes that the adsorbed ions can form with the surface. Ions that form outer-sphere complexes compete for adsorption sites with ions of the supporting electrolyte. In this case a decrease in the adsorption is observed when the electrolyte concentration is increased [33]. Conversely, ions that form inner-sphere complexes are directly coordinated to surface groups and do not compete or compete less with electrolyte ions. Thus, the adsorption is less affected by changing the ionic strength [33]. Moreover, in many cases of inner-sphere complex formation the adsorption increases with increasing electrolyte concentration [31]. This effect is usually attributed to changes in the electric potential in the inter-

face, which decreases the electrostatic repulsion between the charged surface and the anion, and favors the adsorption [4].

3.3. Electrophoresis

Electrophoretic mobilities of goethite particles in absence and presence of phosphate and arsenate in 0.01 M electrolyte are shown in Fig. 4. Model predictions are also drawn here. The isoelectric point (IEP) of goethite in the absence of the anions is 9.3 ± 0.2 . This point is coincident with the PZC of the sample as measured by potentiometric titration (Fig. 1), and with IEP values previously reported in the literature [19,29]. Fig. 4 also shows that the presence of either phosphate or arsenate decreases the zeta potential of

the particles at a given pH, and shifts the IEP of goethite towards lower pH values. The higher the anion concentration, the lower the zeta potential and the IEP. The results shown for phosphate are in agreement with previously published data [12]. No data is available in the literature for electrophoresis of pure goethite in the presence of arsenate. For a goethite with an IEP of 7.8 in KNO_3 , the presence of arsenate at concentrations around 1×10^{-4} M shifted the IEP to values lower than 3 [34]. For an amorphous iron oxide in 0.01 M NaCl, 1×10^{-4} M arsenate shifted the IEP from 9.4 to 5.31 [35]. Although not totally comparable, these shifts are in agreement with those observed in Fig. 4. Shifts in the IEP towards low pH values are characteristic for anion adsorption. Inner-sphere anion complexes are especially effective in decreasing the IEP and producing charge reversal of (hydr)oxide particles [5,36].

3.4. Modeling

Models of the solid–solution interface are applied to understand and predict the reactivity of the surface. These models are usually divided into two main parts: one describing the solid surface, the type and reactivity of surface sites, the adsorbed species, the surface charge, etc., and the other describing the charge distribution and potential decay in the electrical double layer, on the aqueous side of the interface. Among many models that have been applied so far, the CD-MUSIC model [10,37] has become one of the most popular models to describe the surface reactivity of well crystallized materials. This model is an extension of the MUSIC [38,39] and modified MUSIC [40] models. The CD-MUSIC model describes the solid surface as populated with surface groups, which can undergo protonation and can bind ions or molecules from the solution. The type and surface density of the groups can be obtained from crystallographic information of the solid structure and from geometrical information of the size and shape of the solid particles. The intrinsic affinity of surface groups for protons is estimated on the basis of Pauling's rules [41] and bond valences [40]. The charge distribution and potential decay in the electrical double layer is assumed in the CD-MUSIC model to obey a three-plane model (0-plane, 1-plane, and 2-plane; see below) combined with a diffuse Gouy–Chapman layer, which accounts for the electrostatics of the solid–solution interface. The combination of electrostatics with intrinsic affinities allows estimating the effective affinity of surface groups for ions [42].

In this article the CD-MUSIC model is used to describe the charging and adsorptive behavior of goethite. The model was intensively used by Hiemstra et al. and by other authors. Several articles with a complete description of the model were published in this journal [4,10,37]. A very good description of the CD-MUSIC model and its formulation for phosphate adsorption using the readily available and widely used surface complexation program FITEQL were presented by Tadanier and Eick [43]. Therefore, there is no need to

write the whole set of equations conforming to the model, which is available upon request. Only a brief description is given here of the CD-MUSIC model, in which all the considered surface equilibria and adsorption reactions are presented together with some remarks that help to understand the main features of the model.

