

Comparison of Two Methods for the Determination of Stability Constants for Metal-NOM Interactions

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Abstract

The inherent polyfunctional and heterogeneous nature of natural organic matter (NOM) has made the modeling of metal complexation reactions difficult. Historically, a number of modeling approaches have been developed to describe metal complexation by NOM. These models can be grouped into two: chemical and non-chemical. In the present study, we compare a non-chemical model (Schubert's method) to a chemical model (discrete ligand, non-electrostatic approach) to determine the stability constants of metal/NOM complexes. Our analyses of Co/fulvic acid complexation data using Schubert's equation result in an apparent nonintegral number of ligands binding the Co^{2+} ion. The model fit was improved assuming a mixture of 1:1/1:2 Co(II)-ligand complexes. Schubert's method can be used as an effective tool to provide information on reaction stoichiometries and average stability constants over the whole NOM. However, the binding of metals by NOM occurs on specific sites, mostly associated with carboxylic groups. In the discrete ligand approach, NOM is conceptualized as being composed of a suite of monoprotic acids, HL_i , of arbitrarily assigned $\text{pK}_{a(i)}$ values (e.g., 4, 6, 8 and 10). Although the discrete ligand approach is more complex and requires more fitting parameters (i.e. usually more than 5) compared to Schubert's approach, it provides a means of capturing the complexation behavior of metals with specific sites in a framework suitable for use in equilibrium speciation models under variable chemical conditions. In addition, all of the potential mononuclear and polynuclear metal and organic species can be considered within the framework of the chemical model.

Key words: Schubert's method, Stability constants, Chemical model, Complexation, NOM.

Introduction

Humic substances are naturally occurring polyelectrolytes that play an important role in the chemical speciation, bioavailability and mobility of metals in the subsurface environment. In many groundwater systems, natural organic matter (NOM) constitutes an important suite of ligands available for complexing trace metals. NOM contains approximately 10^{-4} to 10^{-3} mol/g of proton-donating functional groups, and numerous studies have shown the abil-

ity of NOM ligands to strongly complex a variety of trace metals and to dominate metal speciation under acid to circumneutral pH conditions (Lenhart and Honeyman, 1999; Murphy et al., 1999). Understanding the environmental behavior of metals in systems containing NOM requires knowledge of metal-NOM complexes. Due to the strong binding of NOM with metals, NOM has also been used as a leaching agent in the remediation of soils contaminated with radioactive and heavy metals (Francis and Dodge, 1998). The complexation of metals with

NOM occurs mainly through carboxylic and phenolic groups. However, molecular structure and the number of available complexing sites of NOM are not well established in the literature. For example, the average fulvic acid contains approximately 4.5-6.0 meq/g carboxyl and 0.5-2.5 meq/g phenolic groups. Humic acids usually contain 20% less carboxyl content than do fulvic acids from the same source (Thurman, 1985; Murphy et al., 1999).

There are different approaches to studying the interaction of a metal ion with an organic ligand. Each method may require different experimental conditions, which may, in turn, create differences in the interpretation of complexation reactions and the stability constants. For example, direct speciation methods (e.g., spectroscopic techniques) are only applicable to metal concentrations ($> 10^{-8}$ M) greater than those observed in the environment. There are also indirect methods that can be employed at environmentally relevant metal ion concentrations (e.g., ion-exchange, solvent extraction, ultrafiltration, titration).

A number of modeling approaches (i.e. interpretation of experimental data from indirect methods) have been developed to describe metal and proton complexation by NOM (e.g., Dzombak et al., 1986; Westall et al., 1995). These models can be grouped into two: chemical and non-chemical. Non-chemical methods are graphical techniques consisting mainly of Schubert's approach (Schubert, 1948; Smith et al., 1986; Lenhart et al., 2000; Kantar and Honeyman, 2005; Kantar et al., 2005), the Bjerrum approach (Stevenson et al., 1993), the Scatchard approach (Mantoura and Riley, 1975; Fitch and Stevenson, 1984; Hintelmann et al., 1997) and the Langmuir approach (Jang et al., 1999). Non-chemical models (e.g., Schubert's technique) are more appropriately used for metal species that are mono-nuclear with respect to either the organic ligand or metal ion.

