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The effects of ternary surface complexes on the adsorption of metal cations and organic acids onto mineral surfaces

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Abstract—Ternary surface complexation, which can be viewed as the co-adsorption of metal cations and organic molecules onto the same mineral surface site, can dramatically enhance both metal cation and organic molecule adsorption under certain pH conditions. In 1990, Schindler (1990) reviewed the experimental studies of ternary complex formation. At that time, only a handful of studies had been conducted, and the only measured thermodynamic stability constants were for Type A (mineral-metal-ligand) complexes. Since 1990, a number of studies have examined both Type A and Type B (mineral-ligand-metal) ternary surface complexation, and in this review I describe the advancement in understanding that has occurred over the past decade. We now have stability constant measurements for both Type A and Type B complexes, but the databases of both are still quite limited. The experimental studies of the past 10 years have reinforced the observation that ternary surface complexation can, under some conditions, control metal and organic mobilities in water-rock systems. In addition, enough data exist to construct predictive techniques for estimating stability constants for ternary surface complexes that have not been directly studied in the laboratory. For Type B complexes, a linear correlation exists between the log stability constant of the ternary surface complex and the sum of the log stability constants of the metal-organic aqueous complex and the organic-surface complex. This relationship can be used to predict whether a mineral-organic-metal surface set is likely to form a ternary surface complex, and it can be used to estimate the extent of adsorption that occurs in such a system. I use this approach to estimate the stability of a goethite-citrate-Co(II) ternary surface complex, demonstrating that the ternary complex can markedly enhance Co(II) adsorption onto goethite over a wide range of pH conditions. Despite having enough data to build predictive models, the accuracy of these models depends strongly on the acquisition of additional data that constrain the thermodynamic stabilities of ternary surface complexes.

1. INTRODUCTION

Metal cations and organic acid ligands co-exist in solution in a wide range of both natural and contaminated water-rock systems. Over the past twenty years, experimental studies have demonstrated that metal cations and organic acid ligands each adsorb to mineral surfaces individually. Furthermore, when present together in contact with mineral surfaces, metal cations and organic ligands can form ternary surface complexes, thereby influencing the adsorptive properties of each solute (e.g., Bowers and Huang, 1986). Prior to 1990, only a small number of studies had documented the formation of ternary metal-organic surface complexes, and even fewer had quantified their thermodynamic stabilities in a surface complexation framework. Schindler (1990) reviewed these early studies, but since 1990 an increasing awareness of metal-organic co-contamination in the subsurface, and an understanding of the influence of natural organic matter on metal cation adsorption, has focussed considerable attention on co-adsorption. The objective of this paper is to review the studies that have been conducted since Schindler's (1990) review, to summarize our current understanding of the stabilities and importance of metal-organic ternary surface complexes, and also to outline what needs to be better understood in order to accurately quantify solute adsorption in metal- and organic-bearing aqueous systems.

2. CHARACTERIZING THE MINERAL SURFACE

Adsorption of solutes onto mineral surfaces can be modeled either with partitioning approaches or with a surface complexation approach. Partitioning approaches describe adsorption in terms of relative amounts in solution and on the mineral surface under a specific set of conditions. Partition coefficients are applicable only to the conditions at which they were determined. Conversely, surface complexation models, which apply the formalism of aqueous ion association reactions to solute adsorption reactions with surfaces, require a detailed understanding not only of the surfaces involved, but also of the adsorption/desorption mechanisms. A surface complexation model treats the adsorbed solute as a distinct thermodynamic entity whose stability can be quantified with an equilibrium constant. The equilibrium constants which describe the extent of adsorption in surface complexation models are *invariant* with respect to most of the parameters which affect partition coefficients. Therefore, one can determine equilibrium constants in systems that isolate specific adsorption reactions, and model complex systems by combining these results into a computational model. Because of the additional components that must be understood and measured, surface complexation modeling is more difficult to apply to adsorption processes than bulk partition modeling. However, the added insight gained from a thorough understanding of the adsorption/desorption mechanisms enables estimation of the extent of adsorption/desorption that occurs under conditions other than those studied in the laboratory.

The pH-dependent surface charge on metal oxides and aluminosilicates can be quantified according to surface complexation theory by the following types of reactions (Hohl and Stumm, 1976; Sposito, 1984):

$$\equiv SOH^o \quad + \quad H^+ \quad \Leftrightarrow \quad \equiv SOH_2^+ \qquad (1)$$

$$\equiv SO^- \quad + \quad H^+ \quad \Leftrightarrow \quad \equiv SOH^o \qquad (2)$$

where $\equiv S$ represents a generic, crystallographically bound metal cation, S, at the surface-water interface. This formalism implies that protons are adsorbed or desorbed onto or from specific surface sites, and that the abundance of protons (or other adsorbed cations) at these sites determines surface charge. These sites are considered distinct thermodynamic entities. That is, the equilibria can be quantified with mass-action equations of the form (written for Eqn. 1):

$$K_{(1)} \quad = \quad \frac{[\equiv SOH_2^+]}{[\equiv SOH^0][H^+]} \qquad (3)$$

where K represents a conditional (or apparent) equilibrium constant for the subscripted reaction at the ionic strength and surface coverage of interest, and brackets denote concentrations in terms of molality.

Acid/base titrations of mineral powder suspensions constrain the equilibrium constant values for surface protonation or deprotonation reactions. Numerous studies have quantified these values for metal oxides, as well as for more complex aluminosilicates. Sverjensky and Sahai (1996) developed a method for estimating these equilibrium constants for oxides and silicates based on known properties of the solids, in conjunction with electrostatic and solvation theories. A wide range of values are observed for the important rock-forming metal cations. For example, the value of $pK_{(1)}$ (at 0.01-0.03 m) ranges from approximately –1.6 for quartz to 7.5 for gibbsite and goethite (Table 3, Sverjensky and Sahai, 1996). Therefore, different mineral surface cation sites can display markedly different surface charges at a given pH.

The advantage of the surface complexation approach lies in the fact that the K values are constant at a given pressure and temperature, so system speciation can be directly calculated at any system composition of interest. Because the surface electric field affects the ability of ions to approach and depart from surface sites, these equilibrium constant values must be adjusted to account for this effect, using the following equation (Stumm and Morgan, 1996):

$$K_{Apparent} \quad = \quad K_{Intrinsic} \exp(-\frac{\Delta ZF\Psi}{RT}) \qquad (4)$$

$K_{Apparent}$ represents the equilibrium constant value valid at a particular surface charge (i.e., eq. 3), while $K_{Intrinsic}$ is the fixed equilibrium constant value for a hypothetically uncharged surface. ΔZ, F, Ψ, R, and T represent the change in the charge of the surface species for the reaction, Faraday's constant, the surface potential, the gas constant, and absolute temperature, respectively.

