Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption

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(Received July 29, 1996; accepted in revised form February 18, 1997)

Abstract—The adsorption of phosphate and sulfate on goethite is studied individually and in combination at solution concentrations of phosphate ranging from $10^{-8}$ to $10^{-4}$ M and of sulfate ranging from $10^{-3}$ to $10^{-3}$ M. For single anion adsorption the influence of pH, ionic strength, and anion:goethite ratio was determined. The anion adsorption data were described well with a model in which surface complexation and electrostatic interaction is taken into account. In systems with both anions, the influence of phosphate on sulfate adsorption was much stronger than vice versa, which reflects the higher affinity of phosphate for the goethite surface. In spite of the rather small competitive effect of sulfate on phosphate adsorption expressed per unit surface area of goethite, a considerable increase in the solution concentration of phosphate was observed at relatively low pH in the presence of sulfate. The relative increase in the phosphate solution concentration was larger at a higher ratio of total concentrations of sulfate and phosphate in the system and when lowering the pH. The data indicate that the competitive interaction of phosphate and sulfate for adsorption may have an important effect on the bioavailability of these anions. The competitive adsorption data were predicted well using model parameters derived for single anion adsorption. Copyright © 1997 Elsevier Science Ltd

I. INTRODUCTION

The adsorption of phosphate and sulfate by metal (hydr)oxides in soils and sediments of aquatic systems influences the bioavailability of these anions (Barrow, 1969; Gehhardt and Coleman, 1974; Mc Callister and Logan, 1978; Solis and Torrent, 1989; Soltan et al., 1993; Filippelli and Delaney, 1996). The bioavailability of anions may also be affected by the interaction between anions for adsorption on metal (hydr)oxides. In general, the extent of this interaction depends on the affinity of the anions for the surface, the relative concentration of the anions, the change in the surface potential upon adsorption, and the pH. Anions with a high affinity for metal (hydr)oxides, like phosphate, decrease the adsorption of inorganic anions with an equal or lower affinity, such as arsenate, selenate, molybdate, selenate, and sulfate, over a wide range of pH (Hinston et al., 1971; Parfit, 1982; Ryden et al., 1987; Manning and Goldberg, 1996). This was also the case when only relatively small amounts of phosphate were present (Hinston et al., 1971).

Experiments in which the effect of sulfate on the adsorption of inorganic anions was studied were usually performed at relatively high total concentrations of sulfate. At total sulfate concentrations of 10–3000 times that of the competing anion, the adsorption of selenate (Benjamin et al., 1982), chromate (Zachara et al., 1987), arsenate (Xu et al., 1988), and phosphate (Hawke et al., 1989; Yao and Millero, 1996) was reduced, but the effects were small with respect to the ratio of total concentrations of the anions. The results also showed that the competitive effect of sulfate on anion adsorption was larger at lower pH.

Only a limited amount of data concerning competition of sulfate and phosphate for adsorption on metal (hydr)oxides is present in literature. The adsorption of phosphate on goethite and on manganese dioxide at low pH was lower when sulfate was present at the high concentration observed in seawater, than in the absence of sulfate (Hawke et al., 1989; Yao and Millero, 1996). When phosphate and sulfate were added in equal total concentrations to goethite the adsorption of sulfate was largely decreased, whereas the effect of sulfate on the amount of adsorbed phosphate was small. Nevertheless, the P solution concentration at low pH was markedly increased in the presence of sulfate, indicating that competitive adsorption of sulfate with phosphate may result in an increased availability of P (Parfit, 1982).

The interaction of anions for adsorption may be caused by direct competition for sorption sites and the influence of anion adsorption on the surface charge of the metal (hydr)oxide. These factors are taken into account in the CD-MUSIC model, in which an electrostatic model and a surface complexation model are combined (Hiemstra and Van Rijmsdijk, 1996), that will be used to describe phosphate and sulfate adsorption. The choice of the adsorption complexes is based on detailed molecular information of adsorption complexes from spectroscopic techniques. For modeling P adsorption on goethite, the adsorption complexes proposed by Tejedor-Tejedor and Anderson (1990) based on in situ cylindrical internal reflection-Fourier transformed infrared spectroscopy data were used (Hiemstra and Van Rijmsdijk, 1996).

