Chemical Modeling of Anion Competition on Goethite Using the Constant Capacitance Model

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ABSTRACT

The constant capacitance model was used to describe phosphate, selenite and silicate adsorption on goethite (α-FeOOH) in single anion systems. The model assumes a ligand exchange mechanism and considers the charge on both adsorbate and adsorbent. It is therefore appropriate for describing the adsorption behavior of these specifically adsorbed anions. The computer program FITEQQL, a program that fits equilibrium constants to experimental data using an optimization technique, was used to obtain optimal values for the anion surface complexation constants on goethite. The model represented adsorption of these anions well over the entire pH range studied (3–12). The main advantage of the model is its ability to represent changes in anion adsorption occurring with changes in pH. Extension of the model to describing anion competition in mixed systems using the anion surface complexation constants from single anion systems was qualitatively successful. In mixed anion systems the model predictions reproduced the shape of the adsorption isotherms well over the pH range 3 to 12. However, phosphate adsorption was overestimated while adsorption of the competing anion was underestimated.

Additional Index Words: phosphate adsorption, selenite adsorption, silicate adsorption, ligand exchange, FITEQQL, MICROQL.


The constant capacitance model of the oxide-water interface was developed by Stumm, Schindler and their co-workers (Stumm et al., 1970; Schindler and Gamsjäger, 1972; Stumm et al., 1976; Stumm et al., 1980). It is a chemical model which differs from the Langmuir and Freundlich adsorption equations in that it explicitly defines surface species and chemical reactions. The adjustable model parameters are the conditional equilibrium constants for the surface reactions as well as the capacitance—an empirical parameter. The effect of pH on the extent of adsorption and on the magnitude of surface charge is included in this model. The model successfully describes the amphoteric behavior of inorganic surface hydroxyl groups as well as the adsorption of specifically adsorbed anions. Anions become specifically adsorbed by undergoing ligand exchange with reactive surface hydroxyl groups. Specific adsorption of anions produces a shift in the zero point of charge (ZPC), of the oxide mineral to a more acid value. A shift in ZPC was observed for adsorption of selenite on goethite (Higdon et al., 1968) and on hydrous alumina (Rajan, 1979) and for silicate adsorption on goethite (Higdon et al., 1972; Sigg and Stumm, 1981) indicating that these ions are adsorbed specifically. For this reason, the constant capacitance model is appropriate for describing the adsorption behavior of these anions. The adsorption behavior of various other anions has been described with the model, including adsorption of the aromatic compounds catechol, salicylic acid, benzoic acid, and phthalic acid on γ-Al₂O₃ (Kummert and Stumm, 1980), and F⁻, SO₄²⁻, acetate, H₂SiO₄⁻, and PO₄³⁻ adsorption on goethite (Sigg and Stumm, 1981). The ability of the model to describe phosphate adsorption on various x-ray amorphous as well as crystalline aluminum and iron oxides was recently demonstrated by Goldberg and Sposito (1984).

Selenium is an essential element in animal nutrition being required in small amounts and producing toxicity symptoms at higher concentrations. Since the concentration range between deficiency and toxicity is narrow, reactions affecting selenium availability have been investigated. Wells (1967) postulated that selenium was retained by the clay size particles, especially gibbsite and iron oxides, since marked selenium accumulation occurred in soil horizons enriched in these colloids. Geering et al. (1968) and Cary and Allaway (1969) found evidence for the retention of selenium by adsorption onto soil iron oxides. Cary and Allaway (1969) indicated that the adsorption complex was a finely divided sesquioxide having a solubility equivalent to or less than freshly precipitated Fe(OH)₃. Hamdy and Gissel-Nielsen (1977) found that selenite was fixed very rapidly by Fe₂O₃ and adsorbed strongly, indicating a major role of iron oxides in selenite retention in soils. Rajan (1979) found that selenite adsorption on hydrous alumina occurs specifically via a ligand exchange mechanism with surface hydroxyl ions. By determining the ratio of hydroxyl ions released to selenite ions adsorbed, Rajan (1979) proposed that selenite forms both monodentate and bridging complexes at low surface coverage but forms almost exclusively monodentate complexes near the experimental adsorption maximum.

