Chapter 19

Sorption of Molybdenum on Oxides, Clay Minerals, and Soils
Mechanisms and Models

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The constant capacitance model was well able to describe multilayer sorption on hematite and iron oxides, clay minerals, and soils as a function of pH. The three-layer model consisted in version 5.1 of the program PTEQ, was used to simultaneously optimize Mo surface complexation constants to Mo sorption data on goethite, gibbsite, 2Al2O3·3SiO2·3H2O, hematite, montmorillonite, and two and three soils as a function of pH (3 to 10.5) and ionic strength (0.01, 0.1, and 1.0 mol L−1 NaCl). This is a new capability of the PTEQ program, and the triple-layer model was well able to describe the υMo values at all pHs on all materials. Because of model sensitivity to the surface site density parameter, we used a surface site density value of 2.01 psu−1 which had been recommended by Davis and Rand (1978). Key, and Mo, 23 (17-268) for natural materials. Triple-layer modeling of Mo sorption was successful on all materials using the site density value. Use of a consistent site density value will facilitate the development of a well-consistent thermodynamic database, especially for heterogeneous natural sorbents such as clay minerals and soils.
Molybdenum is a trace element essential for both plant and animal nutrition. Molybdenum deficiencies are reported throughout the world for many agronomic crops, especially legumes (Murphy and Welsh, 1972). Molybdenum's role in ammonia form is usually taken up by forage plants and can be accessible to a wide dormant or grazing ruminant animals (Reissner et al., 1962). To evaluate pH availability of Mo in soils, knowledge of its adsorption chemistry is required.

Molybdate adsorption has been investigated for a variety of soil minerals and soils. Three adsorbent surfaces include aluminum oxides (Jones, 1957; Reissner et al., 1962; Bremner et al., 1969; Vossius et al., 1990; Sparrs et al., 1992); Bisker and Bregquist, 1994. Sparrs and Lyssek (1995; Goldberg et al., 1996), iron oxides (Jones, 1957; Reissner et al., 1962; Bremner et al., 1969; Lyrta and Javitt, 1967; Kyrtos, 1967; McKee, 1983; Ferrin et al., 1985; Zhang and Sprent, 1989; Bisker and Bregquist, 1994; Goldberg et al., 1996), clay minerals (Jones, 1957; Philips and Mavigil, 1984; Mikkelsen and Tammavas, 1993; Motta and Menard, 1989; Goldberg et al., 1996), and soils (Jones, 1957; Reissner et al., 1962; Barrow, 1970; Thing, 1971; Gottschol et al., 1974; Jarmol and Dawson, 1979; Karimian and Cox, 1978; Roy et al., 1986; Xue and Mackenzie, 1990; Xue et al., 1991; Mikkelsen and Tammavas, 1990a; Goldberg et al., 1996).

Molybdate adsorption on all of the above adsorbents increased with increasing solution pH from pH values of 3 to 4, exhibited a peak near pH 4, and decreased with increasing pH above pH 4. Aluminous and iron oxides represent important molybdate adsorbing surfaces in soils. Molybdate adsorption on soil clay dominantly in kaolinite and illite was decreased by removal of amorphous aluminum and iron oxides (Theng, 1971). Molybdate adsorption in soils was highly correlated with extractable aluminum (Barrow, 1970) and iron (Gottschol et al., 1974; Jarmol and Dawson, 1979; Karimian and Cox, 1978), and decreased after removal of amorphous iron oxides (Jones, 1957).

Ligand exchange is suggested to be the mechanism of molybdate adsorption on aluminum and iron oxide minerals (Jones, 1957; Perren et al., 1982). By this mechanism, ions become adsorbed specifically as inner-sphere surface complexes. Inner-sphere surface complexes, by definition, contain no water molecules between the adsorbing ion and the surface functional group (Sparrs, 1984). The point of zero charge (PZC) is defined as the pH value where there is no net particle charge (Sparrs, 1984). Specific adsorption of anions onto variable-charge minerals, such as oxides, shifts the PZC in a more acidic pH value. Molybdate adsorption lowered the PZC of goethite (McKenzie, 1983), amorphous iron oxide, 5-FeOOH, gibbsite, amorphous aluminum oxide, and kaolinite (Goldberg et al., 1996), indicating specific adsorption on these minerals.

The dependence of ion adsorption on the effect of ion strength has been used
to distinguish between inner- and outer-sphere surface complexes (Hayer and Leckie, 1987; Hayer and others, 1988). Outer-sphere surface complexes, by definition, contain at least one water molecule between the adsorbing ion and the surface functional group (Spoko, 1984). Hayer and others (1988) suggested that some, which showed little ionic strength dependence in their adsorption behavior, was specifically adsorbed on goethite in an inner-sphere surface complex, while others, which showed great ionic strength dependence, was adsorbed non-specifically in an outer-sphere surface complex. Similarly, Zhang and Spoko (1984) found little ionic strength dependence of molybdate adsorption on goethite and interpreted this result as supporting evidence for inner-sphere surface complex formation.

The constant capacitance model (Laum et al., 1980) and the triple-layer model (Dhama et al., 1978) are chemical surface complexation models of the electro-chemical double-layer interface that use a ligand exchange mechanism to describe specific ionic adsorption. These models explicitly define inner- and outer-sphere surface complexes and chemical reactions, and consider the charge on both the adsorbed ion and the adsorbing surface. The constant capacitance model has been used successfully to describe molybdate adsorption on various aluminum and iron oxides via ligand exchange with surface hydroxy groups and on various clay minerals via ligand exchange with aluminum groups as a function of solution pH (Goldberg et al., 1996). The constant capacitance model has successfully described Mo adsorption on clay minerals as a function of equilibrium Mo concentration (Motta and Miranda, 1989). The constant capacitance model was unable to describe Mo adsorption on three soils as a function of solution pH (Goldberg et al., 1996). The triple-layer model has been used successfully to describe molybdate adsorption on goethite as a function of solution pH (Zhang and Spoko, 1985).

