Lead Sorption onto Ferrihydrite. 2. Surface Complexation Modeling

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Few studies have combined molecular- and macroscopic-scale investigations with surface complexation models (SCMs) to predict trace metal speciation and partitioning in aqueous systems over a broad range of conditions. In this work, an extensive collection of new macroscopic and spectroscopic data was used to assess the ability of the modified triple-layer model (TLM) to predict single-solute lead(II) [Pb(II)] sorption onto 2-line ferrihydrite in NaNO₃ solutions as a function of pH, ionic strength, and concentration. Regression of constant-pH isotherm data together with potentiometric titration and pH edge data was a much more rigorous test of the TLM than fitting pH edge data alone. When combined with spectroscopic data, the choices of feasible surface species/site types were limited to a few. In agreement with the spectroscopic data, very good fits of the isotherm data were obtained with a two-species, one-site model using the bidentate-mononuclear/monodentate-mononuclear species pairs, (≡FeO)₂Pb/≡FeOH₅Pb²⁺ and (≡FeO)Pb/ ≡FeOH₅Pb⁺−NO₃⁻. Regressing edge data in the absence of isotherm and spectroscopic data resulted in a fair number of surface species/site-type combinations that provided acceptable fits of the edge data but unacceptable fits of the isotherm data. Surprisingly, best-fit equilibrium “constants” for the Pb(II) surface complexes required adjustment outside the pH range of 4.5−5.5 in order to fit the isotherm data. In addition, a surface activity term was needed to reduce the ionic strength dependence of sorption for the species pair, (≡FeO)₂Pb/≡FeOH₅Pb²⁺. In light of this, the ability of existing SCM s to predict Pb(II) sorption onto 2-line ferrihydrite over a wide range of conditions seems questionable. While many advances have been made over the past decade, much work still needs to be done in fine-tuning the thermodynamic framework and databases for the SCMs.

Introduction

Numerous commercial and public domain geochemical codes exist for predicting trace metal speciation in aqueous systems; however, the existing surface complexation models (SCMs) in these codes often prove inadequate for simulating multisolute sorption reactions in complex industrial systems. One contributing factor is that published thermodynamic parameters for the surface complexes are often based on regressions of a handful of pH sorption edges covering a narrow range of conditions, done without the aid of state-of-the-art spectroscopic techniques to confirm surface speciation.

Extensive studies of metal cation and anion sorption onto amorphous iron (hydr)oxides have been conducted over the years. Dzombak and Morel (1) critically reviewed pre-1990 single-solute sorption data for hydrous ferric oxide (HFO); these data were regressed to obtain best-fit intrinsic equilibrium constants (Kᵢ) for the Generalized Two-Layer Model (GTLM). Interestingly, only 17% of 184 cation/anion data sets were equilibrium isotherms. This suggests that these equilibrium constants will have limited applicability if the pH edges used to determine them did not cover a broad enough range of conditions. Constant-pH equilibrium isotherms, on the other hand, often cover 5−8 orders of magnitude in metal concentration. If generated at multiple pH values, regression of constant-pH isotherm data along with pH sorption edge data is a much more rigorous test of the SCM.

Despite the fact that lead(II) [Pb(II)] is a common constituent found in contaminated soils, sediments, and some groundwater streams, previous studies of single-solute Pb(II) sorption onto HFO/ferrihydrite are somewhat limited (1, 2, 3). All studies report pH edge data except for Scheinost et al. (2), which contains kinetic data for Pb(II) sorption onto 2-line ferrihydrite at pH 5, and Benjamin (3), which provides the only published Pb(II) sorption isotherm for HFO (pH 4.5) prior to this work. Interestingly, Dzombak and Morel (1) regressed only low concentration edge data to obtain a best-fit Kᵢ for Pb(II) sorption onto type 1, high-affinity sites; Kᵢ for type 2, low-affinity sites in the GTLM was estimated based on linear free energy relationships.

Before the advent of in situ spectroscopic and macroscopic techniques, researchers were limited in their ability to probe the surface of mineral oxides to determine surface speciation. As a result, assumptions about surface speciation in early applications of SCMs were largely based on macroscopic observations, such as the shift (or lack thereof) in pH sorption edges with ionic strength (4−8). Dzombak and Morel’s work (1) represented one of the first attempts to use a single SCM to regress a wide cross section of metal sorption data for a single sorbent. Even in recent years, however, pH edge data alone are still being used to obtain best-fit model parameters for SCMs (9−12). Since 1995, some studies have evaluated the applicability of SCMs over a wider range of concentration, pH, and ionic strength conditions (13−15). For example, Katz and Hayes (13, 14) proposed a surface continuum model for simulating cobalt(II) sorption onto Al₂O₃ from 0.05 to 100% surface coverage. Robertson and Leckie (15) evaluated the ability of three different SCMs to predict copper (Cu) sorption onto goethite over 3 and 6 orders of magnitude in Cu surface coverage and solution concentration, respectively, at three different pH values. None of these studies, however, benefited from parallel spectroscopic investigations. A handful of studies have combined spectroscopic and macroscopic analyses with surface complexation modeling to simulate trace metal sorption data (16−18); however, none were found for Pb(II) sorption onto HFO/ferrihydrite.

