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EXPERIMENTAL STUDY OF Cd-CITRATE CO-ADSORPTION ON CORUNDUM

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ABSTRACT

An experimental investigation of metal-organic co-adsorption was conducted using cadmium and citrate in the presence of corundum. The experiments were performed in the pH range 3.0 to 10.0 in a 0.01M NaCl matrix with citrate:Cd ratios of 0.00 and 10.00. The presence of citrate enhances cadmium adsorption between pH 3.5 and 7.2, and reduces it above pH 7.2. The results from the experiments provide constraints on the thermodynamic properties of the surface complexes. The adsorption of Cd is quantified by the competition between aqueous CdCit^{-1} and the surface species $>\text{AlCitCd}^0$, $>\text{AlOCd}^+$, and $>\text{AlOCdCl}^0$. The experimentally determined equilibrium constants provide a means to predict Cd mobilities in groundwater systems by describing the relative stabilities of surface and aqueous metal-organic complexes as a function of metal-to-ligand and solute-to-sorbent ratios.

RÉSUMÉ

La co-adsorption de complexes metal-organiques a été étudiée pour le cas du cadmium et du citrate en présence du corindon. Les expériences ont été menées entre les pH 3.0 et 10.0, avec 0.01M NaCl comme sel de fond et en utilisant des ratios citrate:Cd de 0.00 et 10.00. Le citrate favorise l'adsorption du cadmium entre les pH 3.5 et 7.2 mais le réduit au-dessus de pH 7.2. Les données expérimentales ont été utilisées pour quantifier l'adsorption du Cd et du citrate à l'aide d'équations de masses. L'adsorption du Cd sur le corindon est quantifiée par la compétition entre le complexe aqueux CdCit^{-1} et les complexes de surface $>\text{AlCitCd}^0$, $>\text{AlOCd}^+$, and $>\text{AlOCdCl}^0$. Les constantes d'équilibres calculées dans cette étude peuvent ainsi être utilisées pour prédire le devenir du Cd dans les eaux souterraines en calculant la stabilité des

complexes métal-organiques en solution et à la surface d'(hydr)oxides d'aluminium et ce à différentes concentrations de Cd, de citrate et de sites de surface.

INTRODUCTION

Interactions between crustal fluids and mineral surfaces have important implications to many geological settings. Mineral surfaces are reactive and are known to complex with a number of solutes (e.g., Huang and Stumm, 1973; Hohl and Stumm, 1976; Stumm *et al.*, 1980). These reactions can affect processes such as transport of metals in groundwater (Zachara, 1993) and porosity enhancement in sedimentary basins (Fein and Brady, 1995 and references therein). Contaminated and natural aqueous near-surface crustal fluids can contain large concentrations of dissolved organic matter, and there are numerous possible interactions that may occur between these aqueous organic compounds, mineral surfaces, and dissolved metals. Organic compounds can coat mineral surfaces, enhance/hinder mineral dissolution (Herring, 199X), and enhance/hinder adsorption of dissolved metals (Tipping, 1981; Davis, 1982, 1984). While many studies recognize the importance of organic compounds on the mobility of heavy metals in crustal fluids (e.g., Reuter and Perdue, 1977; Vuceta and Morgan, 1978; Davis, 1982, 1984; Lövgren *et al.*, 1987; Lövgren and Sjöberg, 1989; Lövgren, 1991; Girvin *et al.*, 1993; Jardine *et al.*, 1993) interactions between mineral surfaces, organic compounds, and dissolved metals are still poorly understood and quantified.

An understanding of these metal-organic-mineral interactions is fundamental to better predictions of mass transport in the subsurface. Aqueous geochemical modelling enables the prediction of the mobility of chemicals on the basis of their thermodynamic properties. Geochemical modeling, assuming thermodynamic equilibrium, is an appealing approach as it requires a relatively small number of input

parameters to predict speciation. For instance, a thermodynamic model could simultaneously account for aqueous and surface speciation, precipitation and dissolution in a system, provided the equilibrium constants for the relevant reactions are known. For example, Tessier *et al.* (1996) used hydrolysis constants of metals and surface complexation reactions to describe the sorption of metals to diagenetic iron and manganese oxyhydroxides in two lakes. Thus, thermodynamic models of relevant geochemical reactions, augmented by physical flow models of groundwater, can be powerful tools for assessing mass transport in the subsurface.

The principal goal of this Master's Thesis is to determine the formation constants of surface complexation reactions (adsorption) in mixed aqueous metal-organic acid-mineral surface systems using Cd(II), citrate and corundum. Corundum ($\alpha\text{-Al}_2\text{O}_3$) occurs chiefly in crystalline rocks (e.g. granite, nepheline syenite, gneiss, mica and chlorite schist), however it is an important chemical and structural building block of geological aluminosilicate minerals contacted by groundwater, making it a useful analogue to $>\text{Al-O}$ surface complexation sites. Cd(II) is an EPA priority pollutant (Keith and Telliard, 1979) and because it forms generally weaker bonds than other heavy metals it should also be more mobile. Citrate ($\text{C}_6\text{O}_7\text{H}_8$), a trifunctional carboxylic acid was chosen because it forms strong complexes with metals and is common in soils (Huang and Violante, 1986). While citrate is not a major building block of organic substances, it can serve as an analogue for naturally-occurring or environmentally-important multifunctional organic acids. Note, however, low-molecular weight (LMW) organic acids are not perfect analogues to the more complex organic molecules. They display similar types and orientations of functional groups to

more complicated organic matter, and therefore the two types of molecules should display similar chemical behaviours. However, the effects of the physical characteristics of organic substances on metal speciation, such as electrostatic fields, hydrophobic properties, the colloidal aspect of organic matter, etc. cannot be simulated with LMW organic acids.

This thesis is composed of three chapters. In the first chapter, I present the basic concepts and assumptions relating to solute adsorption onto metal oxides. The first chapter also describes the experimental procedures, and the methodologies employed in modeling adsorption data. The second chapter is the reprint of an article published in *Geochimica et Cosmochimica Acta* (Boily and Fein, 1996) on the co-adsorption of cadmium-citrate on corundum. In this chapter, some topics of the first chapter are also discussed in greater detail. The third and last chapter is the conclusions of the thesis.

CHAPTER 1

BACKGROUND

Surface functional groups

Mineral surfaces display dangling bonds which result from incomplete crystal lattice bonding. In aqueous systems, these dangling bonds are satisfied by binding with water molecules (Davis and Kent, 1990). In general, water molecules that are coordinated to one surface cation are considered to be proton active in the pH of natural waters (e.g. Hiemstra, 1989a,b). That is, they can act as proton donor/acceptors and therefore display pH-dependent properties. Adsorption reactions that take place on metal oxides are mostly ascribed to those sites. Water molecules that are coordinated to more than one surface cation are considered to be unactive, though solutes can interact with these sites by means of chemical interactions.

Acid/base titrations of suspensions of metal oxides can be used to determine the concentration of proton active surface sites for a given aqueous composition and ionic strength. Titration curves are easily visualized with plots of H^+_{consumed} ($H_{\text{consumed}} = C_{\text{acid}} - C_{\text{base}} - 10^{\text{pH}} \cdot (\gamma_{H^+})^{-1} + K_w \cdot \gamma_{H^+} \cdot 10^{\text{pH}}$) as a function of pH. These plots show that the amount of H^+ consumed by the surface reaches a plateau at low pH, indicative of the saturation of proton active surface sites. Typical values of proton active sites are on the order of 1-2 sites per nm^2 (e.g. Lövgren *et al.*, 1990) while calculation of the site density from crystallographic considerations would yield 5-15 sites per nm^2 . Thus, only a fraction of surface cations appear to be coordinated to water molecules which display amphoteric properties. The value of H^+_{consumed} decreases with increasing pH, indicating surface deprotonation. At the $H^+_{\text{consumed}}=0$

region, titration curves display a sub-horizontal trend, indicative of a low buffering capacity. This behaviour is similar to that of diprotic acids whose buffering capacity is at its lowest when the concentrations of L^{-2} and H_2L^0 are equal. Mineral surfaces are also considered to act as diprotic acids with the following equilibrium reactions (Stumm and Morgan, 1981):



where $>Me$ refers to a metal at the mineral surface. This model will be referred as the '2pK model'. Thus the pH at which $H_{consumed}=0$ corresponds to the pH at which the concentration of $>MeOH_2^{1+}$ equals the concentration of $>MeO^{-1}$, or the pH of *zero point of charge*. This point also corresponds to the pH at which the total net charge of the surface is zero and it can coincide with the *isoelectric point*, determined by electrophoresis.

