

Adsorption of Phosphonates onto the Goethite–Water Interface

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The adsorption of one phosphonate, two hydroxyphosphonates, and five aminophosphonates onto the iron (hydr)oxide goethite (α -FeOOH) has been studied as a function of pH. At phosphonate concentrations significantly lower than the total number of available surface sites, nearly 100% adsorption is observed below pH 8.0. Adsorption decreases to negligible levels as the pH is increased to 12.0. Under the conditions just described, adsorption of nitrilotris(methylenephosphonic acid) as a function of pH is nearly independent of the ionic strength (from 1 mM to 1 M). At phosphonate concentrations close to the total number of available surface sites, adsorption decreases over a broader range in pH and reflects the number of phosphonate groups. At pH 7.2, the maximum extent of adsorption decreases as the number of phosphonate groups increases from one to five. Adsorption is modeled using a 2-*pK* constant capacitance model that postulates formation of a 1:1 surface complex involving one surface site and one phosphonate functional group. Denoting the fully deprotonated phosphonate ligand as L^{a-} , different protonation levels for adsorbed phosphonate species are represented by a series of equilibrium constants of the form

$$\beta_{n,\text{surf}} = \frac{[\equiv \text{Fe-L-H}_n^{(a-n-1)-}]}{[\equiv \text{FeOH}] \cdot [L^{a-}] \cdot [\text{H}^{+(n+1)}]}$$

For a phosphonate of charge $a-$, there are $(a - 1)$ possible surface protonation levels. For a surface protonation level n , log $\beta_{n,\text{surf}}$ values derived from this modeling approach are related to the surface complex charge Z through the following linear relationship:

$$\log \beta_{n,\text{surf}} = (11.45 + 7.31 \cdot n) - (2.53 - 0.46 \cdot n) \cdot Z.$$

Using this approach, adsorption as a function of phosphonate concentration and pH can be fully accounted for. © 1999 Academic Press

Key Words: phosphonates; goethite; adsorption; surface complexation; surface protonation.

INTRODUCTION

The adsorption of carboxylic acids onto oxide surfaces has been well studied in recent years. Adsorption has been ex-

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plained by both inner-sphere complexes (mixture of ionic bonding and covalent bonding) and outer-sphere complexes (near-range electrostatic interactions). While monocarboxylic acids exhibit only weak adsorption, increasing the number of carboxylic acid groups leads to increased adsorption (1). Aminocarboxylate compounds which are able to effectively complex Fe(III) or Al(III) in solution such as NTA or EDTA display a strong adsorption onto the respective (hydr)oxide surfaces (2–4).

While adsorption of carboxylic acids has been extensively investigated, only a few studies have focused on the corresponding phosphonates. Phosphonates are effective complexing agents and contain one or more phosphonate groups -C-PO(OH)_2 . Properties such as high water solubility, the ability to complex metals even at high pH, the ability to prevent scale formation and corrosion (5, 6), and good chemical stability make them attractive for use in a variety of industrial applications. Phosphonates are used in oil and gas production, in cooling water, boiler, and desalination systems to inhibit scale formation and corrosion, in the textile industry to stabilize peroxide-based bleaching agents, in industrial and household detergent formulations, and in nuclear medicine as bone-seeking carriers of radionuclides. Approximately 20,000 tons are used in the United States each year (7).

Phosphonates have a strong tendency to adsorb onto a variety of surfaces. Examples include calcite (8), barite (9), cassiterite (10), clays (11, 12), aluminum oxides (13–15), and iron oxides (16). Adsorption has also been studied with natural adsorbents such as sewage sludge (17–19), sediments (12), and soils (20).

Despite the fact that phosphonates are known to adsorb strongly, only few studies have tried to model the adsorption of phosphonates using a surface complexation model. Most authors use a Langmuir isotherm at a given pH (12). Laiti and co-workers (13, 14) have modeled the adsorption of phenylphosphonate (a monophosphonate) onto aluminum oxides. By using three surface complexes ($\equiv \text{XLH}$, $\equiv \text{XL}^-$, and $\equiv \text{XLOH}^{2-}$) they were able to model the acid–base behavior, the pH-adsorption edge, and the adsorption isotherm in the system phenylphosphonate–aged- Al_2O_3 . For the system phenylphosphonate–boehmite, they considered two binuclear surface complexes: $\equiv \text{X}_2\text{LH}$ and $\equiv \text{X}_2\text{L}^-$. Gerbino (15) presented

TABLE 1
Names, Abbreviations, and Structures of the Phosphonates Used in This Study

Abbreviation	Name	Structure
MP	Methylphosphonic acid	$\text{CH}_3\text{-PO}(\text{OH})_2$
AMP	Aminomethylphosphonic acid	$\text{H}_2\text{N-CH}_2\text{-PO}(\text{OH})_2$
HMP	Hydroxymethylphosphonic acid	$\text{HO-CH}_2\text{-PO}(\text{OH})_2$
HEDP	1-Hydroxyethane- (1,1-diphosphonic acid)	$\begin{array}{c} (\text{OH})_2\text{O P} \\ \\ \text{HO-C-CH}_3 \\ \\ (\text{OH})_2\text{O P} \end{array}$
IDMP	Iminodi- (methylenephosphonic acid)	$\begin{array}{c} (\text{OH})_2\text{OP-CH}_2 \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N-H} \\ \quad \quad \quad \diagup \\ (\text{OH})_2\text{OP-CH}_2 \end{array}$
NTMP	Nitrilotris- (methylenephosphonic acid)	$\begin{array}{c} (\text{OH})_2\text{OP-CH}_2 \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N-CH}_2\text{-PO}(\text{OH})_2 \\ \quad \quad \quad \diagup \\ (\text{OH})_2\text{OP-CH}_2 \end{array}$
EDTMP	Ethylenedinitrilotetrakis- (methylenephosphonic acid)	$\begin{array}{c} (\text{OH})_2\text{OP-CH}_2 \quad \quad \quad \text{CH}_2\text{-PO}(\text{OH})_2 \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ \quad \quad \quad \text{N-CH}_2\text{-CH}_2\text{-N} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ (\text{OH})_2\text{OP-CH}_2 \quad \quad \quad \text{CH}_2\text{-PO}(\text{OH})_2 \end{array}$
DTPMP	Diethylenetrinitrilopentakis- (methylenephosphonic acid)	$\begin{array}{c} (\text{OH})_2\text{OP-CH}_2 \quad \quad \quad \text{CH}_2\text{-PO}(\text{OH})_2 \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ \quad \quad \quad \text{N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ (\text{OH})_2\text{OP-CH}_2 \quad \quad \quad \text{CH}_2\text{-PO}(\text{OH})_2 \\ \quad \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \quad \text{PO}(\text{OH})_2 \end{array}$

a limited surface complexation model for the adsorption of polyphosphonates onto aluminum oxide.

This study examines the adsorption of eight phosphonate-containing ligands onto goethite as a function of pH, ionic strength, and phosphonate concentration, using experimental data and a simple surface complexation model (the 2-*pK* constant capacitance model). As shown in Table 1, compounds possessing one (MP, AMP, and HMP), two (HEDP, IDMP), three (NTMP), four (EDTMP), and five (DTPMP) phosphonate groups are included in this study. Four of the phosphonates examined are widely used in technical applications: HEDP, NTMP, EDTMP, and DTPMP (21). Although we are chiefly concerned with how the number of phosphonate groups affect adsorption, the presence of other functional groups (alcoholate and amino groups) and molecular structures plays a role in some instances.