Dissolved silica in soil solution plays an important role in soil development and a beneficial one in plant growth. Silicate was chemisorbed on crystalline aluminum hydroxide (Hingston and Raupach, 1967) and was adsorbed with high affinity on iron and aluminum hydrous oxides (McPhail et al., 1972). McKeague and Cline (1963) found that freshly precipitated iron and aluminum hydroxides exhibited a much higher capacity for removing silicate from solution than did crystalline oxide minerals. They found that silicate adsorption on a bauxite sample containing mostly gibbsite increased with increasing pH over the pH range 4.8 to 9.7. Similar behavior was found for the soils studied by McKeague and Cline (1963) in that silicate adsorption increased over the pH range 4 to 9. Decreases in soil silicate sorption were found above pH 10. Beckwith and Reeve (1963) also found that silicate adsorption behavior on aluminum and iron oxides was very similar to that on soil samples in its pH dependence in the pH range 3 to 9. Obihara and Russell (1972) obtained silicate adsorption curves of soils.
which were in agreement with those obtained by McKeague and Cline (1963) and Beckwith and Reeve (1963) for their soils and very similar to silicate adsorption on goethite found by Hingston et al. (1968).

In all previous studies intrinsic equilibrium constants for the formation of surface species have been obtained by fitting the constant capacitance model to adsorption data. An independent test of the model's ability to describe data is needed. In this study intrinsic surface complexation constants obtained for the adsorption of phosphate, selenite and silicate from single anion systems will be used to predict simultaneous, competitive adsorption from mixtures of two of the anions. Comparison of these predictions with experimental adsorption data will allow additional evaluation of the chemical utility of the constant capacitance model.

DATA AND METHODS

The constant capacitance model is based on the following assumptions: (i) adsorption proceeds via a ligand exchange mechanism; (ii) all surface complexes formed are inner-sphere complexes; (iii) no complexes are formed with ions in the background electrolyte; (iv) a linear relationship exists between net surface charge, \( \sigma \) [\( \text{mol} \text{ m}^{-2} \)], and the surface potential, \( \psi \) [V]:

\[
\sigma = \frac{(CSa/F) \psi}{[\text{mol} \text{ m}^{-2}]} \quad \text{[1]}
\]

where \( C \) (F m\(^2\)) is a capacitance density parameter, \( S \) (m\(^2\) kg\(^{-1}\)) is the specific surface area, \( a \) (kg m\(^{-2}\)) is the concentration of the solid in aqueous suspension, and \( F \) (C mol\(^{-1}\)) is the Faraday constant. In the constant capacitance model the amphoteric behavior of the surface functional group, FeOH, is described by the following two reactions:

\[
\text{FeOH}(s) + H^+(aq) \rightarrow \text{FeOH}^+(s) \quad \text{[2]}
\]

\[
\text{FeOH}(s) \rightarrow \text{FeO}^-(s) + H^+(aq) \quad \text{[3]}
\]

Reactions for the formation of selenite and silicate surface complexes are defined as follows:

\[
\text{FeOH}(s) + H_2\text{SeO}_3(aq) \rightarrow \text{FeHSeO}_3(s) + H_2O \quad \text{[4]}
\]

\[
\text{FeOH}(s) + H_2\text{SeO}_3(aq) \rightarrow \text{FeSeO}_3(s) + H^+ + H_2O \quad \text{[5]}
\]

\[
\text{FeOH}(s) + H_2\text{SiO}_4(aq) \rightarrow \text{FeHSiO}_4(s) + H_2O \quad \text{[6]}
\]

\[
\text{FeOH}(s) + H_2\text{SiO}_4(aq) \rightarrow \text{FeH}_2\text{SiO}_4(s) + H^+ + H_2O \quad \text{[7]}
\]

