Adsorption of EDTA and Metal–EDTA Complexes onto Goethite

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The adsorption characteristics of a variety of divalent and trivalent metal–EDTA complexes onto goethite (α-FeOOH) were examined in aqueous solution. Uncomplexed EDTA is adsorbed as a binuclear complex at low pH and as a mononuclear complex at high pH. Adsorption is ligand-like with a high extent of adsorption at low pH. The process can be described by formation of inner-sphere complexes by the surface complexation model with constant capacitance. The EDTA complexes of the divalent metals Ca, Zn, Ni, Cu, Co(II), and Pb, which are quinqueidentate in solution (free donor atoms bound to the metal ion), all showed the same ligand-like adsorption behavior. Their adsorption as a function of pH and concentration can be described by the formation of one type of ternary surface complex and can be fitted with the same equilibrium constant. Pd(II)EDTA, which is bidentate or quadridentate in solution, is adsorbed more strongly, but also in a ligand-like manner. The EDTA complexes of the trivalent metals LaEDTA and BiEDTA are adsorbed very strongly over the whole pH range. The sexidentate complex of Co(III) is weakly adsorbed at low pH outer-spherically, i.e., by electrostatic interaction only, Fe(III)EDTA is weakly adsorbed over the whole pH range with a predominant non-specific surface complex at low pH and a specific complex at high pH.

Key Words: EDTA; metal–EDTA complexes; goethite; adsorption; ternary surface complexes; surface complexation model.

INTRODUCTION

The anthropogenic complexing agent EDTA (ethylenediaminetetraacetic acid) is widely used in industries (photographic, metal, and other industries). Due to the low biodegradability of EDTA in biological sewage treatment plants (1), it is found in many aquatic environments such as rivers (2), lakes, and groundwater (3). Infiltration from river to groundwater or bank filtration is a source of EDTA in ground or drinking water (3, 4). EDTA forms stable complexes with the major ions Ca and Mg and with heavy metals (e.g., Pb, Zn, and Cd) and can therefore alter the migration of these metals in aquifers, because the anionic complexes show a different adsorption and retardation behavior than the uncomplexed metal. This was shown by Behra (5, 6) to be the case in the mercury–chloride system. Adsorption of complexes, metal exchange, and dissolution reactions may occur in a system with metal–EDTA complexes, but these reactions are not yet well understood in heterogeneous systems (7, 8). Especially the adsorption behavior of metal–EDTA complexes to iron oxides has yet not been investigated accurately.

Adsorption of uncomplexed EDTA on metal oxides (iron oxides, aluminium oxides) has been studied by several authors (9–13). However, in natural waters, EDTA exists only as complexed species (mainly CaEDTA, ZnEDTA, and Fe(III)EDTA (14)). Adsorption of divalent metal complexes was first studied by Bowers and Huang (15). They found that a variety of complexes (Cu, Zn, Cd, Ni, and Ca) are adsorbed on γ-Al₂O₃ in the same ligand-like adsorption behavior. More recently, Girvin et al. (16) reported the adsorption of Co(III)EDTA and Co(II)EDTA to δ-Al₂O₃.

Davis and Kent (7, 8) have conducted tracer tests with several metal–EDTA species (NiEDTA, CuEDTA, PbEDTA, and ZnEDTA) in a sandy aquifer at a rather low pH. Jardine et al. (17) studied the reactions of metal–EDTA species in column systems packed with natural aquifer material, and Szecsody et al. (18) investigated the behavior of Co(II)EDTA with ironoxide-coated sand. In these studies, adsorption and dissolution reactions occurred simultaneously and the exact speciation of EDTA was not known. Likewise, Bryce et al. (19) did not differentiate between adsorption and dissolution reactions in their study of the adsorption of NiEDTA onto hydrous ferric oxide (HFO).

To our knowledge there are no published stability constants for the adsorption of metal–EDTA complexes to (hydr)oxides, except the one by Bryce et al. (19) for NiEDTA onto HFO. Data for the adsorption of EDTA complexes of trivalent metals are rare, although Fe(III)EDTA has been found to be a major species in natural waters (20). No adsorption for Fe(III)EDTA onto magnetite was found (13). Szecsody et al. (18) included adsorption of Fe(III) EDTA into their model, but did not investigate the behavior of this complex in detail.

To elucidate the role of EDTA in the transport of metal ions in aquatic systems, we studied the adsorption of EDTA and metal complexes on α-FeOOH (goethite). We chose goethite as a model mineral surface because its surface chemical properties are well known and because goethite and

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other Fe(III) (hydr)oxides are important interfaces (both as adsorbents and as potentially dissolving solid phases) in aqueous systems (21). The results will be described by the surface complexation model (22, 23), which has been successfully used for the description of the adsorption of anions and cations to surfaces (24–27).

In this paper we will discuss how the adsorption behavior of a metal complex can be related to the structure (coordination and orbital arrangement) of the complex in solution.

The adsorption of the metal–EDTA complexes was studied in batch systems as a function of pH, complex concentrations, adsorbate concentration, and ionic strength. Also competition experiments with phosphate were conducted.

The obtained data sets may be used to explain the adsorption characteristics of metal–EDTA complexes in natural systems, and to predict the effects of EDTA on the mobility of various metals and radionuclides in the subsurface.

THEORY

We have interpreted the adsorption of EDTA and metal–EDTA species in terms of surface complex formation. A general description for the adsorption of sexidentate ligand EDTA$^{4-}$ (abbreviated as $L^{4-}$) at the surface of an iron(III) oxyhydroxide is (≡Fe−OH represents a surface site)

\[ n\text{Fe} = \text{OH} + L^{4-} + (m + n)H^+ \]

\[ \Leftrightarrow \text{Fe}_nLH_m^{(4-n-m)-} + n\text{H}_2\text{O}, \quad K_1 \]  

where \( n \) is the number of surface sites involved and \( m \) is the number of protons involved in the surface complexation. These two parameters are not known a priori and must be determined experimentally.

We imply that the surface complexation given generally in Eq. [1] can occur in terms of three specific equations, indicating the possibility of forming three different surface species:

\[ 2\text{FeOH} + L^{4-} + 2H^+ \Leftrightarrow \text{Fe}_2L^{2-} + 2\text{H}_2\text{O}, \quad K_2 \] \[ 2\text{FeOH} + L^{4-} + 3H^+ \Leftrightarrow \text{Fe}_2LH^- + 2\text{H}_2\text{O}, \quad K_3 \] \[ \text{FeOH} + L^{4-} + H^+ \Leftrightarrow \text{Fe}L^{3-} + \text{H}_2\text{O} , \quad K_4 \]

\( K_2, K_3, \) and \( K_4 \) are the respective equilibrium constants. These reactions differ in their stoichiometry, as related to the number of surface groups and the number of protons involved.

There is some ambiguity, however, in writing the mass action law for the formation of a binuclear surface complex (Eq. [2] and Eq. [3]). Once the first bond is coordinated to one surface group, there is only a small number of available free surface groups for the second bonding. The equilibrium expression for Eq. [2] is then

\[ K = \frac{[\text{Fe}_2L^{2-}]}{[\text{FeOH}]^2 \cdot [L^{4-}] \cdot [H^+]^2} \] \[ \text{[5]} \]

or alternatively

\[ K = \frac{[\text{Fe}_2L^{2-}]}{([\text{FeOH}]_2) \cdot [L^{4-}] \cdot [H^+]^2}. \] \[ \text{[6]} \]

In Eq. [6] the surface group is expressed as a dimer (≡FeOH)$_2$ (24). In (29) and (33) differences between the equations are discussed. Both expressions are used in this paper. All modeling was done according to Eq. [6], whereas evaluation of the number of involved surface sites involved Eq. [5].