The present study is intended to revitalize the ability of the constant capacitance model to describe molybdate adsorption behavior previously constrained by Goldberg et al. (1996) on a variety of soils and soil minerals. A study on oxide and clay minerals—i.e., as a function of solution pH. Molybdate adsorption on various soils was evaluated at a constant solution pH and ionic strength in an effort to reduce adsorption mechanisms. The ability of the triple-layer model to describe all Mo adsorption data simultaneously with one set of outer-sphere surface complexation constants will also be investigated.

II. MATERIALS AND METHODS

Molybdenum adsorption behavior as a function of solution pH and ionic strength was studied on various adsorbents: E-ALO, under the trade name Alumina Oxid C, was obtained from Degussa (Teubron, NJ). Goethite, α-FeOOH,
was synthesized as described by McLoughlin et al. (1981). Gibbsite, \( \gamma \)-Al\(_2\)O\(_3\),
was synthesized according to the procedure of Kyle et al. (1975). No trace con-
taminants were observed in the oxides using X-ray diffraction analysis. Samples
of GC-1 kaolinite and SW-1 montmorillonite were obtained from the Clay Min-
eral Society's Source Clays Repository (Univ. of Missouri, Columbia) and used
without pretreatment. Surface samples of the Pachapa (course-loamy, mixed,
demic, Mollic Hapludalf) and Potrero-ville (fine, montmorillonitic, thermic Typ-
ich Chernozem) soil series consisted of the <0.05-mm fraction. Organic and inor-
ganic carbon analyses were carried out using the method of Nelson and Sommers
(1982). Free aluminum and iron oxides were extracted as described by Coffin
(1965).
Trace impurities in the oxides and clay minerals were determined using X-ray
diffraction powder methods (see Table 1). To obtain dominant clay mineralogy
of the soils, X-ray diffraction peak areas obtained using oriented mounts were con-
verted directly to clay mineral content as described by Klages and Hopper (1982).
Specific surface areas of the clay minerals and oxides were determined with a sin-
gle-point BETN, adsorption isotherm obtained using a Quantachrome Corp.,
Syosset, NY: specific surface areas of the soil samples were obtained using ethylene glycol monoethanol ether (EGME) adsorption
as described by Chichak and Bremner (1979). Points of zero charge and elec-
trophoretic mobilities were determined for all oxides and kaolinite by macroelec-
trophoresis as described by Goldberg et al. (1996). Table 1 presents point of zero
charge and specific surface area data for the oxides and clay minerals. Table II pre-
vents chemical, mineralogical, and specific surface area data for the soils.
Methane adsorption experiments were carried out in batch systems to deter-
mine adsorption/envelopees (amount of N\(_2\) adsorbed as a function of solution pH
per fixed total N concentration). Samples of adsorbent were added to 50-mi
polypropylene centrifuge tubes or 250-nil centrifuge bottles and equilibrated
with alginates (see Table III for solids concentrations) of 0.01, 0.1, or 1.0 mol L\(^{-1}\) NaCl
solution by shaking for 20 hr on a reciprocal shaking at 25 ± 1°C. This solution

<table>
<thead>
<tr>
<th>Table I</th>
<th>Characterization of Oxides and Clay Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Surface area m(^2) g(^{-1})</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>GC-1</td>
<td>32.7</td>
</tr>
<tr>
<td>A-(\gamma)-Al(_2)O(_3)</td>
<td>102.9</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>74.5</td>
</tr>
<tr>
<td>KCl: Fe</td>
<td>9.14</td>
</tr>
<tr>
<td>SW-1 montmorillonite</td>
<td>18.6</td>
</tr>
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</table>

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Table II
Characterization of Soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Inorganic carbon (%)</th>
<th>Organic carbon (%)</th>
<th>Free Fe (mg/g)</th>
<th>Free Al (mg/g)</th>
<th>Surface area (m²/g)</th>
<th>Dominant minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharaoh</td>
<td>0.010</td>
<td>0.49</td>
<td>0.067</td>
<td>0.16</td>
<td>36.3</td>
<td>Ilite, nontronite</td>
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<tr>
<td>Pentzville</td>
<td>0.023</td>
<td>0.08</td>
<td>0.090</td>
<td>1.67</td>
<td>172.2</td>
<td>Ilite, nontronite</td>
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Table III
Solids Concentration and Intrinsic Surface Complication Constants Obtained with the Constant Capacitance Model