where \( \text{FeOH} \) represents 1 mol of reactive surface hydroxyls bound to a metal ion, \( \text{Fe}^{3+} \), in the goethite mineral. Following are the expressions for the intrinsic conditional equilibrium constants describing these reactions (Eq. 2-7), respectively:

\[
K_+(\text{int}) = \frac{[\text{FeO}^+]}{[\text{FeOH}] [H^+]} \exp\left(\frac{F \psi}{RT}\right) \quad \text{[8]}
\]

\[
K_-(\text{int}) = \frac{[\text{FeO}^-] [H^+]}{[\text{FeOH}]} \exp\left(\frac{-F \psi}{RT}\right) \quad \text{[9]}
\]

\[
K_2(\text{int}) = \frac{[\text{FeHSeO}_3]}{[\text{FeOH}] [H_2\text{SeO}_3]} \quad \text{[10]}
\]

\[
K_3(\text{int}) = \frac{[\text{FeHSiO}_4]}{[\text{FeOH}] [H_2\text{SiO}_4]} \quad \text{[11]}
\]

where \( R \) is the molar gas constant, \( T \) is the absolute temperature, and square brackets indicate concentrations (mol m\(^{-3}\)). Surface complexation reactions and intrinsic conditional equilibrium constant expressions defined for the application of the constant capacitance model to phosphate adsorption were given in a previous paper (Goldberg and Sposito, 1984). The chemical equilibrium problem outlined above can be solved using simultaneous equation solution methods after inclusion of appropriate mass balance and charge balance equations.

The mass balance for the surface functional group, FeOH, is:

\[
[\text{FeOH}]+ = [\text{FeOH}^+] + [\text{FeO}^-] + \sum_{i=1}^{n} [\text{FeH}_i A_i^-] + \sum_{i=1}^{n} [\text{FeH}_i A_i A_i^-] + [\text{FeH}_i A_i A_i A_i^-] \quad \text{[14]}
\]

where \( x \) is the number of protons present in the undissociated form of the acid, \( A \) is the completely dissociated form of the acid (PO\(_4^2_\), SeO\(_3^2_\), or SiO\(_4^2_\)), and \( n \) is the number of different adsorbing anions in the system. The last complex in the mass balance is defined only for the phosphate system.

Due to the small magnitudes of the third and fourth dissociation constants of silicic acid only two silicate surface complexes are defined. The charge balance equation is defined as follows:

\[
\sigma = [\text{FeO}^-] - [\text{FeO}^+] - \sum_{i=1}^{n} [\text{FeH}_i A_i^-] - 2[\text{FeH}_i A_i A_i^-] \quad \text{[15]}
\]

The computer program FITEQL (Westall, 1982) was used to calculate the intrinsic surface complexation constants for the anion surface species using adsorption isotherm data from Hingston (1970). FITEQL contains the constant capacitance model and fits equilibrium constants to adsorption data using a least squares optimization technique. The intrinsic surface complexation constants calculated by FIT-TEQL were used in the chemical speciation program MI- CROQL (Westall, 1979) to predict distributions of surface and solution anion species in equilibrium with aqueous solutions containing two competing anions.