Metal cation adsorption onto mineral surfaces is modeled in the surface complexation approach as attachment of the metal cation M^{m+} onto one of the surface species, for example, the deprotonated negatively charged $\equiv SO^-$ site:

$$M^{m+} \quad + \quad \equiv SO^- \quad \Leftrightarrow \quad \equiv SOM^{(m-1)+} \qquad (5)$$

The adsorption of metal cations onto metal oxide or silicate surfaces is typically pH-dependent, with little or no adsorption under low-pH conditions (where H^+ ions can effectively compete with the metal cations for the available surface sites). Adsorption increases with increasing pH as the surface sites deprotonate and the surface becomes more negatively charged. Stability constants for metal-surface complexes can be determined by measuring the amount of metal adsorbed onto a mineral surface. The stoichiometry of the surface complex can be constrained by conducting these experiments as a function of pH, ionic strength, and solute:surface concentration ratio (see, e.g., Dzombak and Morel, 1990, for a thorough review of metal adsorption behavior). Furthermore, information concerning the molecular structure of mineral surface complexes can be gleaned from spectroscopic techniques, such as magnetic resonance, x-ray absorption, and Fourier transform infrared spectroscopies (Motschi, 1987; Brown, 1990; Karthein et al., 1991).

Because many types of surface sites are protonated under low-pH conditions, and hence neutrally or positively charged, organic acid anions tend to adsorb most extensively at low pH, such that there is decreasing adsorption of organic anions with increasing pH. Most studies have observed little organic anion adsorption under conditions at which both the anion and the mineral surface are negatively charged (e.g., Stumm et al., 1980). Similar to metal cation adsorption, the adsorption of organic acid anions onto mineral surfaces can be viewed in terms of interactions between the organic molecules and specific sites on the mineral surface. For example, Fein and Brady (1995) model oxalate adsorption onto Al_2O_3 with the following reaction:

$$\equiv AlOH^o + Ox^{2-} + H^+ \Leftrightarrow \equiv AlOx^- + H_2O \tag{6}$$

Adsorption of metal cations or organic acid anions does not typically render mineral surface sites inert. If adsorption results in charge reversal of the surface site, and if the aqueous system contains both dissolved metal cations and organic ligands, then the formation of metal-organic ternary surface complexes can occur. As described by Schindler (1990), two types of ternary surface complexes may form: Type A complexes in which a metal cation bridges the negative charges of the surface and organic acid ligands; and Type B complexes in which an organic polyfunctional ligand bridges the positive charges of the surface and a metal cation. In Type A complexes, the coordination sphere of the adsorbed metal cation is only partially filled through its interaction with the surface functional group, creating a positively charged site for further adsorption of ligands. A generic reaction that describes the formation of Type A ternary surface complexes is:

$$\equiv SO^- + M^{m+} + L^{y-} \Leftrightarrow \equiv SOML^{(m-y-1)+} \tag{7}$$

Type B complexes form because adsorption of a poly-functional organic acid anion (such as oxalate illustrated in Eqn. 6) creates a negatively charged surface site, thus promoting co-adsorption of a metal cation. The formation of Type B ternary complexes can be represented as:

$$\equiv SOH^o + M^{m+} + L^{y-} + H^+ \Leftrightarrow \equiv SLM^{(m-y+1)+} + H_2O \tag{8}$$

The formation of either type of ternary surface complex can significantly enhance adsorption of both metal cations and organic acid anions. It is clear that in an organic-dominated system, for example, the formation of Type B ternary complexes would cause adsorption of metal cations under conditions otherwise unfavorable to cation adsorption. Similarly, Type A complexes would enhance adsorption of organic acid anions, but enhanced metal adsorption due to Type A complexation has also been observed (Schindler, 1990).

When the review of Schindler (1990) was published, very few studies had been conducted that had determined thermodynamic stability constants for ternary metal-organic surface complexes, and the only ones that were reported were Type A complexes involving either silica or rutile surfaces. Although some experimental evidence suggested the presence of Type B ternary complexes (e.g., Davis and Leckie, 1978; Davis, 1984), no experimental studies had constrained their stability constants. However, in natural geologic settings and in most metal- and organic-contaminated groundwater systems, the presence of polyfunctional organic acid anions (rather than the π-acceptor organic molecule ligands that tend to form Type A complexes) makes it likely that Type B complexes form in these settings. Because of the potential formation of these complexes, and their potential effect on aqueous mass transport, a large number of experimental studies have examined Type B complexation since 1990. The objective of this review is to describe our state of knowledge of both Type A and B ternary surface complexation involving metal cations and organic anions, to summarize the measured thermodynamic stabilities of these complexes, to describe their effects on contaminant transport, and to suggest fruitful lines for future experimentation. While ternary surface complexes exist involving inorganic ligands, such as phosphate and carbonate, this study will focus exclusively on those involving organic molecules.

3. EXPERIMENTAL STUDIES

3.1. Type A Complexation

Since Schindler's review of ternary complexation studies in 1990, a number of studies have been conducted that have examined both Type A and Type B complexation (Table 1). One effect of Type A surface ternary complexes is to increase the extent of metal adsorption onto mineral surfaces. Although the stoichiometry of Eqn. 7 does not indicate the creation of additional binding sites relative to the organic-free systems (Eqn. 5), the presence of organic anions can significantly enhance adsorption over a wide pH range. This is the type of ternary complexation summarized by Schindler (1990). The presence of some organic molecules (in particular π-acceptor ligands) must alter the electron clouds of the sorbing metal cations enough to augment the positive charge of the cation, thereby enhancing the electrostatic attraction with the mineral surface.