<table>
<thead>
<tr>
<th>Solids concentration (g/L, %)</th>
<th>log K₁ ( handlers.)</th>
<th>log K₂ (Al, Fe)</th>
<th>log K₃ (Al, Fe)</th>
<th>log K₄ (Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxides</td>
<td>5.3</td>
<td>7.52</td>
<td>-8.80</td>
<td>0.71</td>
</tr>
<tr>
<td>Hemate</td>
<td>1.25</td>
<td>7.51</td>
<td>-8.80</td>
<td>0.74</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.65</td>
<td>7.51</td>
<td>-8.80</td>
<td>0.51</td>
</tr>
<tr>
<td>Amorphous iron oxide</td>
<td>0.64</td>
<td>7.51</td>
<td>-8.80</td>
<td>0.72</td>
</tr>
<tr>
<td>Average iron oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum oxides</td>
<td>1.25</td>
<td>7.51</td>
<td>-6.09</td>
<td>0.53</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>0.55</td>
<td>7.51</td>
<td>-6.09</td>
<td>0.57</td>
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<tr>
<td>Average (aluminum oxides)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Average (solids)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clays</td>
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<td></td>
</tr>
<tr>
<td>kaolinite</td>
<td>200</td>
<td>4.95</td>
<td>-6.09</td>
<td>7.66</td>
</tr>
<tr>
<td>kaolinite + illite</td>
<td>100</td>
<td>5.99</td>
<td>-6.09</td>
<td>8.08</td>
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<tr>
<td>kaolinite + montmorillonite</td>
<td>50</td>
<td>5.99</td>
<td>-6.09</td>
<td>8.43</td>
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<tr>
<td>kaolinite + montmorillonite</td>
<td>50</td>
<td>5.99</td>
<td>-6.09</td>
<td>8.43</td>
</tr>
<tr>
<td>kaolinite + illite</td>
<td>50</td>
<td>5.99</td>
<td>-6.09</td>
<td>8.43</td>
</tr>
<tr>
<td>Average (clays)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soils</td>
<td>200</td>
<td>7.35</td>
<td>-6.95</td>
<td>8.28</td>
</tr>
<tr>
<td>Phosphorus</td>
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<td>-6.95</td>
<td>9.36</td>
</tr>
<tr>
<td>Portlandite</td>
<td>200</td>
<td>7.35</td>
<td>-6.95</td>
<td>9.00</td>
</tr>
<tr>
<td>Average (total)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Re: concentration.
containment 0.092 mol m\(^{-3}\) of Mo from Na,MoO\(_4\), 2H\(_2\)O (Mallinckrodt, Inc., St. Louis, MO) and had been adjusted to the desired pH values using 1.0 mol L\(^{-1}\) HCl or 1.0 mol L\(^{-1}\) NaOH additions that changed the total volume by 0.2%. Experi-
ments were carried out at 0.092 mol m\(^{-3}\) of Mo to avoid the formation of Mo poly-
mer in solution (Carpena, 1947). The samples were centrifuged at a relative con-
ting of 3000g for 20 min. The supernatant were for pH, filtered through a 0.45-μm Whatman filter, and analyzed for Mo concentrations with in-
ductively coupled plasma (ICP) emission spectrometry.

In an attempt to conﬁrm the Fe–Mo transformation in atr (ATR) Fourier transform infrared (ATR-FTIR) spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, were used to trace the speciation of Mo on a synthetic amorphous iron oxide, Fe(OH)\(_2\)(OH), described by Kux and Szmant (1995). Amorphous Fe–Mo oxide was cho-
ed because it is known to contain large amounts of Mo, and it does not exhibit strong infrared (IR) bands of the region where Mo shows characteristic IR bands. Amorphous iron oxide has a BET surface area of 750 m\(^2\) g\(^{-1}\). The suspensions of Fe(OH)\(_2\)(OH) were prepared by adding 2.0 g of solids to 20 each mL of 1.0 mol L\(^{-1}\) NaCl to pH 6.0, 0.05 mol L\(^{-1}\) Na,MoO\(_4\) + 1.0 mol L\(^{-1}\) NaCl (pH 6.0), or 1.0 mol L\(^{-1}\) Na,MoO\(_4\) + 1.0 mol L\(^{-1}\) NaCl (pH 6.0). Suspension pH was meas-
ured in 6 by frequent additions of 1.0 mol L\(^{-1}\) NaOH or 1.0 mol L\(^{-1}\) HCl. The suspensions were shaken for 24 h at ambient temperature and centrifuged. Eleven milliliters of the supernatant were removed and assayed at the time of the ATR-FTIR study. The solid was recrystallized in the remaining 3 mL of supernatant and used as the sample. A solid concentration of 400 g L\(^{-1}\) was achieved in the sampling ATR reservoir. Concentrations of Mo in the super-
natant were determined by ICP.

Infrared spectra of the aqueous solutions of 1.0 mol L\(^{-1}\) NaCl (pH 6) and 0.05 and 0.10 mol L\(^{-1}\) Na,MoO\(_4\) + 1.0 mol L\(^{-1}\) NaCl (pH 6), and the suspensions of Fe(OH)\(_2\)(OH) treated with Mo, were recorded in the 4000 to 7000 cm\(^{-1}\) range using a Bio-Rad Digilab FTS-7 spectrometer (Bio-Rad Digilab Div., Cambridge, MA). The ATR accessory consisted of a horizontal reservoir and a ZnSe crystal rod with a 45° angle of incidence. Single-beam IR spectra were obtained from 2000 scans using a resolution of 4 cm\(^{-1}\). All final spectra were the result of sub-
tracting the spectrum of the supernatant of 0.05 and 0.10 mol L\(^{-1}\) Na,MoO\(_4\) + 1.0 mol L\(^{-1}\) NaCl (pH 6) from the spectrum of the Fe(OH)\(_2\)(OH) suspensions of or 0.05 and 0.10 mol L\(^{-1}\) Na,MoO\(_4\) + 1.0 mol L\(^{-1}\) NaCl (pH 6), respectively. A subtraction factor of unity was al-
ways used.