A metal ligand complex, $MeL$, can be adsorbed at a mineral surface to form a ternary surface complex either as ≡S−L−$Me$ or ≡S−O−$Me$−L (28), (≡S represents a surface site), depending on whether the surface groups of the oxide can participate in exchanging their OH$^-$ for the metal–ligand complexes, or the ≡SO$^-$ groups directly interact with the complexed metal. Among other factors, this will depend on whether in the $MeL$ complex the coordination shell of the metal is completely filled with the donor atoms of the ligand.

For the adsorption of a metal–EDTA complex (Me$L^{2-}$), the general equation for the ligand-like adsorption behavior is

\[ n\text{Fe} = \text{OH} + MeL^{2-} + (m + n)H^+ \]

\[ \Leftrightarrow \text{Fe}_nLH_m^{(2-n-m)-} + n\text{H}_2\text{O}, \quad K_7 \]  

EDTA is assumed in this case to act as a bridge between the surface ≡Fe and the divalent metal ion $Me^{2+}$.

All equilibria among the metal ion, $H^+$, and ligand have to be considered. With the EDTA complexes of heavy metals, a large fraction of the metal and of EDTA (>99%) are present as $Me$EDTA, but in the case of less stable complexes like CaEDTA and MgEDTA, dissociation of the complex is also important.

\[ MeL^{2-} \Leftrightarrow Me^{2+} + L^{4-} \quad K_8. \] \[ \text{[8]} \]

The surface complex formation for a mononuclear, nonprotonated complex can be written in two ways:

\[ \text{FeOH} + Me^{2+} + L^{4-} + H^+ \]

\[ \Leftrightarrow \text{Fe}−L−Me^{2-} + \text{H}_2\text{O}, \quad K_9 \] \[ \text{[9]} \]

\[ \text{FeOH} + MeL^{2-} + H^+ \]

\[ \Leftrightarrow \text{Fe}−L−Me^{2-} + \text{H}_2\text{O }, \quad K_{10}. \] \[ \text{[10]} \]

The two constants from Eq. [9] and Eq. [10] can be related as follows:
\[
\log K_{10} = \log K_9 - \log K_8. \tag{11}
\]

Furthermore, it is possible that at high pH, the adsorption of the complex is metal-like (15):

\[
\begin{align*}
\text{FeOH} + MeL^{2+} + OH^- &\rightleftharpoons \text{Fe} - O - Me - L^{3+} + H_2O \quad K_{12}. \tag{12}
\end{align*}
\]

In this case, the metal bridges between the surface \(\text{Fe} - O\) and EDTA.

Other explanations for the adsorption of anions are possible. Bowers and Huang (15) have studied the adsorption of divalent EDTA complexes to Al₂O₃. They explained the reaction by hydrogen bonding between the AlOH\(^{2+}\) surface groups and the \(MeL^{2+}\) complexes as follows.

\[
\begin{align*}
\text{AlOH} + MeL^{2+} + H^+ &\rightleftharpoons \text{AlOH}_{\text{ads}} \cdots L^2Me^- \quad K_{13}. \tag{13}
\end{align*}
\]

In contrast to the reaction represented in Eq. [1], this reaction does lead to a much smaller pH shift.

Eq. [13] involves predominantly electrostatic interactions between the protonated surface groups and the metal–EDTA complex, which we will refer to as nonspecific interactions here. In such interactions, negatively charged complexes may be retained within the electrical double-layer near a positively charged surface.

Dissolution of oxides by ligands can be interpreted by ligand-promoted dissolution (25, 26). The first step is the adsorption of the ligand, followed by a release of Fe(III) and the formation of dissolved Fe(III)EDTA.

The dissolution of the iron oxide by EDTA or \(Me\)EDTA can therefore be written in the following way:

\[
\begin{align*}
\text{Fe} - O(\text{OH}) - \text{Fe} - L^{3+} + 2H^+ &\rightarrow \text{FeOH}_{\text{new}} + \text{Fe}(\text{III})L^{-}(\text{aq}) + H_2O. \tag{14}
\end{align*}
\]

In the case of the adsorption of a metal–ligand complex, the exchange reactions of the metal against Fe(III) have to be considered. Such exchange reactions, which can be slow (14), may be written as

\[
\begin{align*}
\text{Fe} - O(\text{OH}) - \text{Fe} - L - Me^- + 2H^+ &\rightarrow \text{FeOH}_{\text{new}} + \text{Fe}L^{-}(\text{aq}) \\
&+ Me^{2+}(\text{aq or adsorbed}) + H_2O. \tag{15}
\end{align*}
\]

DATA EVALUATION

Evaluation of the number of surface sites involved in the reaction \((n)\) is done according to Müller and Sigg (29). More recently Kanungo (30) used the same procedure for the adsorption of Mn, Co, Ni, and Zn onto HFO. Experimentally, an inversion of the surface titration is used. This means that a constant amount of ligand is titrated with goethite at constant pH.

We take Eq. [1]

\[
K = \frac{[L]_{\text{ads}}}{[\text{FeOH}]^n \cdot [H^+]^{(n+m)}} \tag{16}
\]

by setting \(\text{Fe}_nLH_{m}^{(4-n-m)}\) to \([L]_{\text{ads}}\). The equation is rearranged to

\[
\frac{[L]_{\text{ads}}}{[L^+]^n} = K \cdot [\text{FeOH}]^n \cdot [H^+]^{(n+m)}. \tag{17}
\]

We take the logarithm of this equation:

\[
\log \frac{[L]_{\text{ads}}}{[L^+]^n} = \log K + (n + m) \cdot \log[H^+] + n \cdot \log[\text{FeOH}]. \tag{18}
\]

A plot of \(\log \text{FeOH} vs \log ([L]_{\text{ads}}/[L^+]^n)\), often referred as a Kurhatov plot (31), is linear if only one type of surface complex is formed. The slope gives the number of surface sites involved. The log \(K\) value can be obtained as follows:

\[
\log K = \text{intercept} - (n + m) \cdot \log[H^+]. \tag{19}
\]

Values for both \(\text{FeOH} and \(n\) are calculated by iteration according to Eq. [20]:

\[
[\text{FeOH}_{\text{tot}}] = [\text{FeOH}] + [\text{FeO}^-] + [\text{FeOH}_2^-] + n \sum [\text{Fe}_nLH_m]. \tag{20}
\]

Lines with two different slopes as reported by Müller and Sigg (29) for the adsorption of Pb to goethite indicate a change in the type of surface complex formed.

In this study, some adsorption isotherms at constant pH were treated according to Van den Berg and Kramer (32). This is a linearization similar to the Scatchard plot. Differences between the linearization methods are discussed by Müller (33). For the case of the adsorption of uncomplexed EDTA \((L^+)\) on the surface groups \(\text{FeOH}\), the Langmuir adsorption isotherm at a given pH,

\[
K_{\text{ads}} = \frac{\{L\}_{\text{ads}}}{\{\text{Fe}\} \cdot [L]}, \tag{21}
\]

can be written with the assumption \(\{\text{Fe}\} = \{\text{Fe}\}_{\text{tot}} - \{L\}_{\text{ads}}\).
\[
\{ \text{Fe} \} = \{ \text{FeOH} \} + \{ \text{FeO}^- \} + \{ \text{FeOH}_2^- \} \quad [22]
\]
as
\[
\{ L \}_{\text{ads}} = \frac{\{ \text{Fe} \}_{\text{tot}} \cdot K_{\text{ads}} \cdot [ L ]}{1 + K_{\text{ads}} \cdot [ L ]}. \quad [23]
\]
This can be rearranged to
\[
\frac{[ L ]}{\{ L \}_{\text{ads}}} = \frac{1}{K_{\text{ads}} \{ \text{Fe} \}_{\text{tot}}} + \frac{[ L ]}{\{ \text{Fe} \}_{\text{tot}}}. \quad [24]
\]
\([ L ]/\{ L \}_{\text{ads}}\) is plotted versus \([ L ]\) and \{ \text{Fe} \}_{\text{tot}} and \( K_{\text{ads}} \) are determined. Adsorption of \( \text{MeL} \) complexes is treated analogously.