An alternative avenue is the use of chemical equilibrium models that describe metal-ligand complexation through some chemical reactions (Westall et al., 1995; Bolton et al., 1996; Kinniburgh et al., 1996; Ganguly et al., 1999; Murphy et al., 1999; Christl and Kretzschmer, 2001; Weirich et al., 2002; Ge et al., 2005; Kantar and Honeyman 2005; Kantar et al., 2005). Chemical models provide a means of explicitly accounting for the likely suite of reactions in the system under consideration, including polynuclear metal-ion complexes. Furthermore, the use of chemical speciation models can obviate the need to con-

strain experiments to the conditions that would be required for the application of graphical techniques. Chemical models basically differ on 2 points: 1) the use of a discrete ligand vs. a distribution of ligands and 2) whether or not to explicitly consider electrostatics. When electrostatics are explicitly included, terms are invoked to account for the physical aspect of individual NOM molecules, including assumptions about shape (spherical or cylindrical), measured or assumed particle density, and measured particle size and molecular weight (Bartschat et al., 1992; Tipping and Hurley, 1992; De Wit et al., 1993; Benedetti et al., 1996). While the inclusion of electrostatics in model constructs can be more satisfying due to correspondence to physical reality, the need to determine values for model parameters that may or may not be known can limit their use. Another promising approach is the discrete-ligand, non-electrostatic approach (Westall et al., 1995; Bolton et al., 1996; Murphy et al., 1999; Kantar and Honeyman, 2005). In such a model construct, natural organic acids are treated as an assembly of monoprotic acids of assumed pK_a values. Each of the conjugate bases interacts with the metal-ion in a 1:1 stoichiometry.

In the selection of a model to describe metal-ligand interactions, the ultimate goals, as stated by Lenhart and Honeyman (1999), should be as follows:

i) The accurate representation of the experimental data over a range of system conditions. To a certain extent, the degree of model 'correctness' is expressed in the model's predictive capability.

ii) A small and orderly set of adjustable parameters. Westall et al. (1995) provide a framework for the comparison of heterogeneous materials with a minimum of adjustable parameters (i.e. acid concentrations).

iii) Reasonable ease of use with general speciation models.

iv) Insight into the physical nature of the interactions. It is unlikely, though possible, that a model that is fundamentally incorrect will be able to 'predict' the response of a system over a reasonably wide range of system conditions. Clearly, modeling complex systems requires simplification. A chemically 'reasonable' model, even though a simplification of the target system, should be able to provide insight to system properties even if the model is not 'microscopically' accurate.

This paper describes and compares the modeling approaches used for the determination of stability constants for metal-organic ligands. Recent

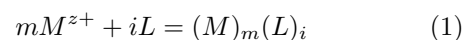
literature concerning the modeling of metal-organic ligand complexation is examined with special emphasis on Schubert's method and chemical equilibrium approach. Among all the non-chemical models, Schubert's approach is described in detail here because it is a classical approach for deriving stability constants for metal-ion/ligand complexes (e.g., Nash and Choppin, 1980): it provides a useful benchmark for comparison to non-traditional techniques. Classical and modified Schubert's methods are compared to the discrete ligand, non-electrostatic approach. In chemical models, on the other hand, the chemical behavior of NOM is described using a discrete ligand approach advocated by several researchers (e.g., Fish et al., 1986; Tipping and Hurley, 1992) and as implemented by Westall et al. (1995) and Murphy et al. (1999). In their models, NOM is represented as 'an assembly' of monoprotic acids with assumed pK_a values and without explicit correction for electrostatic effects. An important attribute of this modeling approach is that no site-site interactions are considered. As such, non-interacting sites titrate as a mixture of monoprotic acids and bases. Furthermore, all of the sites are considered to be part of a single macromolecule; thus, the potentiometric titration curves of the macromolecular ligand are interpreted as that of a polyprotic acid.