Atoms that can become protonated or deprotonated at the surface of (hydr)oxides are oxygen atoms. In the case of goethite, surface oxygen atoms are bound to one, two, or three iron atoms forming singly, doubly or triply coordinated groups respectively. Depending on the pH of the aqueous solution in contact with the surface, oxygen atoms of the groups can be also bound to none, one or two proton ions. The singly, doubly, and triply coordinated groups of the goethite surface are denoted as $\text{FeOH}^{1/2-}$, Fe_2OH^0 , and $\text{Fe}_3\text{O}^{1/2-}$, where the 1/2- and 0 values represent the electric charge associated with each group. This charge can be deduced by applying Pauling's rules to Fe and O atoms at the surface [10,43]. At low pH $\text{FeOH}^{1/2-}$ and $\text{Fe}_3\text{O}^{1/2-}$ groups can become protonated to give $\text{FeOH}_2^{1/2+}$ and $\text{Fe}_3\text{OH}^{1/2+}$ groups, respectively. On the basis of Pauling's rules and bond valences it can be deduced that the Fe_2OH^0 group is inert in a normal pH range and it cannot become either protonated or deprotonated. In addition, since this group is uncharged, its presence at the surface does not affect the charging behavior of the goethite surface, and thus it is not considered in the model.

The protonation reactions of the $\text{FeOH}^{1/2-}$ and $\text{Fe}_3\text{O}^{1/2-}$ groups are written in Table 1, together with the logarithm of their intrinsic protonation constants ($\log K_H$) and other parameters of the goethite–water interface. The $\log K_H$ values are equal to the PZC of the goethite [10]. The two protonation equilibria indicate that at sufficiently high pH the

Table 1
CD-MUSIC model surface equilibrium reactions for adsorption of protons and electrolyte ions on goethite, and other parameters of the goethite–water interface

Surface reactions	$\log K$
Surface protonation	
$\text{FeOH}^{1/2-} + \text{H}^+ = \text{FeOH}_2^{1/2+}$	$\log K_H = 9.3$
$\text{Fe}_3\text{O}^{1/2-} + \text{H}^+ = \text{Fe}_3\text{OH}^{1/2+}$	$\log K_H = 9.3$
Ion-pair formation with electrolyte	
$\text{FeOH}^{1/2-} + \text{K}^+ = \text{FeOH}^{1/2-} \dots \text{K}^+$	$\log K_K = -1$
$\text{FeOH}_2^{1/2+} + \text{NO}_3^- = \text{FeOH}_2^{1/2+} \dots \text{NO}_3^-$	$\log K_{\text{NO}_3} = -1$
$\text{Fe}_3\text{O}^{1/2-} + \text{K}^+ = \text{Fe}_3\text{O}^{1/2-} \dots \text{K}^+$	$\log K_K = -1$
$\text{Fe}_3\text{OH}^{1/2+} + \text{NO}_3^- = \text{Fe}_3\text{OH}^{1/2+} \dots \text{NO}_3^-$	$\log K_{\text{NO}_3} = -1$
Other parameter	Value
$\text{FeOH}^{1/2-}$ site density	3.45 sites/nm ²
$\text{Fe}_3\text{O}^{1/2-}$ site density	2.7 sites/nm ²
C_1	1.4 F/m ²
C_2	5.0 F/m ²

Table 2

CD-MUSIC model surface complexation equilibrium reactions for adsorption of phosphate or arsenate on goethite