Application of a Law of Mass Action (LMA)-based SCM requires the definition of many parameters including site densities and surface areas for the sorbents; equilibrium constants for protonation, deprotonation, metal sorption, and background electrolyte sorption reactions; and, in some
cases, capacitance values. This is in addition to making assumptions about the number and types of sorption sites and surface species (19). In recent years, Sverjensky and coworkers have developed techniques for estimating the values of a number of LMA-based SCM parameters on the basis of the physical and chemical properties of the solutes and sorbents themselves (20–23); however, these predictive techniques are currently limited to crystalline sorbents. For an amorphous sorbent like ferrihydrite, regression of macroscopic data is still necessary. In an attempt to address potential limitations inherent in LMA-based SCMs (most notably, the mass balance constraints on surfacesites), Kulik has developed a multisite Gibbs energy minimization (GEM) approach for surface complexation modeling (24, 25). Two important aspects of this work are the rigorous definition of standard and reference states for surface species and sites and the use of a surface activity term to suppress the concentration of a surface complex as it nears a defined maximum site density.

An in-depth literature review highlighted the scarcity of studies where molecular- and macroscopic-scale data have been coupled with surface complexation modeling to predict metal-cation sorption over a wide range of conditions. In the first paper in this series, Trivedi et al. (26) presented extensive single-solute macroscopic and spectroscopic data for Pb(II) sorption onto 2-line ferrihydrite. In this paper, we highlight the importance of integrating spectroscopic data on surface speciation with macroscopic isotherm and pH sorption edge data covering a wide range of conditions when calibrating a SCM. In addition, we test the ability of the modified triple-layer model to predict single-solute Pb(II) sorption onto 2-line ferrihydrite over a broad range of conditions using a single set of surface complexation modeling parameters.

Methods

Potentiometric Titration and Pb(II) Sorption Data. Modeling studies were based on macroscopic and spectroscopic data for single-solute Pb(II) sorption onto 2-line ferrihydrite (N2 atmosphere, room temperature, and 4-h equilibration time) that are reported and discussed in ref 26. This includes the ferrihydrite preparation method as well as potentiometric titration data for ferrihydrite in 0.001, 0.01, and 0.1 M NaNO3 solutions (N2 atmosphere and room temperature). Raw tabulated titration and Pb(II) sorption data can be found in ref 27. Titration data at each ionic strength were tabulated as excess acid (q, equiv/L) versus pH:

\[ q \text{ (equiv/L)} = C_A - C_B - [H^+] + [OH^-] \]  

where \( C_A \) and \( C_B \) are the total quantity of mineral acid and base, respectively, added at each titration point (in equiv/L). The measured pH values at each ionic strength were used to determine molal concentrations for \([H^+]\) and \([OH^-]\) by taking into account activity coefficients for \(H^+\) and \(OH^-\) and \(H_2O\) activity. The titration curves were then shifted slightly downward along the y-axis so that the common intersection point was at \( q = 0.0 \). All constant-pH isotherm and pH edge data points were individually equilibrated in their own sample vials.

Geochemical Modeling Software. The OLI Software (OLI Systems, Inc., Morris Plains, NJ) is a commercial simulation package that models aqueous electrolyte equilibria including chemical speciation and redox reactions; equilibria between aqueous, vapor, organic liquid, and multiple solid phases; biochemical and inorganic reaction kinetics; and ion exchange, adsorption, and coprecipitation phenomena. The system is built around the OLI Engine, which is the foundation for the Environmental Simulation Program (ESP), Corrosion Simulation Program (CSP), and ProChem. ProChem was used in this study because it models single-stage equilibria at both steady and unsteady states (28).