The surface complexation constant obtained by this method depends on the surface charge, and is therefore an apparent constant that is valid only at the pH where it was determined. In the subsequent interpretations of the overall surface complex formation constants, we used the constant capacitance model to account for the electrostatic correction.

The pH-independent \( K_{\text{ind}} \) can be obtained by the relation
\[
K_{\text{ind}} = \frac{K_{\text{ads}}}{[H^+] \cdot \alpha}, \quad [25]
\]
where \( \alpha \) is the fraction of \( \{ \text{FeOH} \}_{\text{tot}} \) that is present as \( \{ \text{FeOH} \} \). \( K_{\text{ind}} \) is not corrected for surface charge.

The protonation of the surface complex was determined by a proton balance. The reference states are defined as \( \text{FeOH, } H_2L^2^- \) (from dissolution of \( \text{Na}_2\text{HEDTA} \cdot 2\text{H}_2\text{O} \)), \( \text{FeL}^2^- \), and \( \text{Fe}_2L^2^- \) (both calculated with the reference species \( \text{FeOH} \) and \( H_2L^2^- \)). The proton balance for the system goethite–EDTA is then
\[
[H_{\text{tot}}] = [H^+] - [OH^-] + [\text{FeOH}_2^-] - [\text{FeO}^-] + 2[H_2L] + [H_3L^-] - [HL^+] - 2[L^+] + \sum [\text{FeL}^-]. \quad [26]
\]
\( \Sigma [\text{Fe}^-L] \) gives the concentration of protons bound to the surface EDTA complex (see the difference between Eq. [2] and Eq. [3]). The known total concentrations are \( H_{\text{tot}} \) (=added strong acid), \( L_{\text{tot}} \), and \( \text{FeOH}_{\text{tot}} \). pH and dissolved EDTA were measured. The concentrations of the species were calculated with the speciation program MICROQL (34). \( \Sigma [\text{Fe}^-L] \) was then calculated from Eq. [26].
\[
\Sigma [\text{Fe}^-L] = [H_{\text{tot}}] - [H^+] + [OH^-] - [\text{FeOH}_2^-] + [\text{FeO}^-] - 2[H_2L] - [H_3L^-] + [HL^+] + 2[L^+]. \quad [27]
\]
A factor \( p \) is defined as
\[
p = \sum \text{Fe} - L/L_{\text{ads}}. \quad [28]
\]
\( p \) gives the number of protons per adsorbed EDTA in relation to the reference state. If \( p = 0 \), then the surface complexes are either \( \text{FeLH}_2^2^- \) or \( \text{Fe}_2L^2^- \) (reference states). If \( p > 1 \), there are more protons bound to the surface EDTA complex, e.g., \( \text{FeLH}_2^2^- \) and \( \text{Fe}_2L^2^- \); if \( p < 0 \), then less protons are bound, e.g., \( \text{FeL}^3^- \).

MATERIALS AND METHODS

Water was obtained from a Barnstead Nanopure equipment. All chemicals were analytical grade from Merck or Fluka except HNO\(_3\), NaOH, and NaN\(_3\) which were Merck Suprapur quality.

All experiments were done with 0.01 \( M \) NaNO\(_3\) as the background electrolyte with ambient CO\(_2\) concentrations at room temperature (22–24°C). pH was measured with a Metrohm pH-meter with a Metrohm glass electrode, calibrated with standard buffers.

Metal–EDTA solutions were prepared by dissolving the metal–nitrate (except Bi, for which the chloride was used) and Na\(_2\)HEDTA \cdot 2H\(_2\)O in water and boiling for 1 h to be sure that the complexes were completely formed. ZnEDTA and Fe(III)EDTA were prepared by dissolving ZnNa\(_2\)-EDTA \cdot 4H\(_2\)O and NaFeEDTA \cdot 2H\(_2\)O in water, respectively. Co(III)EDTA was prepared according to Ref. (35): Co(II)Cl\(_2\) and EDTA were dissolved in water (100 ml) and 3 times over 24 h 1 ml of 30% H\(_2\)O\(_2\) was added. All stock solutions were 0.01 \( M \). The Fe(III)EDTA was stored in an aluminium covered bottle in the refrigerator to avoid photolysis of the complex (10).

Preparation and Characterization of Goethite

Goethite was synthesized according to Schwertmann and Cornell (36). Fe(NO\(_3\))\(_3\) solution (100 ml of 1 \( M \)) and KOH (180 ml of 5 \( M \)) were put into a polyethylene (PE) bottle and filled with nanopure water to 2000 ml while being stirred. The suspension was aged at 70°C in an oven for 60 h. Twice a day the suspension was stirred for 2 min. The goethite was centrifuged and washed 6 times with nanopure water and stored as a suspension with 20 g/liter of solid. It was checked by X-ray analysis and electron microscopy to be pure crystalline goethite. The specific surface area was determined by BET to be 21 m\(^2\)/g.

The proton exchange capacity was determined in 0.01 \( M \) NaNO\(_3\) by adding 0.1 \( M \) HNO\(_3\) in excess to 4.5 g/liter suspensions of goethite and letting the suspension equilibrate on a shaker for 24 h at 25°C. The protons remaining in the solution were determined by measuring the pH. The exchange capacity was found to be 7.95 \( \times \) 10\(^{-3}\) mol/g. Acid–
base properties of the surface can be described by the reactions

\[
\text{FeOH}_2^+ \leftrightarrow \text{FeOH} + \text{H}^+ \quad K_a \quad [29]
\]

\[
\text{FeOH} \leftrightarrow \text{FeO}^- + \text{H}^+ \quad K_b. \quad [30]
\]

The conditional constants defined above were extrapolated to zero surface charge, yielding the intrinsic constants (24). The values obtained from linearizations of the titrations are 6.25 for \( pK_a^{\text{int}} \) and 8.59 for \( pK_b^{\text{int}} \) with a capacitance of the inner layer of 2 F/m².

The best fits obtained by fitting the titration data with FITEQL (37, 38) are 5.67 for \( pK_a^{\text{int}} \) and 9.01 for \( pK_b^{\text{int}} \) with a capacitance of 4.0 F/m². All the modeling was done with these values. The points of zero charge are 7.42 and 7.34, respectively.

**Adsorption Experiments**

Goethite suspension, NaNO₃, and water were added to 50 ml PE bottles. The pH was adjusted with different buffers: for pH 3–4.5, HNO₃ was used; for pH 5.2–6.8, MES (2-morpholinoethane-sulfonic acid) buffer \((2 \times 10^{-3} \text{ M})\) and NaOH were used, for pH 6.8–8.8, HEPES \((4-(2-	ext{hydroxyethyl})\text{-piperazine}-1-	ext{ethane-sulfonic acid}) (2 \times 10^{-3} \text{ M})\) and NaOH were used, and for pH >8.4, NaOH or NaHCO₃/Na₂CO₃ buffer were used. HEPES was found to have very weak complexing properties (39, 40). In this case, adsorption of the buffer can therefore be neglected. Previous experiments showed that MES has no influence on adsorption of EDTA complexes. Because of the potential adsorption of carbonate on the goethite surface, small error may be introduced by the use of HCO₃⁻/CO₃²⁻ buffers. However, very few data in the pH range of this buffer were interpreted. The suspension was equilibrated at the desired pH value for 1 h before addition of EDTA. Equilibration time was 30 min for most species, except for Fe(III)EDTA which was 3 h and for Cr(III)EDTA which was 48 h. For most of the experiments total EDTA and MeEDTA concentrations were about \( 5 \times 10^{-7} \text{ M} \) and 0.5 g/liter of goethite. Samples were taken with PE syringes and filtered though 0.2 μm cellulose nitrate filters (Sartorius) and analyzed for EDTA and/or metals. Adsorbed concentrations were calculated as the difference between the known total and the measured dissolved concentrations.