The adsorption mechanism of sulfate has since long been a subject of discussion. Infrared (IR) spectroscopy data of dried samples of goethite with adsorbed sulfate have shown that sulfate forms bidentate inner sphere complexes (Parfit and Smart, 1977, 1978). On the other hand, the influence of the ionic strength on sulfate adsorption is rather strong, and this has been interpreted as an indication for outer sphere adsorption (Charlet et al., 1993). Other indications for outer

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sphere adsorption are the low intrinsic energy of sulfate adsorption on goethite (Hansmann and Anderson, 1985) and the observation that sulfate adsorption has no influence on the weathering rate of aluminum oxide surfaces (Charlet et al., 1993). Moreover, in situ extended x-ray absorption fine structure spectroscopy (EXAFS) measurements of adsorbed selenium, which exhibits the same type of adsorption behavior as sulfate (Davis and Leckie, 1980; Baijlsierri and Chao, 1987), also suggested the formation of outer sphere complexes. These EXAFS measurements were carried out at low selenate loading of goethite and pH 3.5, however, the ionic strength was not reported (Hayes et al., 1987). In contrast, in situ EXAFS measurements of selenate adsorption on hydrous ferric oxide and goethite by Manseau and Charlet (1994) have indicated that selenate is adsorbed as a bidentate inner sphere complex with singly coordinated surface groups and, to a lesser extent, as an edge-sharing bidentate complex. These experiments were also carried out at low selenate loading and low pH (pH 2.7 and 3.5), at a known ionic strength of 0.1 M NaNO₃.

Most measurements of P adsorption have been carried out at rather high P solution concentrations, in the range of 10⁻⁴ to 10⁻² M (e.g., Barrow et al., 1980; Bowden et al., 1980). In this study, data are presented of phosphate adsorption on goethite at a wide range of P concentration in solution (10⁻⁸ to 10⁻⁴ M). Sulfate adsorption is determined at solution concentrations ranging from 10⁻⁶ to 10⁻⁴ M. The concentration ranges of phosphate and sulfate that are studied are relevant for a wide range in environmental conditions. Goethite is used because it is an important metal (hydr)oxide in soils and sediments.

The influence of pH, ionic strength, and anion:goethite ratio on phosphate and sulfate adsorption was studied. From these data, model parameters were obtained for the description of the adsorption of sulfate and phosphate on goethite. In systems with both anions, the influence of pH and the ratio of total sulfate and phosphate concentrations on the competitive adsorption of sulfate and phosphate was studied. Competitive adsorption was predicted with the CD-MUSIC model using the model parameters derived from the single anion adsorption experiments.

2. MATERIALS AND METHODS

2.1. Preparation of Goethite

Two goethite batches were prepared by titrating 5 L of 0.5 M Fe(NO₃)₃, 9 H₂O with 2.5 M NaOH, at a rate of 9 mL min⁻¹, to pH 12. The suspension was aged for 4 days at 60°C and subsequently dialyzed with distilled demineralized (DD) water (Hiemstra et al., 1989b). The BET specific surface area was 96.4 m² g⁻¹ for goethite I and 105 m² g⁻¹ for goethite II. The pristine point of zero charge (PPZC) was 9.2 for goethite I and 9.5 for goethite II. The PPZC was determined from the common intersection point of surface charge vs. pH relations at three ionic strengths (Venenma et al., 1996). Goethite I was used in all experiments, except those to determine the sulfate adsorption isotherms, which were carried out using goethite II.

2.2. Adsorption Experiments

Anion adsorption was calculated from the difference in total anion and equilibrium concentration adsorbed (Venema et al., 1996). The amounts of phosphate solution (KH₂PO₄), sulfate solution (K₂SO₄), and goethite suspension that were added, and the total volume per batch experiment were determined by weighing. All solutions were prepared from DD water and stored in plastic bottles to avoid contamination with silica.