The 2pK model has been successful at modeling surface acid/base titration data, and metal ion and organic acid adsorption for a wide range of metal (hydr)oxides. While it offers a poor physical description of the surface sites, it can still be used to explain the acid/base equilibria at the mineral/water interface. Van Riemsdijk (1987) proposed that successive protonation/deprotonation steps involve two different water molecules bound to the same surface cation. This is a well established concept for the hydrolysis of cations in solution where the successive deprotonation of Al^{3+} , for example, involves the deprotonation of a different water molecule at each new protonation level: i.e. $Al(H_2O)_6^{3+} = Al(H_2O)_5OH^{2+} + H^+ = Al(H_2O)_4(OH)_2^{1+} + 2H^+$ and so on. Thus, doubly coordinated aluminum would exhibit

5 protonation levels (Fig. 4 of Chapter 2), of which only 3 are detectable in natural water pHs.

Complexation of cations and anions at the metal oxide/water interface

The acid/base properties of metal oxides, as shown by the above equilibria, indicate that positively-charged surface sites dominate in acidic conditions, and negatively-charged sites in alkaline conditions. Anions should therefore display greater affinities for mineral surfaces in acidic conditions whereas cation adsorption should be favoured under alkaline conditions (Stumm and Morgan, 1981; Stumm *et al.*, 1980). The adsorption of solutes on mineral surfaces is usually described by the association of a proton active surface site with a solute by means of electrostatic/chemical interactions. Adsorbed species also modify the electric potential of the solid/solution interface. For example, a high concentration of multifunctional organic acid anions may drastically reduce the positive surface charge at low pH, thereby reducing coulombic repulsion between aqueous cations and the surface. Cations can therefore sorb more easily either on (1) adsorbed anions or (2) directly on negatively- or neutrally-charged surface sites. For example, polyfunctional organic ligands that adsorb in low pH conditions may exhibit uncomplexed and ionized functional groups onto which cations may adsorb, giving rise to a *surface ternary complex*, i.e. >Me-Ligand-Metal (Schindler, 1990). This type of surface complex is particularly important in organic ligand-bearing fluid/rock systems and can thus play an important role on the mobility of metals.

Citrate, the ligand used in this thesis, is a trifunctional carboxylic aliphatic acid with one OH group. It could sorb to the surface of corundum as mono-, up to tetra-

dentate complexes. Surface binding modes depend the protonation of citrate in solution (and is thus pH dependent), on surface coverage, and on surface electric potential. Citrate molecules adsorbed in mono- or bi-dentate coordination display at least on free carboxylic group with which metals may bind, and thereby form a surface ternary complex. In addition, the flexibility of the citrate molecule could also allow the cadmium-citrate surface complex to reorganize itself in order to reach the highest configurational entropy. The overall stability of this surface complex however depends on the relative stability of the surface and aqueous metal-citrate complex. In this thesis, I present results of experiments for the adsorption of Cd onto corundum in the presence and absence of citrate. The adsorption of Cd and citrate is assumed to take place on proton active sites, as described above. In addition, because the structure of corundum consists of AlO_6 octahedra stacked in hexagonal close-packed coordination, with one vacant octahedron out of three, and that the vacant octahedra are not interconnected through-out the structure, I value that internal absorption of solutes within the structure cannot be possible. Also, while kinks, steps and terrasses are certainly present on the surface of corundum, their effects on Cd and citrate adsorption cannot be quantified, or even considered, with the approached employed in this thesis. The surface is assumed to be flat and devoid of these features.

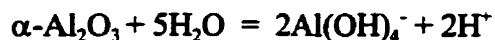
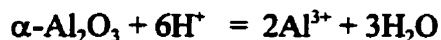
EXPERIMENTAL PROCEDURES

The adsorption of Cd and citrate on corundum (α -Al₂O₃, Aldrich Chem.) was measured as a function of pH at 25 $\pm$ 1°C. The corundum powder was washed with 10% HCl or HNO₃ and 10%NaOH. After acid and base treatment, the powder was rinsed 15 to 20 times with doubly distilled deionized water until the supernatant was at approximately pH 8.5. The solids were then dried at 70-80°C. Washing the solid minimizes the occurrence of ultrafine-grained particles which can cause anomalous aluminum dissolution during the course of the experiments. Surface area was measured by the N₂(g) BET method to be 9.3m²/g (Fein and Brady, 1995). All experiments were conducted with reagent-grade chemicals and doubly distilled deionized water.

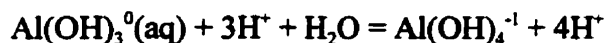
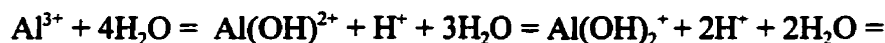
Surface titrations and adsorption experiments were carried out in Teflon bottles with N₂ gas bubbling through the solutions to purge CO₂ from the system. Temperature was controlled by placing the reaction vessel in a water bath, and the solution was mixed using a Teflon-coated stirring bar. H⁺ activity was measured, either with a gel-filled combination electrode or with a glass combination electrode with an outer reference cell of 3M KCl.

Potentiometric surface titrations were carried out with an automated titrator/autoburette assembly with HCl and NaOH titrants, standardized against K-H-Phthalate. A maximum emf drift of 0.1mV/s was allowed by the instrument between each titrant addition. Because of this poor constraint on pH stability, small dilute titrant volumes were required to ensure fast equilibration times. Because corundum

dissolves during the course of the titration, the titration curve can be influenced by dissolution and hydrolysis. In excess acid or base, the dissolution of corundum would take place as follows:



Aluminum hydrolysis would release more H^+ ions as the pH is increased:



To minimize dissolution and hydrolysis two titrations were required to cover the pH range of interest, starting approximately at the pH of the solubility minimum of aluminum hydroxide (pH=5-6) and titrating one suspension with HCl and the other with NaOH.

For the adsorption experiments, Cd, and citrate were introduced to the solution by adding a small volume of concentrated parent solutions. The solutions were allowed to equilibrate for 60 min during which the pH was continuously measured. During the course of the experiments, pH never drifted more than 1.0 pH unit (and no more than 0.1 pH unit in the last 10 minutes of the experiments) and the final pH of the experimental fluids range from 3.0 to 9.0. Two samples for each experiment were taken and filtered with a 0.1 μm cellulose nitrate membrane filter. One sample was acidified with concentrated (70%) HNO_3 to preserve Cd(II), and Al(III) and the other with concentrated NaOH (12M) to preserve and fully deprotonate the citrate for analysis. Final metal concentrations were determined with flame atomic absorption spectrometry, using standard analytical procedures. Citrate concentrations were

determined using ion chromatography, with a 200mM NaOH eluent with a flow rate of 1.1mL/min, and a 0.5N H₂SO₄ regenerant at a flow rate of 4.0mL/min. The analytical uncertainties associated with the analysis of the citrate acids is evaluated to be +/- 5% by ion . Analytical uncertainty for the determination of Cd and Al on atomic absorption spectrometry is +/-1.0%.

THERMODYNAMIC MODELING

In this thesis, adsorption reactions are quantified using measured losses of H (for the acid/base titrations), or Cd and citrate (for the adsorption experiments) from the solution as a function of pH. Equilibrium constants are calculated with the computer program FITEQL 2.0 (Westall 1982a,b).

The standard states that are employed in this study for the solid phase and for water are the pure mineral and fluid, respectively, at 25°C and 1 atm. The standard state for aqueous species is a hypothetical one molal solution which exhibits the behaviour of infinite dilution. Departures from this standard state for charged aqueous species are characterized by molal activity coefficients, calculated within FITEQL 2.0 using the Davies equation (Davies, 1938, 1962) $-\log \gamma_i = -Az_i^2 (I^{0.5}/(1+I^{0.5}) - 0.3 I)$, where γ_i is the activity coefficient for species i , A is the molal Debye-Hückel constant ($A=0.5$) and I ionic strength. Activity coefficients for neutral aqueous species are assumed to be unity. The standard state for surface complexes is a hypothetical site with zero surface potential. Deviations from standard state are due to electrostatic interactions between counterions and are corrected with the Boltzmann accumulation factor (e.g. Parks, 1990):

$$K_{int} = K_{cond} \exp\left(\frac{-F\Psi}{RT}\right)$$

where K_{int} is the ‘intrinsic’ formation constant at standard state, K_{cond} is the ‘conditional’ formation constant uncorrected for coulombic interactions, z is the charge of the surface species, F is Faraday’s constant (96485C mol⁻¹), ψ is the surface potential (in V), R is the molal gas constant, and T is the absolute temperature.