Titrations with goethite at constant pH were done according to Müller (29). To a constant amount of EDTA small increments of goethite suspension were added. This inverse titration leads to very high surface coverage at the beginning of the titration.

Fe(III)EDTA adsorption experiments were conducted in aluminum covered bottles to inhibit photolysis of Fe(III)EDTA (20).

For experiments regarding the competitive adsorption of EDTA and phosphate, the solution was equilibrated at the desired pH for 60 min, EDTA was then added, and the solution was shaken for 30 min. NaH₂PO₄ solution was then added, and after 10 min the samples were taken. Phosphate was measured by the molybdenum blue method.

Metals were measured using a graphite tube atomic absorption spectrometer (GT-AAS, Varian), except for Ca and Zn which were measured with a flame-AAS (Perkin Elmer). Bi, La, Pd, and In were measured by inductively coupled plasma mass spectrometry (Elan 5000 ICP-MS).

**Dissolution Experiments**

Dissolution experiments were performed in aluminum covered 100 ml PE bottles to inhibit the photolysis of Fe(III)EDTA (20). The samples were shaken in a thermostated room at 25°C. pH was kept constant using the same buffers as described for adsorption experiments.

Iiron was measured by GT-AAS or by inductively coupled plasma emission spectrometer (Spectro ICP-AES).

**Analysis of EDTA**

For the determination of EDTA, a HPLC method was used, developed by Kari (20). According to this method, different metal–EDTA complexes were exchanged with Fe(III) to form Fe(III)EDTA that was subsequently separated and specifically detected by UV absorption, as follows: 1 ml samples were evaporated to dryness in an oven at 70–90°C. The residues were dissolved in 1 ml of formate buffer (0.005 M sodium formate and 0.015 M formic acid in water, pH 3.3). A 1 mM Fe(III) solution (20 μl) was added (0.0404 g Fe(NO₃)₃·9 H₂O and 0.2 ml 5 M HNO₃ in 100 ml water) and the solution was heated to 90°C for 1 h (3 h for NiEDTA experiments) in a water bath. The solution was then cooled to room temperature and 40 μl of a 0.04 M tetrabutylammoniumbromide solution (1.312 g TBA–Br in 100 ml buffer) was added to it. The sample was pipetted into autosampler vials. The Fe(III)EDTA complex was separated on a Lichrocard 250-4 C18 column with formate buffer as the eluent \((0.001 \text{ M TBA–Br, 0.005 M sodium formate, 0.015 M formic acid, and 8% acetonitrile, pH 3.3})\).

Detection was made by a UV detector at 258 nm.

Co(III)EDTA, Cr(III)EDTA, and Bi(III)EDTA were detected without complexation with Fe(III) at 225, 535, and 258 nm, respectively. The PdEDTA complex was detected after complexation with Bi(III). Because the PdEDTA complex has about the same stability constant as Fe(III)EDTA, it can, therefore, not be complexed by Fe(III). In contrast to PdEDTA, Bi(III)EDTA can be detected at 258 nm. Instead of the Fe(III) addition, 20 μl of BiCl₃ solution (0.001 M in ethanol) was added. The rest of the procedure was the same as described above.

**FITEQL**

The program FITEQL, version 2 (37, 38), was used to determine the best fit for the log K values. FITEQL is an
iterative optimization program, designed to determine the optimal values of the equilibrium constants for a set of experimental data. An indicator for the goodness of the fit is the overall variance \((V_y = \text{SOS/DF})\) which should be close to 1 (27). Values between 0.1 and 20 indicate a reasonable good fit. The overall variance depends on the experimental error estimates.

In our work the experimental error for pH measurements was set to 0.125 and the error of the EDTA and the metal measurement to \(3 \cdot 10^{-8} \text{M}\).

The standard deviation of log \(K\) depends on the specified experimental error, on the number of data points, and on the goodness of the fit of the model with the data (27).

FITEQL allows us to distinguish between mass action law and mass balance (A-matrix and B-matrix). Different adsorption densities can be modeled with the same concentration of surface sites. Also adsorption of a binuclear complex can be modeled in terms of Eq. [6] using adsorption to a dimer (\(\equiv \text{FeOH}\))

RESULTS

Adsorption of Uncomplexed EDTA

The kinetics of the adsorption was studied first. It was found that uncomplexed EDTA adsorbs fast within a few minutes. After 2 h measurable amounts of dissolved iron were detected, indicating the beginning of the dissolution reaction. Distinction between adsorption and dissolution was therefore easily possible by measuring adsorbed EDTA after 30 min.

The adsorption isotherm at pH 3.45 shows a Langmuir-type behavior with a maximum amount of surface sites of 4.03 \(\cdot 10^{-5}\) mol/g goethite or 1.15 EDTA/nm\(^2\) (Table 1). This is one half of the amount of surface sites determined by acid–base titrations (7.95 \(\cdot 10^{-5}\) mol/g). In Fig. 1, measured and calculated adsorption isotherms are shown. At pH 3.3, adsorbed EDTA can be desorbed by the addition of phosphate (Fig. 2). The stoichiometry of the reaction is 2 mol of phosphate adsorbed for 1 mol of EDTA released.

This process can be modeled with one surface EDTA complex and one surface phosphate complex.

To elucidate the type of surface complex and the stability constant, titrations of EDTA with goethite were performed at constant pH. The linearization was made according to Eq. [18] (Kurbatov plot). Values for \(n\) (numbers of surface sites involved in the reaction) and log \(K\) are listed in Table 2. Examples for linearizations are shown in Figs. 3a and 3b. Two stages can be distinguished: at a pH lower than 6.5 the slope is close to 2 and at pH higher than 6.5 close to 1. This indicates a binuclear complex at low pH and the predominance of a mononuclear complex at higher pH. An average value of the log \(K_s\) for the binuclear complex is 34.94 \pm 0.37.

Protonation of the surface complex was calculated according to Eq. [27] with a proton-balance. In Table 3, measured and computed pH values are shown. The computed values were calculated for a system without adsorption of EDTA. The measured pH shift indicates the consumption of protons according to Eq. [11] and shows that there is a specific interaction with the surface. The factor \(p\), defined in Eq. [28], gives the numbers of protons in the adsorbed EDTA complex in relation to the reference state (\(\equiv \text{Fe}_2\text{L}^2^-\) for a binuclear complex). The binuclear surface complex has therefore one proton more than the reference state and can be written as \(\equiv \text{Fe}_2\text{LH}^-\).

For two different EDTA/surface ratios, surface complexation constants as defined in Eq. [3] and Eq. [4] were calculated according to the constant capacitance model. Best fit was obtained with FITEQL. Intrinsic constants (valid for a potentially uncharged surface) are given in Table 4. The mass action law of Eq. [6] has been used to calculate the constants for the binuclear complex. Therefore, adsorption to the dimer (\(\equiv \text{FeOH}\)) was considered. In the FITEQL mass balance (B-matrix), two sites were included per adsorbed EDTA to get the right stoichiometry.