Schubert's Method

One approach for determining an average stability constant for a metal-ligand system is to use the well-known Schubert equation (Schubert, 1948), which is a linearization technique to analyze complexation data collected at a specific pH and ionic strength, I . This approach can be used effectively to determine binding constants for metal/ligand complexes under environmentally relevant concentrations of metal ions. This method is based on measuring the metal content between the solution phase and a solid phase (e.g., cation exchange resin) in the absence or presence of a metal-complexing ligand. To more accurately apply this method, the metal ion concentration must be negligible compared to the ligand concentration, and neither the ligand nor metal-ligand complex must sorb to the solid phase. In addition, the ratio of metal ion concentration to solid sites should be kept at those that remain on the linear portion of the metal sorption isotherm. While Schubert's method is not valid for the interpretation of all types of data, as in the case of non-integer Schu-

bert slopes (e.g., Lenhart et al., 2000), it is often a useful starting point for the analysis of simple metal ion/organic ligand systems and more complex interactions as described here.

The binding of a metal ion (M^{z+}) to an organic ligand (L) can be described by the following general stoichiometric expression:



with a conditional stability constant, $\beta_{m,i}$:

$$\beta_{m,i} = \frac{[(M)_m(L)_i]}{[L]^i [M^{z+}]^m} \quad (2)$$

The mass balance on dissolved metal ion, in the absence of an organic ligand, is given by

$$[M]_T = M^{z+} + M(OH)^{(z-1)} + \dots = M^{z+} \{1 + \beta_{M(OH)^{(z-1)}} [OH^-] + \dots\} \quad (3)$$

The distribution coefficient, λ_o , which is the solid (e.g., resin)/solution distribution coefficient for metal in the absence of the organic ligand, is defined as follows:

$$\begin{aligned} \lambda_o &= \frac{[M]_{resin}}{[M]_{sol}} \\ &= \frac{[M]_{resin}}{[M^{z+}] \{1 + \beta_{M(OH)^{(z-1)}} [OH^-] + \dots\}} = \frac{[M]_{resin}}{[M^{z+}] \Pi} \end{aligned} \quad (4)$$

where $[M]_{resin}$ has units of moles of metal per gram resin, $[M]_{sol}$ has units of moles of metal per liter (l) of solution and λ_o has units of l/g. The term Π is a constant for a given set of solution conditions (e.g., pH and I), and is used to account for the concentrations of all dissolved metal species with the exception of those with the target ligand. Detailed information on the calculation of Π can be found elsewhere (e.g., Lenhart et al., 2000).

Similarly, a corresponding set of ion-exchange experiments is performed to determine λ , the resin/solution distribution for metal ion in the presence of the target organic ligand. Assuming that the ligand L forms a series of complexes ML_i that are mononuclear with respect to metal ion ($m = 1$), λ is defined as follows (for $i = 1$ to n):

$$\begin{aligned}\lambda &= \frac{[M]_{resin}}{[M]_{sol}} \\ &= \frac{[M]_{resin}}{[M^{z+}]\{\Pi + \beta_{1,1}L + \beta_{1,2}[L]^2 + \dots + \beta_{1,n}[L]^n\}}\end{aligned}\quad (5)$$

where L is the target organic ligand, and $[M]_{sol}$ is the sum of all dissolved metal species, including those with the target ligand under study. The combination of Eqs. (4) and (5) gives

$$\left(\frac{\lambda_o}{\lambda} - 1\right) = \frac{\beta_{1,1}[L] + \beta_{1,2}[L]^2 + \dots + \beta_{1,n}[L]^n}{\Pi} \quad (6)$$

In the case where only metal-ligand complexes of 1:n stoichiometry are formed, Eq. (6) simplifies to

$$\left(\frac{\lambda_o}{\lambda} - 1\right) = \frac{\beta_{1,n}[L]^n}{\Pi} \quad (7)$$

Equation (7) can be linearized by taking the logarithm of both sides as follows:

$$\log\left(\frac{\lambda_o}{\lambda} - 1\right) = \log\left(\frac{\beta_{1,n}}{\Pi}\right) + n\log[L] \quad (8)$$

The value of $\log \beta_{1,n}$ can be determined from a plot of $\log\{(\lambda_o/\lambda)-1\}$ vs. $\log[L]$. The graphical representation is commonly called a Schubert's plot.