At the heart of the OLI Engine are the database, the thermodynamic framework, and the equation solvers (29). The OLI database contains the thermodynamic and physical properties of over 8300 inorganic and organic species. The thermodynamic variables (Gibbs free energy, enthalpy, entropy, and heat capacity) in the database are from six main sources—Glushko et al. (30), Wagman et al. (31), Gurvich et al. (32), Chase et al. (33), Daubert and Danner (34), and Oelkers et al. (35). Each of these sources is an extensive, carefully evaluated, and well-documented calculation of thermodynamic data. The state-of-the-art thermodynamic framework uses generalized correlations based upon re- gressed experimental data in the database to predict the required thermodynamic and physical properties for the chemical system of interest (i.e., infinite dilution, standard-state values for Gibbs free energy, enthalpy, entropy, heat capacity, and volume, liquid-phase activity coefficients for systems at finite concentrations, etc.). The theoretical basis for the thermodynamic framework is explained elsewhere (36, 37). Shock and Helgeson (38) describe the semi-theoretical basis for temperature and pressure extrapolation of standard-state properties along with procedures for estimating missing parameters. The aqueous activity coefficient model is an extension of the work of Bromley and Meissner (i.e., the Bromley–Zemanis framework) and is given in Supporting Information (37, 39). Details on the equation solvers used to solve the nonlinear equilibrium, electroneutrality, and mass balance equations can be found in ref 29. Permissible operating ranges for the software can be found in ref 40. The OLI equilibrium reactions and associated equilibrium constants used in this work are given in Table S1 in the Supporting Information.

Surface Complexation Models. Four different surface complexation models are available in the OLI Software—the nonelectrostatic model (NEM), the constant capacitance model (CCM), the GTLM, and the modified triple-layer model (TLM). In this research, the NEM, GTLM, and TLM were all considered, although the TLM ultimately proved to be the preferred SCM as discussed below. The thermodynamic framework for the NEM, GTLM, and modified TLM are described in Hayes and Katz (41), Dzombak and Morel (1), and Sahai and Sverjensky (42), respectively.

Modeling Protocol. Hayes and Katz (41) served as a basis for the modeling protocol used in this study. First, the OLI Software’s nonlinear regression routine was used to determine a valid set(s) of metal hydroxide surface parameters for the SCM of interest using potentiometric titration data for 2-line ferrihydrite at three different ionic strengths as reported in ref 26. For the GTLM, this was done for a range of site density (N_s) values at a fixed specific surface area (A_s) giving K_{int} and K_{int}' (the surface acidity constants) as a function of N_s. For the modified TLM, Hayes and Katz (41) showed that various combinations of N_s, C_s, and \( \Delta pK_a \) will provide adequate fits of potentiometric titration data for mineral oxides. For this reason, a three-factor, face-centered cube (FCC), response-surface experimental design was used to determine the values of N_s, C_s, and \( \Delta pK_a \) that provide the best fit of the titration data (A_s and C_s were held constant in the model). The experimental design was generated and analyzed using the MINITAB Statistical Software (Minitab Inc., State College, PA). Ranges of values considered for N_s, C_s, and \( \Delta pK_a \) in the experimental design were 0.2–0.9 mol of sites/mol of Fe, 0.6–1.4 faraday/m², and 3.0–6.0, respectively. The criteria for judging the quality of fit were the value of R^2 obtained from the OLI code’s nonlinear regression program, and visual inspection of a plot of the model titration curves with the experimental data. A Marquardt nonlinear optimization algorithm was used throughout this work; the
objective function minimized was the ratio ($R_i$) of the calculated to experimental values (or vice versa, such that $R_i$ is always $>1.0$). $R_i$ values were equally weighted, with a perfect fit being defined as $R_i = 1.0$. OLI has found that this objective function is more robust than least-squares minimization when regressing data values that range over many orders of magnitude, such as in constant-pH isotherms where Pb(II) solution concentrations will vary over 5–7 orders of magnitude. $R_{avg}$ represents the arithmetic average of all $R_i$ values for the regressed experimental data set.

Next, spectroscopic results and the impact of ionic strength on Pb(II) sorption were used to guide the selection of the Pb(II) surface complexation reactions at low to moderate surface coverage. Hayes and Katz (41) note that past X-ray absorption fine structure spectroscopy (XAFS) studies have suggested that mononuclear species predominate at low to moderate surface coverage (0.1–10%) for strongly sorbing metals and at all coverages for weakly sorbing metals. Ionic strength dependence has also been used historically to infer the presence of inner-sphere versus outer-sphere surface complexes (43). In this study, pH edges generated at three different ionic strengths were used to assess the ionic strength dependence of Pb(II) sorption. Spectroscopic results are summarized in ref 26.

Spectroscopic results and the shape of the constant-pH equilibrium isotherms were used to determine the need for multinuclear surface complexation reactions at higher surface coverage (i.e., surface polymers and/or surface precipitates). The constant-pH isotherms were also used to determine a reasonable starting point for $N_s$ and to assess the possibility of site heterogeneity (i.e., the need for more than one site type). Robertson and Leckie (44) found that site heterogeneity is likely if the slope of a constant-pH isotherm curve is less than 1.0 at low surface coverage.