The constants were also fitted by using Eq. [5]. These values can be compared to those of the Kurbatov plot. The values were 15.06 and 34.50 for log \(K_1\) and log \(K_4\), respectively. The values for both log \(K\) differ somewhat from the constants obtained by linearization (Table 2). However, the constants reported in Table 2 are conditional and are pH dependent. Because the mononuclear surface complex has a charge of \(-3\), the electrostatic term is important. For the binuclear surface complex with a charge of \(-1\), the electrostatic term is less important. The value obtained by FITEQL is an intrinsic constant.

In Fig. 4, measured and calculated extents of adsorption as a function of pH (designated as adsorption edge) for uncomplexed EDTA are shown. The two complexes can explain the adsorption behavior of EDTA very well.

The adsorption of uncomplexed EDTA to goethite is explained by an inner-sphere reaction. The consumption of protons (Eq. [11]) during the adsorption was observed. Such anion exchange mechanisms were proposed for the adsorp-
tion of EDTA onto magnetite (13) and lepidocrocite (10). The stoichiometric exchange with phosphate that has been shown to adsorb as an inner-sphere complex (41, 42) indicates adsorption to the same surface sites. Furthermore, it is possible to explain the desorption data by one EDTA–surface complex and one phosphate surface species and adsorption to the same surface sites.

We investigated the dissolution of goethite by EDTA at various pH values. The investigation of the dissolution behavior may give some new insight into the formation of surface complexes. The dissolution rate increases with increasing pH yielding a maximum dissolution rate around pH 8. At pH higher than 8, the dissolution rate decreases (Fig. 5a). The maximum concentration of the mononuclear complex corresponds with the maximum dissolution rate. Stumm and co-workers (43, 44) have postulated the hypothesis that a binuclear surface complex inhibits dissolution while a mononuclear complex enhances it. We explain the dissolution behavior of goethite by EDTA as follows: at low pH the binuclear surface complex dissolves with a slow rate. As the mononuclear complex becomes important at higher pH, the dissolution rate gets faster, decreasing again with decreasing concentration of surface complex (Fig. 4). This two-species adsorption model differs from the results of Bondietti et al. (43) for lepidocrocite and EDTA. These authors fitted the adsorption of EDTA with two species \( \equiv \text{FeL}^{3-} \) and \( \equiv \text{FeLH}^{2-} \). The dissolution rate was fast at a low pH and slow at a high pH. A linear relation between adsorbed EDTA and the dissolution rate was found. The dissolution rate is therefore constant with respect to the adsorbed EDTA. The slower dissolution rate at higher pH is due to a weaker

![Figure 1](image1.png)

**Fig. 1.** Adsorption isotherms of EDTA and of the EDTA complexes of Ni, Pb, Bi, Fe(III), and Al to goethite. Conditions: For EDTA, NiEDTA, PbEDTA, and BiEDTA, goethite 0.17 g/liter, pH 3.45; ZnEDTA, goethite 0.16 g/liter, pH 5.38; Fe(III)EDTA, goethite 1.72 g/liter, pH 3.30. All in 0.01 M NaNO₃. The curves are calculated using the Langmuir constants from Table 1.

![Figure 2](image2.png)

**Fig. 2.** Competition between EDTA and phosphate. Conditions: goethite 0.12 g/liter, EDTA or PbEDTA 9.5 \( \times 10^{-6} \) M, pH 3.35, 0.01 M NaNO₃. The curves are calculated using the adsorption constants of Table 4.

<table>
<thead>
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<th>pH</th>
<th>( n' )</th>
<th>( \log K )</th>
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<td>5.70</td>
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<tr>
<td>5.85</td>
<td>1.74</td>
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</tr>
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<td>8.48</td>
<td>0.93</td>
<td>13.09</td>
</tr>
</tbody>
</table>

\(^{\prime} n \) is the number of surface sites involved in the reaction

**Table 2**

Linearization of the Adsorption Isotherm of EDTA to Goethite According to Eq. [18] (modified Kurbatov plot)
Adsorption. The different surface complexes on goethite and lepidocrocite may be explained by the different structure of goethite and lepidocrocite.

**Adsorption of Divalent Metal–EDTA Complexes**

Adsorption kinetics experiments indicated that the complexes of divalent metals adsorb fast within a few minutes. In these experiments both EDTA and metal concentrations were measured. Adsorption stoichiometry of these complexes to the surface is 1:1, as can be seen in Fig. 6 for the adsorption of PbEDTA, where the data points for adsorbed lead and adsorbed EDTA correspond very well. This is true only for the pH range where nearly 100% of the metal is complexed in solution. Weaker complexes like ZnEDTA or CaEDTA are dissociated at a lower pH and show a decreased adsorption of the metal (Fig. 7). In most of the following experiments either total EDTA or total metal concentrations were measured, depending on the analytical conditions of the used methods. Dissolution reactions according to Eq. [15] become important only after a few hours. Distinction between adsorption and dissolution is therefore easily achieved.

MeL$^2^-$ complexes are adsorbed similarly to noncomplexed EDTA (Fig. 1). Most of the adsorption isotherms were measured at pH 3.5, except for ZnEDTA, because the complex is stable only above pH 5. The lower extent of adsorption is therefore due to the higher pH and the different speciation of the goethite surface. NiEDTA and PbEDTA complexes, however, show the same behavior. In Table 1 the results according to the linearization of Van den Berg (Eq. [24]) are shown. The total amount of surface sites and the conditional log $K$ values are listed. The log $K$ values all have the same order of magnitude. The pH-independent constants were calculated according to Eq. [25]. A mean value for EDTA complexes of divalent metals of 10.79 was found (log $K_{10}$, Eq. [10]).

PbEDTA can be desorbed by phosphate with the same stoichiometry as the uncomplexed EDTA, i.e., one EDTA released for two phosphates adsorbed (Fig. 2). The data can be fitted with the known adsorption constant for PbEDTA (Table 4) and one fitted phosphate adsorption constant, assuming adsorption to the same surface sites. According to Sigg and Stumm (24), a neutral mononuclear surface complex $\equiv$FePO$_2$H$_2$ was used. The fitted constant is in the same range as determined by Sigg and Stumm (24).

A pH shift is observed after addition of PbEDTA to goethite. The pH rises due to the release of OH$^-$ according to Eq. [1]. This pH shift supports the strong evidence for an inner-sphere complex.

Titrations of PbEDTA and ZnEDTA with goethite were performed in the same way as for the uncomplexed EDTA. The results for PbEDTA are shown in Table 5. An example of a linearization is shown in Fig. 3c. In contrast to the

---

**TABLE 3**

Proton Balance for the Adsorption of EDTA to Goethite According to Eq. [27]

<table>
<thead>
<tr>
<th>pH measured</th>
<th>pH calculated without adsorption</th>
<th>$p$ for $n = 2^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.69</td>
<td>4.88</td>
<td>0.97</td>
</tr>
<tr>
<td>6.14</td>
<td>5.42</td>
<td>1.31</td>
</tr>
<tr>
<td>6.43</td>
<td>5.63</td>
<td>0.76</td>
</tr>
</tbody>
</table>

*a* $p$ is defined by Eq. [28].

---

**FIG. 3.** Kurbatov plots of the adsorption of EDTA and PbEDTA to goethite according to Eq. [18]. Conditions: (a) pH 6.47, EDTA 9.10 · 10$^{-7}$ M, goethite 22–110 mg/liter. (b) pH 7.85, EDTA 1.24 · 10$^{-6}$ M, 65–325 mg/liter goethite. (c) pH 5.68, PbEDTA 9.45 · 10$^{-7}$ M, goethite 23–100 mg/liter.
uncomplexed EDTA, the slope of the linearized curve is always about 1, except for the highest pH where adsorption is weak. This indicates that mononuclear complexation is important. The mean value of log K for the adsorption of PbEDTA to goethite determined by titration according to Eq. [18] is 11.21.