Numerical values used in this study for the intrinsic protonation-dissociation constants \( K_+(\text{int}) \) and \( K_-(\text{int}) \) were obtained from a literature compilation of experimental data for iron oxides (See Table 1, Goldberg and Sposito, 1984). A detailed explanation of the procedure for obtaining log \( K_+(\text{int}) \) by plotting titration data as log \( K_+ \) vs. surface charge, \( \sigma \), and extrapolating to \( \sigma = 0 \) is given in Goldberg and Sposito (1984). The relationship between the intrinsic and conditional protonation constants, for example, is given by:
Table 1. Numerical values of model parameters.$§$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Goethite-B</th>
<th>Goethite-C</th>
<th>Goethite-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_i$ (int)</td>
<td>7.31</td>
<td>8.80</td>
<td>1.10</td>
</tr>
<tr>
<td>$C$ (mol m$^{-3}$)</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum adsorption density</td>
<td>0.310</td>
<td>0.534</td>
<td>1.10</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>2.8</td>
<td>3.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Solid concentration</td>
<td>4.00</td>
<td>4.68</td>
<td>4.36</td>
</tr>
<tr>
<td>$K_d$ (int)</td>
<td>10.43</td>
<td>10.49</td>
<td>11.22</td>
</tr>
<tr>
<td>$K_p$ (int)</td>
<td>6.25</td>
<td>6.27</td>
<td>7.06</td>
</tr>
<tr>
<td>$K_{b1}$ (int)</td>
<td>0.17</td>
<td>0.17</td>
<td>0.99</td>
</tr>
<tr>
<td>$K_{b2}$ (int)</td>
<td>10.02</td>
<td>5.36</td>
<td>5.80</td>
</tr>
<tr>
<td>$K_{b3}$ (int)</td>
<td>3.82</td>
<td>4.48</td>
<td></td>
</tr>
<tr>
<td>$K_{b4}$ (int)</td>
<td>-4.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† See Table 1, Goldberg and Sposito (1984).
‡ From Hingston (1970).
§ All intrinsic surface complexation constants were obtained using concentrations in mol L$^{-1}$.

$K_i$ (int) = $C_k$ exp ($F\psi/RT$)  
where $C_k = [\text{FeOH}_2^+]/[\text{FeOH}]\text{[H}^+\text{]}$. 

The capacitance density, $C$, an empirical model parameter, was fixed at 1.06 F m$^{-2}$, the optimal value for $\gamma$-Al$_2$O$_3$ (We-stall and Hohl, 1980). Additional necessary model parameters: specific surface area, $S$, concentration of the solid, $a$, and the maximum adsorption density, $[\text{FeOH}]$, had been determined experimentally by Hingston (1970). Table 1 presents numerical values of these model parameters as well as values for the intrinsic surface complexation constants fit with the FITEQL program.

RESULTS AND DISCUSSION

The ability of the constant capacitance model to fit phosphate adsorption data on two goethite minerals is illustrated in Fig. 1. The model produces a close fit to the experimental data over the entire pH range studied, as had previously been found for phosphate adsorption on goethite-E (Goldberg and Sposito, 1984, Fig. 4). Plots of the maximum amount of selenite adsorption versus pH ("adsorption envelopes") on two goethites are shown in Fig. 2. The selenite adsorption envelopes resemble those for phosphate, showing a steady decrease with increasing pH value. However, selenite adsorption, in contrast to phosphate adsorption, exhibits a rapid decline with increasing pH starting around pH 8 to 9. The constant capacitance model reproduces this rapid decline of selenite adsorption in fitting the data. Adsorption envelopes for silicate on two goethite minerals are shown in Fig. 3. Adsorption increases gradually with increasing pH values, reaches a maximum value near pH 9 and then decreases rapidly. Again the constant capacitance model represents the experimental data well, fitting a smooth curve through the data. In the model calculations for all three of these anions the surface protonation-dissociation constants and the capacitance density parameter were fixed at identical values. Therefore the only adjustable parameters were the surface complexation constants: three constants for phosphate and two each for selenite and silicate. The ability of the model to represent changes in adsorption over the entire pH range studied with two or three adjustable parameters is its main advantage over the Langmuir and Freundlich adsorption isotherm approach.
In the simulations for anion competition all parameters were maintained at the same values as in the single anion systems. In other words, no parameters were fit, all intrinsic surface equilibrium constants were fixed at constant values and a simple chemical speciation was carried out. Anion adsorption envelopes for the phosphate-selenite system are shown in Fig. 4 and 5. The model predicts the shape of the isotherms over the entire pH range studied, however phosphate adsorption is overestimated while selenite adsorption is underestimated. It is evident from Fig. 5 that the model predictions improve as the total concentration of phosphate in solution decreases. Figures 6 and 7 show anion adsorption envelopes for the silicate-phosphate system. Here again phosphate adsorption is overestimated while the adsorbed amount of silicate is underestimated. It is interesting to note that silicate adsorption is predicted by the model to become significant only after pH 7.5. This behavior is consistent with the experimental adsorption data for goethite-B (Fig. 6). Experimental data for silicate adsorption on
goethite-E (Fig. 7) indicate that the adsorbed amounts are considerably larger than those predicted by the model. However, as observed before for phosphate-silicate competition the shape of the adsorption envelope predicted by the model is similar to that of the experimental adsorption envelope.