A submilliliter of 1.0 mL of the solid suspension (400 g L\(^{-1}\)) was washed twice with 30 mL of deionized water and air dried before DRIFT microscopic analysis. DRIFT spectra of samples dispersed with KBr (5% sample in 95 mg KBr) were recorded from 4000 to 300 cm\(^{-1}\) at a 4 cm\(^{-1}\) resolution over 500 scans. A subsam-
ples of the washed solids was examined by X-ray diffraction and subsequently dis-
solved in 0.5 mol L\(^{-1}\) HNO\(_3\) and analyzed for Mo entranation by ICP.
A CONSTANT CAPACITANCE MODELING

The constant capacitance model (Strem et al., 1980) was used to describe the hygroscopic behavior on the adsorbent as a function of solution pH in a 2x3 ground electrode of 0.1 mol L⁻¹ NaCl. The computer program (PETROG, version 3.3) (Herbert and Wexler, 1999) has been used to fit anisotropic model data to compare the surface complexation constants to the experimental adsorption data as presented in Goldberg et al., (1997). In the present study the data from Goldberg et al. (1997) are mainly used and modified with a 'dummy' component. Using this procedure we obtained as improved fit and were able to use the computer grid format to check the goodness-off-the of the model to the data. Additional explanation on the use of the adsorbed ion in a 'dummy' component is provided by Herbert and Wexler (1999).

Methylbenzene occurs as MoO₄²⁻ over most of the pH range. The acid-base reactions undergone by polyol electrolyte are

\[ \text{H}_2\text{MoO}_4^{2-} \rightarrow \text{H}_2\text{O} + \text{HMO}_4^{3-} \]  
\[ \text{H}_2\text{O} + \text{HMO}_4^{3-} \rightarrow 2\text{H}_2\text{O} + \text{MO}_4^{2-} \]  

with pK values of 4.00 and 8.24, respectively (Linard, 1979).

In the constant capacitance model the protonation and dissociation reactions for the surface functional group, SOH (where SOH represents a reactive surface hydroxy bound to a metal ion, S (Al or Fe), in the oxide mineral or as an aluminosilicate at the clay mineral edges) are defined as

\[ \text{SOH} \rightarrow \text{H}_2\text{O} + \text{SOH} \]  
\[ \text{SOH} \rightarrow \text{SO}^\text{H} + \text{H}_2\text{O} \]  

The constant capacitance model contains the assumption that all surface species are inter-related. Therefore the surface complexation reactions for methylene blue adsorption are defined as

\[ \text{SOH} \rightarrow \text{H}_2\text{O} + \text{HMO}_4^{3-} \]  
\[ \text{SOH} \rightarrow \text{SO}^\text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} \]  

The relative equilibrium constants for protonation and dissociation reactions of the surface functional group are

\[ K_{\text{SOH}} = \frac{[\text{SOH}]}{[\text{SOH}^\text{H}]} \exp(-\Phi_\text{p} / RT) \]  
\[ K_{\text{SOH}} = \frac{[\text{SOH}]}{[\text{SOH}]} \exp(-\Phi_\text{p} / RT) \]  

where \( \Phi_p \) is the Faraday constant (C mol⁻¹ V⁻¹), \( V \) is the surface potential (V), \( \rho \) refers to the surface plane of adsorption, \( R \) is the molar gas constant (J mol⁻¹ K⁻¹), \( T \) is the temperature (K), and

\( K_{\text{SOH}} \) is the association constant for the surface functional group.

\( K_{\text{SOH}} \) is the acid-base reaction constant for the surface functional group.
is the absolute temperature (K), and square brackets represent concentrations (mol L⁻¹). The intrinsic equilibrium constants for the molybdate surface complexation reactions are

\[ K_{\text{eq},i}^{\text{MSO}_4^{-}} = \left[ \frac{[\text{MSO}_4^{-}][\text{H}_2\text{SO}_4]}{[\text{MSO}_4^{-}][\text{H}_2\text{SO}_4]} \right] \exp(-\Delta G_{i}/RT) \]

where the subscript "i" refers to inner-sphere surface complexation.

The mass balance expression for the surface functional group is

\[ [\text{SOH}] = [\text{SOH}] + [\text{SOH}]^2 + [\text{SO}^-] + [\text{S(OH)}_2^-] + [\text{S(OH)}_3^2^-] \]

where [SOH] is the surface acid site density, N_S is the surface area (m² g⁻¹), C_S is the solids concentration (g L⁻¹), N_A is Avogadro's number, and N_A has units of cm⁻² kg⁻¹.

The charge balance expression is

\[ q_e = [\text{SOH}]^+ - [\text{SO}^-] - [\text{S(OH)}_2^-] \]

where q_e represents the surface charge (mol L⁻¹). The relationship between surface charge and surface potential is

\[ \sigma_e = \frac{C_S}{A_S} \phi_e \]

where C is the capacitance (F m⁻²).

In our application of the constant capacitance model, the surface site density was treated as molybdate reactive site density and set to the maximum Mo adsorption obtained in our experiments. Numerical values of the intrinsic protonation constant, K_{iprotonation}, and the intrinsic dissociation constants, K_{iod}, were obtained from the literature compilation of experimental values for aluminum- and iron oxides of Goldberg and Spotsin (1984a). The intrinsic protonation and dissociation constants were initially fixed at log K_{iprotonation} = 1.31 and log K_1 (int) = -8.80 for gibbsite; log K_2 (int) = 7.16 and log K_3 (int) = -9.09 for gibbsite and the clays (Goldberg and Spotsin, 1984a); and log K_2 (int) = 7.55 and log K_3 (int) = -9.85 for octasils (Goldberg and Spotsin, 1984a). For the kaolinite and two of the montmorillonites it was subsequently necessary to optimize log K_{iprotonation} or log K_1 (int) and log K_2 (int) as well as the molybdate surface complexation constants using the MINUIT program. The capacitance density was fixed at C = 1.06 F m⁻², considered optimum for γ-MOCl₂ by Westall and Hitch (1980). It is prefer-
able to minimize the number of adjustable parameters by obtaining values of log $K_{n, \text{int}}$ and log $K_{m, \text{int}}$ experimentally from isotherm data when available.