Surface potential is measured with difficulty. It is possible to measure the potential drop across the diffuse layer of the mineral/water interface by means of electrophoresis, for example. However assumptions on the location of the slipping plane do not allow electrokinetic potentials to be equal to the surface potential (Stumm and Morgan, 1981). Instead, the surface potential can be modeled using the constant capacitance model, CCM, (Schindler and Gamsjäger, 1972) by:

$$\psi = \sigma C^{-1}$$

where σ is the surface charge, C is the specific capacitance (in Fm⁻², where F=Farad=CV⁻¹). The molal surface charge is obtained by the sum of the moles of charges exhibited by the surface species. In electrostatic terms, σ is expressed by:

$$\sigma = T_{\sigma} F s^{-1} a^{-1}$$

where T_{σ} is the total surface charge, F is Faraday’s constant, s is the specific surface area (m² g⁻¹), and a is the solid concentration (g l⁻¹). The surface potential is then calculated by:

$$\psi = T_{\sigma} F s^{-1} a^{-1} C^{-1}$$

The CCM describes the double layer as a parallel plate condenser, separated by a distance δ :

$$C = \epsilon_m \epsilon_0 / \delta^{-1}$$

where ϵ_m and ϵ_0 are the relative permittivities of the compact layer and vacuum, respectively. The value of the capacitance is controlled by the dominant electrolyte ions that bind to the surface because the size of the hydrated electrolytes influences the thickness of the double layer. For example, non-specific adsorption of the hydrated Na ion will result in a higher theoretical C than the hydrated Cl ion. And because adsorption of Na and Cl are pH dependent, the value of C is also pH dependent. However, for practical purposes, it is considered to be constant. Thus, it becomes appealing to calculate the capacitance with above equations. However, the value of the dielectric constant of the mineral water interface can range from 5 to 78, making the choice of a suitable capacitance difficult.

Instead, the value of C is found by trial and error when using the titration data to optimize for the acid/base properties of the surface, and for the total surface site. The chosen C should be the one that provides the best fit to the data, but must also be 'substantiated by the chemist's intuition' (Westall, 1982b). Decreasing C increases the calculated surface potential and thereby the electrostatic repulsion between the surface and ions of same sign. The concentration of proton active surface sites can be controlled both by (1) the availability of singly-coordinated water molecules (Davis and Kent, 1990), and (2) coulombic repulsion between a positive surface site and H^+ . The adsorption of anions (such as Cl^-) reduces surface potential (e.g. Gunneriusson, 1994) and can induce the protonation of additional sites at low pH. Thus, provided singly-coordinated water molecules are widespread on the surface of corundum, one could assume that surface potential can control surface protonation. This could

explain why only a fraction of the crystallographically available sites for mineral suspensions in quasi-indifferent electrolytes (e.g. NaClO_4 , NaNO_3 or NaCl) are in fact proton active. The correct capacitance must therefore reflect the maximum capacity of a surface to take up protons at a given ionic strength and fluid composition. The chosen capacitance must provide a good fit to the data but must also yield reasonable values of total surface sites. If one obtains a value for total surface sites of, say, 0.1 moles/l for a coarse-grained suspension, then the 'chemist's intuition' must come into play. The same holds if the obtained capacitance is out of the range permitted by theoretical considerations.

In the CCM, all adsorbed species are assumed to be in inner-sphere coordination with the surface. The CCM ignores outer sphere complexes and the diffuse layer. Thus, the surface potential in the CCM decreases linearly away from the surface. Because of these limited views, formation constants calculated with the CCM pertain strictly to the ionic strength of interest. In addition, the values of the formation constants should also pertain only to the medium used (in this thesis NaCl) because the effects of adsorbed electrolyte ions on surface potential are not distinctively accounted for in the CCM. Nonetheless, the CCM is equally good at modelling adsorption and acid/base titration data for a constant ionic strength as any more complicated model (e.g. Westall and Hohl, 1980). The CCM model is therefore used in this thesis because the experiments were conducted at constant ionic strength.

CHAPTER 2

Experimental study of cadmium-citrate co-adsorption onto α -Al₂O₃

a copy of the paper published in
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Experimental study of cadmium-citrate co-adsorption onto α - Al_2O_3

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Abstract—An experimental investigation of metal-organic co-adsorption was conducted using cadmium and citrate in the presence of corundum. The experiments were performed in the pH range 3.0 to 10.0 in a 0.01 M NaCl matrix with citrate:Cd ratios of 0.00 and 10.00. The presence of citrate enhances cadmium adsorption between pH 3.5 and 7.2, and reduces it above pH 7.2. The results from the experiments provide constraints on the thermodynamic properties of the surface complexes. We model the adsorption of Cd by quantifying the competition between aqueous CdCit^- and the surface species, $>\text{AlCitCd}^+$, $>\text{AlOCd}^+$, and $>\text{AlOCdCl}^+$. The experimentally determined equilibrium constants provide a means to predict Cd mobilities in groundwater systems by describing the relative stabilities of surface and aqueous metal-organic complexes as a function of metal-to-ligand and solute-to-sorbent ratios.

1. INTRODUCTION

Mineral surface complexation can control the mobility of dissolved metals in natural and contaminated water-rock systems. The co-occurrence of dissolved metals and organic compounds is widespread in both natural waters and in contaminated groundwater systems (Leenheer et al., 1976; Girvin et al., 1993). In these systems, organic ligands can strongly influence speciation of dissolved metals (e.g., Reuter and Perdue, 1977; Davis and Leckie, 1978a; Vuceta and Morgan, 1978; Davis, 1982, 1984; Lövgren et al., 1987; Lövgren and Sjöberg, 1989; Lövgren, 1991; Girvin et al., 1993; Jardine et al., 1993) and can, thus, play a determining role in controlling the mobility of dissolved metals. Many investigators have focused on the adsorption of either heavy metals (e.g., Huang and Stumm, 1973; Hohl and Stumm, 1976; Davis and Leckie, 1978b; Gunneriusson et al., 1994) or organic acids (e.g., Kummert and Stumm, 1980; Cambier and Sposito, 1991; Violante et al., 1991; Fein and Brady, 1995) on metal oxides and their polymorphs. Few studies, however, have applied equilibrium thermodynamics to quantify adsorption in mixed metal-organic systems.

Aqueous organic ligands in contaminated groundwater can either promote or inhibit metal adsorption on mineral surfaces. For instance, under acidic conditions, metal oxide surface sites are positively charged (Stumm et al., 1980) and adsorption of cations does not generally occur. However, multifunctional organic ligands that adsorb onto oxide surface sites in acidic to neutral conditions can change the surface charge from positive to neutral to negative, thereby creating adsorption sites for metal cations (Davis and Leckie, 1978a; Tipping 1981; Tipping et al., 1983). Conversely, under neutral to basic conditions, organic ligands do not adsorb as extensively as in acidic conditions. Under those conditions, organic ligands can compete with the negatively charged surface sites for the available metals in solution, and thereby enhance metal mobilities.

In this study, we examine the mechanisms and the extent of metal-organic co-adsorption, using citrate, cadmium, and α - Al_2O_3 (corundum). Citric acid, a tricarboxylic acid, is present in some contaminated groundwater systems (e.g., the Hanford site, USA; Zachara et al., 1993). In addition, citrate leaching of heavy metal from contaminated soils has been proposed as a remediation technique (Oak Ridge National Laboratory, 1993). A better understanding of the effects of citrate on metal adsorption is, therefore, crucial for understanding the speciation of metals in both natural and contaminated systems. Cadmium was chosen not only because it is an EPA priority pollutant (Keith and Telliard, 1979), but also because organic ligands should strongly influence its adsorption properties, especially under acid conditions. Cadmium typically forms weaker aqueous and surface complexes than do other heavy metals, and therefore Cd should exhibit a higher mobility under slightly acidic conditions. Aluminum oxide was used in the adsorption experiments because aluminum-(hydr)oxide and aluminosilicate minerals are common, and, along with Fe-(hydr)oxides, are among the most reactive surface sites contacted by surface and ground waters. The objectives of the experimental study were to document the nature and extent of metal-organic co-adsorption, to determine the conditions under which adsorption competes with aqueous metal-organic complexation, and to quantify the interactions using equilibrium thermodynamics.

2. EXPERIMENTAL PROCEDURES

The adsorption of cadmium and citrate onto α - Al_2O_3 was measured at 25°C in a 0.01 M NaCl electrolyte as a function of pH at citrate:Cd ratios of 0.00 and 10.00, and at a corundum:solution ratio of 1:10 (by weight). Reagent-grade α - Al_2O_3 was successively washed with 10% HCl or HNO₃ and 10% NaOH. After acid and base treatment, the powder was rinsed 15 to 20 times with doubly distilled deionized water until the supernatant was at approximately pH 8.0–8.5. The washed solids were then oven-dried at 70–80°C. Washing the solids minimizes the occurrence of ultrafine-grained particles which can cause anomalous aluminum dissolution during the course of the experiments. Surface area of the washed corundum was determined by the BET method to be 9.3 m²/g (Fein and Brady,

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1995). Reagent-grade chemicals and doubly distilled deionized water were used in all the experiments.