CONCLUSIONS

Phosphate, selenite and silicate adsorption on goethite in single anion systems can be quantitatively described with the constant capacitance model. The model considers both the charge on the adsorbing ion and the adsorbent goethite surface and therefore predicts adsorption over the entire pH range studied using the same set of surface complexation constants. The ability of the model to predict the changes in adsorption occurring with changes in solution pH represents an advancement over the Langmuir and Freundlich adsorption isotherm approach. This improvement is especially evident for the case of selenite and silicate adsorption because the number of adjustable parameters used in the constant capacitance model is the same as in the Freundlich equation and the single-surface Langmuir equation.

The constant capacitance model is able to represent mixed phosphate-selenite and phosphate-silicate anion systems only qualitatively but it does reproduce the shape of the adsorption envelopes over the entire pH range studied. The model overestimates phosphate adsorption while at the same time underestimating adsorption of the competing anion. Hingston (1970) had interpreted his anion competition data by postulating three sets of goethite surface sites: one group of sites available to both anions and two additional groups each specific to one of the anions. He described the competition using Langmuir equations. Russell et al. (1975) suggested that phosphate-selenite competition may involve only one set of sites. They postulated that while the phosphate and selenite anions do not adsorb on every reactive hydroxyl site in single anion systems, they may do so in mixed systems thereby increasing the total amount of adsorption.

The constant capacitance model is based on the assumption that adsorption occurs at only one type of site. While this assumption has been adequate for the modeling of single anion systems this study indicates that it is very likely an oversimplification. Benjamin and Leckie (1980, 1981) have found evidence for site heterogeneity on amorphous iron oxyhydroxide and \( \gamma \)-FeOOH. Benjamin and Leckie (1981) were able to explain competitive adsorption of trace metal ions by postulating limited groups of sites having high selectivity for specific metal ions. By postulating a small group of sites which are selective for selenite and silicate it is possible to explain the underprediction of selenite or silicate and the overprediction of phosphate adsorption. This group of sites would be occupied preferentially with selenite or silicate leaving less sites for which phosphate can compete. The effect of the selenite specific sites would be greatest at high phosphate adsorption. Figure 5 indicates that, indeed, as the amount of phosphate adsorbed decreases the model fit improves considerably. The constant capacitance model also contains the assumption that adsorption proceeds up to a monolayer coverage. If phosphate adsorption had continued beyond a monolayer in the single anion system the model would overpredict phosphate adsorption in the mixed system. Because the model is capable of representing the shape of the anion adsorption envelopes from mixed solution qualitatively, it appears likely that it is an appropriate representation of anion competition. However, quantitative verification of the model's ability to describe anion competition using a single set of reactive sites will not be possible without improvements in certain model parameters. Independent experimental determination of the maximum adsorption density, \( \left[\text{FeOH}\right]_F \), and experimental determination of log \( K_a(\text{int}) \) on the specific oxide mineral studied are expected to improve the predictions obtained with the model. Additional experiments are also necessary to establish whether site heterogeneity exists on goethite and can explain adsorption in mixed anion systems.

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Chemical Modeling of Arsenate Adsorption on Aluminum and Iron Oxide Minerals

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All surface constant values given in Table 1 in both papers are for log $K_i$(int) not $K_i$(int).