Due to the bridging of the cation in Type A ternary surface complexes, this complexation can augment

Table 1. Experimental Evidence for Ternary Surface Complexes – post Schindler (1990)

Reference	**Type**	**Mineral**	**Metal**	**Organic**	**Surface Complexation Interpretation**
Lövgren (1991)	A	Goethite	Al	Phthalate	Yes
Stadler & Schindler (1993)	A	Ca-Montmorillonite	Cu	5 & 6 member chelate rings	Yes
Ludwig & Schindler (1995)	A	Anatase	Cu	Chelates with N donor atoms	Yes
Girvin et al. (1996)	A	Gibbsite	Co(II)	NTA	No
Boily & Fein (1998)	A	Corundum	Pb	Benzenecarboxylates	Yes
Nowack & Stone (1999)	A	Goethite	Ca	Phosphonates	No
Boily (1999)	A	Goethite	Cd	Phthalate	Yes
Girvin et al. (1993)	B	δ-Al_2O_3	Co(II)	EDTA	No
Bryce et al. (1994)	B	HFOs	Ni	EDTA	Yes
Nordén et al. (1994)	B	Alumina, Quartz	Eu, Sr	Fulvic Acid	No
Szecsody et al. (1994)	B	Fe-oxide coated Sand	Ca, Co(II) Fe(III)	EDTA	No
Zachara et al. (1994)	B	Assemblage[1]	Co(II)	Humic Acid	No
Zachara et al. (1995)	B	Goethite	Co(II)	EDTA	Yes
Ali & Dzombak (1996)	B	Goethite	Ca, Cu	Phthalate, Chelidamate	Yes
Boily & Fein (1996)	B	Corundum	Cd	Citrate	Yes
Nowack & Sigg (1996)	B	Goethite	Metals[2]	EDTA	Yes
Nowack et al. (1996)	B	Al, Fe oxides[3]	Ni, Pd, Fe(III)	EDTA	Yes
Vohra & Davis (1997)	B[4]	TiO_2	Pb	NTA	Yes
Redden et al. (1998)	B	Goethite	U(VI)	Citrate	No
Vohra & Davis (1998)	B[4]	TiO_2	Pb	EDTA	Yes
Yang & Davis (1999)	B	TiO_2	Cu, Cd	EDTA	Yes

[1] **A clay-sized isolate from a natural subsurface sample.**

[2] **Ca, Zn, Ni, Cu, Pb, Co(II), Co(III), Pd, Fe(III), Al.**

[3] **δ–Al_2O_3, crystalline and non-crystalline iron-oxides.**

[4] **Also found evidence for a Type A complex.**

the extent of organic adsorption onto mineral surfaces that are otherwise not conducive to anionic adsorption (Lövgren, 1991; Ludwig and Schindler, 1995; Girvin et al., 1996; Boily and Fein, 1998; Nowack and Stone, 1999). It should be noted that enhanced organic adsorption in the presence of aqueous metal cations does not necessarily require the presence of Type A ternary surface complexes. It is possible that Type B complexes could also account for this behavior because the diminished electronegativity associated with a Type B complex (relative to organic-surface complexes themselves) could enable enhanced adsorption of the organic anion due to diminished surface repulsion. For example, Nowack and Stone (1999) demonstrate that the adsorption of some phosphonates, which are used widely as industrial complexing agents, onto goethite is dramatically increased when cations such as Ca^{2+} and Zn^{2+} are present in excess concentrations relative to that of the phosphonates. Fig. 1, from Nowack and Stone (1999), depicts the adsorption of nitrilotris-methylenephosphonic acid (NTMP) onto goethite in the absence of Ca, and with 10 – 1000 μM Ca. The experiments clearly demonstrate that the presence of Ca can significantly increase the adsorption of NTMP in the basic pH range. Nowack and Stone (1999) state that the observed adsorption behavior could be explained by the formation of ternary surface-phosphonate-Ca complexes, but they do not provide thermodynamic stability constants for these complexes. It is likely that the data could also be explained by the formation of a Type A ternary surface complex. Contaminated groundwater systems can possess high concentrations of rock-forming divalent cations (such as Ca^{2+}, Mg^{2+}, Fe^{2+}), as well as contaminant metals (such as Cd^{2+}, Zn^{2+}, etc.). Therefore, especially when concerned with organic contaminant mobility, the formation of Type A surface ternary complexes clearly must be accounted for. However, Type A complexes can also augment the adsorption of metal cations, as observed by Boily (1999). Boily (1999) uses a combination of bulk chemistry analyses with infrared and EXAFS spectroscopies to identify a Type A goethite-Cd-phthalate ternary surface complex and to quantify its thermodynamic stability. However, remarkably few stability constants for Type A complexes have been determined (see Schindler, 1990, and Table 1), so our ability to model these effects is extremely limited.

3.2. Type B Complexation

Type B ternary surface complexation can dramatically affect both metal and organic molecule mobilities in metal- and organic-bearing geologic systems. As the stoichiometry of Eqn. 8 indicates, Type B complexes involve multi-functional organic acid anions. A large number of these types of molecules are found with aqueous metals as contaminants in groundwater systems, and many anthropogenic organic acids are listed as Environmental Protection Agency (E.P.A.) Priority Pollutants (Keith and Telliard, 1979). Organic acids, such as EDTA, citrate, and tributylphosphate, are also common constituents with metals and radionuclides as contaminants in soils (e.g., at U.S. Department of Energy (D.O.E.) sites; Riley et al., 1992), and humic and fulvic acids are naturally-occurring complex organic acids that are virtually ubiquitous in near-surface environments. Therefore, Type B ternary surface complexation is likely to be even more widespread and significant than Type A complexation. For this reason, Type B complexation has received considerable attention over the past 10 years (Table 1).

A number of studies have identified the general effects of organic acid anions on metal adsorption onto mineral surfaces (Fig. 2). As noted by a number of workers in this area (e.g., Davis, 1984; Murphy and Zachara, 1995; Ali and Dzombak, 1996; Boily and Fein, 1996), under low pH conditions the formation of Type B ternary surface complexes enhances the adsorption of aqueous metal cations onto positively- or neutrally-charged mineral surfaces. Conversely, under higher pH conditions, mineral surface sites deprotonate to a greater extent, causing a net decrease in the mineral surface charge, and hence a decrease in the amount of organic anions that can adsorb. The non-adsorbed organic acid anions in solution under these higher pH conditions can form highly stable aqueous metal-organic complexes,