The total surface capacity for metal–EDTA complexes is about the same as for the uncomplexed EDTA although for a mononuclear complex it could be twice as high. We explain this by the size of the complex that covers several surface sites, so that they are not accessible for other complexes.

The influence of ionic strength was investigated for Pb-EDTA. A decrease in the ionic strength from 0.01 to 0.001 M NaNO₃ had little effect; it only altered the shape of the adsorption edge. At an ionic strength of 0.1 M NaNO₃, the adsorption was weaker (Fig. 8). This weak dependence on ionic strength gives further evidence of inner-sphere complexation of PbEDTA with surface FeOH.

Using this information, the adsorption edges of several metal–EDTA complexes were fitted with FITEQL. The metals (Zn, Cu, Pb, Ni, and Co(II)) show all the same adsorption behavior (Fig. 9). In Table 4 the fitted constants are given according to Eq. [9] and Eq. [10]. The mean value for Eq. [10] for 5 species (Ni, Zn, Pb, Cu, Co(II)) is 11.08. This is very close to 11.21 that was determined for PbEDTA by linearization of the adsorption isotherm at constant pH.

The EDTA complex of the divalent palladium shows a very strong adsorption (Fig. 9). This behavior is clearly anionic, however, but it must be due to specific adsorption because the PdEDTA complex adsorbs up to pH 10, well above the point of zero charge (7.4). It was found that both Pd and EDTA were adsorbed together. The adsorption edge can be fitted with a log K of 15.08.

The adsorption edge for CaEDTA is shown in Fig. 7. In this system, the adsorption of both complexed and uncomplexed EDTA has to be considered. Adsorption of Ca²⁺ is very weak (24) and was not taken into account. At low pH, the CaEDTA complex is dissociated and the uncomplexed EDTA is adsorbed, whereas at a higher pH there is a competition between CaEDTA and EDTA for the surface sites. The experimental data were fitted by FITEQL with the reactions above (adsorption of the CaEDTA complex and formation

---

**TABLE 4**

<table>
<thead>
<tr>
<th>Species</th>
<th>log K{sub}c</th>
<th>log K{sub}i</th>
<th>log K{sub}i</th>
<th>log K{sub}i</th>
<th>log K{sub}i</th>
<th>log K{sub}i</th>
<th>SOS/DF{sup}a</th>
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</thead>
<tbody>
<tr>
<td>EDTA (Exp. 1)</td>
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<td>14.99 ± 0.1</td>
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<td></td>
<td>0.24</td>
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<td>EDTA (Exp. 2)</td>
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<td>15.05 ± 0.11</td>
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<td></td>
<td>0.24</td>
</tr>
<tr>
<td>Ca</td>
<td>10.28</td>
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<td>22.36</td>
<td>12.08</td>
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<tr>
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<td>11.08 ± 0.03</td>
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<tr>
<td>Cu (Exp. 2)</td>
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<td>30.03</td>
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<td>1.31</td>
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<tr>
<td>Pb (Exp. 2)</td>
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<td>Co(II)</td>
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<tr>
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<tr>
<td>Fe(III)</td>
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<td>9.70</td>
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<tr>
<td>Co(III)</td>
<td>42.90</td>
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<td></td>
<td>8.32 ± 0.14</td>
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<tr>
<td>Al(III)</td>
<td>18.00</td>
<td></td>
<td></td>
<td>26.73 ± 0.11</td>
<td>2.50</td>
<td></td>
<td></td>
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</table>

{sup}a Values from Martell and Smith (61), calculated for 0.01 M.

{sup}b Value for the goodness of the fit. Between 0.1 and 20, the fit is reasonably good (26).

{sup}c Maximum adsorption capacity only 1/80. This value was set in the B-matrix in the mass law.

{sup}d Value for the metal-like species after Eq. [12].

---

**FIG. 4.** Extent of adsorption as a function of pH (adsorption edge) of EDTA to goethite. The curves are calculated using the constants from Table 4. Conditions: goethite 0.46 g/liter, EDTA 4.6 × 10⁻⁷ M, 0.01 M NaNO₃, MES/HEPES buffer.
Adsorption of EDTA and Metal–EDTA Complexes

The pH of Table Conditions: buffer. very 6 dissolution of 7.9 a substantial change in pH 7.9 to 8. The slower dissolution is a direct consequence of the weaker adsorption at a higher pH. This behavior is similar to that observed for other ligands.

Adsorption of Trivalent Metal–EDTA Complexes

Adsorption kinetics experiments indicated that the adsorption of Fe(III)EDTA was substantially slower at pH 8 than at pH 3, or than for the divalent species (adsorption complete after 1 h). At pH 7.9 the Fe(III)EDTA complex was adsorbed with a first-order kinetic with a half life of 24 min. This indicates a specific process at high pH and presumably involves a change in the coordination of Fe(III). Fe(III)EDTA in solution was found to have slow exchange kinetics with other metals, e.g., Zn (14). Also Cr(III)EDTA showed very slow adsorption kinetics. This again indicates a change in the coordination of the Cr(III) which has an extremely slow water exchange rate.

Adsorption isotherms at low pH were performed using BiEDTA and Fe(III)EDTA (Fig. 1). BiEDTA adsorbs simi-

### TABLE 5
Linearization of the Adsorption Isotherm of PbEDTA to Goethite According to Eq. [18]

<table>
<thead>
<tr>
<th>pH</th>
<th>n°</th>
<th>log K</th>
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<tr>
<td>3.35</td>
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<td>4.22</td>
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<tr>
<td>6.18</td>
<td>1.08</td>
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<tr>
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<td>6.96</td>
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</tr>
<tr>
<td>8.08</td>
<td>0.62</td>
<td>12.26</td>
</tr>
</tbody>
</table>

° n is the number of surface sites involved in the reaction.
Influence of ionic strength on the adsorption of Co(III)EDTA and PbEDTA to goethite. The curves are calculated using the constants from Table 4.

Conditions: Co(III)EDTA, goethite 0.46 g/liter, Co(III)EDTA $4.6 \times 10^{-7}$ M, MES/HEPES buffer; PbEDTA, goethite 0.16 g/liter, PbEDTA $9.4 \times 10^{-7}$ M, MES/HEPES buffer.

Similarly to the divalent complexes, whereas the maximum adsorption capacity for Fe(III)EDTA is about 50 times smaller than that for PbEDTA (Table 1).

Adsorption edges were determined for the complexes of the trivalent metals Fe, Al, Co, Cr, In, La, and Bi (Figs. 10a and 10b). The differences in the adsorption behavior of these complexes range from very weak adsorption for Co(III)-EDTA to very strong for BiEDTA. Adsorption decreases with increasing stability in solution in the order Al, Cr, and Co(III). Fe(III)EDTA shows weak adsorption over the whole pH range from 3 to 10. In the case of Fe(III)EDTA, an $\equiv$Fe-O-Fe-$L$ type of ternary complex is probably formed at a higher pH, where adsorbent surface and adsorbate are both negatively charged. Adsorption cannot be explained by electrostatic interaction. The adsorption equi-

FIG. 8. Influence of ionic strength on the adsorption of Co(III)EDTA and PbEDTA to goethite. The curves are calculated using the constants from Table 4. Conditions: Co(III)EDTA, goethite 0.46 g/liter, Co(III)EDTA $4.6 \times 10^{-7}$ M, MES/HEPES buffer; PbEDTA, goethite 0.16 g/liter, PbEDTA $9.4 \times 10^{-7}$ M, MES/HEPES buffer.