On the basis of the above analyses of the macroscopic and spectroscopic data, an appropriate set of oxide surface parameters ($N_s$, $C_i$, $C_2$, $\Delta pK_a$, and $A_s$) and Pb(II) surface complex species were assumed for the SCM of interest. These surface parameters/species were used to regress the constant-pH isotherm data to obtain a set of best-fit equilibrium constants for single-solute Pb(II) sorption. The best-fit $K$ values were then used to assess how the model predicted the pH edge data at multiple ionic strengths and initial Pb(II) concentrations. Various combinations of viable Pb(II) surface complexes were considered to evaluate the sensitivity of the model fits to the speciation assumptions. The minimum numbers of site types and species that provided the best fit of the isotherm and pH edge data were considered the optimum. Again, $R_{avg}$ values for both $x$ (total Pb(aq)) and $y$ (mol of Pb/mole of Fe) data from the nonlinear regression program together with visual inspection of graphical output were used to judge the quality of the fits. This step was an iterative process whereby the oxide surface parameters were adjusted if $N_s$ was altered.

Results and Discussion

Potentiometric Titration Data. The point of zero net proton charge ($pH_{PZPC}$) for 2-line ferrihydrite was determined to be 7.91, which falls within the range of point of zero charge values reported by others (1). Figure S1a,b in the Supporting Information and Figure 1 present best fits of the potentiometric titration data for the NEM, GTLM, and TLM, respectively. Corresponding model parameters are given in Table 1. In all cases, $A_s$ was fixed at 600 m$^2$/g. The NEM fit provides no functionality with ionic strength, and it significantly overpredicts surface charge as pH moves away from the $pH_{PZPC}$. The GTLM was better than the NEM and TLM at capturing the sharp curvature in the titration data at the pH extremes; however, it was inferior to the TLM in predicting the more linear surface-charging behavior over the pH range of 5–9. Regardless of the number of site types and $N_s$, the general shape of the GTLM-predicted titration curves did not change substantially.

The modified TLM produced titration curves (Figure 1) that were more linear over a wider pH range, especially as ionic strength increased. Unlike the NEM and GTLM, outer-sphere surface complexes involving the background electrolyte ions are included in the TLM; these complexes dominate surface charge, producing less curvature in the titration curves. The optimum fit shown in Figure 1 along with the associated model parameters in Table 1 were obtained with the help of the three-factor, FCC, response–surface experimental design. The quality of the fits based on $R_{avg}$ was highly sensitive to the value of $C_i$. On the other hand, the impacts of $\Delta pK_a$ and $N_s$ on $R_{avg}$ were moderate and small, respectively. In all cases, the TLM could not reproduce the sharp increase (decrease) in proton surface charge at pH $\sim$4.5 (see Figure 1 in ref 26). In general, the quality of the TLM fit deteriorated at the pH extremes and as ionic strength increased. For this reason, the model fit of the titration data was optimized over the pH range of 4.5–9.0.

To validate the quality and consistency of the data, ferrihydrite titrations in 0.01 and 0.1 M NaNO$_3$ solutions were repeated two more times each in separate runs as discussed in ref 26. In all cases, these new titrations occurred 1 year after the original titrations used for the model regressions and used a different batch of ferrihydrite. The additional titrations in 0.01 M NaNO$_3$ solution were conducted over the pH range of 4–10 to examine the effects of a longer equilibration time (15 vs 2 min in original titrations) and a higher solids concentration (10 vs 1 g/L in original titrations). The impact of equilibration time alone was small at 1 g of ferrihydrite/L, suggesting that kinetics was not a significant factor. The combination of a higher solids concentration and longer equilibration time, on the other hand, shifted the 0.01 M NaNO$_3$ titration curve to a lower surface charge and provided some dampening of the sharp curvature at the pH extremes. At this high solids concentration, however, mass transfer limitations were likely. Regardless, the new data did not substantially improve the ability of the TLM to fit the titration data over the entire pH range of 4–10. The 0.1 M NaNO$_3$ titrations were repeated over a narrower pH range (pH 5–9 vs pH 4–10) than the original titration and were conducted from both low-to-high and high-to-low pH. Figure S2 (Supporting Information) shows excellent agreement...
between the triplicate 0.1 M NaNO₃ runs, indicating that the
ferrihydrite preparation and experimental titration methods
are reproducible. The results were also similar regardless of
the initial conditions. On the basis of the triplicate 0.1 M
NaNO₃ data, the average coefficient of variation (1
~10°) for the ~100 titration steps between pH 5 and pH 9 was ~8%. Error
bars corresponding to ± 2σ are shown in Figure 1. In addition,
independent solubility measurements for 2-line ferrihydrite
in 0.01 M NaNO₃ solutions over the pH range of 3–5 showed
that sorbent dissolution could not account for the sharp
increase in acid consumption between pH 5 and pH 4.
Ferrihydrite solubility was nondetect, 1.7 ppb, and 6.5 ppb
at pH 5, 4.5, and 4, respectively. Ongoing investigations are
examining the possibility that the sharp change in slope of
the titration curves below pH 4.5 and above pH 9 is due to
a change in ferrihydrite morphology and, hence, in the surface
area available for reaction with acid or base.