Sulfate adsorption isotherms were determined by adding appropriate small volumes of 0.1 M K₂SO₄ to goethite (II) suspensions (14–16 g/L) of 0.1 M NaNO₃, having pH values of 7.0, 4.3, 3.8, or 3.5. After being left overnight the pH of the samples was readjusted. Subsequently, the samples were shaken for 2 h, followed by a second pH adjustment before centrifugation at 22000 g. Total S was measured using ICP. The adsorption was reversible when samples were brought to a pH of 12.

Phosphate and sulfate adsorption edges were determined at a pH ranging from 5.3 to 10. After addition of one of the anions, or of both anions simultaneously in competitive adsorption experiments, suspensions were shaken in an end-over-end shaker for 20 h. When the influence of the order of anion addition on competitive adsorption was studied, one anion was added 24 h after the other, after which the suspensions were shaken for another 20 h. Subsequently the anion solution concentration and the pH were determined.

Phosphate adsorption in 0.01 M KNO₃ was determined for five total goethite ratios. For a goethite ratio of 50%, phosphate adsorption was also determined in 0.5 M KNO₃. In the experiments with the lowest three total P concentrations, 2.6–160 kg P carrier free ³²P was added, resulting in a ratio of ³²P:³⁰P larger than 6.8 x 10⁻³. After shaking, part of the suspension was centrifuged for 10 min at 15000 g after which the supernatant was centrifuged for another 10 min. The ³²P concentration in the second supernatant was determined by Cerenkov counting. The samples, with an aimed activity of 200 disintegrations per min or higher, were counted for 10 min. Since disintegration occurs randomly and hence has a Poisson distribution, the standard error of activity measurements is 1/sqrt(N), where N is the total number of disintegrations counted. For an aimed N larger than 2000 the standard error is maximum 2.2%. For one in every five suspensions, two separate samples were centrifuged, and ³²P in the supernatant was determined. The median of the standard error of two duplicates, which included the error for disintegration, was 2.1%. The P solution concentration was computed using the ³²P:³⁰P ratio corrected for disintegration. For the other experiments, samples were centrifuged at 22000 g and the P solution concentration was determined spectrophotometrically using the manual malachite green method (for concentrations up to 9 µM) (Novozamsky et al., 1993) or the molybdenum blue method.

Sulfate adsorption edges in 0.01 M KNO₃ were determined for a total sulfite concentration of 1.0 x 10⁻⁴ M at a goethite suspension density of 0.5 g L⁻¹ and for 1.0 x 10⁻⁵ M total sulfate at 4.0 g goethite L⁻¹. For the latter system, sulfate adsorption experiments were also carried out in 0.5 M KNO₃. After shaking, part of the suspension was centrifuged at 22000 g. Total S in the supernatant was determined using ICP.

Competitive adsorption was studied in a background solution of 0.01 M KNO₃. Phosphate adsorption in the presence of 1.0 x 10⁻⁴ M total sulfate was determined at three total P:goethite ratios. For one ratio, P adsorption was also determined in the presence of 1.0 x 10⁻³ M. For the lowest two total P concentrations, 1.1–45 kBq carrier free ³²P was added resulting in a ratio of ³²P:³⁰P higher than 2.9 x 10⁻⁶. Sulfate adsorption was determined for a total sulfite concentration of 1.0 x 10⁻⁴ M at a goethite suspension density of 0.5 g L⁻¹ in the presence of 7.9 x 10⁻⁵ and 1.0 x 10⁻⁴ M P. The influence of the order of addition of the two anion solutions on adsorption was studied for total P concentrations of 2.2 x 10⁻⁴ and 1.0 x 10⁻⁴ M with a total sulfite concentration of 1.0 x 10⁻⁴ M.

2.3. Modeling Anion Adsorption

The CD-MUSIC model of Hiemstra and Van Riemsdijk (1996), in which an electrostatic model and a surface complexation model are combined, was used to describe anion adsorption. A description of the most important characteristics is given.