Non-linear analysis of Schubert-type data

Several metal-NOM complexation studies suggest deviations from linear behavior (Lenhart et al., 2000; Murphy, 2000; Kantar and Honeyman, 2005). The results of these studies indicate that a non-linear regression technique may be required to more accurately describe the complexation reactions. For this purpose, the data is transformed to non-linear expressions to simulate metal/NOM binding. In this technique, the data can be simulated by 1) a model postulating the formation of a single 1:n model [Eq. (7)]; and 2) a model postulating a combination of 1:1 and 1:2 metal-ligand complexes. Based on the formation of a mixture of 1:1 and 1:2 complexes, Eq. (6) can be transformed into

$$\left(\frac{\lambda_o}{\lambda} - 1\right) = \frac{\beta_{1,1}[L] + \beta_{1,2}[L]^2}{\Pi} \quad (9)$$

Application of 1:n model to Schubert-type data

In the present work, we also tested the applicability of the 1:n model to simulate Co(II) binding by fulvic acid as a function of pH and I. For these simulations, the Co(II) complexation data were taken from the work of Dong et al. (1999) and analyzed using the 1:n model. Figure 1a, b show the resulting simulations. The non-linear simulations were performed using Eq. (7), assuming the existence of 1:n metal-ligand complex. The non-linear simulations were performed using the software Scientist (Micromath, Inc). In these simulations, $(\frac{\lambda_o}{\lambda} - 1)$ is the dependent variable, and fulvic acid concentration (eq/l) is the independent variable. The best fit values for $\log \beta_{1,n}$ and the statistical parameters (e.g., coefficient of determination (R^2), relative error (RE) and model selection criteria (MSC)) are shown in Table 1. The best fits of the models are those that minimize the sum of the squared residuals:

$$S = \sum_{i=1}^n (y_i^{exp} - y_i^{calc})^2 \quad (10)$$

where y_i^{exp} represents the experimental value of a variable Y and y_i^{calc} is the computed value of Y from the model at a particular setting of an independent variable.

In most cases, the values of n from the resulting simulations (Figure 1a,b) are significantly different from 1.0, indicating that the complexation process is more complicated than a simple 1:1 metal/ligand stoichiometry. This makes the use of conventional linearized Schubert method [Eq. (8)] impossible, since it requires values of n near unity. As discussed by Clark and Turner (1969), Schubert's method is appropriate only for systems that exhibit integer slope values, i.e., where the ligand number is 1, 2 or 3, etc. The non-integer slopes are common for metal-NOM complexation, and have been reported elsewhere. For example, Lenhart et al. (2000) reported a slope of 1.46 for the complexation of U(VI) with humic acid at pH 4. The modeling results also suggest that the Co(II)-fulvic acid binding varies with changing experimental conditions (e.g., pH and I). This indicates that the complexation behavior of fulvic acid may change depending on the experimental conditions. As indicated by Lenhart et al. (2000), the 1:n model is not suitable for metal-NOM systems with non-integer slopes.

Table 1. Model parameters and statistics for the Co(II)-fulvic acid system (data from Dong et al. (1999)).

Model	pH	I (M)	MSC ^a	R ^{2b}	Parameters
1 : n	5.2	0.001	3.62	0.986	$\log \beta_{1,n} = 4.66 \pm 0.25; n = 1.09 \pm 0.10$
	5.2	0.01	5.46	0.998	$\log \beta_{1,n} = 4.90 \pm 0.11; n = 1.06 \pm 0.04$
	5.2	0.1	4.72	0.996	$\log \beta_{1,n} = 3.91 \pm 0.12; n = 0.83 \pm 0.04$
	3.8	0.01	5.69	0.998	$\log \beta_{1,n} = 6.01 \pm 0.12; n = 1.12 \pm 0.039$
	5.8	0.01	5.48	0.998	$\log \beta_{1,n} = 4.75 \pm 0.10; n = 1.06 \pm 0.039$
	6.8	0.01	1.65	0.9138	$\log \beta_{1,n} = 3.66 \pm 0.37; n = 0.76 \pm 0.18$
1 : 1/1 : 2	5.2	0.001	3.83	0.989	$\log \beta_{1,1} = 4.29 \pm 0.07; \log \beta_{1,2} = 6.88 \pm 0.24$
	5.2	0.01	5.58	0.998	$\log \beta_{1,1} = 4.68 \pm 0.03; \log \beta_{1,2} = 6.75 \pm 0.20$
	5.2	0.1	----	----	
	3.8	0.01	6.3	0.999	$\log \beta_{1,1} = 5.49 \pm 0.02; \log \beta_{1,2} = 8.38 \pm 0.08$
	5.8	0.01	5.58	0.998	$\log \beta_{1,1} = 4.54 \pm 0.03; \log \beta_{1,2} = 6.45 \pm 0.21$
	6.8	0.01	----	----	