MATERIALS AND METHODS

The goethite used in this study was synthesized and characterized as described in (22) and was stored as a slurry contain-

ing 44 g/L goethite. MP, AMP, HEDP, IDMP, and NTMP in the acid form were obtained from Fluka (>97% purity). EDTMP (Dequest 2041, 95% purity), HMP, and DTPMP were provided by Monsanto (St. Louis, MO).

Adsorption experiments were carried out in 30-mL glass vials in a 25 ± 0.2°C constant temperature bath. A goethite loading of 0.42 g/L was used in all experiments. For most experiments, 10 mM NaNO₃ was used to maintain constant ionic strength conditions. In one set of experiments, the ionic strength was varied by adding 1, 10, and 100 mM and 1.0 M NaNO₃. Prior to phosphonate addition, carbon dioxide was excluded by sparging suspensions with argon. Following phosphonate addition, suspensions were stirred for 1 h using a Teflon-coated stir bar before pH measurement and sample collection. Each sample was filtered using 0.2 micrometer pore-diameter polycarbonate filters (Nuclepore Corp.) prior to analysis.

The pH-adsorption edge experiments employed 10 and 40 μM phosphonate concentrations. No buffer was used in these experiments. Instead, NaOH and HNO₃ additions were used to

TABLE 2
Equilibrium Constants Describing the Acid–Base Properties
of Goethite from Ref. (27)

$\equiv\text{FeOH} + \text{H}^+ = \equiv\text{FeOH}_2^+$	$\log K: 7.47$
$\equiv\text{FeOH} = \equiv\text{FeO}^- + \text{H}^+$	$\log K: -9.51$
Total specific capacitance	$1.28 \text{ F}\cdot\text{m}^2$
Site density	$1.7 \text{ sites}/\text{nm}^2$
BET surface area ^a	$47.6 \text{ m}^2/\text{g}$

^a From Ref. (22).

vary the pH. Constant pH experiments employed either 1.0 mM acetate (pH 4.6) or 1.0 mM MOPS (pH 7.2) buffers.

Experiments examining adsorption–desorption kinetics began by adding 10 μM NTMP to goethite suspensions buffered to pH 7.2 (1.0 mM MOPS). These buffers were selected because of their poor ability to complex metals ions (23). Aliquots were taken as a function of time and filtered for analysis. In one experiment, desorption was initiated 1 h after phosphonate addition by raising the pH to 12.2 using 1 M NaOH. In a second experiment, the phosphonate remained in contact with goethite for 7 days prior to raising the pH to 12.2.

HEDP, NTMP, EDTMP, and DTPMP in filtered solutions were measured using an ion-pair HPLC method described in Nowack (24). Each phosphonate was complexed with Fe(III) at low pH and then separated on a polymer reversed-phase column. The eluent contained the tetrabutylammonium counterion, bicarbonate buffer (pH 8.3), and acetonitrile. Using a UV/visible detector set at 260 nm, detection limits of this technique are 0.1 μM for NTMP, EDTMP, and DTPMP, and 0.5 μM for HEDP.

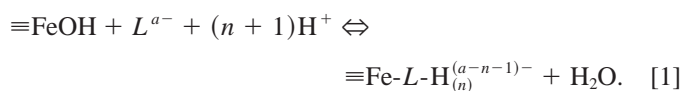
IDMP, AMP, HMP, and all phosphonates included in the 40 μM pH–adsorption edge experiments were quantified by measuring total phosphorus. A filtered sample was digested for 2 h with potassium peroxodisulfate at 100°C and measured as orthophosphate by the molybdenum blue method (25). Absorbance was measured spectrophotometrically at 720 nm.

DATA TREATMENT

FITEQL 3.1 (26) was used to model equilibrium speciation. The pK_a values for dissolved phosphonate species were selected from the CRITICAL database (23) and were corrected to 0.01 M ionic strength using the Davies equation. Acid–base properties of free- and phosphonate-bound surface sites and electrostatic aspects of the (hydr)oxide–water interface were modeled using the 2- pK constant capacitance model. The surface area of this goethite preparation was determined previously to be 47.6 m^2/g (22). Lövgren *et al.* (27) reported surface site density, first and second protonation constants, and total specific capacitance values for their goethite preparation in 0.10 M NaNO_3 . It is assumed that these same values (shown in Table 2) also apply to our goethite preparation in 0.010 M NaNO_3 .

In order to account for phosphonate adsorption within the 2- pK constant capacitance model, it is necessary to specify the number of surface sites, adsorbing anions, and protons that comprise each surface species. Results from the Sjöberg group (13, 14, 28) are especially pertinent here. Phenylphosphonate adsorption onto aged Al_2O_3 (13) and onto AlOOH (boehmite) (14) has been examined using acid–base titration and FTIR (28). Phenylphosphonate ($\text{C}_6\text{H}_5\text{PO}_3^{2-}$) possesses two anionic oxygen groups. The most recent appraisal of the experimental evidence (28) concluded that adsorbed phenylphosphonate makes contact with one surface-bound Fe^{III} atom (i.e., mononuclear surface complex) and is capable of existing in three protonation levels ($\equiv\text{AILH}$, $\equiv\text{AIL}^-$, and $\equiv\text{AIlOH}^{2-}$).

For the sake of simplicity, we have made the assumption that the equation formulated by Sjöberg’s group for monophosphonate adsorption onto Al (hydr)oxides also applies to the adsorption of phosphonate-containing compounds onto FeOOH (goethite):



As far as the mathematical formulation of FITEQL is concerned, this equation allows for mononuclear complex formation and disallows multinuclear complex formation. It makes no distinction between monodentate and multidentate mononuclear surface complexes. Using Eq. [1], two protonation levels are possible for the monophosphonates MP and HMP (deprotonated and protonated), three for AMP (taking into account protonation of the amine group), four for the diphosphonate HEDP, five for IDMP, seven for NTMP, ten for EDTMP, and 13 for DTPMP. As subsequent sections will indicate, Eq. [1] provided a reasonable representation of the experimental data, and hence equations accounting for multinuclear surface complexes were not employed.

In solution, chelate ring formation is usually required in order for multidentate complexes to be significant. Five-membered rings are most stable, followed by six-membered rings; larger rings are substantially less stable (29). Assuming that surface complexes are analogous to solution complexes, generalizations can be made about the viability of multidentate surface complexes involving the eight compounds included in our study (Table 1). The alcohol groups in HMP and HEDP probably do not participate in bond formation, owing to their high pK_a values. Six of the compounds listed in Table 1 possess amine groups which are near enough to phosphonate groups to allow the formation of five-membered chelate rings. If amine groups are *not* involved in coordination, ring sizes become prohibitively large (i.e., involving eight or more atoms.)