The site density of the reactive surface groups is derived from the crystal structure of goethite. The O, OH, or H₂O surface groups may be coordinated to one, two, or three Fe atoms in the goethite crystal. Depending on the number of these Fe atoms (n), the surface groups are denoted singly (n = 1), doubly (n = 2), or triply (n =
3) coordinated surface groups. The doubly coordinated surface groups are considered to be in the normal pH range (Hiemstra et al., 1989a), and it has been reasoned that only one third of the triply coordinated surface groups is reactive for protons (Hiemstra and Van Riemsdijk, 1996). For goethite, the overall site density of the singly coordinated surface groups is 3.45 sites nm⁻² and of the reactive tripoly coordinated surface groups 2.7 sites nm⁻².

The protonation of the singly and tripoly coordinated surface groups of goethite is described by one-pK reactions (Table 1, Eqn. 1). The log Kₛ values of both reactive groups are unknown but assumed to be comparable and are, therefore, set equal to the PPZC of goethite (Hiemstra and Van Riemsdijk, 1996). The ions of the electrolyte solution are assumed to form ion pairs (Table 1, Eqns. 2 and 3), that are present at the head end of the diffuse double layer (DDL) and are regarded as point charges. The log K for ion pair formation is set to −1. In the absence of specifically adsorbing ions, the Stern layer between the surface and the head end of the DDL is charge free (Hiemstra and Van Riemsdijk, 1996).

Specifically adsorbed ions approach the surface more closely than ion pairs, since the anion and the surface share ligands. For the description of inner sphere complexes in the model, an additional plane (1-plane) within the Stern layer is introduced. The charge of the outer sphere complexes is considered to be spatially distributed. Therefore, a fraction f of the charge of the central cation and the charge of the surface oriented ligands is attributed to the 0-plane, whereas the remaining charge of the central cation and the charge of the solution oriented ligands is attributed to the 1-plane (Hiemstra and Van Riemsdijk, 1996).

The capacitances of the two layers are related to the overall Stern layer capacitance according to \( C = 1/C₁ + 1/C₂ = 1/C \). The three plane model used in the CD-MUSIC model differs strongly from the triple layer model of Davis et al. (1978) because the position of the ion pairs and the value of C₂ is different (Hiemstra and Van Riemsdijk, 1991, 1996); goethite has a Stern layer capacitance of approximately 0.9 F m⁻² and fitting of phosphate adsorption data determined at different ionic strengths has resulted in a C₂ value of 5 F m⁻². This capacitance corresponds with a distance between the 0-plane and the head end of the DDL of a half to one water molecule (Hiemstra and Van Riemsdijk, 1996).

Phosphate adsorption was modeled using bidentate, protonated bidentate, and monodentate surface complex formation of P with singly coordinated surface groups (Table 1, Eqns. 4, 5, and 6). For the description of sulfate adsorption, bidentate complex formation with singly coordinated surface groups was assumed (Table 1, Eqn. 7). Also, a description of sulfate adsorption assuming ion pair formation (outer sphere complexes) or a combination of bidentate complexation and ion pair formation was made, since these were the adsorption mechanisms based on IR spectroscopy and EXAFS data suggested in literature (Parfitt and Smart, 1977, 1978; Hayes et al., 1987; Manoeau and Charlet, 1994).

The model description of the adsorption data was optimized by trial and error, aided by plots of the experimental and modeled data. First the charging curves were modeled (C, log Kₛ), then the description of phosphate and sulfate adsorption in single anion systems was optimized (log Kₛ, f values) while the parameters for the charging behavior were fixed.

### 3. RESULTS

The experimental PPZC and charging curves of goethite were comparable with data for similar goethite preparations (Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) and were described well with the CD-MUSIC model using a Stern layer capacitance of 0.9 F m⁻² (data not shown).

#### 3.1. Phosphate Adsorption

From the measured P adsorption edges in 0.01 M KNO₃, adsorption isotherms at pH 2.5, 4.0, 5.5, 7.0, and 8.5 were obtained by interpolation (Fig. 1). Phosphate adsorption on goethite was nonlinearly related to the P solution concentration, even at a low P loading of goethite. At relatively high P solution concentration, P adsorption decreased with higher pH. However, at very low P solution concentration, P adsorption was lower at pH 2.5 than at pH 4.0.