The goodness-of-fit criterion is the overall variance, $V$, in Y (Herbelin and Westall, 1994).

$$V_n = \frac{\text{SOS}}{\text{DF}}.$$  \tag{15}$$

where SOS is the weighted sum of squares of the residuals and DF is the degrees of freedom.

\section*{B. TRIPLE-LAYER MODELING}

The triple-layer model allows ion adsorption as either inter-sphere or outer-sphere surface complexes. In addition to the protonation-dissociation reactions, Eqs. (3) and (4), the triple-layer model considers outer-sphere surface complexation reactions for the background electrolyte:

$$\text{SOR}_n + \text{Na}^+_{\text{aq}} = \text{SO}_n\text{R}^n_{\text{aq}} + \text{H}^+_{\text{aq}} \quad \tag{16}$$

$$\text{SOR}_n + \text{H}_3\text{O}^+_{\text{aq}} = \text{SO}_n\text{R}^n_{\text{aq}} + \text{H}_2\text{O} \quad \tag{17}$$

In the triple-layer model, inner-sphere surface complexation reactions and intrinsic equilibrium constant expressions for molybdate are given by Eqs. (3), (6), (9), and (10), as for the constant capacitance model. The outer-sphere surface complexation reactions for molybdate adsorption are

$$\text{SOR}_n + \text{H}_2\text{O}^+\text{M} = \text{SO}_n\text{R}^n_{\text{aq}} + \text{H}_2\text{O} + \text{M} \quad \tag{18}$$

$$\text{SOR}_n + \text{H}_3\text{O}^+\text{M} = \text{SO}_n\text{R}^n_{\text{aq}} + \text{H}_2\text{O} + \text{M} \quad \tag{19}$$

The intrinsic equilibrium constants for outer-sphere surface complexation are

$$K_{n, \text{int}} = \frac{[SO_nR^+] [H_2O^+]^{\alpha} \exp \left(F \Phi - \frac{\Delta G}{RT} \right)}{[SORn][Na^+]^\beta} \quad \tag{20}$$

$$K_{n, \text{int}} = \frac{[SO_nR^+] [H_3O^+]^{\beta} \exp \left(F \Phi - \Delta G \right)}{[SORn][H_2O^+]^\alpha} \quad \tag{21}$$

$$K_{m, \text{int}} = \frac{[SO_nR^+] [H_2O^+]^{\alpha} \exp \left(F \Phi - \Delta G \right)}{[SORn][H_3O^+]^\beta} \quad \tag{22}$$

$$K_{m, \text{int}} = \frac{[SO_nR^+] [H_2O^+]^{\beta} \exp \left(F \Phi - \Delta G \right)}{[SORn][H_3O^+]^\alpha} \quad \tag{23}$$

where $\beta$ refers to the place of outer-sphere adsorption and the subscript "ms" refers to outer-sphere surface complexation.
The net balance for the surface functions group is

\[
[\text{SOH}]_1 = [\text{SOH}] + [\text{SOH}]^- + [\text{SO}^-] + [\text{SiMgO}_2] + [\text{SiMeO}_2^-] \\
+ [\text{SO}^-\text{Na}]^- + [\text{SO}^-\text{Cl}^-] \\
\text{[24]}
\]

The charge balance expressions are

\[
s_1 + s_2 + s_3 = 0 \text{ \quad [25]}
\]

\[
s_1 = [\text{SOH}] + [\text{SOH}]^- + [\text{SOH}]^-\text{MgO}_2^- + [\text{SOH}]^-\text{MeO}_2^- \\
+ [\text{SO}^-\text{Cl}^-] - [\text{SO}^-] - [\text{SiMgO}_2^-] - [\text{SO}^-\text{Na}]^- \\
- [\text{SO}^-\text{Cl}^-] \\
\text{[26]}
\]

\[
s_2 = [\text{SO}^-\text{Na}]^- + [\text{SO}^-\text{MgO}_2^-] - 2[\text{SOH}]^-\text{MgO}_2^- + [\text{SO}^-\text{Cl}^-] \\
- [\text{SO}^-\text{Cl}^-] \\
\text{[27]}
\]

The relationships between the surface charge and the surface potentials are

\[
s_1 = \frac{C_2}{\varepsilon} \left( \Phi_2 - \Phi_b \right) \text{ \quad [28]}
\]

\[
s_2 = \frac{C_2}{\varepsilon} \left( \Phi_2 - \Phi_b \right) \text{ \quad [29]}
\]

\[
s_3 = \frac{N_2}{\varepsilon} \left( \Phi / \text{DRT} \right) \left( \Phi / \text{DRT} \right) \\
\text{[30]}
\]

where \( C_2 \) and \( C_3 \) are capacitances, \( d \) refers to the plane of the diffuse ion swarm, \( \varepsilon \) is the permittivity of vacuum, \( D \) is the dielectric constant of water, and \( F \) is the ionic strength.