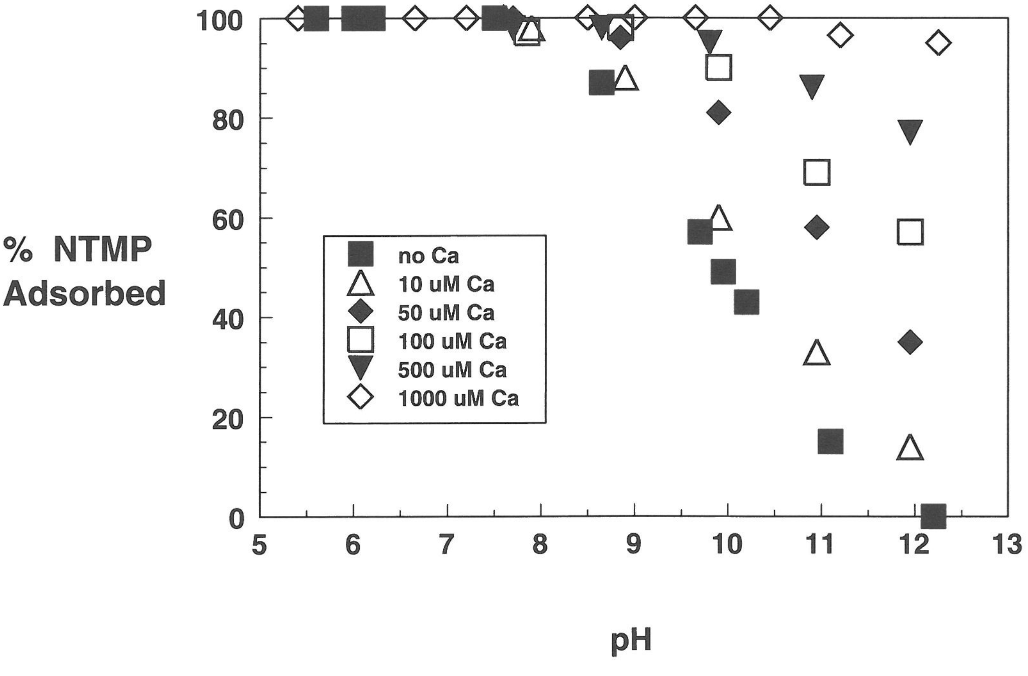

Fig. 1. Experimental data from Nowack and Stone (1999) showing the effect of aqueous Ca^{2+} (from 0 to 1000 μM) on the adsorption of nitrilotris-methylenephosphonic acid (NTMP) onto goethite, with 9.8 μM NTMP and 0.42 g/L goethite in 0.01 M $NaNO_3$. Nowack and Stone (1999) ascribe the adsorption enhancement to a ternary goethite-Ca-NTMP surface complex.

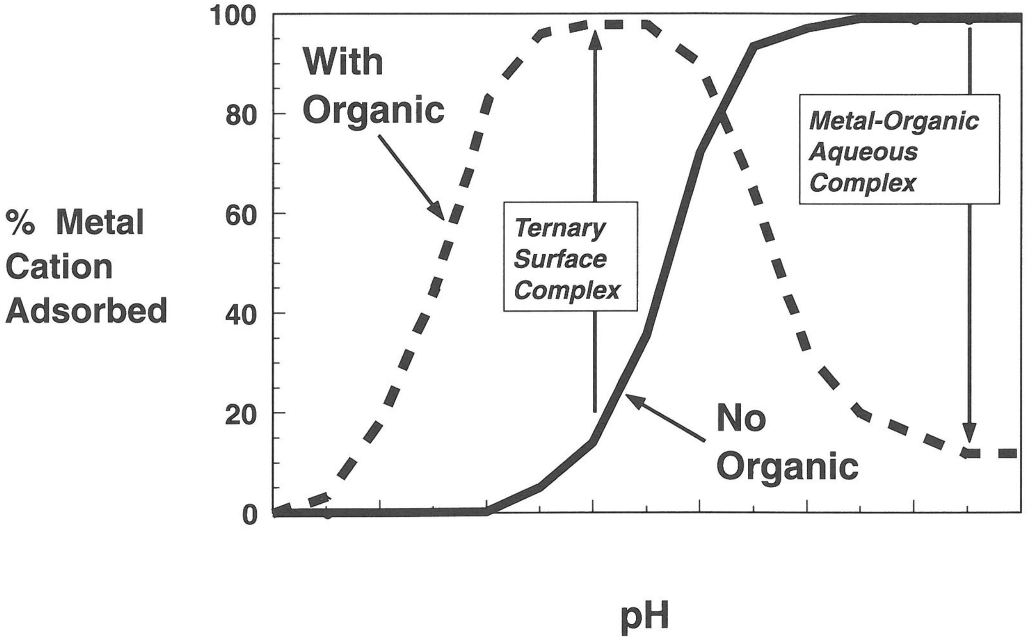

Fig. 2. The generalized effects of dissolved organic acid anions on the adsorption of aqueous metal cations onto an oxide-type mineral surface. The organic anions enhance adsorption under lower pH conditions through the formation of Type B ternary surface complexes, and diminish adsorption at higher pH values by competition involving metal-organic aqueous complexes.

thereby competing with the mineral surface for the available metal and reducing the amount of metal that can adsorb.

A number of field studies have demonstrated that aqueous metals can strongly bind to adsorbed organic matter on mineral surfaces (e.g., Balistrieri et al., 1981; Tessier et al., 1996), qualitatively showing the importance of Type B ternary surface complexes. In addition, experimental studies have been conducted that document the enhancement of metal cation adsorption in the presence of humic and fulvic acids and simpler organic acids (Table 1); however, few provide quantitative constraints on the thermodynamic stabilities of the important ternary surface complexes. Type B ternary surface complexes are formed because adsorption of multi-functional organic acid anions onto positively- or neutrally-charged mineral surfaces creates additional sites for metal cation adsorption on the surface. For example, Zachara et al. (1994) measured over 80% removal of 11 mg/L leonardite humic acid onto 1.3 g/L of subsurface isolates throughout the pH range of their experiments (~4.5 to 8.0), in metal-free, humic acid-mineral systems. In these systems, the adsorption of the humic acid significantly decreased the electrophoretic mobility of the mineral isolates, despite the overall net negative charge of the mineral surfaces. In Co- and humic acid-bearing systems, the extent of Co^{2+} adsorption was significantly higher than that observed in the absence of humic acid, with the maximum amount of adsorption enhancement occurring at approximately pH 6 – 6.5. Zachara et al. (1994) attribute these observations to the adsorption of the humic acid onto positively-charged Al- and Fe-(hydr)oxide sites within the mineral isolates, and subsequent exposure of ionized carboxylate groups to the solution. The net effect of humic acid adsorption is to augment the concentration of negatively-charged surface sites, thereby accounting for both the enhanced electronegativity of the mineral surfaces in humic-only systems, and the elevated Co^{2+} adsorption in the metal and humic experiments. Due to the complex chemistry of both the humic acid and the mineral assemblages used in the experiments, Zachara et al. (1994) could not easily apply a surface complexation approach to quantify the thermodynamic stability of the observed ternary surface complexes. Rather, they applied a linear additivity composite K_d approach to modeling the data.