The log K and f values used for modeling P adsorption are listed in Table 2. Phosphate adsorption was described with the model parameters of Hiemstra and Van Riemsdijk (1996) and with the adjusted model parameters that were used in this study (Fig. 1). The prediction of P adsorption with the model parameters of Hiemstra and Van Riemsdijk (1996) was rather good, except for P adsorption at P solution concentrations below 10⁻⁸ M, particularly at pH 2.5, where adsorption was overestimated. Changing the model parameters improved the model prediction, especially at pH 4 and 5.5, but at pH 2.5 P adsorption was still overestimated at low P solution concentration. Equal adsorption at pH 2.5 and pH 4.0 was predicted at a P loading of 1 μmol m⁻², whereas experimentally a value of about 1.5 μmol m⁻² was found.

In Fig. 2 the influence of ionic strength on P adsorption is shown. For low P loading at low pH almost all P was
Table 2. Model parameters used for the description of charging behavior of goethite, and for phosphate and sulfate adsorption on goethite. Also the P adsorption model parameters used by Hiemstra and Van Riemsdijk (1996) are listed.

<table>
<thead>
<tr>
<th>Charging behavior</th>
<th>This study</th>
<th>Hiemstra and Van Riemsdijk</th>
</tr>
</thead>
<tbody>
<tr>
<td>site density</td>
<td>3.45 nm⁻²</td>
<td>3.45 nm⁻²</td>
</tr>
<tr>
<td>density_effect</td>
<td>2.7 nm⁻²</td>
<td>2.7 nm⁻²</td>
</tr>
<tr>
<td>log K_effect</td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td>log K</td>
<td>-1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>log K_0</td>
<td>8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Stern layer capacitance, C</td>
<td>0.9 F m⁻²</td>
<td>0.9 F m⁻²</td>
</tr>
<tr>
<td>inner layer capacitance, C_i</td>
<td>1.1 F m⁻²</td>
<td>1.1 F m⁻²</td>
</tr>
<tr>
<td>outer layer capacitance, C_o</td>
<td>5.0 F m⁻²</td>
<td>5.0 F m⁻²</td>
</tr>
</tbody>
</table>

Phosphate adsorption

| log K_0 | 30.0        | 29.2        |
| log K_p | 35.5        | 35.4        |
| log K_0 | 20.5        | 20.8        |
| f_r     | 0.55        | 0.50        |
| f_p     | 0.60        | 0.60        |
| Sulfate adsorption |
| log K_0 | 19.5        | 19.5        |
| f_0     | 0.62        | 0.62        |

adsorbed, and, therefore, the influence of ionic strength on the amount of P adsorbed per unit surface area (Fig. 2a) was less clear than on the P solution concentration (Fig. 2b). Increasing the ionic strength resulted in a decrease in P adsorption at low pH and an increase in P adsorption at high pH. The pH at which the effect of the ionic strength on adsorption reversed decreased with higher P loading of goethite.

The model description of P adsorption in a background of 0.5 M KNO₃ was rather good, although P adsorption for the intermediate and high level of P loading was underestimated in the pH range between 5 and 8.

3.2. Sulfate Adsorption

The pH dependence of sulfate adsorption was much larger than that of phosphate adsorption, and no sulfate was adsorbed above the PPZC (Figs. 3, 4). The influence of the ionic strength on the adsorption of sulfate was strong and resulted in a lower adsorption at higher ionic strength over the whole range of pH below the PPZC (Fig. 4).

The pH dependence, salt dependence, and the influence of the sulfate solution concentration on sulfate adsorption was described well with the model, assuming bidentate complex formation with singly coordinated surface groups with a log K_0 of 19.5 and a f_0 value of 0.62 (Figs. 3, 4).

3.3. Competitive Adsorption

The competitive interaction of phosphate and sulfate at equal total concentrations in the system (1·10⁻⁴ M) is shown in Fig. 5. The influence of sulfate on phosphate adsorption was small (Fig. 5a), whereas sulfate adsorption was decreased largely when phosphate was present (Fig. 5b). In the presence of a lower total concentration of phosphate (7.9·10⁻⁵ M) the decrease in sulfate adsorption was smaller (Fig. 5b, inset).