The surface parameters listed in Table 2, combined with the FeOOH loading of 0.42 g/L, can be used to calculate a surface site loading (S_T) of 58 μM . Hence, 40 μM phosphonate

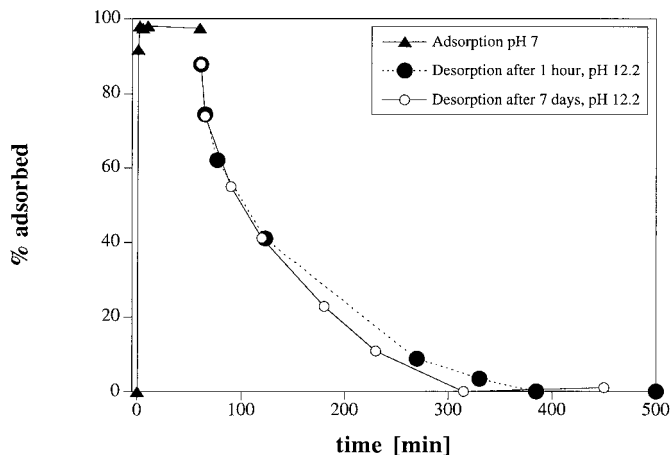


FIG. 1. Adsorption of NTMP onto goethite at pH 7 and desorption at pH 12.2 as a function of time. NTMP was adsorbed for 1 h or for 7 days, respectively, before addition of NaOH. Conditions: 9.8 μM NTMP, 0.42 g/L goethite, 1 mM MOPS-buffer, 0.01 M NaNO_3 , addition of 1 M NaOH after 60 min and 7 days.

concentrations are comparable in magnitude to S_T . Experiments performed at this phosphonate concentration were used, if possible, to determine stability constants for surface complexes, since adsorption was sensitive to changes in pH. In contrast, 10 μM phosphonate concentrations result in an excess of surface sites and nearly 100% adsorption below approximately pH 8.0. Experiments performed using 10 μM phosphonate concentrations were only used to fit the adsorption of the fully deprotonated surface complex at pH values above 10.

Once stability constants for surface complexes had been determined, their values were used to calculate the amount of adsorption expected in 10 μM phosphonate experiments and in adsorption isotherm experiments at pH 7.2 using the speciation program *Mac μ QL* (30).

The iterative algorithm employed by *FITEQL* fails with data from EDTMP and DTPMP adsorption experiments, owing to the large number of possible surface complexes. The stability constants of these surface complexes were adjusted manually using the speciation program *Mac μ QL*. All surface complexes were considered equally important so that no surface complexes were overrepresented. Again, the 40 μM data were fitted and subsequently the 10 μM data and the adsorption isotherms were calculated.

RESULTS

Adsorption Kinetics

The adsorption of 10 μM NTMP onto 0.42 g/L goethite at pH 7 is very fast and complete within a few minutes (Fig. 1). If the pH is raised to 12.2 after 1 h of contact time, a slow desorption process takes place. All NTMP can be desorbed within 5 h, and therefore the adsorption reaction is completely reversible. If NTMP is adsorbed onto goethite at pH 7 for 7

days, the same desorption behavior is observed after raising the pH to 12.2. This suggests that NTMP is adsorbed as a surface complex and that no phase transformation into an iron(III)-NTMP precipitate took place. Precipitates of phosphonates with Fe(III) have been observed for NTMP at pH 2–7 (31) and glyphosate (a mixed phosphonate–carboxylate ligand) at pH 7 (32).

Ionic Strength Dependence

The adsorption of 10 μM NTMP onto 0.42 g/L goethite at four different concentrations of the background electrolyte NaNO_3 is shown in Fig. 2. NTMP adsorption increases with decreasing pH. There is no influence of the background NaNO_3 concentration on the adsorption in the range from 1 mM to 1 M NaNO_3 . Whereas the presence of an ionic strength effect does not necessarily mean that outer-sphere complexes are formed, the absence of an effect points clearly toward an inner-sphere complex (33). The line in Fig. 2 represents the model calculation for the 0.01 M system with the constants from Table 3.

Adsorption as Function of pH

Two data sets were obtained for all phosphonates. The 10 μM phosphonate data represent an excess of surface sites over the phosphonates, while the 40 μM data represent a surface site concentration and phosphonate concentration that are comparable in magnitude.

Figure 3 shows the results for the monophosphonate MP. Two surface complexes, $\equiv\text{FeL}^-$ and $\equiv\text{FeLH}^0$, are sufficient for modeling the data. Both complexes are assumed to be mononuclear surface complexes involving bond formation between one O of the phosphonate group and one surface $\equiv\text{FeOH}$ group as proposed for phenylphosphonate and alumina (13). The two complexes very well represent the plateau at low pH and the decrease in adsorption toward higher pH.

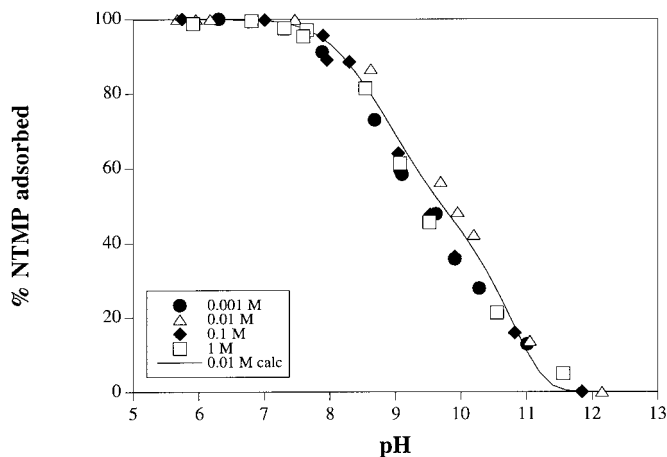
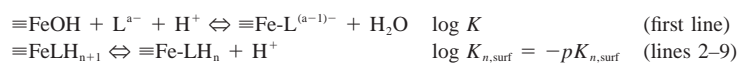


FIG. 2. Adsorption of NTMP onto goethite as a function of the concentration of the background electrolyte. Conditions: 9.8 μM NTMP, 0.42 g/L goethite, NaNO_3 as background electrolyte.

TABLE 3
Stability Constants for Goethite–Phosphonate Surface Complexes ($I = 0.01 \text{ M NaNO}_3$, 25°C)

Surface complex		MP	HMP	AMP	HEDP	IDMP	NTMP	EDTMP	DTPMP
$\equiv\text{FeL}$	$\log K$	13.31	13.26	14.14	18.8	18.91	23.85	30.05	41.0
$\equiv\text{FeLH}$	$pK_{1,\text{surf}}$	6.06	5.90	7.65	6.2	6.12	6.2	7.6	8.0
$\equiv\text{FeLH}_2$	$pK_{2,\text{surf}}$			5.94	4.8	5.47	5.6	6.2	7.2
$\equiv\text{FeLH}_3$	$pK_{3,\text{surf}}$				3.2	4.05	4.8	5.6	6.6
$\equiv\text{FeLH}_4$	$pK_{4,\text{surf}}$						3.5	5.0	6.0
$\equiv\text{FeLH}_5$	$pK_{5,\text{surf}}$						2.4	4.0	5.0
$\equiv\text{FeLH}_6$	$pK_{6,\text{surf}}$							2.7	4.0
$\equiv\text{FeLH}_7$	$pK_{7,\text{surf}}$								2.8
$\equiv\text{FeLH}_8$	$pK_{8,\text{surf}}$								1.6

Note. Log K is defined by the equations:



Adsorption becomes negligible above pH 10. The data from 10 μM total MP experiments can also be described using the two log K values obtained from the 40 μM total MP data.

HMP, which possesses a phosphonate group and a hydroxyl group, adsorbs as a function of pH in a manner that is quite similar to MP (Fig. 3). Again, the surface complexes $\equiv\text{FeL}^-$ and $\equiv\text{FeLH}^0$ yield reasonable modeling results; log K values for HMP and MP are similar (see Table 3).

Adsorption of AMP, which possesses a phosphonate group and an amino group, cannot be modeled using $\equiv\text{FeL}^-$ and $\equiv\text{FeLH}^0$ alone; a third surface complex, $\equiv\text{FeLH}_2^+$, must be postulated in order to obtain a good fit to the experimental data. The surface complex $\equiv\text{FeL}^-$, with a deprotonated amino-group, is only predicted to occur in low concentrations at high pH. The surface complex $\equiv\text{FeLH}^0$ corresponds to a surface complex with a protonated amino group and a deprotonated phosphonate group. $\equiv\text{FeLH}_2^+$ corresponds to a complex with a protonated amino-group and a singly protonated phosphonate group. This description is reasonable since the first protonation of AMP occurs on the amino-group, which is not believed to form a bond to the surface. The pH adsorption isotherm for AMP exhibits a maximum near pH 4 with a small decrease toward pH 3, which was not found for MP and HMP (Fig. 3).