Surface titrations and adsorption experiments were carried out in Teflon bottles with N_2 gas bubbling through the experimental solutions to purge CO_2 from the system. Each reaction bottle contained initial suspensions of 5.0 g of washed corundum in 50 mL of the electrolyte solution for the titration experiments, and 10.0 g in 100 mL for the adsorption experiments. Temperature was controlled by placing the reaction vessel in a water bath, and the solution was mixed using a Teflon-coated stirring bar. H^+ activity was measured, in the adsorption experiments, with a gel-filled combination electrode and, in the surface titration, with a glass combination electrode with an outer reference cell filled with 3 M KCl.

The surface titrations were conducted with an automated titrator/autoburette assembly with HCl and NaOH titrants, standardized against K-H-Phthalate. A maximum pH stability of 0.1 mV/s change (the maximum stability allowed by the instrument) was attained before each titrant addition. Due to this constraint, addition of small volumes of dilute titrant were required to ensure fast equilibration times between each titrant addition. Because corundum can dissolve during the course of the titrations, the titration curve can be influenced by corundum dissolution and aqueous Al hydrolysis. Titrations carried out from acidic to basic conditions should display a strong dependance on metal hydrolysis because aqueous Al produced by acid dissolution would hydrolyze as pH increases. To minimize dissolution and hydrolysis, two titrations were required to cover the pH range of interest. The first titration was carried out with the HCl titrant and covered the pH range from 5.9 to 2.9 and the second, using a new suspension and the NaOH titrant, covered the pH ranging from 4.1 to 10.7.

For the adsorption experiments, cadmium and citrate were introduced in a 0.01 M NaCl solution by adding a small volume of a concentrated cadmium-citrate solution. The initial cadmium and citrate concentrations in the reaction bottle were 10^{-4} M and 10^{-3} M, respectively. Another set of experiments was conducted in the same electrolyte concentration and solid:solution ratio using citrate-free solutions in which the initial Cd concentration was also 10^{-4} M. The duration of each experiment was 60 min, during which the pH of the solution was controlled by manually pipetting 1.0 M HCl or NaOH into the experimental solution when the pH readings drifted more than 0.1 pH unit from the desired value. Final ionic strength, however, was never increased more than two values greater than 0.015. The kinetics of the adsorption reactions were determined by conducting repeat experiments, varying the duration time between 5 and 120 min. These experiments (conducted at pH 4.0, 6.5 and 8.0) show that the concentrations of citrate and Cd in solution remain constant beyond 60 min of experimentation time. Therefore, a run duration of 60 min is sufficient for the adsorption reactions to equilibrate, but it is short enough not to significantly alter the ionic strength or speciation of the solution due to the addition of buffering agents or by extensive corundum dissolution. In fact, aluminum concentrations of the experimental fluids were all below the detection limit (10^{-14} M Al) of the spectrometer, indicating that Al-citrate complexation did not significantly affect the Cd or the citrate speciation in the experiments.

At the end of each experiment, two samples were extracted from each reaction bottle and filtered through 0.45 μ m cellulose nitrate membranes; 0.1 mL of concentrated HNO_3 (70%) was added to one of the samples for Cd and Al analyses and, 0.1 mL of 12 M NaOH was added to the other for citrate analysis and storage. Citrate concentrations were determined using ion chromatography, with a 200 mM NaOH eluent with a flow rate of 1.1 mL/min, and a 0.5 N H_2SO_4 regenerant at a flow rate of 4.0 mL/min. Cadmium and aluminum concentrations were determined by flame atomic absorption spectrometry. Analytical uncertainties are $\pm 5\%$ for the ion chromatograph and $\pm 1\%$ for the atomic absorption spectrometer. Because the kinetics of adsorption are much faster than the dissolution of corundum, adsorption reactions reached equilibrium before the dissolution reaction could proceed to a significant extent.

3. RESULTS

3.1 Potentiometric Titration

The titration curve of a suspension of 100 g/L of $\alpha-Al_2O_3$ in 0.01 M NaCl is shown in Fig. 1, which depicts the net

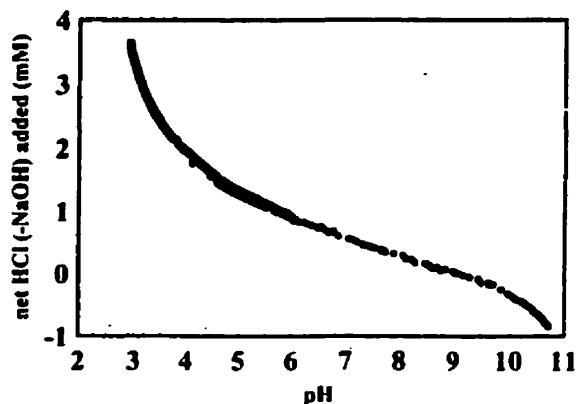


FIG. 1. Titration curve of a suspension of 100 g/L corundum in a 0.01 M NaCl solution.

proton molality added to the solution as a function of pH. Acidity caused by carbonic acid was assumed to be negligible because the experiments were all conducted in a nitrogen atmosphere. The titration curve intersects the no net acid line ($y = 0$ in Fig. 1) between pH 9.0 and 9.1, yielding a pH_{nc} which is in excellent agreement with experimental and theoretical studies by Davis and Kent (1990) and Sverjensky (1994), respectively.

3.2. Cadmium and Citrate Adsorption

The percent of Cd adsorbed onto corundum as a function of pH, is shown for the citrate-free experiments, and for the citrate-bearing experiments, in Fig. 2. The percent of citrate adsorbed as a function of pH for the mixed Cd-citrate experiments is shown in Fig. 3. The experimental results are compiled in Appendix A. For each experiment, the concentrations of adsorbed Cd and citrate were calculated by subtracting measured final concentrations from the initial concentrations. The solubility of solid $\beta-Cd(OH)_2$ in a citrate-free solution is 10^{-14} M Cd at pH 9.0, and decreases to 10^{-16} M Cd at pH 10.0 (Baes and Mesmer, 1976). Our calculations indicate that in the presence of 10^{-3} M of citrate, the solubility of solid $\beta-Cd(OH)_2$ at pH 9.6 is 10^{-14} M Cd. Therefore, the citrate-free adsorption experiments and the citrate-bearing experiments (both with 10^{-4} M Cd) were conducted at pH values below 9.0 and 9.6 (except for one experiment at pH 10.0), respectively, yielding experimental solutions that were never supersaturated with respect to $\beta-Cd(OH)_2$. Furthermore, since the experimental solutions were, in principle, free of dissolved CO_2 , $CdCO_3(s)$ precipitation was assumed to be insignificant.

The adsorption of Cd in the citrate-free system (Fig. 2a) is characterized by an adsorption edge ranging from 5% adsorption at pH 4.0 to 99% adsorption at pH 8.3. The system containing citrate (Fig. 2b), shows enhanced Cd adsorption relative to that in the citrate-free system under acidic conditions, but less adsorption than in the citrate-free system under more basic conditions. In Fig. 3, all of the citrate adsorbs at pH values less than 6.0, but the fraction of adsorbed citrate

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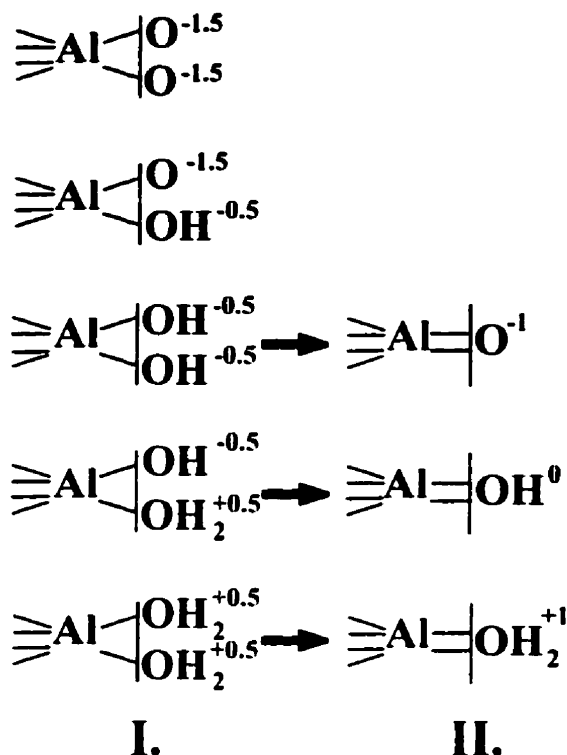


FIG. 4. Surface alumina coordination models at the 100 crystal plane at the α -corundum/water interface (100 crystal plane). Diagram I shows five doubly coordinated surface alumina with different degrees of protonation (each line surrounding an Al atom represents one Al-O bond). Diagram II shows the equivalent species commonly used in the literature, represented as a single Al-O bond (after Van Riemsdijk et al., 1987).