While none of the SCMs could predict the shape of the
titration curves over the entire pH range (pH 4–10), the TLM
provided the best fits of the ferrihydrite titration data over
the pH range of environmental significance (pH 4.5–9). There
are several important points to keep in mind regarding the
quality of the titration data fits. First, while optimizing the
model fit of the titration data over different pH ranges (pH
5–8, 4.5–9, and 4–10) resulted in different sets of best-fit
oxide surface parameters (i.e., C₁, log K⁺,(NO₃)²⁻, and log K⁺,(OH)²⁺),
these unique sets of parameters gave essentially identical
fits of the constant-pH isotherm data (i.e., log K values for the
Pb(II) surface complexes). Second, the model predictions
are also bounded by a level of uncertainty. Figure 1 displays
the 95% prediction intervals for the model titration curves
on the basis of the results of a rigorous error propagation
analysis using the uncertainty analysis module in the OLI
code (27). Assumed input thermodynamic uncertainties (1σ)
were C₁ (10%), C₂ (10%), pH (0.03 unit), total ferrihydrite
(10%), total H₂O (3%), total NaNO₃ (10%), total NaOH (2.5%), total
HNO₃ (2.5%), log K⁺,(NO₃)²⁻ (0.125 log unit), log K⁺,(OH)²⁺ (0.125 log
unit), log K⁺,(Na)²⁺ (0.125 log unit), and log K⁺,(H₂O)²⁻ (0.125 log unit).
When uncertainties in the data and model are both
considered, the experimental data points fall well within the
uncertainty bands for the model curves. Third, extensive
uncertainty analyses of the Pb(II) isotherm and pH edge
model fits in Dyer (27) revealed that input uncertainties in
log K⁺,(NO₃)²⁻ and log K⁺,(OH)²⁺ have little impact on the predicted
output uncertainties in Pb(II) sorbed and Pb(II) in solution
over the majority of the pH, Pb concentration, and ionic
strength space covered by this study. Only in the narrow pH
range of 3.5–4.5 at low Pb(II) surface (~10⁻³ mol/mol) and
solution (~1 ppm) concentrations did uncertainty in the
titration data fit have a significant impact on predicted
Pb(II) partitioning. More importantly, this was true only
when the 1σ uncertainties in log K⁺,(NO₃)²⁻ and log K⁺,(OH)²⁺ were
greater than 0.24 log unit (i.e., a 2σ uncertainty ~148% in K space).
In all other cases, uncertainties in Pb(II) concentrations
were not sensitive to the fit of the titration data. On the basis
of consideration of R(avg), visual inspection of the fits, extensive
uncertainty analyses, and results of past TLM modeling efforts

with HFO (4, 8, 45), Figure 1 was defined as the “best fit” to

carry forward for the regression of the Pb(II) sorption data.

Pb(II) Sorption Isotherms and Edges. Analysis of mac-
rosopic and spectroscopic data from ref 26 for Pb(II) sorption
onto 2-line ferrihydrite provided several insights to help focus
the SCM development. First, pH edge data for 50 mM Pb(II)
charged with 1 g of ferrihydrite/L in 0.001 M NaNO₃ solution;
Pb(II) added as Pb(NO₃)₂; 4-h equilibration time; room temperature;
N₂ glovebox.

FIGURE 2. Optimized triple-layer model fits of pH 4.5, 5.5, and 6.5
equilibrium isotherm data for single-solute Pb(II) sorption onto 2-line
ferrihydrite assuming the species pairs (a) (FeO)₂Pb/FeOH₂Pb²⁺
[log K⁺,(FeO)₂Pb/FeOH₂Pb²⁺ = -4.98 (pH 4.5, 5.5) and 6.16 (pH 6.5); log K⁺,(FeO)₂Pb²⁺/FeOH₂Pb²⁺ = -8.76 (pH 4.5, 5.5) and -5.27 (pH 6.5)] and (b) (FeO)₂Pb²⁺/FeOH₂Pb²⁺
[log K⁺,(FeO)₂Pb²⁺/FeOH₂Pb²⁺ = -5.02 (pH 4.5, 5.5) and -5.95 (pH 6.5); log K⁺,(FeO)₂Pb²⁺/FeOH₂Pb²⁺ = -2.17 (pH 4.5, 5.5) and -0.18 (pH 6.5)]. Experimental
conditions: 0.1 and 1.0 g of ferrihydrite/L in 0.01 M NaNO₃ solution;
Pb(II) added as Pb(NO₃)₂; 4-h equilibration time; room temperature;
N₂ glovebox.