^a The model selection criteria (MSC) relate the coefficient determination to the number of model parameters in order to evaluate the appropriateness of the model. The higher values indicate a more appropriate model.

^b In this paper R² refers to the coefficient of determination.

Application of 1:1/1:2 model to Schubert-type data

Due to non-integer slopes, a number of studies have used a modeling approach based on the assumption of the formation of complexes with mixed stoichiometries. For example, Fukushima et al. (2001) and Lenhart et al. (2000) show that divalent metal ions bind with NOM in terms of a mixture of 1:1 and 1:2 metal-ligand complexes. The main advantage of this approach is that it can easily be tested and incorporated into the current modeling framework through the use of Eq. (9). For these simulations, the Co(II) complexation data were taken from the work of Dong et al. (1999) (Figure 1a, b). Non-linear regressions were performed for the model ligands and Co(II) based on the formation of 1:1 and 1:2 complexes using the software Scientist. In these simulations, $(\frac{\lambda_e}{\lambda} - 1)$ is the dependent variable, and fulvic acid concentration (eq/1) is the independent variable. The best fit values for $\log \beta_{1,1}$ and $\log \beta_{1,2}$ are shown in Table 1. The statistical values from the resulting simulations were better than those with the 1:n model in most cases.

For some experimental conditions (e.g., pH 5; I = 0.1 M and pH 6.8; I = 0.01 M), the value of n for the 1:n model is less than one, indicating the formation of polynuclear species with respect to Co²⁺ ion. The

value of n usually provides valuable information on types of complexes formed and reaction stoichiometries. The 1:1/1:2 approach is not appropriate for systems with n values less than one since it is more accurately used for systems with mononuclear complexes with respect to either the metal ion or the ligand. Chemical models, which will be discussed below, can be used to deal with such complex polynuclear systems.

Discrete ligand model for proton and metal binding of NOM

Alternative to non-chemical models (e.g., Schubert's method) are chemical equilibrium models. The inherent complex polyfunctional and heterogeneous nature of NOM led Westall et al. (1995) to develop an approach in which the natural organic matter is conceptualized as a compound of a suite of monoprotic acids, HL_i, of arbitrarily assigned pK_a. Due to the complex structure and reactivity of NOM molecules, the approach used by Westall et al. (1995) may not correspond to a strict physical or chemical model of natural organic matter. However, it provides a consistent evaluative framework for the simulations of interactions of NOM with soil surfaces and ions (Lenhart, 1997; Murphy et al., 1999).