Oxyanion (AO_4^{3-}) ^a adsorption reactions		PO_4^{3-}		AsO_4^{3-}	
		log K	f	log K	f
Monodentate inner-sphere complexes					
$\text{FeOH}^{1/2-} + \text{H}^+ + \text{AO}_4^{3-} = \text{FeOAO}_3^{2.5-} + \text{H}_2\text{O}$	K_1	20.8	0.25	–	–
$\text{FeOH}^{1/2-} + 2\text{H}^+ + \text{AO}_4^{3-} = \text{FeOAO}_3\text{H}^{1.5-} + \text{H}_2\text{O}$	$K_{1\text{H}}$	–	–	25.0	0.25
Bidentate inner-sphere complexes					
$2\text{FeOH}^{1/2-} + 2\text{H}^+ + \text{AO}_4^{3-} = \text{Fe}_2\text{O}_2\text{AO}_2^{2-} + 2\text{H}_2\text{O}$	K_2	30.2	0.50	28.8	0.35
$2\text{FeOH}^{1/2-} + 3\text{H}^+ + \text{AO}_4^{3-} = \text{Fe}_2\text{O}_2\text{AO}_2\text{H}^- + 2\text{H}_2\text{O}$	$K_{2\text{H}}$	36.4	0.60	36.3	0.65

^a A means either P or As.

surface is mainly populated with $\text{FeOH}^{1/2-}$ and $\text{Fe}_3\text{O}^{1/2-}$ groups, resulting in a net negative surface charge. At sufficiently low pH, the surface is mainly populated with $\text{FeOH}_2^{1/2+}$ and $\text{Fe}_3\text{OH}^{1/2+}$ groups, resulting in a net positive surface charge.

Charged surface groups can form ion pairs with oppositely charged electrolyte ions [10,43]. The ion-pair formation reactions between singly and triply coordinated groups and electrolyte ions are also written in Table 1.

Adsorption of oxyanions at the goethite–water interface is described in the CD-MUSIC model as forming inner-sphere surface complexes with singly coordinated $\text{FeOH}^{1/2-}$ groups. Reactions with Fe_2OH^0 and $\text{Fe}_3\text{O}^{1/2-}$ groups seem not to take place [4,10]. A phosphate anion, for instance, can form a monodentate inner-sphere complex, where one oxygen of the anion binds directly the Fe atom of a $\text{FeOH}^{1/2-}$ group, releasing the attached OH^- , or a bidentate inner-sphere complex, where two oxygens of the anion bind two Fe atoms of two adjacent $\text{FeOH}^{1/2-}$ groups. Additionally, phosphate in both monodentate and bidentate complexes can be protonated or deprotonated. This leads to the formation of four different inner-sphere surface complexes: monodentate nonprotonated, monodentate protonated, bidentate nonprotonated, and bidentate protonated [43]. A schematic representation of the goethite–water interface with these four surface complexes is shown in Fig. 5. The surface reactions that lead to the formation of the complexes are given in Table 2. These equilibria indicate that protonated complexes become more important at low pH than the corresponding nonprotonated complexes. The presence of even more inner-sphere surface complexes could be postulated. Tadanier and Eick [43], for example, considered the presence of a monodentate diprotonated phosphate complex. In principle, other similar species could also be formed with Fe_2OH^0 and $\text{Fe}_3\text{O}^{1/2-}$ groups, but they do not seem to be important for arsenate and phosphate adsorption on goethite.

The electrical double layer is described in the CD-MUSIC model as formed by three planes and a diffuse layer. They are also represented in Fig. 5. The three planes, termed 0-, 1-, and 2-planes, locate the charges associated

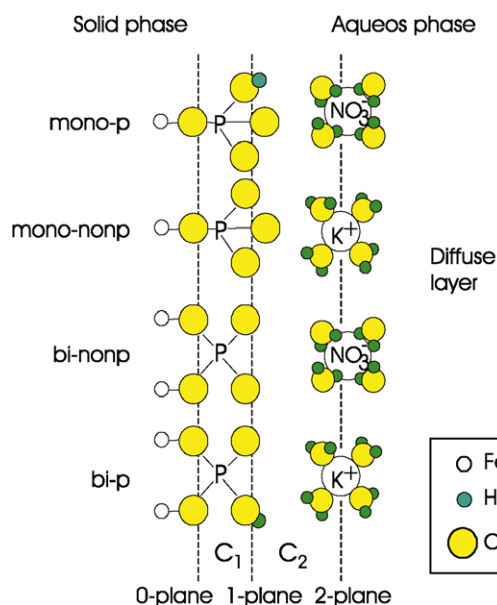


Fig. 5. Scheme of the goethite–water interface with adsorbed inner-sphere phosphate complexes. Monodentate protonated, mono-p; monodentate nonprotonated, mono-nonp; bidentate nonprotonated, bi-nonp; bidentate protonated, bi-p. Analogous complexes can be drawn for arsenate.