The surface site density was set at a value of 2.31 sites \( \text{nm}^{-2} \). This value has been recommended by Davis and Lott (1990) for natural materials. Numeric values for the intrinsic protonation and dissociation constants and the \( \text{SOH}^- \text{MeO}_2^- \) equilibrium constants were obtained from the literature. For \( \text{SiMeO}_2^- \) these constants were \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -4.3 \), \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -9.8 \), \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -9.3 \), and \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -9.4 \) as obtained by Zhang and Sparks (1990b). For silanol oxides, clays, and soils these constants were \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -5.0 \), \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -11.2 \), \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -8.6 \), and \log \( K_{\text{SiMeO}_2^-} (\text{M}) = -7.2 \) as obtained by Strykow (1990a,b) on \( >\text{SiMeO}_2^- \). Molybdate surface complexation constants were fit simultaneously to the adsorption data at three diffuse layer ionic strengths using either inverse sphere or outer sphere adsorption mechanisms. It was subsequently necessary to optimize log \( K_{\text{Mo}^-\text{MeO}_2^-} (\text{M}) \) and log \( K_{\text{Mo}^-\text{MeO}_2^-} (\text{M}) \) as well as the molybdate surface complexation constant using the GETMOL program. The capacitances were fixed at \( C_1 = 1.2 \text{F} \text{m}^{-2} \) and \( C_2 = 0.2 \text{F} \text{m}^{-2} \), values considered optimum for goethite by Zhang and Sparks (1990). It is preferable to minimize the number of adjustable parameters by ob-
III. RESULTS AND DISCUSSION

The fit of the constant capacitance model to the data of Goldberg et al. (1996) using Mocardo as a "dummy" component is indicated in Figures 1 to 5. Molybdate adsorption on all minerals exhibited a maximum at low pH (3 to 5). With increasing solution pH, adsorption decreased rapidly, with little adsorption occurring above pH values of 7 to 8. The constant capacitance model was well able to describe molybdate adsorption on all iron and aluminum oxides studied, with some deviations occurring at low and high pH values (Figs. 1 and 2). Use of Mocardo as a "dummy" component improved the model fit for all oxides except aluminum (iron and aluminum oxides compared to Fig. 9 of Goldberg et al. (1996)). Molybdate adsorption on the oxides was described with the model when only the molybdate surface complexes' constants, \( K_{sp}(\text{ox}) \) and \( K_{sb}(\text{ox}) \), were optimized.

The constant capacitance model was well able to describe molybdate adsorp-
Figure 2: Molybdate adsorption on aluminum oxides as a function of solution pH: \( \text{Fe}-\text{Al(OH)}_3 \text{, } Z_n = 3.5 \), \( \text{Fe}-\text{Al(OH)}_3 \text{, } Z_n = 3.0 \). All experimentally determined data; 

ion on the kaolinite with no improvement observed by use of the "dummy" component (compare Fig. 3 to Figs. 1a and 6b of Goldberg et al. (1996)). The ability of the model to describe molybdate adsorption on 2:1 clay minerals is indicated in Figure 4. Use of the "dummy" component improved the fit for SA-1 and STS-1 montmorillonite, and degraded it for SWy-1 montmorillonite and Bb-1 (finite compare Fig. 4 to Figs. 6a, 6d, and 6f of Goldberg et al. (1996)); however, the latter comparison is deceptive because unlike in the previous study (Goldberg et al., 1996), log \( K_n \) (in) and log \( K_{ inté } \) were not optimized for SWy-1 montmorillonite and Bb-1. The model optimized with the non-linear surface compensation constants in describing adsorption on the kaolinite off the STS-1 montmorillonite. For the SA-1 montmorillonite, log \( K_n \) (in) was optimized as well.

The constant capacitance model was able to describe molybdate adsorption on the three soils studied with some deviations occurring especially at low pH values (Fig. 5). The model was unable to describe molybdate adsorption on the Hespera soil below pH 4 where large deviations from the data were observed. In their application of the model, Goldberg et al. (1990) were unable to provide any of the soil data once convergence of the FITVER computer program (Herbertin and Westall, 1994) either could not be obtained or provided a very bad fit.
Figure 3. Molybdate adsorption on barite as a function of solution pH. (a) XGaq-barite, \( V_r = 68.7 \); (b) XGq-2 barite, \( V_r = 188 \). Circles represent experimental data. Crosses represent model results as represented by triangles and solid lines.

Figure 4. Molybdate adsorption on 2:1 clay minerals as a function of solution pH. (a) Na-1 montmorillonite, \( V_r = 66 \); (b) Na-2 montmorillonite, \( V_r = 41 \); (c) Na-1 beidellite, \( V_r = 271 \); (d) Na-1 illite, \( V_r = 327 \). Circles represent experimental data. Crosses represent model results as represented by triangles and solid lines.
Table III provides values of the methylate surface complexation constants obtained using the constant-capacitance model in the FITTOOL program for all materials. To fit the methylate adsorption data we never required more than two adjustable parameters for any adsorbent. This number of adjustable parameters compares very favorably with the empirical Langmuir and Freundlich adsorption isotherm approaches. The good fit of the model to methylate adsorption on oxides, kaolinite, two of the clay minerals, and two of the soil samples indicates that inter-layer surface complexation is the appropriate adsorption mechanism for these materials. The magnitude of the methylate surface complexation constants for these materials were similar in magnitude (see Table III). Averages for the methylate - surface complexation constants obtained with the constant-capacitance model for all materials, iron oxides, clay minerals, and soils were not statistically different at the 95% level of confidence, suggesting a common adsorption mechanism.