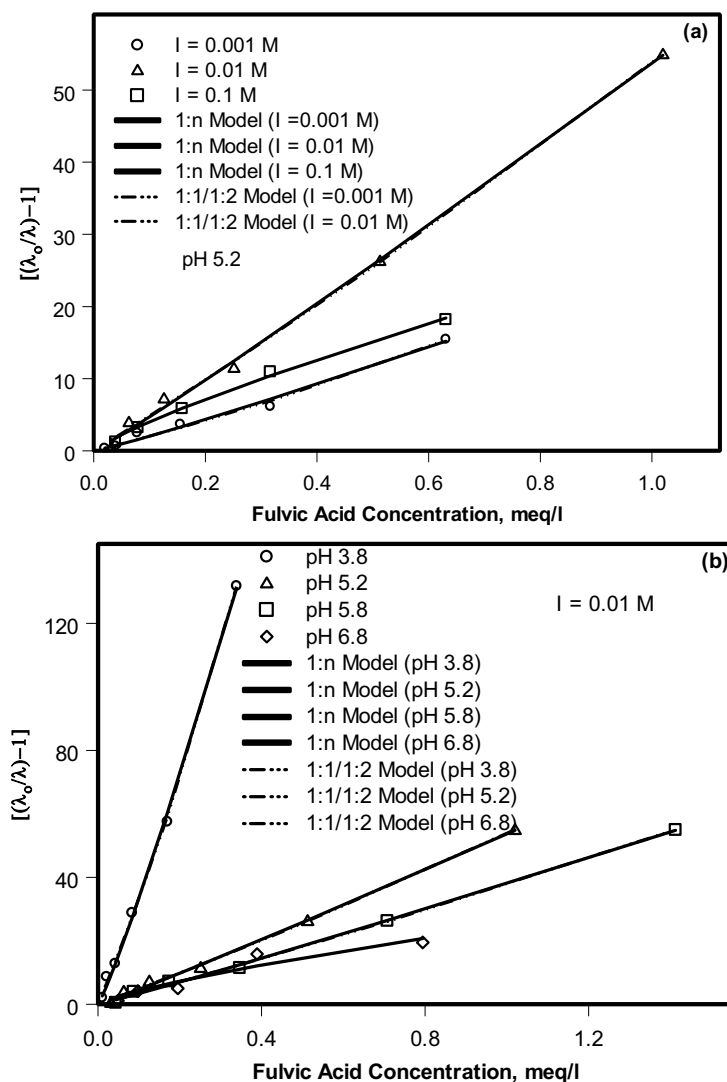


Figure 1. Plots of $[(\lambda_0/\lambda) - 1]$ vs. fulvic acid concentration (a) at different ionic strengths (I) and pH = 5.2 (b) at different pH values, I = 0.01 M. Experimental data were taken from Dong et al. (1999) and reanalyzed with the 1:n and 1:1/1:2 approaches. Lines represent best fit model simulations with the models.

In the discrete ligand approach, the metal/NOM complexation data can be used to determine binding constants for metal-ion/ HL_i complexes. A main advantage of this approach is that the resulting metal/ligand complexes can easily be incorporated into solution/surface speciation models (Kantar, 2001) to more accurately simulate metal ion behavior in environmental systems containing NOM. The number of acidic groups is selected to properly describe the acid/base characteristics of NOM.

The concentration of each of these individual groups, as well as the electrolyte association term (K_{Na}), are usually determined through the optimization of potentiometric titration data. The development of models for the discrete ligand approach can be found in detail elsewhere (e.g., Murphy et al., 1999). In this approach, the titration data are simulated in a chemical equilibrium model using the following sets of reactions for each site to determine the acid/base characteristics of NOM:

Table 2. Leonardite humic acid solution-phase reactions (from Westall et al. (1995)).

Reaction	T_{HLi} (mmol/g) ^a	log K (I = 0)
$HL_1 = L_1^- + H^+$	2.9	-4
$HL_2 = L_2^- + H^+$	1.3	-6
$HL_3 = L_3^- + H^+$	0.9	-8
$HL_4 = L_4^- + H^+$	1.2	-10
$HL_2 + Co^{2+} = CoL_2^+ + H^+$	-	5.38 ^b
$HL_3 + Co^{2+} = CoL_3^+ + H^+$	-	6.38 ^b
$HL_i + Na^+ = NaL_i + H^+$		1.71

*Determined from discrete ligand model simulation of titration data represented in Figure 2.

^a The concentration of all functional groups (T_{HLi}) as determined from the model fit is 6.3 mmol/g.

^b Determined from discrete ligand model simulation of complexation data represented in Figure 3. The simulations use acid/base reactions for LHA determined through optimization of titration data given in Figure 2.

$$HL_i = H^+ + L_i^- \quad K_{a(i)} = \frac{[H^+][L_i^-]}{[HL_i]} \quad (11)$$

$$Na^+ + L_i^- = NaL_i \quad K_{Na(i)} = \frac{[NaL_i]}{[L_i^-][Na^+]} \quad (12)$$

The basic constraint equations for evaluating the titration data are the proton balance:

$$T_H^{calc} = [H^+] - [OH^-] - \sum [L_i^-] - \sum [NaL_i] \quad (13)$$

and the mass balance for ligand, i:

$$T_{HL(i)} = [HL_i] + [L_i^-] + [NaL_i] \quad (14)$$

The experimental value of T_H (i.e., T_H^{exp}) is evaluated as follows:

$$T_H^{exp} = C_a - C_b + T_H^o = \Delta T_H + \Delta T_H^o \quad (15)$$

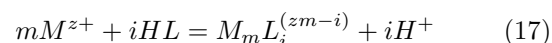
The most difficult and critical part of simulations of potentiometric titration data of natural polyacids is the determination of T_H^o , the initial value of strong acid or base in the system. Westall et al. (1995) treat T_H^o as an adjustable parameter in the simulations.