Dissolved polyphosphonates are known to undergo numerous changes in protonation level as a function of pH (25) and hence it is quite reasonable to postulate multiple protonation levels for adsorbed polyphosphonates. In our modeling work, it is necessary to increase the number of protonation levels as the number of phosphonate groups and amino groups on the molecule is increased. IDMP and HEDP require four protonation levels, NTMP requires six, EDTMP requires seven, and DTPMP requires nine.

Experiments employing 40 μM concentrations of IDMP (Fig. 3) and HEDP (Fig. 4) require protonation levels that range from $\equiv\text{FeLH}_3^0$ at low pH to $\equiv\text{FeL}^{3-}$ at high pH. Each protonation level dominates surface speciation within a fixed

pH range; at higher (or lower) pHs it is superseded by another surface species with lower (or higher) numbers of bound protons. Although concentrations for a particular surface species are quite sensitive to pH, the sum of all adsorbed phosphonate species decreases very slowly as the pH is increased.

The point of zero charge for goethite has been reported to be pH 8.5 (23). With IDMP and HEDP, both 10 and 40 μM data indicate considerable adsorption at and above this pH value. The 10 μM adsorption data, for example, show that there is still 90% adsorption of HEDP and IDMP at the point of zero charge.

Six surface complexes are needed to describe NTMP adsorption (Fig. 4). The complexes range from the neutral $\equiv\text{FeLH}_5^0$ at low pH to $\equiv\text{FeL}^{5-}$ with a charge of -5 at high pH. Although the surface of the goethite is negatively charged at pH 9, there is still strong adsorption of the highly negative NTMP anion (HNTMP^{5-} is prevalent at this pH). The log K values obtained at 40 μM NTMP are able to explain the 10 μM data as well.

When 10 μM concentrations are employed, the adsorption of EDTMP and DTPMP decreases linearly as the pH is increased from 3 to 12 (Fig. 4). EDTMP requires seven surface species and DTPMP requires nine surface species to reproduce this pH dependence. The neutral surface complexes $\equiv\text{FeLH}_7^0$ for EDTMP and $\equiv\text{FeLH}_9^0$ for DTPMP were not considered because apparently they are only needed below pH 3. The completely deprotonated and highly charged complexes $\equiv\text{FeL}^{7-}$ and $\equiv\text{FeL}^{9-}$ occur only at very low concentrations above pH 10. The 10 μM data can be described as well with the set of log K values obtained from the 40 μM data.

Adsorption Isotherms at Constant pH

Adsorption was also studied as a function of phosphonate concentration at constant pH. Experiments were conducted at pH 7.2 for all phosphonates and at three additional pH values

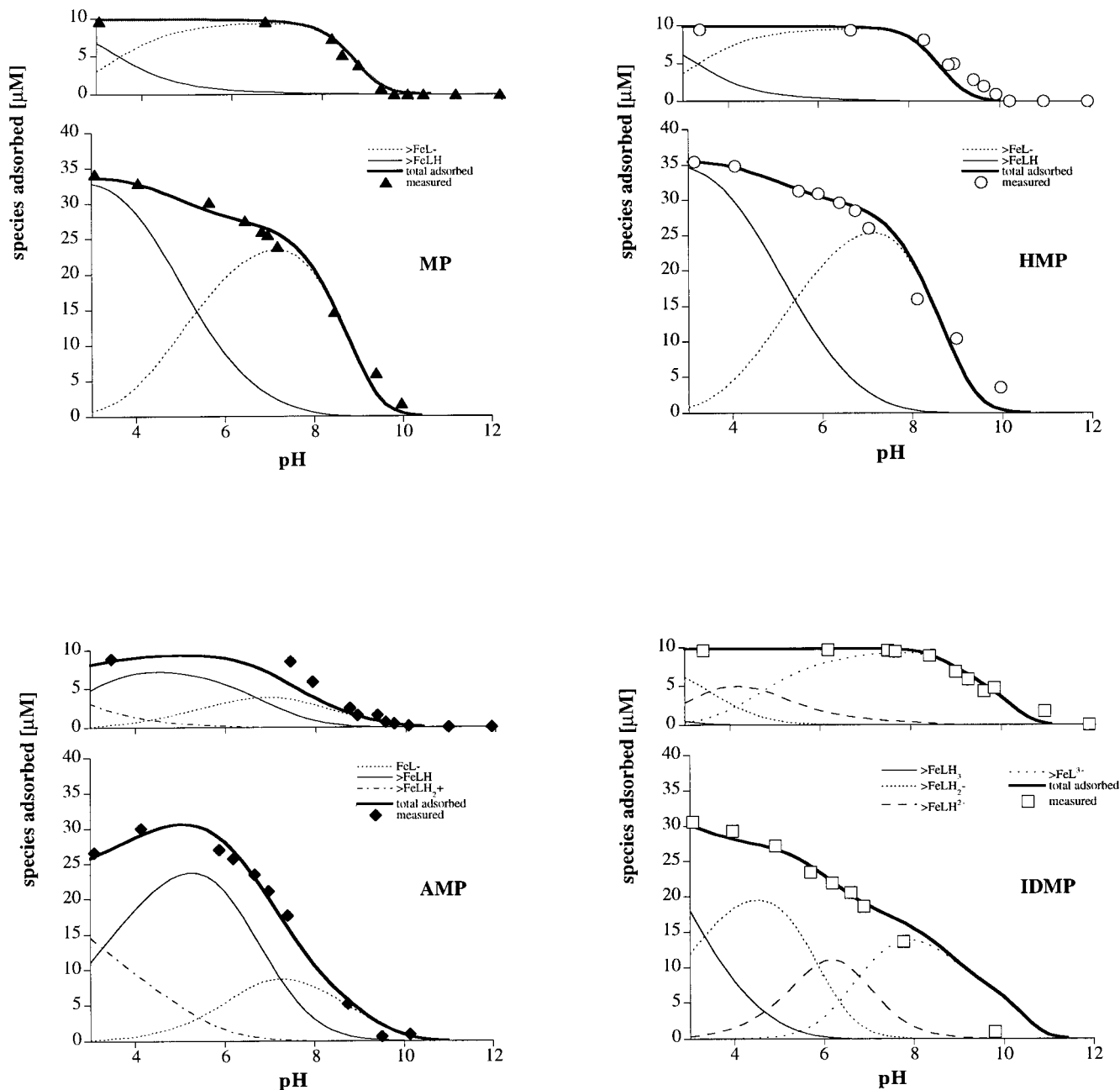


FIG. 3. Adsorption of the monophosphonates MP, HMP, AMP and the diphosphonate IDMP onto goethite as a function of pH using an excess of phosphonates (bottom) and an excess of surface sites (top). Conditions (all phosphonates): 38.7 μM (bottom) and 9.8 μM (top), 0.42 g/L goethite, 0.01 M NaNO₃. The lines are calculated with the constants from Tables 2 and 3.

for NTMP. The adsorption isotherms were also modeled using log *K* values from the pH dependence experiments and do not involve further adjusting of the parameters.