with surface groups, specific adsorbed ions, and supporting electrolyte ions. Surface groups with their adsorbed protons are located in the 0-plane, the charge of specific adsorbed ions such as phosphate and arsenate is distributed between the 0-plane and the 1-plane, and supporting electrolyte ions are assumed to be point charges located in the 2-plane [10,43]. From this last plane the diffuse layer starts and extends toward the bulk solution. The three electrostatic planes describe two interfacial regions that behave as molecular capacitors arranged in series with capacitances C_1 and C_2 for the regions defined by the 0- and 1-planes and by the 1- and 2-planes, respectively. The reported values for C_1 are between 1 and 1.6 F/m^2 [4,8,37,44]. C_2 is between 3 and 5 F/m^2 [4,8,44]. The combination of C_1 and C_2 values leads to an overall Stern-layer capacitance, C_{St} , given by $1/C_{\text{St}} = 1/C_1 + 1/C_2$, of about 1 F/m^2 . Together with the respective dielectric constants of approximately 30 and 80, the values of C_1 and C_2 lead to thicknesses of ap-

proximately 2.8 and 1.7 Å for the regions described by the three planes, which are consistent with the sizes of phosphate and electrolyte ions [43]. In the CD-MUSIC model the diffuse layer is assumed to behave according to the Gouy–Chapman equation.

An important aspect of the CD-MUSIC model is the spatial distribution of the charge of the inner-sphere complexes at the surface. This distribution of charge is an extension of Pauling's rules to the solid–water interface. A fraction f of the charge of the central cation (P or As, in the cases analyzed in this article) of the adsorbed species and the charge of the surface-oriented ligands are attributed to the 0-plane, whereas the remaining charge of the central cation and the charge of the solution-oriented ligands are attributed to the 1-plane. If Pauling's rules are assumed to be strictly obeyed by phosphate and arsenate at the goethite–water interface, phosphorus and arsenic in the monodentate non-protonated complex of Fig. 5 will distribute 25% of their charge in the 0-plane and the remaining 75% in the 1-plane; thus $f = 0.25$ [10,43]. Similarly, since phosphorus or arsenic in the bidentate nonprotonated complex of Fig. 5 has two ligands oriented to the surface and two ligands oriented to the solution, they should locate 50% of their charge in the 0-plane and 50% in the 1-plane; thus $f = 0.50$. As stated by Hiemstra and Van Riemsdijk [10] and by Tadanier and Eick [43], nonsymmetrical neutralization of the central cation charge is possible. This could be due, for example, to a shift in the electron density in the adsorbed species caused by protonation of an oxygen ligand. It is also possible that changes in the charge of the goethite surface due to protonation reactions such as those written in Table 1 cause polarization of the adsorbed anion and shift of the electron density. If this is the case, the shift in the electron density and therefore the f value would change by changing the pH because the surface charge and the surface potential are changing. These changes are not considered in this article. The values of f are treated as fitting parameter and assumed to be constant for a given surface complex irrespective of the pH or electrolyte concentration.

The CD-MUSIC model has several parameters whose values need to be estimated from independent measurements, taken from previous published data or evaluated by fitting surface charge vs pH curves, electrokinetic data or anion adsorption curves. The parameters to be estimated are $\log K_H$, $\log K_K$, $\log K_{NO_3}$, the different $\log K$ for surface reactions that lead to the formation of phosphate and arsenate complexes, the surface densities of $FeOH^{1/2-}$ and $Fe_3O^{1/2-}$ groups ($N_{s,1}$ and $N_{s,2}$, respectively), C_1 , C_2 , and the values of f for each inner-sphere surface complex. Fortunately, there is much information about the goethite surface and the goethite–water interface in the literature; thus many of the parameters can be known or estimated a priori. The surface density of $FeOH^{1/2-}$ and $Fe_3O^{1/2-}$ groups was deduced from the crystal structure of goethite, assuming that 90% of the particle surface is composed by the 110 face and that the remaining 10% is composed by the 021 face [37,45]. $\log K_H$