The effect of EDTA on aqueous metal cation adsorption onto mineral surfaces has received much attention because EDTA has been used to decontaminate nuclear reactors and various nuclear waste processing facilities. At several D.O.E. sites, aqueous radionuclides and metals can exist predominantly as anionic EDTA complexes in groundwater (e.g., Means et al., 1978), suggesting that ternary surface complexation could significantly affect contaminant mobilities. A number of studies have focussed on the effects of EDTA on metal sorption (e.g., Girvin et al., 1993; Szecsody et al., 1994); the structure of EDTA-bearing surface ternary complexes has been investigated using EXAFS (Schlegel et al., 1997), and several studies have quantified the thermodynamic stabilities of the important ternary surface complexes (Bryce et al., 1994; Zachara et al., 1995; Nowack and Sigg, 1996; Nowack et al., 1996; Vohra and Davis, 1998; Yang and Davis, 1999).

The common feature of each of these studies is the general anionic-type of adsorption behavior of the metal or radionuclide involved. Each experiment documents maximum metal adsorption under low-pH conditions, with adsorption decreasing in most cases to negligible amounts at higher pH values. For example, Nowack and Sigg (1996) measured stability constants for EDTA and metal-EDTA (for Ca, Zn, Ni, Cu, Co(II), Pd, Pb, Fe(III), Co(III), and Al) goethite surface complexes. The pH dependence of the adsorption behavior of most of the metals mimics, in general, the adsorption of EDTA alone, indicating that the metal-EDTA complex adsorption is controlled by the same processes that control the adsorption of non-complexed EDTA. The metals that do not follow the typical anion-type trend are ones that form weaker complexes with EDTA, such as Ca, and some of the trivalent metal cations. Ca-EDTA complexes are mostly dissociated under lower pH conditions, and hence Ca adsorption behavior is cation-like under these conditions.

Similar anion-type adsorption behavior for metal-EDTA complexes was observed by Bryce et al. (1994), who measured Ni adsorption onto a hydrous ferric oxide in the presence of EDTA, and by Nowack et al. (1996), who measured Ni- and Pd-EDTA adsorption onto a range of crystalline and non-crystalline metal oxides. Each of these studies modeled the observed adsorption behaviors using the following reaction stoichiometry:

$$\equiv SOH^o \quad + \quad M^{m+} \quad + \quad EDTA^{4-} \quad + \quad H^+ \quad \Leftrightarrow \\ \equiv S - EDTA - M^{(m-3)-} \quad + \quad H_2O \qquad (9)$$

using FITEQL (Westall, 1982) to solve for the equilibrium constant for Eqn. 9. Zachara et al. (1995) measured Co(II)-EDTA adsorption onto goethite, as well as onto a number of fluvial sediments. The goethite adsorption behavior observed by Zachara et al. (1995) is consistent with that observed by Nowack and Sigg (1996). That is, between pH values of approximately 5 and 10, adsorption decreases with increasing pH. In addition, Zachara et al. (1995) extended their experiments to lower pH conditions than did Nowack and Sigg (1996), observing a dramatic decrease in metal adsorption with decreasing pH below approximately pH 4 – 5. Zachara et al. (1995) attribute the decreased adsorption below pH 5 to competitive effects of aqueous Fe^{3+}, which, due to goethite dissolution, was present in increasing concentrations with decreasing pH below pH 5 in these experiments. This implies that competition for the available $EDTA^{4-}$ between Co^{2+} and Fe^{3+} caused increasing displacement of Co^{2+} from goethite-EDTA-Co(II) ternary surface complexes, and therefore a decrease in Co adsorption with decreasing pH. Zachara et al. (1995) noted a positive correlation between Co adsorption and iron oxide content of the sediments used in the experiments, but the correlation was weaker than would be predicted based on the goethite experiments alone. It is likely that the diminished adsorption was due again to competitive complexation by Al^{3+} and Fe^{3+} liberated from the minerals by dissolution. This example indicates that accurate use of a surface complexation approach to quantifying solute adsorption requires determination of all important stability constants in the system. The amount of incorporation of Co(II) in ternary surface complexes can only be predicted if the tendency for other system cations to form such complexes is also known.

Type B ternary surface complexation has also been observed involving poly-functional organic acids other than EDTA. Boily and Fein (1996) measured the adsorption of Cd, in the presence and absence of citrate, onto α-Al_2O_3. Enhanced Cd adsorption between approximately pH 4 and 7 in the citrate systems relative to that observed in the organic-free experiments was best accounted for by the formation of the $\equiv$ Al-Cit-Cd^o ternary surface complex. Diminished Cd adsorption was observed in the presence of citrate at higher pH values due to formation of aqueous Cd-citrate complexes, and the inability of citrate to adsorb onto Al-mineral surface sites under high pH conditions. Redden et al. (1998) confirm the existence of a goethite-citrate-U(VI) surface ternary complex using EXAFS and FTIR spectroscopies. Ali and Dzombak (1996) found similar effects of phthalic and chelidamic acids on the adsorption of Cu^{2+} and Ca^{2+} onto goethite, also using a surface complexation approach to quantify the thermodynamic stability of the ternary surface complexes. These studies, and the others involving metal-EDTA systems, demonstrate that the effect of multi-functional organic acids on metal adsorption is strongly pH-dependent, and that it is incorrect to assume that the presence of dissolved chelating agents will always cause increased metal mobility in the subsurface.

Enhanced metal adsorption in the presence of organic acids is not always caused by the formation of ternary surface complexes. Adsorption of organic acid anions onto positively-charged mineral surfaces will offset at least some of the positive charge of the surface, thereby reducing the electrostatic repulsion between the surface and positively-charged aqueous cations (Boily and Fein, 1998; Nowack and Stone, 1999) and enabling cation adsorption to occur on exposed surface sites that are not involved in organic anion adsorption. For example, Nowack and Stone (1999) observed enhanced Cu uptake onto goethite in the presence of a number of different phosphonates from approximately pH 3 to 6. The observed adsorption enhancement was modeled, not with the presence of a distinct ternary surface complex, but rather by accounting for the effects of the adsorbed organic anions on the electric field of the mineral surface. Adsorption of the negatively-charged phosphonates was sufficient to diminish the positive charge of the goethite surface under the low pH conditions. This electric field effect increased the ability of Cu^{2+} to approach and bind to the goethite surface on separate sites from those responsible for phosphonate adsorption. Enhanced Cd adsorption onto goethite in the presence of phosphate was observed by Venema et al. (1997), and was also successfully modeled without the need for a ternary surface complex. Conversely, Boily and Fein (1998) demonstrated that the observed enhancement of Pb adsorption in the presence of benzenecarboxylates was greater than could be accounted for simply due to electric field effects associated with organic anion adsorption, using this as key evidence for the presence of ternary surface complexes involving Pb and the benzenecarboxylates.