Adsorption isotherms for MP, HMP, and AMP at pH 7.2 are shown in Fig. 5a. MP reaches a surface coverage of 60 μmole/g, and HMP reaches a surface coverage of 70 μmole/g. The *S_T* value reported earlier (58 μM) corresponds to 140 μmole H⁺/g. Thus, the maximum extent of MP and

HMP adsorption corresponds to approximately half of the H⁺ binding sites. AMP is unlike the other two monophosphonates. Because of its amino group, the dianion (*L*²⁻) to a monoanion (*HL*⁻) transition in solution occurs near pH 10, several log units higher than for MP and HMP. As shown in Fig. 5a, AMP adsorption is substantially lower than for the other two monophosphonates. Adsorption data for all three monophosphonates are successfully modeled

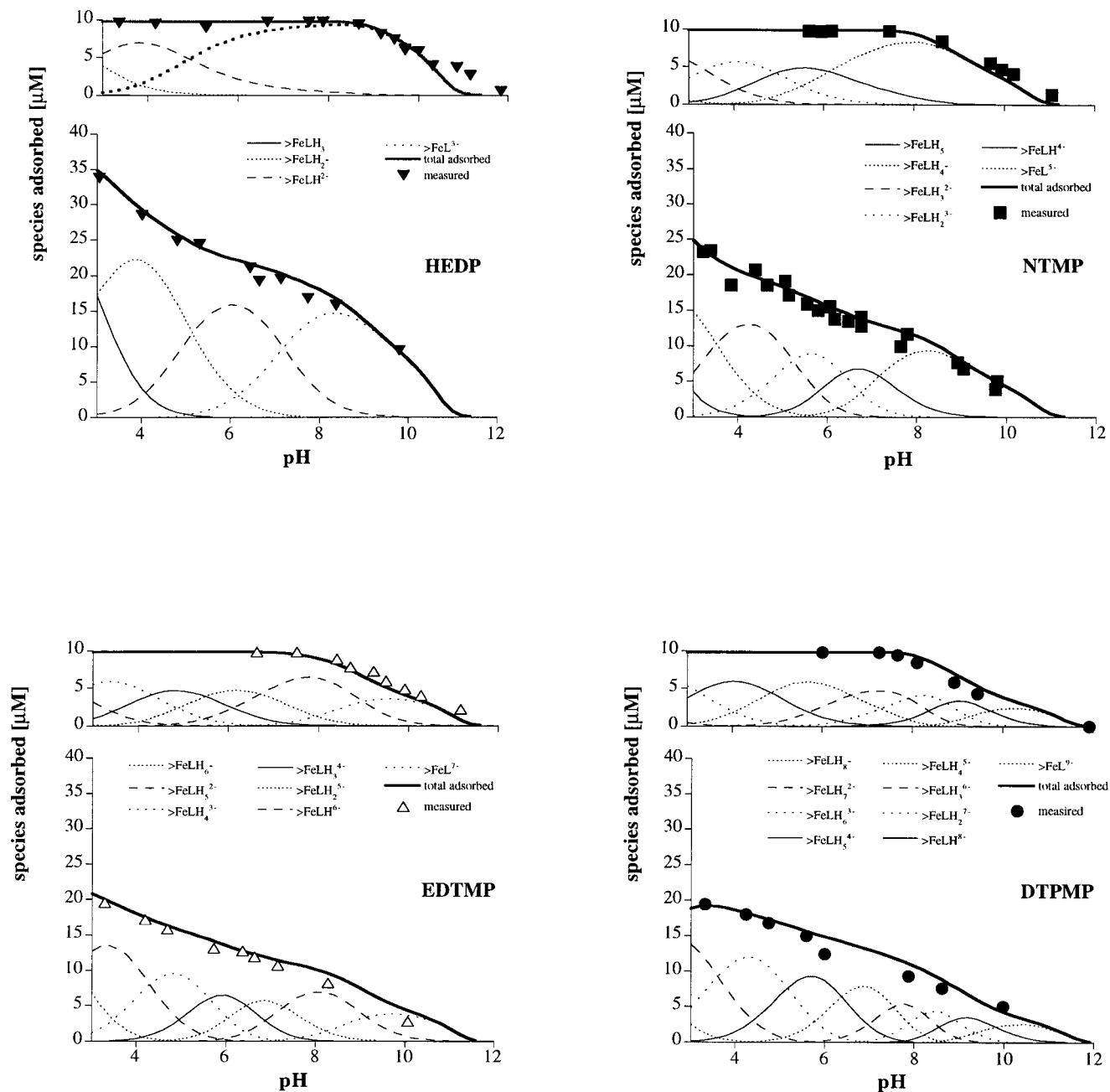


FIG. 4. Adsorption of the polyphosphonate HEDP, NTMP, EDTMP, and DTPMP onto goethite at as a function of pH using an excess of phosphonates (bottom) and excess of surface sites (top). Conditions (all phosphonates): 38.7 μM (bottom) and 9.8 μM (top), 0.42 g/L goethite, 0.01 M NaNO₃. The lines are calculated with the constants from Tables 2 and 3.

using stability constants derived from adsorption versus pH experiments (40 μM total phosphonate).

As shown in Fig. 5b, adsorption of the diphosphonate HEDP and the aminodiphosphonate IDMP rises sharply as their concentration is increased, but reach maximum extents of adsorption that fall short of values observed for MP and HMP. Low concentrations of HEDP and IDMP do, however, yield higher extents of adsorption than AMP.

For the three remaining compounds, maximum extents of adsorption continue to decrease as the number of phosphonate groups is increased: NTMP (one amine group, three phosphonate groups) > EDTMP (two amine groups; four phosphonate groups) > DTPMP (three amine groups; five phosphonate groups). The adsorption isotherms are well represented by the model calculations shown in Fig. 5b.

Maximum extents of NTMP adsorption (Fig. 6) decrease as

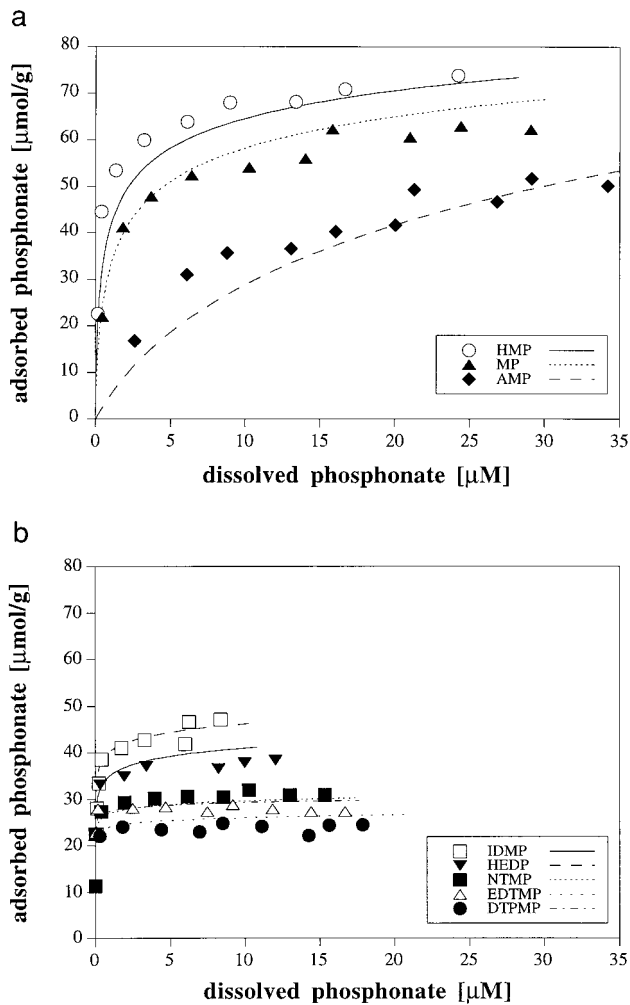


FIG. 5. Adsorption isotherms of phosphonates onto goethite at pH 7.2. Experimental data and model lines are shown. (a) Adsorption of the monophosphonates MP, HMP, and AMP at pH 7.2. Conditions: Goethite 0.42 g/L, 1 mM MOPS-buffer, 0.01 M NaNO₃. The lines are calculated with the constants from Tables 2 and 3. (b) Adsorption of the polyphosphonates IDMP, HEDP, NTMP, EDTMP, and DTPMP at pH 7.2. Conditions: Goethite 0.42 g/L, 1 mM MOPS-buffer, 0.01 M NaNO₃. The lines are calculated with the constants from Tables 2 and 3.

the pH is increased: 50 μmol/g at pH 3.0, 42 μmol/g at pH 4.6, 30 μmol/g at pH 7.2, and 4 μmol/g at pH 10.4. Calculated lines included in Fig. 6 indicate that the adsorption isotherms are very successfully modeled using stability constants derived from adsorption versus pH experiments.