TABLE 1. Model Parameters for the NEM, GTLM, and TLM Based on Regression of Potentiometric Titration Data for 2-Line
Ferrihydrite at Room Temperature in N₂ Atmosphere

<table>
<thead>
<tr>
<th>Model</th>
<th>Nₛ (mol/mol)</th>
<th>C₁ (faraday/m²)</th>
<th>C₂ (faraday/m²)</th>
<th>log K⁺,(NO₃)²⁻</th>
<th>log K⁺,(OH)²⁺</th>
<th>log K⁺,(Na)²⁺</th>
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<td>NEM</td>
<td>0.8</td>
<td>na</td>
<td>na</td>
<td>-4.43</td>
<td>-11.52</td>
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<td>GTLM</td>
<td>0.8</td>
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<td>na</td>
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<td>-8.89</td>
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<tr>
<td>TLM</td>
<td>0.8</td>
<td>0.725</td>
<td>0.2</td>
<td>-5.41</td>
<td>-10.41</td>
<td>-7.59</td>
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* a = FeOH₂⁺ = FeOH + H°, where K⁺,(FeOH) = a₁ = [FeOH] exp(-FV/R)\[FeOH\]; b = FeOH = FeO + H°, where K⁺,(FeO) = a₂ = [FeO] exp(-FV/R); c = FeOH⁻ = FeO⁻ + NO₃⁻, where K⁺,(Na) = a₃ = [FeO⁻] exp(FV/7)\[NO₃\]; d = FeOH⁻ + Na⁺ + H° = FeOH + Na⁺, where K⁺,(Na) = a₄ = [FeOH] exp(FV/7)\[Na\]; e = na, not applicable.
It can be shown that $K_{int}$ arises with multidentate complexes because of the definition of the standard state for surface species in molality rather than molar fraction. This peculiarity arises with multidentate complexes because of the definition of the standard state for surface species in molality rather than molar fraction. It can be shown that $K_{int}$ is actually a conditional $K$ that depends on sorbent solids concentration, $C_s$, regardless.

**Table 2.** TLM Parameters for Single-Solute Pb(II) Sorption onto 2-Line Ferrihydrite (fh) at Room Temperature in N$_2$ Atmosphere

<table>
<thead>
<tr>
<th>Species Pair</th>
<th>pH</th>
<th>$\log K_{(FeO)Pb}$ at 1 g fh/L</th>
<th>$\log K_{(FeOPb)^+}$ or $K_{(FeOPb)^-}$</th>
<th>$R_{avg}$ (Pb$_{edge}$)</th>
<th>$R_{avg}$ (K$^{int}$)</th>
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<td>($\equiv$Fe)$_2$Pb/$\equiv$FeOPb$^{2+}$</td>
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<tr>
<td>($\equiv$Fe)$_2$Pb/$\equiv$FeOPb$^-$/$\equiv$NO$_3$</td>
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<td>5.02</td>
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* For bidentate-mononuclear surface complexes, $K^{int}$ is actually a conditional $K$ that depends on sorbent solids concentration, $C_s$, regardless. ** For bidentate-mononuclear surface complexes, $K^{int}$ is actually a conditional $K$ that depends on sorbent solids concentration, $C_s$, regardless.