Al sites should display five protonation levels (Fig. 4), three of which are likely to exist under the pH conditions of interest. Hiemstra et al. (1989a,b) argue that complete deprotonation of an oxygen in these groups can only occur under extremely alkaline conditions. Therefore, under the pH conditions of the experiments, $>\text{AlO}_2^-$ and $>\text{Al}(\text{O})(\text{OH})^-$ will not be significant. The remaining three groups, $>\text{Al}(\text{OH})_2^+$, $>\text{Al}(\text{OH})(\text{OH}_2)^0$, and $>\text{Al}(\text{OH})_2^+$ can be represented as $>\text{AlO}^-$, $>\text{AlOH}^0$, and $>\text{AlOH}_2^+$, respectively (Van Riemsdijk et al., 1987). Therefore, reactions 1 and 2 may reasonably be used to model the acid/base behaviour of the corundum/water interface.

5. THERMODYNAMIC MODELING

5.1. Data Treatment

Equilibrium constants for surface complexation reactions were calculated with the computer program FITEQL 2.0 (Westall, 1982a,b) using the constant capacitance model (Schindler and Gamsjäger, 1972). The standard states that are employed in this study for the solid phase and for water are the pure mineral and fluid, respectively, at 25°C and 1

atm. The standard state for aqueous species is a hypothetical one molal solution which exhibits the behaviour of infinite dilution. Departures from this standard state for charged aqueous species are characterized by molal activity coefficients, calculated within FITEQL 2.0 by the Davies equation (Davies, 1938, 1962). Activity coefficients for neutral aqueous species are assumed to be unity. Because the addition of NaOH and HCl during the course of the experiments increased ionic strength to, on average, 0.013 (never more than 0.015), we model the experiments using a constant 0.013 M NaCl electrolyte. The standard state for surface complexes is a hypothetical site with zero surface potential. Deviations from standard state due to electrostatic interactions between counterions and the surface are corrected with the Boltzmann accumulation factor (e.g., Parks, 1990).

5.1.1. Equilibria at the corundum/water interface

In this study, we test the ability of a number of different possible surface complexation reactions to account for the data. References to the stability constant of $>\text{AlO} \pm \text{H} \pm \text{Cd} \pm \text{citrate} \pm \text{Cl} \pm \text{OH}$ surface complexes refer to

$$a > \text{AlOH}^0 + b\text{Cd}^{+2} + c\text{Cit}^{-3} + d\text{Cl}^{-1} + e\text{H}_2\text{O} = \\ (>\text{AlO}(\text{H})_{11-11})_s\text{Cd}_b\text{Cit}_c\text{Cl}_d\text{OH}_e^{2b-3c-d-e} \\ + (e+f)\text{H}^+, \quad (3)$$

where binding of a cation to $>\text{AlO}^{-10}$ necessarily implies that a bidentate surface complex is being formed. For $>\text{Al} \pm \text{H} \pm \text{Cd} \pm \text{citrate}$ we write

$$a > \text{AlOH}^0 + b\text{Cd}^{+2} + c\text{Cit}^{-3} + d\text{H}^+ = \\ >\text{Al}_a\text{H}_{a-11}\text{Cd}_b\text{Cit}_c\text{OH}_{c-11-2b-1}^{2b-3c-1} + \text{H}_2\text{O}, \quad (4)$$

The fit parameter that is calculated by FITEQL 2.0, $V(Y)$, is used as a criterion for determining which reaction or reactions best fit the data. For each data point, FITEQL calculates Y , the error in the mass balance (the difference between experimental and calculated values). The weighted sum of squares of the error is normalized accounting for the number of data points, n_p , the number of chemical components for which both total and free concentrations are known, n_n , and the number of adjustable parameters (i.e., formation constants and total concentration of components), n_a , to give the overall variance, $V(Y)$, in Y :

$$V(Y) = \frac{\sum \left(\frac{Y}{S_y} \right)^2}{n_p \cdot n_n - n_a},$$

where S_y is the default experimental error given by FITEQL 2.0 (Westall, 1982b, p. 62). According to Westall (1982b), a good fit to the data should yield a $V(Y)$ value between 0.1 and 20. In this study, the species combinations chosen to fit the experimental data are those that yield the lowest $V(Y)$ values.

5.1.2. Equilibria in solution

The values of the equilibrium constants for the aqueous complexation reactions at 25°C used in the calculations are

Table 1. Formation constants of aqueous species (I=0M, 25°C)

	log K
$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{CdOH}^{+1} + \text{H}^{+}$	-10.1
$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2^0 + 2\text{H}^{+}$	-20.3
$\text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^{-1} + 3\text{H}^{+}$	-31.7
$\text{Cd}^{2+} + \text{Cl}^{-} \rightleftharpoons \text{CdCl}^{+1}$	2.0
$\text{Cd}^{2+} + 2\text{Cl}^{-} \rightleftharpoons \text{CdCl}_2^0$	2.6
$\text{Cit}^{3-} + \text{H}^{+} \rightleftharpoons \text{HCit}^{2-}$	6.4
$\text{Cit}^{3-} + 2\text{H}^{+} \rightleftharpoons \text{H}_2\text{Cit}^{-1}$	11.2
$\text{Cit}^{3-} + 3\text{H}^{+} \rightleftharpoons \text{H}_3\text{Cit}^0$	14.3
$\text{Cit}^{3-} + \text{Na}^{+} \rightleftharpoons \text{NaCit}^{2-}$	1.3
$\text{Cit}^{3-} + \text{Cd}^{2+} \rightleftharpoons \text{CdCit}^{-1}$	5.9 ^a
$\text{Cit}^{-1} + \text{Cd}^{2+} + \text{H}^{+} \rightleftharpoons \text{CdHCit}^0$	10.0 ^b
$\text{Cit}^{-1} + \text{Cd}^{2+} + 2\text{H}^{+} \rightleftharpoons \text{CdH}_2\text{Cit}^{+1}$	13.5 ^b
$2\text{Cit}^{-1} + \text{Cd}^{2+} \rightleftharpoons \text{Cd}(\text{Cit})_2^{-4}$	5.3
$\text{Na}^{+} + \text{Cl}^{-} \rightleftharpoons \text{NaCl}^0$	-0.8
$\text{Na}^{+} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH}^0 + \text{H}^{+}$	-14.2
$\text{H}^{+} + \text{Cl}^{-} \rightleftharpoons \text{HCl}^0$	-0.7
$\text{H}^{+} + \text{OH}^{-} \rightleftharpoons \text{H}_2\text{O}$	14.0

All values are from Martell and Smith (1976a,b) and Smith and Martell (1982). The reactions were rewritten according to the formalism imposed by FITEQL 2.0 and the values of the formation constant were recalculated accordingly.

a. Re-evaluated (see text and Table 2)

b. These formation constants are from experiments conducted at 20°C (Smith and Martell, 1982).

those compiled by Martell and Smith (1976a,b) and Smith and Martell (1982) corrected to $I = 0$ M and presented in Table 1. The formation constant for the reaction $\text{Cd}^{2+} + \text{Cit}^{3-} = \text{CdCit}^{-1}$, given by Martell and Smith (1976a) is from the experiments of Treumann and Ferris (1958), who measured the stability of the aqueous CdCit^{-1} complex at different ionic strengths using a potentiometric technique. Treumann and Ferris (1958) extrapolated the apparent equilibrium constants at finite ionic strengths (from 0.039 to 0.195 molal) to infinite dilution using a linear Debye-Hückel relationship, $\log \gamma_i = -6A'\sqrt{I}$ (where A' is the molal Debye-Hückel constant, and I represents the ionic strength) to obtain a value of 5.35. We have re-evaluated the data of Treumann and Ferris (1958), using the Davies equation with a 0.3 I term (Davies, 1938, 1962) and obtain a value of 5.9 for the log stability constant of CdCit^{-1} (Table 2). We use this recalculated value in our calculations.

Neglecting mineral surface species, the two dominant aqueous Cd species in the citrate-free system are Cd^{2+} and CdCl^{+1} . In the aqueous citrate-bearing system, the dominant Cd species are Cd^{2+} , below pH 4.4, and CdCit^{-1} above this value. The species CdHCit^0 and $\text{CdH}_2\text{Cit}^{+1}$ together constitute less than 11% of the total Cd, but only below pH 4.5. Above this value, the concentrations of these two species are insignificant. The major citrate species are H_3Cit^0 , $\text{H}_2\text{Cit}^{-1}$, HCit^{2-} , Cit^{3-} , CdCit^{-1} , and NaCit^{2-} . It should also be noted that the formation constants for the species CdHCit^0 and $\text{CdH}_2\text{Cit}^{+1}$ are reported for experiments con-

Table 2. logK CdCit^{-1} (I=0)

I	logK ^a	logK ^b
0.195	5.0	5.8
0.031	4.8	5.8
0.023	4.9	5.8
0.027	4.9	5.8
0.027	4.9	5.9
0.032	4.8	5.9
0.037	4.8	5.9
0.039	4.8	5.9
mean logK ^b : 5.9		

a. Conditional K (at finite I) reported from the experiments of Treumann and Ferris (1958).

b. Recalculated K (I=0) using the Davies equation (see text).

ducted at 20°C (Smith and Martell, 1982). No attempt has been made to extrapolate these values to 25°C because the enthalpies of these reactions are not available.