DISCUSSION

Ideally, a quantitative model for predicting phosphonate adsorption should accurately depict: (i) the protonation behavior of unoccupied and occupied surface sites, (ii) the electrical potential gradient and distribution of ions within the (hydr)oxide-water interface, (iii) the number of bonds made between

the phosphonate molecule and the surface, along with details concerning the monodentate versus multidentate and the mono-nuclear versus multinuclear nature of the surface complex; and (iv) the protonation level and net charge of the phosphonate-surface complex. It must be kept in mind, however, that several of the system attributes just listed are either inaccessible experimentally or available only through indirect means and through inferences made about system chemistry. All models are provisional, and most models contain enough fitting parameters that adsorption data can be adequately modeled even though the system is not depicted correctly.

In the present work, different TOTL (total phosphonate concentration) values pose different challenges for interpretation and quantitative modeling. To highlight these challenges, adsorption as a function of pH is replotted in Figs. 7a and 7b for five phosphonates possessing one, two, three, four, and five phosphonate groups. At 10 μM TOTL (Fig. 7a), surface sites are in excess and nearly 100% adsorption is observed below pH 8.0. Adsorption of MP decreases somewhat more sharply than the others as the pH is increased to 12.0, but the similarity in adsorption behavior for IDMP, NTMP, EDTMP, and DTPMP is quite striking. At pH 9, for example, the extent of adsorption for these four phosphonates is virtually the same, despite an enormous dissimilarity in the protonation level and net charge of the predominant species in bulk solution: HL³⁻ for IDMP, HL⁵⁻ for NTMP, H₂L⁶⁻ for EDTMP, and H₂L⁸⁻ for DTPMP.

At TOTL concentrations of 40 μM (Fig. 7b) and above (Figs. 5 and 6), phosphonate molecules and surface sites are present at comparable concentrations. The maximum extent of phosphonate adsorption decreases as the number of phosphonate function groups is increased. In contrast to the behavior at 10-μM TOTL, adsorption as a function of pH at 40 μM TOTL

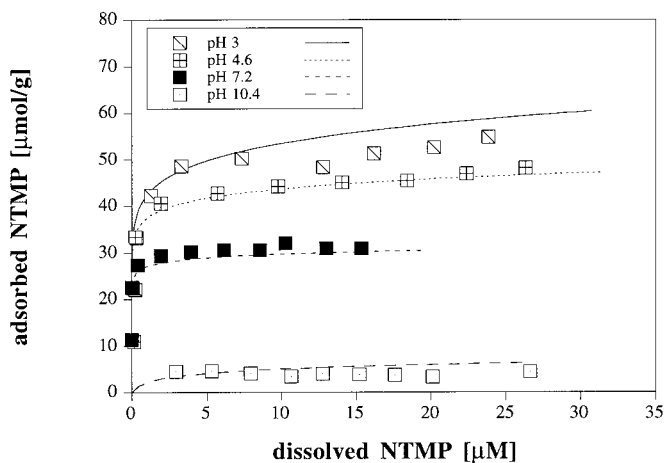


FIG. 6. Adsorption of NTMP at different pH values. Experimental data and model calculations are shown. Conditions: 0.42 g/L goethite; pH 3, addition of HNO₃; pH 4.6, 2 mM acetate-buffer; pH 7.2, 1 mM MOPS; pH 10.5, NaOH; 0.01 M NaNO₃. The lines are calculated with the constants from Tables 2 and 3.

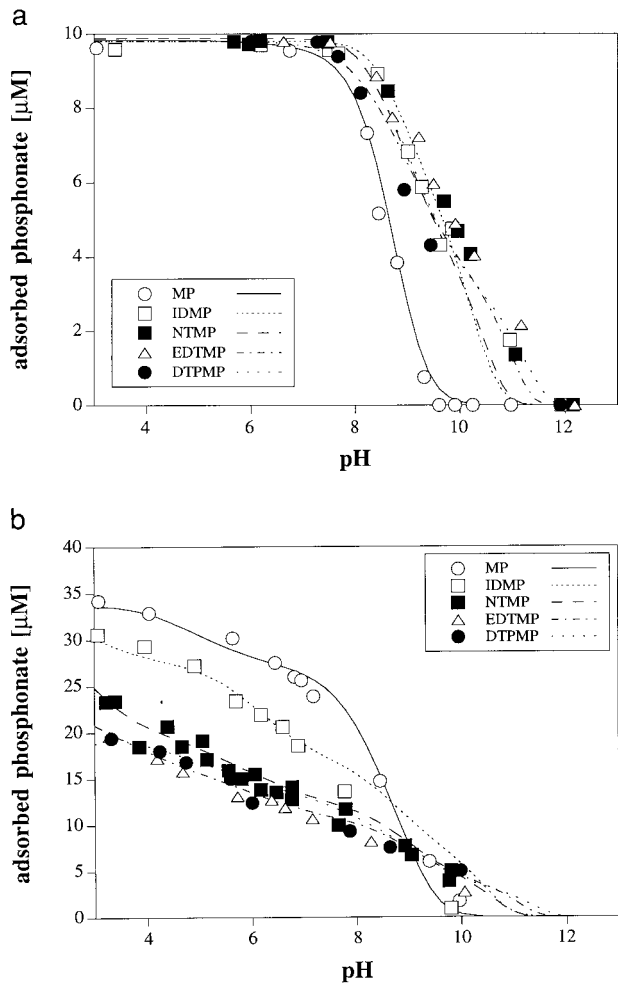


FIG. 7. Comparison of the adsorption of the monophosphonate MP and the polyphosphonates IDMP, NTMP, EDTMP, and DTPMP onto goethite at $9.8 \mu\text{M}$ and $38.7 \mu\text{M}$ total phosphonate with model calculation according to Tables 2 and 3. Conditions: see Figs. 3 and 4.

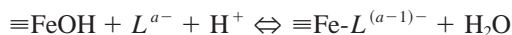
results in a very gradual decrease in adsorption as the pH is increased from 3 to 12. When TOTL is high, the higher fraction of surface sites occupied and the negative charge deposition on the surface through phosphonate adsorption disfavor adsorption of additional phosphonate molecules. From a modeling perspective, however, it is not clear whether the area occupied by each phosphonate molecule arises from (i) the mono-, di-, or tri-nuclear properties of the surface complex, or (ii) the charge of the surface complex, which in turn is affected by its protonation level. The fact that the maximum extent of NTMP adsorption (and by inference, all eight phosphonates) changes as a function of pH indicates that area occupied, protonation level, and charge of the surface complex are strongly interdependent.