**Figure 3.** Comparison of constant-pH isotherm and pH sorption edge data to modified triple-layer model predictions for single-solute Pb(II) sorption onto 2-line ferrihydrite assuming the species pair ($\equiv$Fe)Pb/$\equiv$FeOPb$^{2+}$ \(|\log K_{(FeO)Pb}| = 2.44, 3.39, 4.28, 4.98, 5.67, 6.16 \) and $K_{(FeOPb)^+}$. The $R_{avg}$ values were plotted with isotherm data on the same graph. Figure 3 shows excellent agreement between the pH edge and the isotherm data, indicating that the data are internally consistent. Interestingly, Figure 3 suggests that a reduction in spacing between the constant-pH isotherms should be expected on the basis of the inherent shape of a pH sorption edge. More specifically, d[Pb$_{edge}$/d$\log$K$^{int}$] changes significantly over the course of a pH sorption edge. At low and high values of percent of Pb sorbed, the change in sorbed Pb(II) and, hence, in total Pb(II)(aq) is relatively small for a unit change in pH (i.e., d[Pb$_{edge}$/d$\log$K$^{int}$] is small). However, over a narrow pH range, the change in sorbed Pb(II) with pH increases substantially (i.e., d[Pb$_{edge}$/d$\log$K$^{int}$] is large).
Edge occurs over the pH range of 4–5.5 where $d\left[\text{pH}\right]$ is large. For Pb(II), the steep slope of the pH sorption edge has begun to plateau, and $d\left[\text{pH}\right]$ is 0.5 or less. The constant-pH isotherm curves for pH 3, 3.5, 4, and 6 shown in Table 2. Although not shown, results for the (FeO)Pb/FeOPb$^+$ species pair are very similar; conditional equilibrium constants for each pH value are given in Table 2. The pH 5 isotherm data. This is an artifact of the modified TLM thermodynamic framework itself. First, bulk solution concentrations and activity coefficients for the sorbing ions (i.e., $H^+$, NO$_3^-$, Na$^+$, and Pb$^{2+}$) are used in the mass law expressions (because we know how to measure and estimate them, respectively) rather than true surface species activities themselves (44). Second, lacking a way to directly determine the activity of a surface complex as well as a predictive model for estimating surface activity coefficients, the ratio of the activity coefficients for the surface species (i.e., $\left[\text{FeO}\right]_{\text{Pb}/\text{FeOH}}$, and $\left[\text{FeOH}\right]_{\text{Pb}/\text{FeOPb}}$) are used in the mass law expressions (because we know how to measure and estimate them, respectively) rather than true surface species activities themselves (44). Second, lacking a way to directly determine the activity of a surface complex as well as a predictive model for estimating surface activity coefficients, the ratio of the activity coefficients for the surface species (i.e., $\left[\text{FeO}\right]_{\text{Pb}/\text{FeOH}}$, and $\left[\text{FeOH}\right]_{\text{Pb}/\text{FeOPb}}$) is assumed to equal 1.0. In essence, this represents only a “partial correction” for nonidealities at the surface. To correct...
for the overprediction of the ionic strength dependence, a surface activity term ($\gamma_s$) was used in the OLI model to better match the pH edge data. Interestingly, the best agreement between the predicted curves and the actual data was obtained when $\gamma_s$ was set equal to $\gamma_{sw}^{s*}$, the bulk solution activity coefficient for the Pb$^{2+}$ ion. The $\gamma_s$ term was also used during regression of the isotherm data for the (FeO)$_2$Pb$\rightleftharpoons$FeOH$\cdot$Pb$^{2+}$ species pair; therefore, the equilibrium constants given in Table 2 include this correction.

Interestingly, ionic strength dependence is less with the species pair, (FeO)$_2$Pb$\rightleftharpoons$FeOH$\cdot$Pb$^{2+}$, as shown in Figure 4b. Criscenzi and Sverjensky (51) found that surface species of the form $\equiv$FeOPb$^{+}$/$\equiv$NO$_3$-, $\equiv$FeOH$\cdot$Pb$^{2+}$/-$\equiv$NO$_3$-, etc. better represented the ionic strength dependence of metal sorption in nitrate solutions. At the present time, spectroscopy is unable to confirm whether this type of surface species actually exists at the surface or whether it is necessary because of the construct of the TLM thermodynamic framework itself.

Figure 4c,d displays TLM predictions for both species pairs when pH-adjusted K values are used rather than the best-fit equilibrium constants for pH 4.5-5.5 only. In other words, log K values for the Pb surface complexes in the model were adjusted with pH as reported in Table 2. In addition, Figure 4c includes the $\gamma_s$ correction. Note the good agreement between the model curves and the actual data. The better fit at pH <4 was accomplished without introducing a second, high-affinity site type or additional surface species as has often been done in past modeling studies that are based on pH edge data only. Although not shown, introducing a second, high-affinity site to account for the elevated Pb(II) sorption at pH <4 resulted in unacceptable fits of the isotherm data at low Pb(II) concentrations. Instead, when considered together, the isotherm and edge data suggest that a single, two-species model is sufficient but that the best-fit equilibrium constants are valid over a limited pH range only. Additional pH edge data from ref 26 at different Pb(II):Fe ratios were also compared against the TLM-predicted edges (Figures S9 and S10, Supporting Information).