5.2. Acid-Base Properties of α -Al₂O₃

The acidity constants of the surface functional groups were evaluated using the molalities of the titrants and activities of free H^{+} as constraints. The first and second acidity constants and the total surface site concentration were calculated simultaneously using a capacitance of 1.05 F/m² (Table 3). This value yields the best fit to the experimental data. The values of the logarithm of the calculated first and second acidity constants are 7.4 and -10.7, respectively, yielding a calculated pH_{pzc} of 9.1. This value is in good agreement with both theoretical and experimental determinations of the pH_{pzc} of α -Al₂O₃, which give values of 9.37 (Sverjensky, 1994) and 9.1 (Davis and Kent, 1990), respectively.

5.3. Cadmium Adsorption in the Citrate-Free System

Figure 2a illustrates that the Cd adsorption edge can be divided into two distinct regions. At the high pH end (at pH

Table 3 Equilibria at α -Al₂O₃/water interface

	log K	V(Y)
$>\text{AlOH}^0 + \text{H}^{+} \rightleftharpoons >\text{AlOH}_2^{+}$	7.4	51.4
$>\text{AlOH}^0 \rightleftharpoons >\text{AlO}^{-} + \text{H}^{+}$	-10.7	

$\kappa=1.05\text{F/m}^2$; $[>\text{AlOH}_2^{+}]=2.7\text{mM}$;
 $S^{\circ}=9.3\text{m}^2/\text{g}$; $\alpha\text{-Al}_2\text{O}_3=100\text{g/l}$

a. Capacitance

b. Total surface sites (calculated)

c. Surface area (Fein & Brady, 1995)

values greater than 6.5), the adsorption edge is steep, while at the low pH end (below pH 6.5), the slope is more shallow. This change in slope suggests that more than one Cd surface complex is important in the system. Surface complexation reactions which liberate protons exhibit steep adsorption edges due to a strong pH dependence of the stability of the complex. Conversely, surface complexation reactions that do not liberate protons yield adsorption curves with shallow slopes. In acidic conditions, the Cd surface complexes require a low charge in order to avoid strong electrostatic repulsion with the dominant $>\text{AlOH}_2^+$ surface sites.

We tested all reasonable Cd surface species combinations by determining their ability to account for the observed adsorption behaviour. The results of these tests are reported in Appendix B. The species $>\text{AlOCD}^+$, $>\text{AlOHCd}^{2+}$ and $>\text{AlOCD}^{2+}$ either taken alone, or in combination, provide large misfits to the experimental data. On the other hand, some of the surface cadmium chloride complexes yield significantly lower $V(Y)$ values. Chloride nonspecific adsorption lowers charge at the oxide/water interface (Gunneriusson, 1994; Gunneriusson et al., 1994) and, as a result, cation adsorption may be promoted in chloride-bearing fluids. In fact, Gunneriusson (1994) measured more Cd adsorption onto goethite in NaCl than in NaNO_3 , and he modeled the system with the species $>\text{FeOHCdCl}^+$, $>\text{FeOHCd}^{2+}$, $>\text{FeOCDCl}^+$, and $>\text{FeOCD}^+$. As shown in Appendix B, any of the species combinations not involving $(>\text{AlOH})_2\text{CdCl}_2^0$ yield $V(Y)$ values larger than 20. Using the species $(>\text{AlOH})_2\text{CdCl}_2^0$, instead of $>\text{AlOHCdCl}_2^0$, significantly improves the fit to the data. This species is the only one that provides a good fit to the low pH adsorption data. It may be regarded as a bidentate CdCl_2^0 complex onto two adjacent $>\text{AlOH}^0$ sites (Fig. 5). The complex CdCl_2^0 may form due to the lower dielectric constant of water at the mineral/water interface (Sposito, 1984, p. 70). Conversely, this species may represent the binding of Cd onto two adjacent $-\text{OH}^{0.5}$ groups from two adjoining $\text{Al}(\text{OH})(\text{OH}_2)^0$ sites (equivalent of AlOH^0) sites, coupled with Cl nonspecific adsorption on the $-\text{OH}_2^{0.5}$ groups.

The five species combinations that provide the best fits to the data are reported in Table 4. With $(>\text{AlOH})_2\text{CdCl}_2^0$, the species $>\text{AlOCD}^+$, $>\text{AlOHCd}^{2+}$, and $>\text{AlOCDCl}^+$, either taken alone or in pairs, equally fit the whole adsorption edge. The data from the citrate-free system are not sufficient to discriminate between the possibilities. However, the citrate-bearing system provides additional constraints and, for reasons explained below, species combination D (Table 4) is the chosen model.

5.4. Cadmium Adsorption in Citrate-Bearing Systems

The experiments indicate that the presence of citrate enhances Cd adsorption under acidic conditions, most likely through the formation of a Cd-citrate ternary surface complex. In quantifying the stability of the ternary complex, we must consider the presence of other surface citrate complexes. The stabilities of the surface citrate and surface Cd-citrate complexes are simultaneously determined sequentially using the values of the stability constants for the five species combinations that best fit the citrate-free system (Ta-

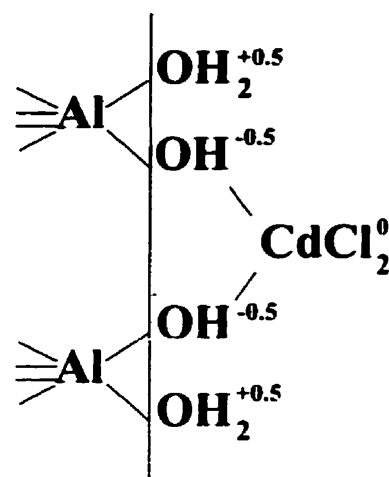


FIG. 5. Schematic representation of the complex $(>\text{AlOH})_2\text{CdCl}_2^0$. (Each line surrounding an Al atom represents one Al-O bond.)

ble 4). As indicated in Appendix A, not all the samples were analyzed for citrate. Because of the consistent trend in citrate adsorption between pH 3.0 and 6.0 (more than 10^{-10} M adsorbed), we interpolated these results for the data points in that range so that the corresponding Cd adsorption data could be used for thermodynamic modeling. The samples with pH values above 6.0 that were not analyzed for citrate were not used to constrain the thermodynamic parameters.

One possibility for the stoichiometry of the Cd-citrate ternary surface complex is $>\text{AlOCDCit}^{2-}$. However, FITEQL does not converge using this stoichiometry, indicating an inability to account for the Cd-citrate adsorption data. The other reasonable stoichiometry for the ternary complex is $>\text{AlCitCd}^0$. The results of the calculations involving the Cd-citrate experimental data, using $>\text{AlCitCd}^0$ as the ternary complex, are reported in Table 5. All five species combinations that fit the citrate-free Cd adsorption edge (denoted as species combination A, B, C, D, and E) were sequentially used to fit the citrate-bearing Cd adsorption data. We obtain a reasonable fit to the data using $>\text{AlCitCd}^0$ with both $>\text{AlCit}^{2-}$ and $>\text{AlCitH}^+$, as the complexes representing adsorbed citrate (Figs. 2b and 3, Table 5). Including the species $>\text{AlH}_2\text{Cit}^0$, $>\text{AlHCitCd}^{+1}$, or $>\text{AlH}_2\text{CitCd}^{+2}$ with $>\text{AlCitCd}^0$, $>\text{AlCit}^{2-}$, and $>\text{AlHCit}^+$ does not significantly improve the fit to the data. The best-fitting curves from models A, B, C, and D in the citrate-bearing system are shown in Fig. 2b. Model D best accounts for the Cd and citrate adsorption data, yielding a $V(Y)$ value of 16.0. The $V(Y)$ values for the models A, B, and C are 23.7, 18.1, and 21.5, respectively (model E fails to converge). The chosen model is reported in Table 6. Our model indicates that the ternary complex $>\text{AlCitCd}^0$ dominates Cd surface complexation at pH values less than 7.9, and that $>\text{AlOCD}^+$ and $>\text{AlOCDCl}^+$ dominate above 7.9. The species $(>\text{AlOH})_2\text{CdCl}_2^0$, which was required in order to account for the low pH adsorption data in the citrate-free system,

Table 4. Surface speciation modeling (citrate:Cd=0.0)

	log K	V(Y)
A. 110000 >AlOHcd ²⁺	5.4	14.6
210200 (>AlOH) ₂ CdCl ₂ ⁰	9.4	
B. 110001 >AlOCd ⁺	-2.6	14.9
210200 (>AlOH) ₂ CdCl ₂ ⁰	9.5	
C. 110101 >AlOCdCl ⁰	-1.7	13.9
210200 (>AlOH) ₂ CdCl ₂ ⁰	9.4	
D. 210200 (>AlOH) ₂ CdCl ₂ ⁰	9.4	14.6
110001 >AlOCd ⁺	-3.4	
110101 >AlOCdCl ⁰	-1.7	
E. 210200 (>AlOH) ₂ CdCl ₂ ⁰	9.4	15.2
110000 >AlOHcd ²⁺	5.3	
110001 >AlOCd ⁺	-3.3	

The listed species combinations are the ones that best account for the observed adsorption (A, B and C are taken from Appendix II). The numbers preceding each species correspond to the stoichiometric coefficients denoted by the letters a, b, c, d, e and f of equation 3. For each species combination listed, the formation constants for the complexes have been simultaneously determined. The calculations yield a formation constant for that complex and the variance, V(Y), associated with the calculated fit to the data.

becomes insignificant in the presence of citrate. Cambier and Sposito (1991) also modeled the adsorption of citrate on pseudo-boehmite with a constant capacitance model and obtained constants for the surface species >AlCit⁻² and >AlHCit⁻¹ ($10^{12.80}$ and $10^{17.71}$, respectively) that are in good agreement with those presented in Table 5.