The CCM model provides an accurate depiction of protonation level of the free goethite surface as a function of pH in 0.10 M NaNO_3 medium (27). The CCM model has been

successfully applied in 0.010 M NaNO_3 (34). The capacitance at 0.01 and 0.1 M NaNO_3 was found to be nearly identical (35).

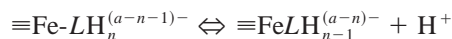
Depicting phosphonate adsorption within a CCM is much more of a challenge. Our approach: (i) considers only mono-nuclear surface complexes, (ii) assumes that the entire charge of the phosphonate-surface complex should be assigned to the zero plane, and (iii) uses multiple protonation levels and corresponding $\log K$ values to fit adsorption as a function of pH. How appropriate are each of these assumptions? At low surface coverages, assumption (i) should be relatively unimportant, since free surface sites are plentiful. This assumption will, however, be problematic at high surface coverages if adsorbed phosphonate molecules actually occupy two or more surface sites. Assumptions (ii) and (iii) are strongly interconnected. Protonation level affects charge, and charge affects the nature of the (hydr)oxide-water interface.

As the figures presented so far indicate, assumptions (i)–(iii) lead to a simple model that quite adequately depicts phosphonate adsorption as a function of pH and TOTL. Inspection of the adsorption constants developed using this model (listed in Table 3 for all eight phosphonates) is also informative. Complex formation constants listed in the first row correspond to the lowest possible protonation level,



$$K = \frac{[\equiv\text{Fe-L}^{(a-1)-}]}{[\equiv\text{FeOH}] \cdot [L^{a-}] \cdot [\text{H}^+]}, \quad [2]$$

while the following constants correspond to the protonation reactions



$$K_{n,\text{surf}} = \frac{[\equiv\text{FeLH}_{n-1}^{(a-n)-}] \cdot \text{H}^+}{[\equiv\text{Fe-LH}_n^{(a-n-1)-}]}, \quad [3]$$

where $-\log K_{n,\text{surf}}$ is equal to the $pK_{n,\text{surf}}$ of the surface complexes and allows a comparison to the $pK_{a(n)}$ of the phosphonates in solution. The overall complex formation constant $\beta_{n,\text{surf}}$ is defined as

$$\log \beta_{n,\text{surf}} = \log K_{L,\text{surf}} + \sum pK_{n,\text{surf}} \quad [4]$$

$\beta_{n,\text{surf}}$ is therefore defined as

$$\beta_{n,\text{surf}} = \frac{[\equiv\text{Fe-L-H}_n^{(a-n-1)-}]}{[\equiv\text{FeOH}] \cdot [L^{a-}] \cdot [\text{H}^{(n+1)}]} \quad [5]$$

We can now ask if there is a relation between the $\log K$ and the number of phosphonate groups. A plot of the number of functional groups against $\log K$ shows a linear behavior (not shown). We can also express this fact in terms of the charge of

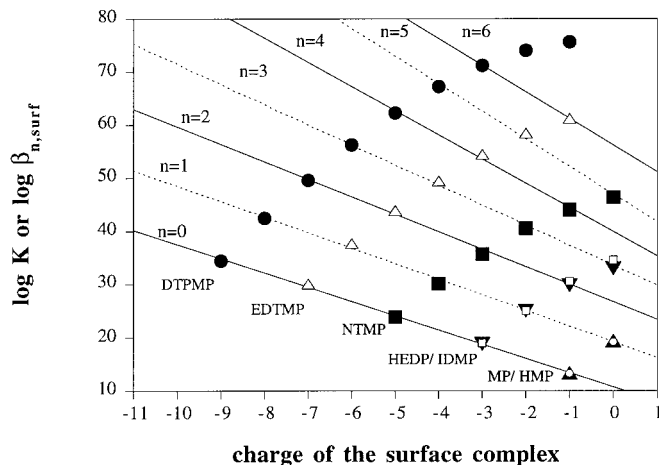


FIG. 8. Plot of the charge of the surface complex against $\log K$ and $\log \beta_{n,\text{surf}}$ for all studied phosphonates (except AMP). The lines are the linear regressions for each surface protonation level n .

the surface complex that is formed. Figure 8 shows a plot of the charge of the surface complex versus the $\log \beta_{n,\text{surf}}$ values. For each protonation level (n), a linear relationship between the $\beta_{n,\text{surf}}$ and the charge of the complex exists.

$$\text{Log } \beta_{n,\text{surf}} = a + b \cdot Z \quad [6]$$

where Z is the charge of the surface complex. Both the intercept a and the slope b are also linearly dependent on Z . By using a multiple linear regression, we can come up with the equation ($r = 0.999$)

$$\log \beta_{n,\text{surf}} = 11.45(\pm 0.33) - 2.53(\pm 0.07) \cdot Z + 7.31(\pm 0.11) \cdot n - 0.46(\pm 0.03) \cdot n \cdot Z \quad [7]$$

where the $\log \beta_{n,\text{surf}}$ is solely dependent on the charge Z of the surface complex. This is a surprising result because it means that regardless of the number of phosphonate groups and their 3-dimensional arrangement, the $\log K$ and $\log \beta_{n,\text{surf}}$ for one surface protonation level of any phosphonate-surface complex are only dependent on the charge of the formed surface complex. The $\log K_{a(n,\text{surf})}$ values are therefore independent of corresponding $\log K_{a(n)}$ values in solution. This can be seen for the two diphosphonates HEDP and IDMP which have almost the same $\log K$ (18.8 and 18.91) and $\log \beta_{1,\text{surf}}$ (25.0 and 25.03) despite quite different $\log K_{a(1)}$ values in solution (10.14 and 11.29).

Laiti *et al.* (13) determined the adsorption constant for the adsorption of phenylphosphonate (a monophosphonate) onto aged Al_2O_3 . The $\log K$ values cannot directly be compared to our values because a different oxide with different surface parameters was used. pH values where protonation-deprotonation occur may, however, be comparable. $pK_{a(1,\text{surf})}$ for phe-

nylphosphonate adsorption onto aged Al_2O_3 was found to be 6.64, which can be compared to the value of 6.06 for MP adsorption and the value of 5.9 for HMP adsorption onto FeOOH (goethite). In their study involving AlOOH (boehmite), Laiti *et al.* (14) modeled phenylphosphonate adsorption using a binuclear surface complex. The $pK_{a(1,\text{surf})}$ of the surface complex was 6.97, which is again very close to our values for MP and HMP adsorption onto FeOOH (goethite).

Our study provides the opportunity to compare the adsorption of compounds with an increasing number of phosphonate groups. The $\log K$ values of the surface complexes increase with increasing charge. This is probably an indication that assignment of charge within the (hydr)oxide-water interface has not been done correctly. If some of the charged groups of an adsorbed phosphonate molecule extend out into bulk water, for example, their associated charge should not receive the same electrostatic correction that is applied to groups located at the zero plane.

Is another modeling approach possible at this time? Figure 7a (10 μM TOTL) suggests that adsorption of IDMP, NTMP, EDTMP, and DTPMP is fundamentally similar, yet distinct from MP. To account for this, we could postulate that two phosphonate groups should be assigned to the zero plane, with any additional groups (including amino groups) assigned to bulk water. Thus, two groups would receive the electrostatic correction imposed by the CCM model, while additional groups are dealt with using the Davies equation. Figure 7b (40 μM TOTL) suggests that NTMP, EDTMP, and DTPMP adsorb in the same way, yet IDMP and MP must be treated differently. To account for this, perhaps we could postulate up to three phosphonate groups at the zero plane, with additional groups assigned to bulk water.