4. PREDICTIVE TECHNIQUES

The above review of the experimental studies that have focussed on metal-organic ternary surface complexes illustrates the limitations of our understanding of this adsorption phenomenon. Until a more comprehensive database is assembled, predictive techniques are required to estimate the thermodynamic stabilities of environmentally and geologically important ternary surface species. Schindler (1990) outlines a predictive approach that is based on a statistical treatment of the coordination chemistry of the metal-ligand pair of interest. Although this approach can successfully account for the available experimental data for Type A complexes, it requires a detailed understanding of the coordination chemistry of the adsorbed species.

Linear free energy correlations have been used successfully to relate organic adsorption stability constants to measured stability constants of metal-organic aqueous complexes (e.g., Stumm et al., 1980), and such an approach has also been applied to equilibrium constants for metal-mineral (Langmuir, 1979) and metal-bacteria adsorption reactions (Fein et al., 1997; Fowle and Fein, 2000). In the present study, I concentrate on Type B ternary surface complexes, attempting to relate the overall stability constant of the surface complex to the thermodynamic stabilities of the adsorbed organic species, and the tendency for the aqueous metal cation and the organic to form an aqueous complex. Ternary complexation can be expressed as follows:

$$\equiv SOH^o + M^{m+} + L^{-L} + H^+ \Leftrightarrow \equiv S-L-M^{(m-L+1)} + H_2O \qquad (10)$$

(where L^{-L} represents the fully deprotonated organic acid anion). The organic anion adsorption reaction can be expressed as:

$$\equiv SOH^o + L^{-L} + H^+ \Leftrightarrow \equiv S-L^{(1-L)} + H_2O \qquad (11)$$

and the aqueous metal-organic complexation reaction can be written:

$$M^{m+} + L^{-L} \Leftrightarrow ML_{(aq)}{}^{(m-L)} \qquad (12)$$

Fig. 3 depicts measured values of the logarithm of the equilibrium constant for Eqn. 10 (log $K_{Ternary}$), plotted as a function of the sum of the log stability constants for Eqns. 11 and 12. The stability constants used in this correlation are listed in Table 2.

As indicated in the present literature review, most measured stability constants for Type B ternary surface complexes are those of metal-EDTA species. The log stability constant value for the Co(II)-EDTA complex from Zachara et al. (1995) was reported as 5.13 for the following reaction:

$$\equiv FeOH_2{}^+ + Co(II)EDTA^{2-} \Leftrightarrow \equiv FeOH_2-EDTA-Co(II)^- \qquad (13)$$

This was altered to the stoichiometry of Eqn. 10 by addition of the surface protonation reaction:

$$\equiv FeOH^o + H^+ \Leftrightarrow \equiv FeOH_2{}^+ \qquad (14)$$

Table 2. Stability Constant Correlation Values

M-L-Solid Set	Log $K_{Ternary}$ Eqn. 10	Log $K_{Solid\text{-}L}$ Eqn. 11	Log $K_{M\text{-}L(aq)}$[1] Eqn. 12	Reference[2]
Cd-citrate-Al_2O_3	16.8	13.5	5.9	a
Ca-EDTA-FeOOH	22.4	15.0	11.0	b
Zn-EDTA-FeOOH	28.4	15.0	18.2	b
Ni-EDTA-FeOOH	30.7	15.0	20.3	b
Cu-EDTA-FeOOH	31.1	15.0	20.5	b
Pb-EDTA-FeOOH	30.0	15.0	19.7	b
Co(II)-EDTA-FeOOH	28.1	15.0	18.1	b
Pd-EDTA-FeOOH	41.7	15.0	20.7	b
Al-EDTA-FeOOH	26.7	15.0	19.1	b
Fe(III)-EDTA-FeOOH	36.9	15.0	27.6	b
Co(III)-EDTA-FeOOH	52.3	15.0	44.0	b
Pd-EDTA-HFO[3]	32.0	15.0[4]	20.7	c
Co(II)-EDTA-FeOOH	28.8	15.0[5]	18.1	d
Ni-EDTA-HFO	28.8	15.0[6]	20.3	e
Pb-NTA-TiO_2	33.5	14.4	12.7	f

Notes:

1 Values for $K_{(12)}$ adjusted to I=0 where necessary (see text).

2 a=Boily and Fein (1996); b=Nowack and Sigg (1996); c=Nowack et al. (1996); d=Zachara et al. (1995); e=Bryce et al. (1994); f=Vohra and Davis (1997).

3 HFO = hydrous ferric oxide.

4, 5, 6 Values of 15.0 are assumed because these studies do not report EDTA adsorption using the same stoichiometry as in Eqn. 11.

and the reaction describing the formation of the Co(II)EDTA aqueous complex:

$$Co^{2+} + EDTA^{-4} \Leftrightarrow CoEDTA^{-2} \qquad (15)$$

assuming that the $\equiv FeOH_2$-EDTA-Co(II) species is thermodynamically equivalent to $\equiv$ Fe-EDTA-Co(II). Ali and Dzombak (1996) model enhanced Cu adsorption onto goethite in the presence of phthalate and chelidamate as ternary surface complexes involving a hydrated surface Fe atom ($\equiv$ FeOH-Cu-ligand), rather than the form used in Eqn. 10. Therefore, inclusion of their data in this treatment is impossible. The correlation that is derived below is valid only for the ternary surface complex stoichiometry described in Eqn. 10. Values of the aqueous metal-organic stability constants are taken from Martell and Smith (1974; 1977; 1982), with values corrected to the reference state of zero ionic strength using the extended Debye-Hückel equation and parameters given by Helgeson et al. (1981). Uncertainties in the relationship arise not only from uncertainties in the measured values of the equilibrium constants for Eqns. 10-12, but also from differences in models used to quantify the electrostatic effects of the mineral surface.