FIG. 9. Adsorption of the EDTA complexes of Pb, Ni, Cu, Zn, Co(II), and Pd to goethite. The curves are calculated using the constants from Table 4. Conditions: goethite 0.46 g/liter, MeEDTA $4.6 \times 10^{-7}$ M, 0.01 M NaNO$_3$, MES/HEPES buffer.

FIG. 10. (a) Adsorption of trivalent metal–EDTA species to goethite. Conditions: goethite 0.46 g/liter, MeEDTA $4.6 \times 10^{-7}$ M, 0.01 M NaNO$_3$, MES/HEPES buffer. (b) Adsorption of LaEDTA and BiEDTA to goethite. Conditions: goethite 0.12 g/liter, MeEDTA $2.30 \times 10^{-6}$ M, 0.01 M NaNO$_3$, MES/HEPES buffer.
librium at high pH is attained slowly, and the effects of the ionic strength (high effect at low pH and little effect at high pH) are compatible with such an explanation (Fig. 11).

In (III)EDTA, with a log K in solution similar to Fe(III)-EDTA shows a similar adsorption behavior. The two complexes BiEDTA and LaEDTA both adsorb very strongly over the whole pH range (Fig. 10b). Both metal and EDTA were measured for the LaEDTA experiment. Both BiEDTA and Bi were measured for the BiEDTA experiment. The overlap of the adsorbed metal and EDTA shows again the formation of a ternary complex.

The strong influence of ionic strength on the adsorption of Co(III)EDTA at low pH indicates that electrostatic interactions are probably predominant for this complex (Fig. 8).

It is possible to desorb trivalent complexes by adding phosphate. AIEDTA, as well as Fe(III)EDTA, can be completely desorbed by phosphate.

Also, the strongly adsorbing LaEDTA and BiEDTA compete with phosphate for surface sites. Phosphate (0.002 M) is able to desorb completely $2 \cdot 10^{-6} \text{ M}$ these species, as well at pH 5 as at pH 8.

DISCUSSION

Distinction between adsorption and dissolution reactions was a major task of this work. Because of the fast dissolution of $\delta$-$\text{Al}_2\text{O}_3$, Girvin et al. (16) had to include the adsorption of AIEDTA in his EDTA adsorption studies. Szecsody et al. (18) could not as well measure the adsorption of EDTA alone on iron oxide-coated sand, due to the fast dissolution kinetics. Also Bryce et al. (19) should have included the formation of Fe(III)EDTA in their system with EDTA/HFO or NiEDTA/HFO. In our study, these difficulties could be excluded by the fast adsorption rate and the slow dissolution of the goethite. Adsorption of uncomplexed EDTA as well as of metal–EDTA complexes could, therefore, be studied without interferences.

The binding of EDTA–metal complexes to the goethite surface is influenced by the relative thermodynamic stability of the complexes in solution and at the surface, as well as by the steric structure of the complexes in solution and at the surface, which may be more or less favorable for different metal ions.

The following adsorption mechanisms may be distinguished:

— specific adsorption of anionic type, with one or several functional groups of EDTA bound to one (or two) surface $\equiv$Fe in inner-sphere complexes;
— specific adsorption of cationic type, with a cation bound to one (or two) surface $\equiv$FeOH and EDTA linked to the surface over the cation;
— predominantly unspecific electrostatic adsorption.

Electrostatic interaction is superimposed in any case on chemical (inner-sphere) interaction. These various mechanisms are observed for various metals.

For the adsorption of EDTA and metal–EDTA complexes, four types of adsorption mechanisms can be distinguished: (i) uncomplexed EDTA, (ii) NiEDTA-like, (iii) LaEDTA-like, and (iv) Co(III)EDTA-like.

Uncomplexed EDTA

The uncomplexed EDTA is adsorbed as an inner-sphere complex, as indicated by the release of $\text{OH}^-$ during adsorption and by the competition experiment with phosphate. It is adsorbed as a binuclear complex at low pH values and as a mononuclear complex at high pH values. The inhibitory effect on the dissolution rate of the binuclear surface complex can be seen in the slower dissolution at a low pH than at a higher pH with a maximum in the dissolution rate at
pH 8. At even higher pH values (9 to 10) the dissolution is slower due to a very weak adsorption.

**NiEDTA-like**

The NiEDTA-like adsorption behavior occurs with small divalent metals (with the exception of the large Pb, which behaves in the same way). These complexes have either a sexidentate structure, where two N and four O are coordinated to the metal or a quinquedentate structure, where one carboxyl group is uncomplexed and one water is coordinated to the metal center. Various authors have studied the structure of NiEDTA (45–47). Depending on the method and on the conditions (sometimes high ionic strength (0.5 M)), they found either the sexidentate or the quinquedentate to be more important in the pH range of 4 to 8. In the most recent investigation, Everhart and Evila (46) concluded from NMR studies of NiEDTA and Co(II)EDTA that the complex is quinquedentate (Fig. 12a). Girvin et al. (16) explained the adsorption behavior of Co(II)EDTA to δ-Al₂O₃ by a hydrogen bonding mechanism. Bowers and Huang (15) also related the adsorption behavior of NiEDTA onto γ-Al₂O₃ to this quinquedentate structure. Girvin et al. (16) found slight effects of ionic strength on the adsorption and concluded therefore that the Co(II)EDTA adsorbs as an outer-sphere complex. We found for the adsorption of Pb-EDTA a small effect of ionic strength in the range from 0.01 to 0.001 M NaNO₃. A tenfold increase in NaNO₃ concentration to 0.1 M caused a significant decrease in the adsorption. This decrease can be an effect of ionic strength on the structure of the complex. Matwijoyf et al. (45) noted in their study of the structure of NiEDTA that the ionic strength has an influence on the chemical shifts (and therefore on the structure) in the NMR study. It may be possible that at a high ionic strength, the sexidentate structure becomes more important than the quinquedentate structure. The free carboxyl group of the quinquedentate complex can adsorb as an inner sphere complex to the surface as shown for benzoate, salicylate, oxalate and other ligands (44, 48).

A possible structure for such a complex is the formation of a bridge by EDTA between metal ion and surface Fe(III). Bridging structures of EDTA between metal ions are known in solution as reaction intermediates (49).

PdEDTA with the same anionic, but stronger, adsorption behavior has another structure. The reported structure of PdEDTA is bidentate or quadridentate (50, 51). The structure of the PdEDTACl₂ complex is shown in Fig. 12b. This complex has therefore a different structure than divalent
metal complexes (e.g., Ni). The strong adsorption of this complex can be explained by the possibility of a bidentate or binuclear surface complex, because two or four carboxyl groups are free. The complexes of Pt(II) should adsorb in the same way as PdEDTA, because they have the same structure (51).

**LaEDTA-like**

A third type of adsorption is the LaEDTA-like adsorption with strong adsorption over the whole pH range. Both LaEDTA and BiEDTA show the same behavior. The LaEDTA complex has about the same stability constant as ZnEDTA, whereas BiEDTA has a higher stability constant than Fe(III)EDTA. The lanthanum in the LaEDTA complex has a coordination number of 10, where four additional water molecules are coordinated (52). The EDTA cannot encircle the ion completely because of the large ionic radius (Fig. 12c). It may be possible that LaEDTA adsorbs by the coordination of lanthanum to the surface OH and the replacement of one or several water molecules by the surface groups. Such ternary complexes were proposed by Schindler (28) for the adsorption of Cu–glycine and Cu–2,2′-bipyridine complexes on amorphous silica. This behavior of the lanthanides is important for the adsorption behavior of heavy radionuclides. Their adsorption behavior may be different from that of the Co(III)EDTA that is widely investigated (16, 17, 18). Both LaEDTA and BiEDTA can be desorbed totally with phosphate, indicating adsorption to the same surface sites. Adsorption of LaEDTA must be specific, because no nonspecific adsorption of a negatively charged complex is possible at pH 10.