6. DISCUSSION

Aqueous metal-organic complexation can successfully compete with surface metal-organic complexation, even at low pH, whenever the concentration of aqueous organic anion overwhelms the capacity of the surface to adsorb it. Figure 6 depicts Cd adsorption edges that are calculated for

Table 5. Surface speciation modeling (citrate:Cd=10.0)

	A	B	C	D	E
log K(1111 >AlCitCd ⁰)	16.2	16.8	17.0	16.8	no conv.
log K(1011 >AlCit ⁻²)	13.3	13.5	13.6	13.5	
log K(1012 >AlHCit ⁻¹)	17.7	18.0	18.2	18.0	
V(Y)	23.7	18.1	21.5	16.0	

The four numbers preceding each species correspond to the stoichiometric coefficients, denoted a, b, c, and d, of equation 4. The letters A, B, C, D and E refer to the species combinations that match the data for the citrate free system (listed in Table 4) and are used to model the data of the citrate-bearing experiments. The models A, B, C and D all yield similar formation constants for the species >AlCitCd⁰ but do not equally fit the data. Model D is the chosen model because it provides the best statistical fit. 'no conv.' means that the optimization procedure cannot converge.

Table 6. Chosen Model

	log K
210200 (>AlOH) ₂ CdCl ₂ ⁰	9.4
110001 >AlOCd ⁺	-3.4
110101 >AlOCdCl ⁰	-1.7
1111 >AlCitCd ⁰	16.8
1011 >AlCit ⁻²	13.5
1012 >AlHCit ⁻¹	18.0

The numbers preceding the three first species correspond to the stoichiometric coefficients denoted by the letters a, b, c, d, e and f of equation 3; those of the following three species are for letters a, b, c, and d of equation 4.

systems that contain various citrate: Cd ratios at a constant Cd concentration of 10^{-4} M. The figure shows different adsorption plateaus for each concentration of citrate that is considered. The adsorption plateau represents the balance between the stabilities of the aqueous CdCit⁻¹ complex and the surface complex >AlCitCd⁰.

With increasing citrate concentration, both enhancement of Cd adsorption and aqueous competition increase relative to Cd adsorption in the citrate-free system. That is, as citrate concentration increases, the Cd adsorption edge shifts to lower pH values, indicating increased formation of >AlCitCd⁰. However, this is accompanied by a decrease in the level of the adsorption plateau as aqueous Cd-citrate complexation increasingly competes with surface Cd-citrate complexation. The adsorption enhancement is limited by the amount of citrate that can adsorb onto the surface. For instance, at a citrate concentration of 10^{-2} M (citrate:Cd ratio of 100) the surface sites are saturated with adsorbed citrate,

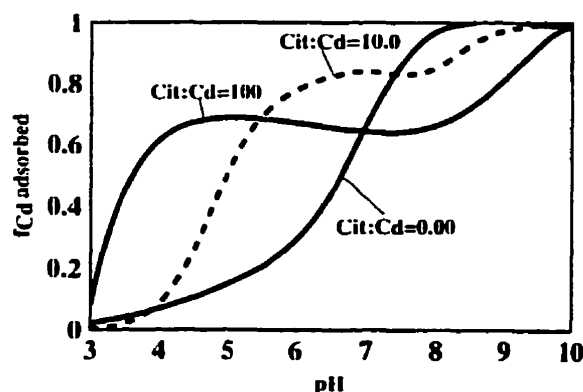


Fig. 6. Calculated extent of Cd adsorption as a function of pH at citrate:Cd ratios of 0.00, 10.0 and 100 (total Cd = 10^{-4} M) for a corundum suspension of 100 g/l and a 0.013 M NaCl electrolyte.

and at higher citrate concentrations, additional adsorption of citrate, and thus additional $>AlCitCd^0$ formation, is not possible. Once the concentration of citrate overwhelms the capacity of the surface to adsorb it, excess citrate remains in solution and is available to form aqueous $CdCit^-$, which then competes with the surface for the available Cd^{+2} . This discussion however, does not take into account the effects of aqueous Al-citrate complexation that arise from enhanced mineral dissolution due to the high concentrations of citrate. Nevertheless, this example illustrates the influence of ligand-to-metal ratios on the extent of co-adsorption of aqueous $CdCit^{-1}$ onto aluminum surface sites. These mechanisms should also pertain, at least qualitatively, to any fluid-rock system containing strongly complexing multifunctional organic acid anions, such as humic or fulvic acids.

7. CONCLUSION

Citrate exerts two opposing effects on the adsorption of Cd. At low pH values, the formation of the ternary surface complex $>AlCitCd^0$ enhances the adsorption of Cd onto the surface. Conversely, at higher pH values, the Al surface sites deprotonate, less citrate can adsorb, and $>AlOCd^+$ and $>AlOCdCl^0$ become more stable than $>AlCitCd^0$. The additional citrate in solution, in forming and $>AlOCdCl^0$ become more stable than $>AlCitCd^0$. The additional citrate in solution, in forming aqueous $CdCit^-$, competes with the surface sites for the available Cd, reducing the amount of Cd that can adsorb onto the surface. Therefore, depending upon the pH, citrate (and by analogy, other multifunctional organic anions) can play different roles in affecting metal mobilities in the subsurface. At low pH, the presence of citrate impedes migration of metals by enhancing metal adsorption; at higher pH values, citrate enhances metal mobilities through increased aqueous metal-citrate complexation.

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APPENDIX B. Surface speciation modeling (citrine: Cd=0.0)

	logK	V(Y)		logK	V(Y)		logK	V(Y)		logK	V(Y)
110000 >AlOHcd ²⁺	5.8	80.8	110000 >AlOHcd ²⁺	no convergence		110001 >AlOcd ³⁺	no convergence		110001 >AlOcdCl ²⁺	no convergence	
110000 >AlOHcdCl ¹⁺	6.5	34.5	110001 >AlOHcdCl ¹⁺			110001 >AlOcdCl ²⁺			110001 >AlOHcdCl ¹⁺		
110000 >AlOHcdCl ₂ ⁰	7.0	333	110000 >AlOHcd ²⁺	5.5	20.3	110001 >AlOcd ³⁺	no convergence		110001 >AlOcdCl ²⁺	-1.6	17.7
			110000 >AlOHcdCl ₂ ⁰	6.5		110001 >AlOcdCl ₂ ¹⁺			110001 >AlOHcdCl ₂ ⁰	6.4	
210000 (>AlOH) ₂ cd ³⁺	8.5	86.9	110000 >AlOHcd ²⁺	equ. are sing.		110001 >AlOcd ³⁺	-3.656	35.03	110001 >AlOcdCl ²⁺	no convergence	
210000 (>AlOH) ₂ cdCl ²⁺	9.2	41.8	210000 (>AlOH) ₂ cd ³⁺			110001 >AlOHcdCl ¹⁺	6.394		210000 (>AlOH) ₂ cd ³⁺		
210000 (>AlOH) ₂ cdCl ₂ ⁰	9.8	194	110000 >AlOHcd ²⁺	no convergence		110001 >AlOcd ³⁺	-2.427	23.49	110001 >AlOcdCl ²⁺	no convergence	
			210000 (>AlOH) ₂ cdCl ²⁺			110001 >AlOHcdCl ₂ ⁰	6.537		210000 (>AlOH) ₂ cdCl ²⁺		
110001 >AlOcd ³⁺	-2.1	105	110001 >AlOHcd ²⁺	5.4	14.6	110001 >AlOcd ³⁺	equ. are sing.		110001 >AlOcdCl ²⁺	-1.7	13.9
110001 >AlOcdCl ²⁺	-0.2	105	210000 (>AlOH) ₂ cdCl ₂ ⁰	9.4		210000 (>AlOH) ₂ cd ³⁺			210000 (>AlOH) ₂ cdCl ₂ ⁰	9.4	
110001 >AlOcdCl ₂ ¹⁺	-0.7	40.1	110000 >AlOHcd ²⁺	equ. are sing.		110001 >AlOcd ³⁺	-3.877	43.92	110001 >AlOcdCl ²⁺	no convergence	
			110001 >AlOcd ³⁺			210000 (>AlOH) ₂ cdCl ²⁺	9.194		110001 >AlOcdOH ⁰		
110001 >AlOcdOH ⁰	-10.0	119	110000 >AlOHcd ²⁺	no convergence		110001 >AlOcd ³⁺	-2.560	14.87			
			110001 >AlOcdCl ²⁺			210000 (>AlOH) ₂ cdCl ₂ ⁰	9.456				
			110000 >AlOHcd ²⁺	equ. are sing.		110001 >AlOcd ³⁺	equ. are sing.				
			110001 >AlOcdCl ₂ ¹⁺			110001 >AlOcdOH ⁰					
			110000 >AlOHcd ²⁺	equ. are sing.							
			110001 >AlOcdOH ⁰								