Fig. 3 illustrates that a strong correlation exists between the log of the stability constant of Type B ternary surface complexes (as expressed by Eqn. 10) and the sum of the logs of the equilibrium constants for Eqns. 11 and 12. This sum represents both the tendency for the organic anion to adsorb onto the mineral surface (Eqn. 11) and for the metal and the organic anion to interact (Eqn. 12). The correlation holds for an extremely wide range of stability constant values (over 30 orders of magnitude with respect to the value of $K_{(10)}$). The correlation appears valid for a wide range of metals, for different metal oxide surfaces, and it appears successful for the Cd-citrate data of Boily and Fein (1996), as well (open square in Fig. 3). In addition, although Nowack and Sigg (1996) note significant differences between the ternary complexation behavior involving divalent and trivalent cations, the relationship holds for both types of cations. The circle significantly above the line corresponds to the measured goethite-EDTA-Pd stability constant of Nowack and Sigg (1996). Note that the hydrous ferric oxide-EDTA-Pd stability constant of Nowack et al. (1996) agrees well with the correlation. It is not possible to include the stability constants for Pb-, Cu-, and Cd-EDTA-TiO_2 from Vohra and Davis (1998) and Yang and Davis (1999) in the relationship depicted in Fig. 3 because the stoichiometries these authors use to characterize the surface ternary complexes are different than that shown in Eqn. 10.

Although the correlation depicted in Fig. 3 appears robust over a wide range of stability constant values, it is uncertain whether such a relationship can accurately predict stability constants for

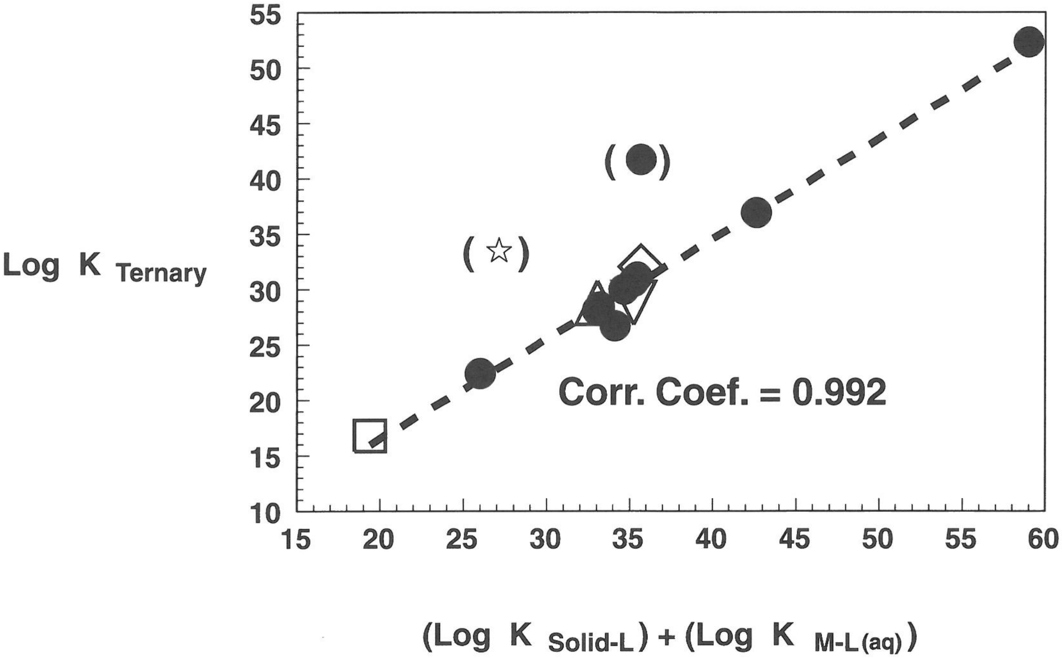

Fig. 3. Correlation plot between the log of the stability constant of ternary surface complexes (Eqn. 10) as a function of the sum of the log of the stability constants of the organic-mineral surface complex (Eqn. 11) and the metal-organic aqueous complex (Eqn. 12). The data are compiled in Table 2: filled circles represent data from Nowack and Sigg (1996); open square from Boily and Fein (1996); open diamond from Nowack et al. (1996); upward pointing triangle from Zachara et al. (1995); and downward pointing triangle from Bryce et al. (1994). The linear regression is calculated neglecting the data (in parentheses) which fall significantly above the correlation line.

Type B ternary surface complexes involving metals and organic acid anions not studied directly in the laboratory. Another system which appears to be inconsistent with this relationship is one involving gibbsite-NTA-Co(II). Girvin et al. (1996) found that NTA does not significantly affect Co(II) adsorption onto gibbsite under low pH conditions, and therefore does not form a Type B ternary surface complex as EDTA does with Co(II) (Girvin et al., 1996, did observe a higher pH effect on NTA adsorption caused by Co(II), and concluded that this was caused by the formation of a Type A gibbsite-Co(II)-NTA complex). Vohra and Davis (1997) find evidence for both Type A and Type B TiO_2–NTA-Pb surface ternary complexes, yet the stability constant (represented by the star in Fig. 3) for the Type B complex does not fit the illustrated correlation. With so few measurements involving organic anions other than EDTA, it is unclear whether citrate or NTA, or both, generally deviate from the correlation in Fig. 3. It is possible that the relationship depicted in Fig. 3 applies only to EDTA, and that the position of the citrate point is coincidental.

In the absence of experimental data, the relationship shown in Fig. 3 can be used to estimate the effects of organic acids on the mobility of aqueous metal cations. For example, Fig. 4 depicts the estimated effects of citric acid on the adsorption of Co(II) onto goethite. The thermodynamic stability of the surface goethite-citrate species has not been determined, so the calculation was conducted assuming that the stability constant value is equivalent to the value determined by Boily and Fein (1996) for the surface species $\equiv AlCit^{-2}$ (with a log stability constant value of 13.5). Stability constant values for ≡ Al-ligand surface complexes are reasonably close to those for ≡ Fe-ligand complexes (Stumm et al., 1980). The stability of the aqueous Co-citrate complex is taken from Martell and Smith (1977), and with an ionic strength correction, the log stability constant is taken as 6.3. The sum of the two aforementioned log stability constant values is 19.8. Using the linear relationship shown in Fig. 3, the sum of 19.8 yields an estimated log stability constant for the ternary surface complex (≡ FeCitCo) of 16.6. This value, along with equilibrium constants for the other important reactions between the goethite surface, dissolved citrate, and dissolved Co(II), can be used to calculate the distribution of Co in the system as a function of pH. The calculation, conducted using FITEQL (Westall, 1982), used stability constant values for aqueous complexes from Martell and Smith (1977; 1982); and for Co(II)-goethite surface species from Zachara et al. (1995).