The adsorption of both complexes could be explained either by a very strong anionic adsorption or by a combination of an anionic and a cationic type of surface complex as formulated in Eq. [10] and Eq. [12].

**Co(III)EDTA-like**

A fourth type of adsorption is Co(III)EDTA-like adsorption. In this case, the adsorption is weak. We observed the same behavior as Girvin et al. (16), namely that Co(III)EDTA is adsorbed much weaker than Co(II)EDTA. They explained this behavior by the presence of different structures in solution. Co(III)EDTA in solution is sexidentate (50), and the Co(III)EDTA complex is extremely stable. The adsorption of the sexidentate Co(III)EDTA is very weak because no carboxyl group is free to coordinate with the surface (Fig. 12d). There is a great influence of decreased ionic strength on the adsorption. The complex adsorbs by nonspecific interaction. AIEDETA, which has the same overall charge, is much more strongly adsorbed. Electrostatic interaction is therefore not suitable for the explanation of all trivalent metal–EDTA complexes. Only complexes with sexidentate structures like (Co(III)EDTA, Cr(III)EDTA, and Fe(III)EDTA) show a weak adsorption.

Stone et al. (53) showed that at an ionic strength of 0.01 M, hardly no nonspecific adsorption of a monovalent anion to the goethite surface should occur at above pH 4. At an ionic strength of 0.1 M, nonspecific adsorption is negligible. These findings both support the explanation with inner-sphere complexes. Hayes and Leckie (54) have used the ionic strength dependence of sorption isotherms as a criterion for the formation of outer-sphere complexes. Recently, however, Manceau and Charlet (55) questioned the relevance of ionic strength effects on the sorption isotherms. They found selenate to be adsorbed inner-spherically to goethite, although there is a strong effect of ionic strength on the adsorption.

Fe(III)EDTA also adsorbs weakly over the whole pH range. At pH > 7 Fe(III)EDTA adsorbs more strongly than most Me(II)EDTA complexes. Its structure in the solution was found to be sexidentate with one additional water molecule coordinated (56, 57). It has therefore no uncomplexed carboxyl group to coordinate with the surface. Its structure is shown in Fig. 12c. At low pH values, we found a strong influence of ionic strength on the adsorption of Fe(III)EDTA, probably indicating nonspecific adsorption. At a high pH, both slow adsorption kinetics and the absence of an effect of ionic strength support the explanation of an inner-sphere complex. We can therefore hypothesize two different surface complexes: at low pH an outer-sphere complex,

\[
\equiv \text{FeOH} + \text{FeL}^- + \text{H}^+ = \equiv \text{FeOH}_2^++\text{LFe}^-, \quad [31]
\]

and at higher pH a specific, cation-like surface-complex,

\[
\equiv \text{FeOH} + \text{FeL}^- + \text{OH}^- \Rightarrow \\
\equiv \text{Fe} \text{--O--Fe} \equiv \text{L}^2^- + \text{H}_2\text{O}. \quad [32]
\]

Blesa et al. (13) found no adsorption of Fe(III)EDTA to magnetite, but probably a weak adsorption was not detected. Fe(III)EDTA is the most prevalent adsorbing species at higher pH values compared to the metal–EDTA complexes, that occur in natural systems (14, 20), such as calcareous aquifers with pH values between 7 and 8.

For AIEDETA, both sexidentate and quinque dentate structures have been discussed (58). Our results indicate that AIEDETA adsorption to goethite is weaker than that for NiEDTA but stronger than that for Fe(III)EDTA. An influence of ionic strength was found. Nonspecific adsorption of the sexidentate and specific adsorption of the quinque dentate complex perhaps occurs simultaneously.

**Stability Constants**

The stability constants for the different surface complexes that were obtained by several methods in this work show a good agreement among one another and with the few published values. The mean log \( K \) values for the adsorption of \( Me(II) \)EDTA complexes were 11.21, as determined from
the Kurbatov plot (for PbEDTA), 10.79 as determined from the Van den Berg plot (NiEDTA, ZnEDTA, and PbEDTA), and 11.08 for the best fit obtained by FITTEQL for the adsorption edge (ZnEDTA, NiEDTA, CaEDTA, PbEDTA, Co(II)-EDTA). From the work of Szecsoedy et al. (18), the conditional Langmuir constants for the adsorption of Co(II)-EDTA and CaEDTA at pH 4.5 and 6.5 were recalculated as intrinsic constants according to Eq. [25]. The acid–base properties of the amorphous iron oxide were taken from Dzombak and Morel (27). Average values for Co(II)EDTA and CaEDTA were 11.8 and 11.7, respectively. These values are within the same order of magnitude as determined in this work. Bryce et al. (19) found a log $K$ of 8.38 for the adsorption of NiEDTA to hydrous ferric oxide, which is much smaller than the values of Szecsoedy et al. (18).

**Consequences for the Transport Behavior of EDTA in Aquifers**

The results show that the transport of EDTA complexes may be affected by mainly two factors: The extent of adsorption of the uncomplexed EDTA and of the metal–EDTA complexes of small metal ions (Ca, Mg, Zn, Ni, Pb, Cu, and Co(II)) is pH dependent and decreases toward neutral pH values. Adsorption in natural systems is commonly thought to be controlled by reactions with iron and aluminum oxides (21). Davis and Kent (7, 8) found a significant retardation of NiEDTA in their field study in groundwater with a pH of 6. This is still in a range where the complexes of divalent metals are adsorbed to a great extent. In calcareous aquifers with pH values between 7 and 8, retardation of these complexes is minor. The transport of metals like lead or cadmium is therefore enhanced.

The adsorption behavior of the complexes of the heavier ions like Pd, La, or Bi is totally different. The strong adsorption up to pH 10 may have an influence on the retardation behavior of such complexes in the subsurface. In this case, complexation by EDTA does not increase the mobility of the metal. This is of great importance for the mobility of radionuclides in groundwater. EDTA complexes of $^{90}$Co and $^{90}$Sr have been studied to a great extent (17, 18), but the extrapolation to the behavior of other radionuclides like Am or Pu cannot be made.

**CONCLUSIONS**

The adsorption of a variety of divalent and trivalent metal–EDTA complexes onto goethite was examined. Depending on the structure of the complex in solution, several adsorption mechanisms were observed. Adsorption is explained by a specific process as indicated by release of OH$^-$, competition with the specifically adsorbing phosphate, and only minor effects of ionic strength. Adsorption edges can be modeled assuming the formation of one ternary surface complex for $Me^{2+}$EDTA ($Me^{2+} =$ Ca, Zn, Ni, Cu, Co(II), and Pb). These complexes are quinquestadentate in solution. Sexidentate complexes, such as Co(III)EDTA and Cr(III)-EDTA are adsorbed only weakly by electrostatic interactions. Fe(III)EDTA is adsorbed weakly over the whole pH range, probably by forming cation-like complexes at higher pH values. At a pH higher than 7, Fe(III)EDTA adsorbed more strongly than the divalent complexes. The complexes of the large ions La and Bi are adsorbed totally over the whole pH range.

The adsorption behavior of EDTA in subsurface systems depends therefore very strongly on the type of complexed metal, ranging from very weak adsorption for Co(III)EDTA to very strong adsorption for LaEDTA.

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