was directly obtained from the PZC of the sample [4,10,43], and the values of $\log K_K$, $\log K_{NO_3}$, and C_2 were estimated by Hiemstra et al. [4,10] from the fitting of surface charge vs pH data at different electrolyte concentrations. C_1 was used as an adjustable parameter in order to attain good fit of surface charge data. The values of the parameters that describe the basic charging behavior of the used goethite are tabulated in Table 1.

Calculations started by fitting surface charge and electrophoresis data in KNO_3 solutions with parameters of Table 1. Model predictions are shown in Fig. 1 for surface charge data and in Fig. 4 for zeta potential data. The quantitative interpretation of the zeta potential with the model is not straightforward. It was assumed here that the zeta potential equals the electric potential at a distance of 2.2 Å of the 2-plane, which resulted in good fit of data. A very good fit of experimental data could be achieved with the mentioned parameters. The parameters are similar to those reported by other authors, indicating that the behavior of the used goethite is similar to other studied goethites [4,10,43].

Phosphate and arsenate adsorption was modeled assuming that monodentate (protonated and nonprotonated) and bidentate (protonated and nonprotonated) inner-sphere complexes could in principle be formed at the goethite–water interface. The adsorption of each anion was treated separately and only the parameters corresponding to the anions ($\log K_1$, $\log K_{1H}$, $\log K_2$, $\log K_{2H}$, and the corresponding f values) were allowed to vary in the fitting, using a trial and error procedure. Parameter values reported in the literature for phosphate [4,10,43] and arsenate [4] were used as initial estimates. The following values of acid dissociation constants in aqueous solution were also used: phosphoric acid $pK_{a1} = 2.15$, $pK_{a2} = 7.12$, $pK_{a3} = 12.35$; arsenic acid $pK_{a1} = 2.24$, $pK_{a2} = 6.96$, $pK_{a3} = 11.50$. The fit started by assuming that only one of the four complexes was formed at the surface. If the fit of adsorption and electrophoresis data was not good, combination of two or three complexes were tried. The aim was to achieve good fit of experimental data with the lowest amount of inner-sphere complexes.

Phosphate adsorption and electrophoresis in presence of phosphate could be reasonably well fitted using three different surface complexes: monodentate nonprotonated, bidentate nonprotonated and bidentate protonated. The best-fit parameters are shown in Table 2, and model predictions for phosphate adsorption and electrophoresis are shown in Figs. 2, 3, and 4. The results are very similar to previously reported ones [4,10,32], where it was also necessary to consider the three mentioned inner-sphere complexes to achieve good fit. These results are also in good agreement with spectroscopic evidence [12]. Tadanier and Eick [43] used two more surface complexes (monodentate protonated and monodentate biprotonated) in order to fit phosphate adsorption on goethite in 0.01 M $NaClO_4$ solutions in the pH range 3–12. However, the contribution of the monodentate biprotonated complex was very small, and good fit could also be