Figure 4 shows that citrate, which is a co-contaminant with Co at a number of D.O.E. sites (Riley et al., 1992), may significantly affect the mobility of Co(II) through the formation of a ternary surface complex. The presence of citrate dramatically enhances the adsorption of Co over a wide range of pH conditions. For example, at pH 6.0 with no citrate present, less than 10 percent of the total Co in the system is adsorbed onto the goethite surface. In the citrate-bearing system, the formation of the ternary surface complex causes the concentration of adsorbed Co to increase to over 97 percent of the total. Clearly, such a dramatic change in the adsorption behavior of Co(II) would markedly change the estimated mobility of Co(II) in groundwater systems. This example shows that ternary surface complexation can dominate the chemical behavior of trace metals in the environment. However, it should also be noted that under some conditions, ternary surface complexes are not likely to significantly alter metal mobilities. For example, a similar estimation of the thermodynamic stability of the ≡Fe-oxalate-Co ternary surface complex on goethite yields a log stability constant of 12.7. Speciation calculations using this value indicate that oxalate causes only a relatively small enhancement of Co(II) adsorption onto goethite due to ternary surface complex formation (Fig. 4). Even with two orders of magnitude more oxalate than Co(II) in the system, the ≡Fe-oxalate-Co ternary surface complex comprises no more than 20 percent of the total Co budget at any pH value, and shifts the Co adsorption edge to more acid pH values by less than 0.5 pH units.

5. CONCLUSIONS AND FUTURE WORK

Although a number of studies have been conducted since Schindler's 1990 review of ternary surface

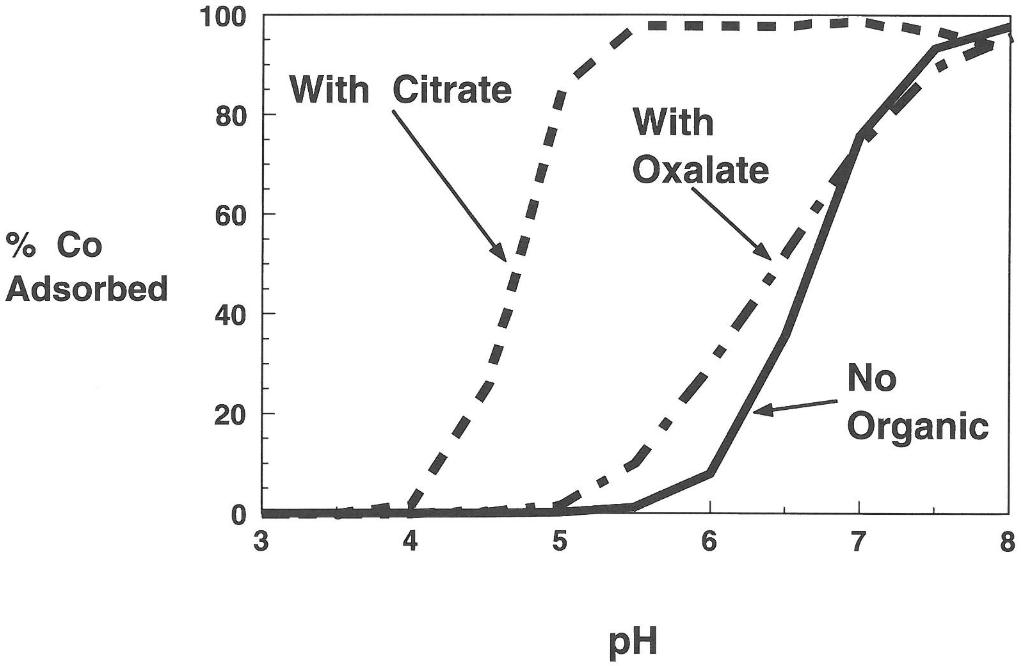

Fig. 4. Calculated adsorption behavior of Co(II) onto goethite in the presence and absence of citric acid. The stability constant for the goethite-citrate-Co(II) ternary surface complex was estimated from the linear relationship depicted in Fig. 3. Calculation conducted for the following conditions: 10^{-5} *m* total Co(II), 2.7 x 10^{-3} *m* total Fe surface sites, 0.01 *m* $NaNO_3$. Solid curve corresponds to a system with no organic acid; dashed curves correspond to those containing either 10^{-3} *m* total citric or oxalic acid.

complexes, our understanding of this adsorption process is still limited. Although Type A complexation (mineral-metal-organic) can significantly enhance the adsorption of aqueous metal cations onto mineral surfaces, these ternary complexes are more likely to affect organic molecule distributions. A number of studies have demonstrated that the presence of aqueous metal cations in organic anion bearing systems can augment the extent of adsorption of the anions through charge reversal due to cation adsorption onto the mineral surface. Despite these potentially large effects, thermodynamic stability measurements for Type A surface complexes are extremely scarce. Because of this lack of data, it is difficult to construct predictive models that enable accurate estimation of the thermodynamic stability of these complexes. Future work quantifying stability constants of Type A complexes would begin to alleviate this problem.

Type B ternary surface complexation (mineral-organic-metal) can significantly enhance metal adsorption under mildly acidic to neutral pH conditions. This enhancement has been demonstrated, and quantified in terms of surface complexation theory, by a number of experimental studies over the past 10 years. Although measurements of the thermodynamic stabilities of Type B ternary surface complexes are still fairly limited, enough exist to enable estimations to be made of the controls on the stabilities of these complexes. A strong linear correlation exists between the log stability constant of Type B ternary surface complexes and the sum of the log stability constants of the metal-organic aqueous complex and the organic-surface complex of the components. The number of experimental studies that constrain this relationship is limited, and the primary goal of future experimental work should be to expand the data set to include metals and organic acid anions that are environmentally or geologically important, and have yet to be studied. The observed relationship enables the thermodynamic stability of Type B ternary surface complexes to be estimated, and the resulting changes in metal adsorption behavior to be determined for various conditions. These changes in adsorption behavior can be large, as in the case illustrated in this study for goethite-citrate-Co(II) complexation, or they can be negligible, as for oxalate (see Fig. 4). At present, due to the small data set that constrains the behavior, the uncertainties associated with the estimated stability constant values are unknown, but are likely to be large. Clearly, in order to more accurately determine whether Type B ternary complex formation is important in a given system, a much larger data set must be used to constrain this relationship, so future work should be focused toward this end.

Ternary surface complexation between mineral surfaces, organic molecules, and metal cations can dramatically affect the fate and transport of both organic molecules and metals in geologic systems. The thermodynamic stabilities of a handful of ternary surface complexes have been measured over the past decade. Our ability to estimate the importance of ternary surface complexation in systems not directly studied in the laboratory has improved since 1990, but it is still limited in scope and accuracy. Due to the common occurrence of metals and organic molecules as co-contaminants, it is crucial that we improve our understanding of ternary surface complexes in order to accurately model the mobility of contaminants in the subsurface.

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