The effect of ionic strength on methylate adsorption on a variety of adsorbents is illustrated in Figure 3 to 12. Solution ionic strength was varied by two orders of magnitude, from 0.01 to 1.0 M NaCl. On all materials, adsorption of methylate was consistently lowest for the highest ionic strength. The adsorbents exhibited different behavior in their ionic strength dependence. Geothite and montmorillonite showed relatively little ionic strength dependence, suggesting the formation...
of inner-sphere surface complexes. An inner-sphere adsorption mechanism for goethite had already been indicated by the electrochemical reversibility measurements of Goldberg et al. (1996). The soils showed little ionic strength dependence except at both low and high pH values. Gibbsite, B-200%, and kaolinite exhibited quasi-constant ionic strength dependence. However, this behavior is in contrast to the inner-sphere adsorption mechanism suggested by these materials by the electrochemical reversibility results of Goldberg et al. (1996). This discrepancy highlights the importance of relying on macroscopic chemical information to deduce adsorption mechanisms.

The triple-layer model was used to describe the adsorption of melamine on goethite, gibbsite, B-200%, KCl 1 kerosene, 5%/1 nonionic, and two oils in a function of sodium-pH and ionic strength. All ionic strength and pH data were optimized simultaneously. Figures 6 to 12 indicate the ability of the triple-layer model to describe melamine adsorption using both an inner-sphere and an outer-sphere adsorption mechanism. The surface site density and the cationization were set at identical values for all adsorbents. Log Kd, (int) and Log Kd, (int) values were obtained from the literature and set at 3 for all values for all materials having NaCl as the reactive functional group (i.e., gibbsite, B-200%, kerosene, montmorillonite, and soils). Different values were used for the goethite having FeCl₃ as the reactive functional group. The ability of the triple-layer model to describe melamine adsorption on...
gohite and gibbsite is presented in Figures 6 and 7, respectively. For both oxides the fit of the model was improved using the inner-sphere adsorption mechanism. For goethite this result is in agreement with the electrophoretic mobility and ionic strength results. For gibbsite the ionic strength effect data suggest an outer-sphere adsorption mechanism, in contrast to the modeling and electrophoretic mobility results. For 8-ALO$_3$ the quality of the triple-layer model fit is comparable to inner-sphere and outer-sphere adsorption mechanisms (Fig. 8).

Figures 9 and 10 present the ability of the triple-layer model to describe molybdate adsorption on kaolinite and montmorillonite, respectively. For kaolinite the quality of the model fit is improved using an inner-sphere adsorption mechanism (Fig. 9). This result is in agreement with the electrophoretic mobility results that correlate the ionic strength dependence data. For montmorillonite an acceptable model fit could be obtained only using an outer-sphere adsorption mechanism (Fig. 10). This finding is in contradiction with the inner-sphere adsorption mechanisms implied by the small ionic strength dependence of the adsorption data. For the soils (Figs. 11 and 12), the quality of the model fit is slightly better for the inner-sphere adsorption mechanism in agreement with the small ionic strength dependence in the intermediate pH range.

Table IV provides values of the molybdate inner- and outer-sphere surface complexation constants obtained using the triple layer model in the FITEQK program for all materials. For goethite with both mechanisms, and for gibbsite using an in-
Figure 8: Molybdate adsorption on Fe(III) as a function of solution pH and ionic strength. Filled squares represent experimental data. Triple square symbols denote data obtained by open loops. \( V_1 = 44 \) for inner-sphere adsorption and \( V_2 = 28 \) for outer-sphere adsorption.

Figure 9: Molybdate adsorption on Fe(III) as a function of solution pH and ionic strength. Filled circles represent experimental data. Tripio square symbols denote data obtained by open loops. \( V_1 = 23.5 \) for inner-sphere adsorption and \( V_2 = 41 \) for outer-sphere adsorption.
Figure 10. Molybdate adsorption on Pyro-3 montmorillonite as a function of solution pH and ionic strength. Filled symbols represent experimental data. Triple-layer model results are represented by open triangles. $V_0 = 400$ for inner-sphere adsorption and $V_0 = 78$ for outer-sphere adsorption.

Figure 11. Molybdate adsorption on Upton soil as a function of solution pH and ionic strength. Filled symbols represent experimental data. Triple-layer model results are represented by open triangles. $V_0 = 50.0$ for inner-sphere adsorption and $V_0 = 125$ for outer-sphere adsorption.
In sphere adsorption mechanism, only two adjustable parameters were optimized, the molybdate surface complexation constant. This number of adjustable parameters, again, compares very favorably with the empirical Langmuir and Freundlich adsorption isotherm approach. For all other materials we optimized the surface complexation constants for Na⁺ and C³⁻ along with the molybdate surface complexation constants, increasing the number of adjustable parameters to four. The surface site density suggested by Davis and Kent (1969) for natural materials was found appropriate for modeling molybdate adsorption in a variety of soils, clay minerals, and rocks. The triple-layer model was able to simultaneously fit molybdate adsorption at several ionic strengths with one set of surface complexation constants.

Triple-layer modeling suggests an inner-sphere adsorption mechanism for goethite, gibbsite, kaolinite, and the soils, and an outer-sphere adsorption mechanism for montmorillonite. Lack of agreement between various indirect methodologies of inferring adsorption mechanisms—are point of charge shifts, ionic strength effects, and surface complexation modeling—underlies the necessity for direct spectroscopic elucidation of adsorption mechanisms. It is then to obtain spectroscopic evidence for the presence of particular surface complexes. Prior to postulating them in surface complexation models.