When constructing such a model, we run into a practical difficulty: which particular functional groups (with associated pK_a values in solution) should be assigned to the zero plane, and which should be assigned to bulk water? Should the highest pK_a groups be assigned to the surface (their high basicity yields the strongest Fe^{III} -phosphonate bonds) or to bulk water? However these assignments are made, $\log K_{a(n,\text{surf})}$ values still would be treated as adjustable parameters, since proximity of surface-bound Fe^{III} can still induce deprotonation.

In parallel with the development of this alternative model, additional adsorption experiments should also be conducted that explore the interrelationships between numbers of phosphonate groups, their spacing within ligand molecules, and their adsorption behavior. Molecules with sufficient numbers of anionic groups (e.g., NTMP, EDTMP, DTPMP) might be appropriately treated as “polyelectrolytes.” Such molecules very likely protonate in a diffuse, cloud-like way, for example. The use of SF theory, where a lattice representation is used to account for the placement of charge at progressively greater distances from the surface (36) might give the most realistic description of the system.

Despite all these limitations of the used model, we can use

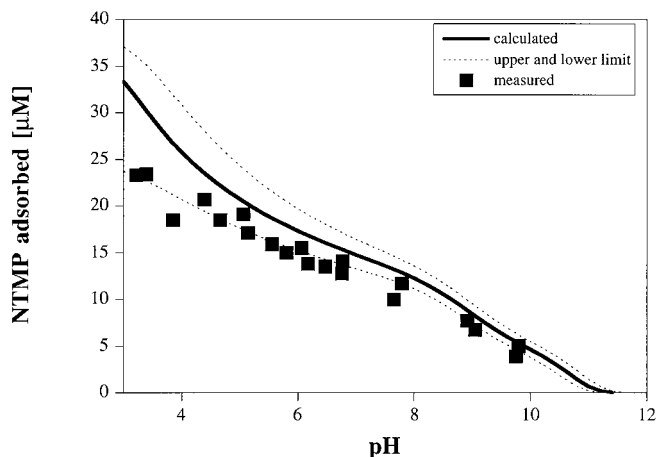


FIG. 9. Predictive modeling of phosphonate adsorption. Prediction of NTMP adsorption based on Eq. [7] with the experimental data from Fig. 4. The range of adsorption based on the error of the coefficients in Eq. [7] is shown in dotted line.

Eq. [7] for a successful predictive modeling of adsorption behavior. If we calculate the $\log K$ values for NTMP adsorption and then calculate the adsorption for the 40 μM experiments, we can predict the adsorption behavior very well. Figure 9 compares the calculated adsorption curve with the experimental values. The highest discrepancy exists at low pH, where the error of the calculated $\log K$ becomes significant. However, all data points are in the range of the $\log K$ values predicted by the error of Eq. [7].

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REFERENCES

- Filius, J. D., Hiemstra, T., and Van Riemsdijk, W. H., *J. Colloid Interface Sci.* **195**, 368 (1997).
- Bowers, A. R., and Huang, C. P., *J. Colloid Interface Sci.* **105**, 197 (1985).
- Girvin, D. C., Gassman, P. L., and Bolton, H., *Clays Clay Min.* **44**, 757 (1996).
- Nowack, B., and Sigg, L., *J. Colloid Interface Sci.* **177**, 106 (1996).
- Ralston, P. H., *J. Petrol. Technol.* **21**, 1029 (1969).
- Davis, R. V., Carter, P. W., Kamrath, M. A., Johnson, D. A., and Reed, P. E., in "Mineral Scale Formation and Inhibition" (Z. Amjad, Ed.), pp. 33–46. Plenum Press, New York, 1995.
- Gerbino, A. J., "The Adsorption of Diethylenetriamine penta(methylene-phosphonic acid) on Clay and Metal Oxide Surfaces." Masters Thesis, Rice University, Texas, 1994.
- Xyla, A. G., Mikroyannidis, J., and Koutsoukos, P. G., *J. Colloid Interface Sci.* **153**, 537 (1992).
- Black, S., Bromley, L. A., Cottier, D., Davey, R. J., Dobbs, B., and Rout, J. E., *J. Chem. Soc. Faraday Trans.* **87**, 3409 (1991).
- Kuys, K. J., and Roberts, N. K., *Colloids and Surfaces* **24**, 1 (1987).
- Morillo, E., Undabeytia, T., and Maqueda, C., *Environ. Sci. Technol.* **31**, 3588 (1997).
- Fischer, K., *Chemosphere* **22**, 15 (1991).
- Laiti, E., Öhman, L.-O., Nordin, J., and Sjöberg, S., *J. Colloid Interface Sci.* **175**, 230 (1995).
- Laiti, E., and Öhmann, L.-O., *J. Colloid. Interface. Sci.* **183**, 441 (1996).
- Gerbino, A. J., "Quantifying the Retention and Release of Polyphosphonates in Oil and Gas Producing Formations Using Surface Complexation and Precipitation Theory." Dissertation, Rice University, Texas, 1996.
- Day, G. M., Hart, B. T., McKelvie, I. D., and Beckett, R., *Environ. Technol.* **18**, 781 (1997).
- Fischer, K., *Chemosphere* **24**, 51 (1992).
- Steber, J., and Wierich, P., *Chemosphere* **15**, 929 (1986).
- Horstmann, B., and Grohmann, A., *Vom Wasser* **70**, 163 (1988).
- Held, S., *Textilveredlung* **24**, 394 (1989).
- Gledhill, W. E., and Fejitel, T. C. J., in "The Handbook of Environmental Chemistry" (O. Hutzinger, Ed.), Vol. 3, Part F pp. 261–285. Springer-Verlag, Berlin/Heidelberg, 1992.
- Coughlin, B., and Stone, A. T., *Environ. Sci. Technol.* **29**, 2445 (1995).
- Martell, A. E., Smith, R. M., and Motekaitis, R. J., "Critically Selected Stability Constants of Metals Complexes Database, Version 4.0," NIST, 1997.
- Nowack, B., *J. Chromatogr. A* **773**, 139 (1997).
- American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," 17th ed., 1989.
- Herbelin, A. L., and Westall, J. C., "FITEQL—A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data." Report 94-01, Department of Chemistry, Oregon State University, Corvallis, 1994.
- Lövgren, L., Sjöberg, S., and Schindler, P. W., *Geochim. Cosmochim. Acta* **54**, 1301 (1990).
- Persson, P., Laiti, E., and Öhman, L.-O., *J. Colloid Interface Sci.* **190**, 341 (1997).
- Martell, A. E., and Hancock, R. D., "Metal Complexes in Aqueous Solutions," Plenum, NY, 1996.
- Müller, B., "MacμQL, V. 1.2, A Program to Calculate Chemical Speciation and Adsorption," EAWAG report, Dübendorf, Switzerland, 1993.
- Zholnin, A. V., Zudov, V. G., Leitsin, V. A., Nosova, R. L., and Smirnov, E. M., *J. Appl. Chem. USSR* **63**, 803 (1990).
- Sundaram, A., and Sundaram, K. M. S., *J. Environ. Sci. Health. B* **32**, 583 (1997).
- Lützenkirchen, J., *J. Colloid. Interface. Sci.* **195**, 149 (1997).
- Müller, B., and Sigg, L., *J. Colloid Interface Sci.* **148**, 517 (1992).
- Müller, B. Ph. D. Thesis, Swiss Federal Institute of Technology, Zürich, Switzerland, 1989.
- Au, K.-K., Yong, S., and O'Melia, C., *Environ. Sci. Technol.* **32**, 2399 (1998).