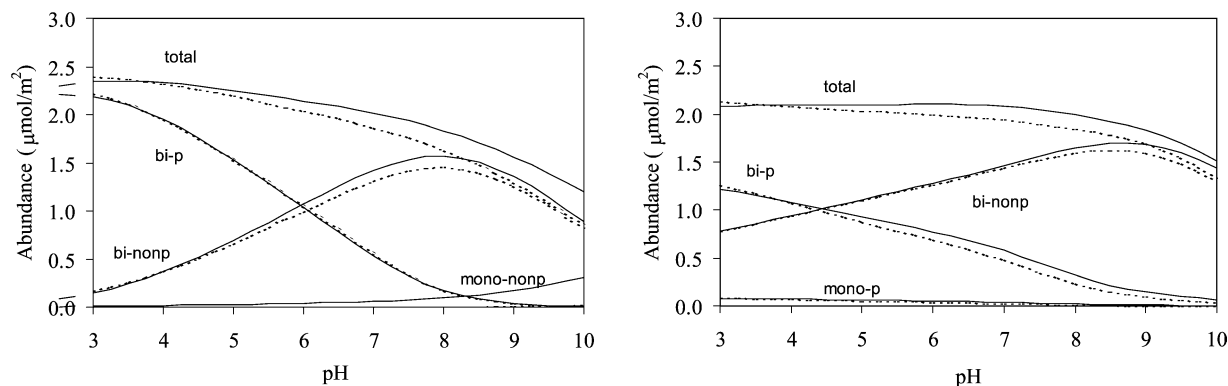


Fig. 6. Abundance of inner-sphere complexes of phosphate (left) and arsenate (right) at the goethite surface, according to the CD-MUSIC model. Solid lines, 0.1 M KNO_3 ; dotted lines, 0.01 M KNO_3 . The total concentration of arsenate or phosphate species in solution is 10^{-4} M.

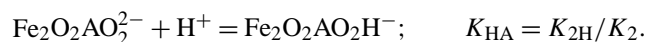
achieved with four complexes. The good fit of adsorption data and the relatively good fit of zeta potential data at different pH and electrolyte concentrations with inner-sphere surface complexes whose presence has been spectroscopically detected gives high credibility to the model.

Arsenate adsorption and electrophoresis in the presence of arsenate could be reasonably well fitted using only the two bidentate complexes. A slight improvement of the fit was achieved by allowing the formation of a small amount of the monodentate protonated complex. The model works well for pH 4.5, 9.0, and 10, but it overestimates somewhat the adsorption at pH 7.0. We are not sure about the cause of this overestimation. Perhaps the model used fails at this pH and a reformulation of the equilibria should be done; perhaps we failed in finding the right set of parameters to describe arsenate adsorption with the trial and error procedure that we have employed here. In spite of this small failure, the model performance can be still considered good for arsenate adsorption.

Conversely to what was found for phosphate, if the monodentate nonprotonated complex was allowed to be present at the surface in significant abundance, the fit of either adsorption or electrophoresis would be poorer. The best-fit parameters are shown in Table 2, and model predictions for arsenate adsorption and electrophoresis are shown in Figs. 2, 3, and 4. The $\log K_2$ value was somewhat smaller for arsenate than for phosphate, whereas the $\log K_{2H}$ values were very similar. It must be noted that the value of f for the bidentate nonprotonated complex is significantly lower for arsenate. This low value was important for predicting low salt dependency in the case of arsenate adsorption. Hiemstra and Van Riemsdijk [4] could successfully fit arsenate adsorption on goethite by using the same complexes as for phosphate with only small changes in $\log K$ values. This is in variance with the results presented in this article. The fit performed by Hiemstra and Van Riemsdijk was done only to data obtained in 0.1 M NaCl, and no effect of the ionic strength was investigated [4]. The parameters informed by these authors for arsenate adsorption would predict a higher salt dependence than the one found in this article.

Fig. 6 shows the abundance of surface species for phosphate and arsenate in the pH range 3–10 at 0.1 and 0.01 M electrolyte concentration according to the CD-MUSIC model with parameters optimized in this article. The total solution concentration of arsenate or phosphate was 10^{-4} M for these calculations. The dominant species is the bidentate one, which is protonated at low pH. This is in agreement with previous findings for phosphate adsorption modelling [10] and spectroscopic data [12]. In addition, the fact that mainly bidentate complexes of arsenate seem to adsorb at the goethite–water interface reinforce the conclusions already obtained by Fendorf et al. [15] and Waychunas et al. [16]. Arsenate and phosphate adsorb mainly as bidentate complexes at high surface loading because under these conditions bidentate species locate more charge at the surface than monodentate ones, allowing a lower electrostatic repulsion between the adsorbed species in the 1-plane [4]. At low surface loadings the monodentate species begins to be important.