For P adsorption edges determined in the presence of 1·10⁻⁴ M sulfate the fraction of total phosphate adsorbed on goethite was almost 1, and, therefore, the influence of sulfate on P adsorption was evaluated on the basis of the P solution concentration (Fig. 6a). At relatively low pH the presence of 1·10⁻⁴ M sulfate resulted in an increase of the P solution concentration. The pH below which the P solution concentration was affected by the presence of sulfate increased with an increasing ratio of total concentrations of sulfate and phosphate in the system. Furthermore, at a higher SO₄²⁻/P ratio, the relative increase in P solution concentration at low pH due to the presence of sulfate was larger (Fig. 6a, b). The P solution concentration at pH 4, in a system with a total P concentration of 2.2·10⁻⁵ M and a goethite suspension density of 0.2 g l⁻¹, was eight times higher in the presence of 1·10⁻⁴ M sulfate and thirty times higher in the presence of 1·10⁻³ M sulfate (Fig. 6b).

For a system with a total concentration of 2.2·10⁻⁵ M P and 1.0·10⁻⁴ M sulfate, the addition of sulfate 24 h after P resulted in lower P solution concentrations than vice versa.
Simultaneous addition of P and sulfate yielded intermediate P solution concentrations (Fig. 6b). For a total concentration of both phosphate and sulfate of $1 \times 10^{-4}$ M, no influence of the order of addition on the adsorption of sulfate and phosphate was observed (data not shown since markers coincide).

The competitive adsorption of sulfate and phosphate on goethite was predicted well with the model when the model parameters derived for single anion adsorption were used (dashed lines in Figs. 5 and 6).

4. DISCUSSION

4.1. Phosphate Adsorption

For P loadings of goethite ranging from 1.2 to 2.4 μmol m$^{-2}$, the P solution concentrations ranged from $10^{-3}$ to $10^{-4}$ M (Figs. 1 and 4). Phosphate adsorption data described in literature have generally been determined at P solution concentrations above $10^{-3}$ M, however, in natural systems P solution concentrations are usually much lower. Model calculations indicated that over the whole range of P solution concentration examined, the observed P adsorption could be described with the same adsorption processes. Hence, there was no indication for the presence of high affinity phosphate adsorption complexes. For P adsorption determined in 0.01 M KNO$_3$ at higher P solution concentrations, the pH and concentration dependence is comparable to that determined by Bowden et al. (1980) and Hiemstra and Van Riemsdijk (1996).

The log $K$ and $f$ values for the three phosphate surface species that were used by Hiemstra and Van Riemsdijk (1996) for the description of phosphate adsorption (Table 2) were obtained by fitting P adsorption data measured at P solution concentrations of $10^{-3}$ to $10^{-1}$ M (Table 2). The description of our data was improved for low P solution concentrations (Fig. 1) by enlarging the $f_p$ value for the bidentate surface complex to 0.55, which results in a changed contribution of the electrostatic energy to adsorption and consequently affects the log $K_{p}$ value. These changes resulted in an overestimation of P adsorption at high pH, but...
by adjusting the $f_{\text{v}}$ value to 0.24, this was compensated. Using the adjusted model parameters, also the P adsorption phenomena that were modeled by Hiemstra and Van Riem- 
dijk (1996) could be described well.

At low P loading of goethite in 0.01 M KNO$_3$, an increase in the P solution concentration, and thus a small decrease in P adsorption, was observed when lowering the pH from 4 to 2.5 (Figs. 1 and 4). When the adsorption experiments at the two lowest levels of P loading were repeated, comparable results were obtained. Possibly the observed increase in P solution concentration at low P loading and low pH was caused by incomplete separation of the solid and solution phase, although much care was taken to centrifuge the samples properly. Phase separation is more difficult at low P loading, very low pH, and low ionic strength, since these factors together result in a relatively high total charge of the solid and a widely extending DDL stabilizing the colloid system. Another explanation might be a contamination of goethite with anions that compete with P for adsorption at low pH. Furthermore, the P concentration in solution may be increased at low pH due to the presence of iron phosphate complexes in solution. However, model calculations using the solubility product of goethite (Lindsay, 1979) indicated that the P solution concentration was not markedly affected.