The advantage of the constant capacitance model over the triple-layer model is its simplicity and small number of adjustable parameters. The advantage of the triple-layer model is its ability to describe ion adsorption as a function of solution...
| Compound          | 
|-------------------|-------------------|
|                  | CH$_2$CH$_2$OCH$_3$ | CH$_3$CH$_2$OCH$_3$ | CH$_3$CH$_2$OCH$_2$CH$_2$OCH$_3$ | CH$_3$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_3$ |
| C$_2$H$_4$O$_2$   | 1.23              | 1.95              | 1.02                            | 0.52                            |
| C$_3$H$_6$O        | 0.52              | 0.62              | 0.47                            | 0.50                            |
| C$_4$H$_8$O$_2$   | 0.52              | 0.52              | 0.52                            | 0.52                            |
| C$_5$H$_10$O$_2$  | 0.25              | 0.25              | 0.25                            | 0.25                            |

The table above represents the relative concentrations of different compounds, with the values normalized for comparison purposes.
Na$_2$MoO$_4$, compared to that at 0.05 mol L$^{-1}$ Na$_2$MoO$_4$ (499 mpsal kg$^{-1}$), corresponding to 90-1 and 90-6% of sorption of added Mo, respectively. The molar ratio of released OH to sorbed Mo was 1.36 at 0.1 mol L$^{-1}$ Na$_2$MoO$_4$ and 1.81 at 0.05 mol L$^{-1}$ Na$_2$MoO$_4$, suggesting a mixture of monodentate and bidentate species of complexed Mo at the mineral surface. It is evident that ligand-exchange (inner-sphere complexation) is a mechanism for Mo sorption on Fe(III)$_2$(OH)$_6$. X-ray diffraction analysis of Fe(III)$_2$(OH)$_6$ after Mo sorption showed no crystalline solid phase. This microscopic result is in agreement with the molybdate results obtained for the iron oxide, goethite, using zero point charge shifts, isoelectric strength effects, and triple-layer modeling.

Two washings with deionized water desorbed 14 and 29% of the initially sorbed Mo from Fe(III)$_2$(OH)$_6$ for the 0.05 and 0.1 mol L$^{-1}$ Na$_2$MoO$_4$ treatments, respectively. DRS/FTIR difference spectra of Fe(III)$_2$(OH)$_6$ show the spectrum of the supernatant was subtracted from the spectra of the solid suspension as affected by Mo sorption. Solid concentration was 400 g L$^{-1}$. The amount of sorbed Mo was ca. 400 mg, 499, and 600 mg kg$^{-1}$ of Mo for total Mo concentrations of 0.1, 0.05, and 0.05 mol L$^{-1}$ Na$_2$MoO$_4$, respectively, at 1.4 cm$^{-1}$ (peak at 6).

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Figure 14: ATR-FTIR difference spectra of Fe(III)$_2$(OH)$_6$ (the spectrum of the supernatant was subtracted from the spectra of the solid suspension as affected by Mo sorption. Solid concentration was 400 g L$^{-1}$. The amount of sorbed Mo was ca. 400 mg, 499, and 600 mg kg$^{-1}$ of Mo for total Mo concentrations of 0.1, 0.05, and 0.05 mol L$^{-1}$ Na$_2$MoO$_4$, respectively, at 1.4 cm$^{-1}$ (peak at 6).
pansion more bands were observed for the maghemite grade $\text{Fe}_3\text{O}_4\cdot 2\text{H}_2\text{O}$ (fig. 15c). A model mononitrate complex $[\text{Cu}\text{NH}_3\text{H}_2\text{O}_2\text{Cu}]^{2+}$ shows three IR bands at 310, 677, and 833 cm$^{-1}$, whereas a bidentate chelate $[\text{Cu}\text{NH}_3\text{H}_2\text{O}_2\text{Cu}]^{2+}$ exhibits four bands at 920, 866, 845, and 795 cm$^{-1}$ (Dor, 1972). An initiation of the relative distribution of mono- and bisvogel complexes is difficult due to overlapping bands of the compounds. Nevertheless, it is highly possible that both types of complexes exist on the surface of Fe(III)O$_2$ as supported by both IR spectra and the molar ratio of OH released to Mo sorbed.

IV. SUMMARY

Molybdate adsorption on all materials exhibited a maximum at low pH (3 to 5). With increasing solution pH, adsorption decreased rapidly, with little adsorption occurring above pH values of 5 to 8. Molybdate adsorption was lowest for the...
highest solution ionic strength; ionic strength dependence on molybdate adsorption was slight on goethite, montmorillonite, and $\mu=0.01$, suggesting in inner-sphere adsorption mechanism. Ionic strength dependence of molybdate adsorption was observed on gibbsite. Aluminimum Oxide (B) and kaolinite, suggesting at inner-sphere adsorption mechanism.

The constant capacitance model was able to describe molybdate adsorption on the oxides, clay minerals, and soils as a function of solution pH. Averaged for the molybdate adsorption capacitance constants obtained with the constant capacitance model for soils, clay minerals, and soils were not statistically different at the 0.05 level of confidence.

The two-layer model was able to describe molybdate adsorption on goethite, gibbsite, aluminum Oxide C, kaolinite, montmorillonite, and two soils as a function of solution pH and ionic strength using a universal site density value of 2.31 sites $\cdot$ $10^{-5}$ cm$^{-2}$ (recommended for natural materials). Good fit of the model to the data were obtained using both inner-sphere and outer-sphere adsorption mechanisms for all materials except montmorillonite, where an acceptable fit was obtained only with an outer-sphere mechanism.

Results from the FTIR spectroscopy indicate that ligand exchange is a mechanism for Mo adsorption on hematite. Hydroxyl release suggests a mixture of goethite and hematite on surface complexes.

REFERENCES