See explanatory text under Table 4. When one complex is shown, it is the only one considered, and the calculations yield a formation constant for that complex and the variance, V(Y), associated with the calculated fit to the data. For each species combination listed, the formation constants for the complexes have been simultaneously determined and the calculations yield one V(Y) value. The first column represents the fits tried with only one species. The three other columns are species combinations involving >AlOHcd²⁺, >AlOcd³⁺, and >AlOcdCl²⁺ respectively. 'no convergence' means that the optimization procedure cannot converge, indicating a severe misfit between the data and the best-fitting model for the given stoichiometry. 'equ. are sing.' (equations are singular) means that one of the adjustable parameters is insignificant to the speciation.

CHAPTER 3

CONCLUSIONS

In this thesis, new results on metal-organic interactions in mixed fluid/rock systems were presented. Citrate can have a strong effect on the speciation and solution concentrations of Cd(II). At low pH, citrate enhances Cd adsorption, relative to citrate-free systems, by forming the surface ternary complex $>AlCitCd^0$. This could not have been predicted without these experiments because not all multifunctional organic acids behave in this fashion. EDTA, for example, forms strong aqueous complexes with metals but cannot serve as a strong coadsorbates because all of its four functional groups are devoted to the metal to which it is bound. (Of course, the oxidation state of the metal will affect the degree to which Me-EDTA remains in solution (see Girvin *et al.*, 1993)). Using the constants presented in Chap. 2 Cd adsorption was modeled at different citrate:Cd ratios. Model calculations show that with increasing citrate:Cd ratios, Cd adsorption increases in low pHs. The enhancement is however limited by the quantity of citrate sorbed. When the surface of corundum is saturated with respect to citrate, residual aqueous citrate is available to form aqueous Cd-citrate, thereby reducing Cd adsorption is reduced. Thus, one of the general conclusions of this thiesis is that competition between aqueous and surface metal-organic complexes can have an important role on the mobility of metals in mixed metal-organic fluid/rock systems.

This thesis has also dealt, though indirectly, with problems associated with electrolyte binding to corundum and the adsorption of $Cd(Cl)_x^{2-x}$ complexes. Adsorbed electrolytes tend to neutralize the surface potential which results from adsorbed H^+ and OH^- . Thus, the electric potential experienced by a solute is not

necessarily as large as what is modeled by the CCM. Consequently, solutes may approach the surface more easily than modeled. Furthermore, different electrolyte ions neutralize surface charge to different extents. For example, the chloride ion neutralizes surface charge more effectively than the nitrate ion (e.g. Gunneriusson, 1994a,b). In this thesis, modeling Cd adsorption required a cadmium-surface complex with a charge less than 1. In other words, the modeled surface potential needed to be lowered in order to account for the experimental data. To satisfy the low surface potentials required by the CCM we needed to invoke a surface CdCl complex. Complexes of this type were also modeled by Gunneriusson (1994a,b), however they are yet not supported by *in situ* surface spectroscopic observations. Alternatively, it could be argued that the $>Al_3O^{-0.5}$ sites would be responsible for the low pH Cd adsorption data. For example, an EXAFS study of Pb(II) surface complexes on corundum and goethite (Bargar, 1996) suggests that lead can bind to two $>Al_3O^{-0.5}$ or two $>AlO^{-1.5}$ sites or a mixture of both. There is also an indication of outer-sphere (hydrogen bonding) Pb complexation on the 001 crystal plane. Cd(II) could potentially behave in a similar fashion. However modeling these specific interactions is not possible using conventional wet chemistry methods because the complexes involve non-proton active sites.

The models presented in this thesis contribute to the enlarging database of equilibrium reactions which describe complexation of solutes at the fluid/rock interface. This database can be used to build predictive models of contaminant transport in fluid/rock systems. In addition, this thesis has examined the effects of electrolyte adsorption on surface potential and the adsorption of CdCl complexes.

There is still considerable uncertainty regarding these processes, and resolution is likely to involve additional techniques such as mineral surface spectroscopy, potentiometric titrations and electrophoresis. However, to model bulk mass transport in fluid-rock systems, the simplest, but adequate model, is sufficient.

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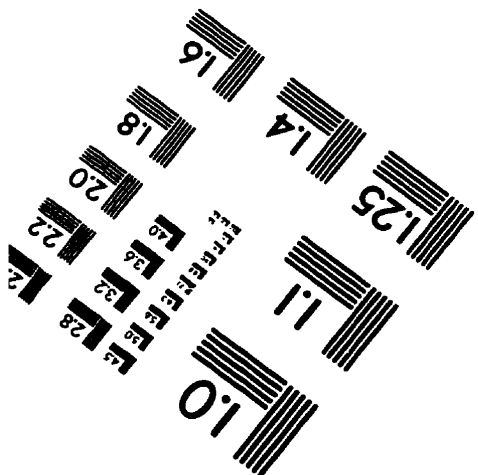
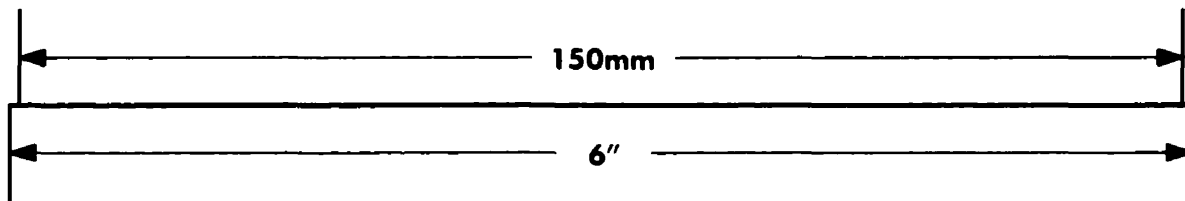
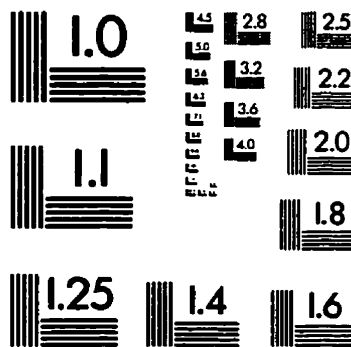
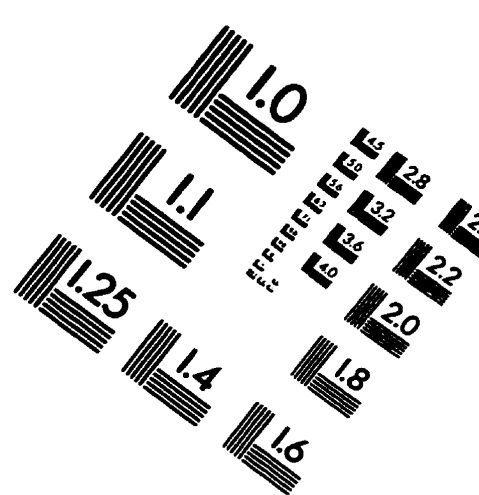
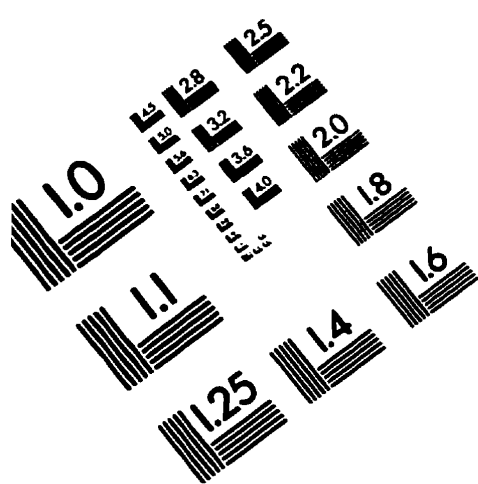
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IMAGE EVALUATION TEST TARGET (QA-3)



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