The increase in P solution concentration when lowering the pH from 4 to 2.5 was predicted by the model, however, at lower P loading than observed experimentally (Fig. 1). The predicted increase in P solution concentration was due to the formation of H$_2$PO$_4^-$ in solution at very low pH.

The effect of increasing ionic strength on P adsorption agrees with results of Barrow et al. (1980). The pH at which the ionic strength has no influence on adsorption indicates the isoelectric point (IEP). At pH values below the IEP, P adsorption is decreased with higher ionic strength and at pH values above the IEP, P adsorption is increased with higher ionic strength. Due to this effect, the pH dependence of P adsorption is smaller at higher ionic strength. At low P loading of goethite, P adsorption in 0.5 M KNO$_3$ showed no pH dependence below pH 6. This effect was described well by the model (Fig. 2b).

4.2. Sulfate Adsorption

The observed pH and salt dependence of sulfate adsorption on goethite agrees with previous studies (Hingston et al., 1972; Balistrieri and Murray, 1981; Zhang and Sparks, 1990; Hoins et al., 1993; Ali and Dzombak, 1996).

Sulfate adsorption on goethite was described poorly when outer sphere adsorption, using ion pair formation treating sulfate as a point charge, was assumed or when a combination of ion pair formation and bidentate complexation was used. Assuming only bidentate complexation yielded a good description of sulfate adsorption (Figs. 3, 4). In this approach, a considerable part of the charge of the central cation in the SO$_4^{2-}$ ion ($f_{\text{SO}_4} = 0.62$) was attributed to the surface. This charge distribution was necessary to describe the pH dependence of sulfate adsorption.

The macroscopic OH/SO$_4$ ratio of sulfate adsorption, predicted with the model, depended on the pH and the amount of sulfate adsorbed on goethite. For a suspension containing $1 \times 10^{-3}$ M sulfate and 4.0 g goethite $1^{-1}$, the OH/SO$_4$ ratio increased from 0.98 to 1.76 for pH 3 to 9, respectively, which is comparable to experimentally obtained OH/SO$_4$ exchange ratios (Turner and Kramer, 1991). The lower values of the exchange ratio at decreasing pH are due to the increased protonation of the surface (He et al., 1996). A good description of the pH dependence and the OH/anion exchange ratio of anion adsorption is essential for predicting anion transport in poorly buffered media containing metal (hydr)oxides (Meeussen et al., 1996).

With increasing pH, the goethite surface becomes less positively charged. Therefore, the strong decrease in sulfate adsorption with increasing pH indicates that the adsorption of sulfate on goethite is dominated by coulombic energy and that the chemical energy is low. This is also reflected in the low value of the log $K_{SO_4}$ used to describe the data. Since almost no sulfate is adsorbed at the PPZC, the IEP is virtually unaffected. At higher ionic strength the positive surface potential decreases at pH values below the IEP = PPZC, re-
sulting in a lower adsorption of anions, such as sulfate, that are sorbed on positive surfaces (Dzombak and Morel, 1990). In contrast, P adsorbs on goethite with a high chemical energy and, at pH values above the IEP, phosphate is adsorbed against coulombic forces. The increase in P adsorption at high ionic strength at pH values above the IEP can be explained by the less negative potential in the plane of adsorption (Barrow et al., 1980).

4.3. Competitive Adsorption of Phosphate and Sulfate

Phosphate has a higher affinity for adsorption on goethite than sulfate and, therefore, is a stronger competitor. At total concentrations of 1 \cdot 10^{-4} M for both anions, P adsorption is only slightly decreased at pH values below pH 4, whereas sulfate adsorption is much lower over the whole range of pH below the PPZC (Fig. 5). This corresponds with results of competitive adsorption of phosphate and inorganic anions with a lower affinity than phosphate (Hingston et al., 1971; Parfitt, 1982). For soils, it was shown that the competitive adsorption of phosphate and sulfate makes sulfate more available for plant uptake and more susceptible to leaching (Kamprath et al., 1956; Metson and Blakemore, 1978; Bolan et al., 1988).