From the corresponding values of K_2 and K_{2H} the equilibrium constant for protonation of the bidentate species can be calculated:



The constant of this reaction is $10^{6.2}$ for phosphate and $10^{7.5}$ for arsenate, suggesting that the adsorbed bidentate complex of arsenate has a somewhat higher proton affinity. However, this is not conclusive. A rather good fitting of arsenate adsorption could also be achieved by increasing $\log K_{1\text{H}}$ and simultaneously decreasing $\log K_{2\text{H}}$, resulting in more similar K_{HA} values. The value of K_{HA} can be used to estimate whether the monodentate nonprotonated species can become important for arsenate. We carried out this estimation, assuming that the protonation constant $K_{\text{HA}} = 10^{7.5}$ found for the bidentate complex is also valid for the monodentate one, yielding $\log K_1 = 17.5$ for arsenate. Calculations with this value for $\log K_1$ and $f = 0.25$ indicate that the abundance of the monodentate nonprotonated species is negligibly small in the pH range 3–10 and electrolyte concentrations at 0.1 and 0.01 M. It could become

important at higher pH and higher electrolyte concentrations.

One of the main differences between phosphate and arsenate adsorption is the effect of ionic strength: whereas phosphate adsorption is affected, especially at high pH, arsenate adsorption is less modified when the salt concentration is changed. It is clear that in both cases the effects are much smaller than those usually found for adsorption of outer-sphere surface complexes, where there is an important competence with supporting electrolyte ions [46]. For inner sphere complexes, the salt dependency can be understood by inspecting the effects of ionic strength on the abundance of surface species. For phosphate, the salt dependency at high pH is mainly due to changes in the abundance of the monodentate nonprotonated species (see Fig. 6). At intermediate pH, however, the effects are mainly due to changes in the abundance of the bidentate nonprotonated species: changing the salt concentration affects mainly the abundance of this species for phosphate (Fig. 6). This is due to different f values for this species: $f = 0.35$ for arsenate indicates that this anion locates most of its negative charge at the 0-plane, whereas $f = 0.5$ for phosphate indicates that half of its negative charge is located in the 1-plane. This excess of charge in the 1-plane for phosphate with respect to arsenate makes phosphate adsorption more sensitive to changes in the ionic strength, because the electrostatic potential in the 1-plane depends more on the salt concentration than the potential in the 0-plane [4]. At the moment, we have no clear explanation for the fact that f values for arsenate are lower than for phosphate. Perhaps the larger size of arsenate makes it more propense to a nonsymmetrical neutralization of its charge.

As was indicated in the Introduction, there was contradictory information about which anion, phosphate or arsenate, adsorbs more at the goethite–water interface. The adsorption behavior of both anions reveals that there is not a unique answer to this fact. Phosphate is more sensitive to changes in pH and ionic strength than arsenate. The combined effects of pH and ionic strengths result in higher phosphate adsorption in acidic media at most ionic strengths, but result in lower phosphate adsorption in basic media and at low ionic strengths.

4. Summary and conclusions

The surface properties of a well-crystallized synthetic goethite have been studied by acid–base potentiometric titrations, electrophoresis, and phosphate and arsenate adsorption at different pH and electrolyte concentrations. The experimental results were fitted with the CD-MUSIC model. The charging behavior of the goethite surface is characteristic of a pure sample with no surface carbonate contamination ($PZC = 9.3 \pm 0.1$ and $IEP = 9.3 \pm 0.2$). Phosphate and arsenate adsorption decrease as the pH increases in either 0.1 or 0.01 M electrolyte. However, the effects of pH and elec-

trolyte concentration are more pronounced for phosphate than for arsenate. Arsenate adsorption is almost independent on the electrolyte concentration. These differences in the adsorption behavior explain why several reports indicate that arsenate adsorbs more than phosphate on goethite whereas other reports indicate the opposite phenomenon.

Acknowledgments

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