**Implications for Surface Complexation Modeling**

This study highlights the benefits of combining comprehensive molecular- and macroscopic-scale studies conducted by the same researcher in the same laboratory with surface complexation modeling. Regressing constant-pH isotherm data together with potentiometric titration and pH edge data is clearly a much more rigorous test of the SCM. When combined with spectroscopic data on surface speciation, the scope of feasible surface complexes and site types becomes much more limited. In this work, application of the triple-layer SCM led to the same conclusions about Pb(II) speciation on the ferrihydrite surface as did analysis of the spectroscopic data in ref 26. More specifically, the authors found that regressing pH edge data in the absence of isotherm and spectroscopic data resulted in a much larger number of surface-species and site-type combinations that provided acceptable fits of the edge data. However, when these same assumptions were used to predict the constant-pH isotherms, the agreement between model and data was poor in most cases. Finally, the results of this research suggest that a single set of SCM thermodynamic parameters is unable to predict single-solute Pb(II) sorption onto ferrihydrite over a wide range of conditions. While many advances have been made over the past decade, much more work still needs to be done in fine-tuning the thermodynamic framework and databases.

**Acknowledgments**

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**Supporting Information Available**

Two graphs showing NEM and GTLM fits of potentiometric titration data; graph showing triplicate sets of 0.1 M NaNO$_3$ potentiometric titration data; three graphs showing TLM fits of constant-pH isotherm data using a one-species model; one graph showing TLM isotherm fits using the species pair, $\equiv$FeOPbOH/$\equiv$FeOPb$^{2+}$; two graphs showing GTLM fits of isotherm data; two graphs showing TLM fits of additional pH-sorption-edge data using the species pairs, (FeO)$_2$Pb$\rightleftharpoons$FeOH$\cdot$Pb$^{2+}$ and (FeO)$_2$Pb$\rightleftharpoons$FeOpb$^{2+}$/-$\equiv$NO$_3$; table of equilibrium reactions and associated equilibrium constants used in OLI code; OLI activity coefficient model. This material is available free of charge via the Internet at http://pubs.acs.org.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i$</td>
<td>activity of species i</td>
</tr>
<tr>
<td>$A_s$</td>
<td>specific surface area of sorbent (m$^2$/g)</td>
</tr>
<tr>
<td>$C_A$</td>
<td>quantity of mineral acid added during potentiometric titration of sorbent (equiv/L)</td>
</tr>
<tr>
<td>$C_B$</td>
<td>quantity of mineral base added during potentiometric titration of sorbent (equiv/L)</td>
</tr>
<tr>
<td>$C_1$</td>
<td>inner-layer capacitance term for triple-layer model (faraday/m$^2$)</td>
</tr>
<tr>
<td>$C_2$</td>
<td>outer-layer capacitance term for triple-layer model (faraday/m$^2$)</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant (96 485 C/mol)</td>
</tr>
<tr>
<td>$[H^+]$</td>
<td>hydrogen ion molal concentration (mol/kg of H$_2$O)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>conditional equilibrium constant</td>
</tr>
<tr>
<td>$K_i^{\text{int}}$</td>
<td>intrinsic or thermodynamic equilibrium constant</td>
</tr>
<tr>
<td>$K_i^{\text{ex}}$</td>
<td>intrinsic acidity constant for the surface deprotonation reaction: $\equiv$FeOH$^-$ $\rightleftharpoons$ $\equiv$FeO$^-$ + $H^+$</td>
</tr>
<tr>
<td>$N_s$</td>
<td>surface site density (mol of sites/mol of sorbent)</td>
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<tr>
<td>$[OH^-]$</td>
<td>hydroxyl ion molal concentration (mol/kg of H$_2$O)</td>
</tr>
<tr>
<td>$q$</td>
<td>excess acid added during potentiometric titration (equiv/L)</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant (8.314 J K$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$R_{\text{avg}}$</td>
<td>arithmetic average of nonlinear regression fit parameters obtained from the OLI Software (R for each data point is the ratio of the model-calculated value to the experimental value (or vice versa), such that R is 1.0 or higher)</td>
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<tr>
<td>$T$</td>
<td>absolute temperature (K)</td>
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<tr>
<td>$\Delta pK_s$</td>
<td>equals ($pK_s^{\text{calc}}$ - $pK_s^{\text{ex}}$) when the protonation/deprotonation reactions are written as dissociation reactions</td>
</tr>
<tr>
<td>$\gamma_s$</td>
<td>lumped surface activity coefficient used in OLI model to account for nonidealities of the surface complex species</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>surface loading (mol of Pb(II)/mol of Fe)</td>
</tr>
</tbody>
</table>
electric potential at $\alpha$-plane in TLM or at surface in GTLM

electric potential at $\beta$-plane in TLM

Literature Cited


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