The order of addition of phosphate and sulfate to goethite had a small influence on adsorption when sulfate was added at a higher total concentration than P (ratio SO_4\_2^-:P = 4:5:1) (Fig. 6b). The observed effect of the order of addition was much smaller than reported by Violante et al. (1991) and Ali and Dzombak (1996). However, Violante et al. (1991) used noncrystalline aluminum oxide, which may have caused partially irreversible sorption. In the experiments of Ali and Dzombak (1996), chelating acid and sulfate, with a comparable affinity for the goethite surface, were used. Chelating acid showed slow sorption kinetics in the presence of sulfate (ratio sulfate:chelating acid = 20:1), which was explained by the reduction in surface sites due to the adsorption of sulfate. Similarly, our data suggested that the sorption kinetics of the anion that was added 24 h after the other anion were slightly slower than when both anions were added simultaneously.

Competitive adsorption may result from direct competition for sorption sites and from electrostatic effects due to the change in charge of the solid upon adsorption. The site density of the singly coordinated surface groups, which are supposed to be reactive for phosphate and sulfate, is 3.45 sites nm\(^{-2}\) or 5.73 \(\mu\)mol m\(^{-2}\). Since the single coordinated surface groups are present in rows on the 110 and 021 face of the goethite crystal, a maximum of 2.86 \(\mu\)mol complexes m\(^{-2}\) can be formed when only bidentate complex formation with phosphate and sulfate is assumed. The observed maximum adsorption of P or sulfate is well below this maximum value indicating the influence of electrostatic interaction (Figs. 1, 3). For a system with both P and sulfate, as shown in Fig. 5, without any interaction a coadsorption of 3.6 \(\mu\)mol m\(^{-2}\) would be expected at pH 2.5, i.e., 2.0 \(\mu\)mol m\(^{-2}\) P and 1.6 \(\mu\)mol m\(^{-2}\) SO\(_4\). However, this value is above the theoretical adsorption maximum of 2.9 \(\mu\)mol m\(^{-2}\), indicating that competition for sorption sites occurs.

Although the competitive effect of sulfate on phosphate adsorption was small, with respect to the amount of P adsorbed per unit surface area of goethite (Fig. 5), it may be of great importance for the bioavailability of phosphate since it caused a substantial increase in the P solution concentration (Fig. 6; Parfitt, 1982). The magnitude of the effect of sulfate on P adsorption and the pH below which P adsorption is affected depends on the relative concentrations of phosphate and sulfate.

5. CONCLUSIONS

Phosphate adsorption on goethite is nonlinearly related to the P solution concentration, even at very low solution concentrations of 10\(^{-6}\) M. Assuming one set of adsorption reactions, the adsorption of P was described well over the whole range of P solution concentrations examined.

The adsorption behavior of sulfate on goethite, that shows strong pH and salt dependence and no adsorption at pH values above the PPZC, was described well using only one inner sphere surface complex.

In competitive adsorption systems with phosphate and sulfate, phosphate is a stronger competitor for adsorption on goethite than sulfate, which is consistent with the higher affinity of phosphate for the surface compared to sulfate. In the presence of phosphate, the adsorption of sulfate is largely reduced over the whole range of pH below the PPZC. On the other hand, the presence of sulfate causes only a small decrease in P adsorption per unit area surface of goethite at relatively low pH, which, nevertheless, results in a substantial increase in the P solution concentration. The interaction of phosphate and sulfate for adsorption was predicted well with the model using the parameters derived for single anion adsorption.

Acknowledgments—The authors thank Dr. B.J.M. Verduin of the Department of Virology, Wageningen Agricultural University, for allowing us to use the facilities of the isotope laboratory. Mr. A.J. Korteweg, Department of Colloid and Physical Chemistry (WAU), is acknowledged for performing the BET surface area measurements. René Rietra is thanked for carrying out the potentiometric titrations of goethite. The reviewers of Geochimica et Cosmochimica Acta are thanked for their helpful comments on the manuscript.

Editorial handling: L. S. Balistieri

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