Westall et al. (1995) tested the applicability of discrete ligand non-electrostatic approach to determine the acid/base characteristics of leonardite humic acid (LHA) system. Figure 2 shows a typical

acid-base titration of NOM and the resulting simulation with a discrete non-electrostatic approach. The values for the parameters determined from the discrete ligand model optimization of titration data are shown in Table 2. In this approach, the number of fitting parameters required to describe proton binding by NOM depends on the number and types of sites used in the simulations. As given in Table 2, Westall et al. (1995) used 6 adjustable parameters: $4T_{HL(i)}$, $4K_{a(i)}$, $4K_{Na(i)}$ and T_H^o . In their model, the $pK_{a(i)}$ values were arbitrarily set to 4, 6, 8 and 10. Typically, ligands with pK_a values less than 8 can operationally be defined as ‘‘carboxyl’’ and those with pK_a values of 8 or higher correspond to phenolic groups (Lenhart and Honeyman, 1999), although the actual structure of NOM is not fully determined. The values of the adjustable parameters are determined through minimization of the difference function, Y , in a chemical equilibrium model:

$$Y = T_H^{calc} - T_H^{exp} \quad (16)$$

Li et al. (1980) and Higgs et al. (1993) reported that the metal binding by NOM is an ion-exchange reaction through the protons of the free carboxylic and phenolic functional groups of NOM. Thus, the association of a metal ion with NOM can be expressed by the reaction:



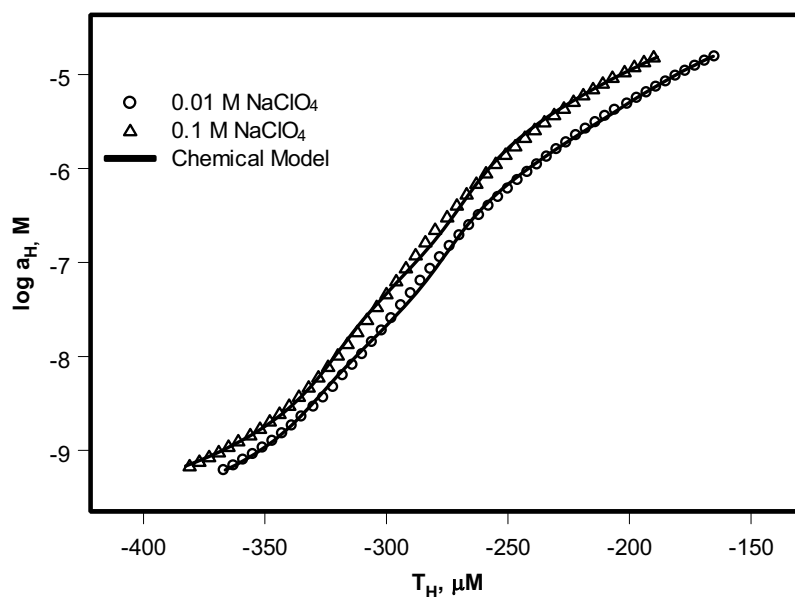


Figure 2. Acid-base titrations of leonardite humic acid (LHA) in 0.01 and 0.1 M NaClO₄, with initial LHA concentration of 41.2 mg carbon/l. Experimental values of hydrogen activity ($\log a_H = -\text{pH}$) are plotted against experimental and calculated values of T_H . Modeled with 4 discrete-site pK_a spectra: $\text{pK}_a = 4, 6, 8$ and 10 with 1 constant for the exchange of sodium for hydrogen; acid-base reactions and constants listed in Table 2 (Westall et al.(1995)).

The equilibrium constant for Eq. (17) can be determined by applying the chemical model to the results of metal/ligand complexation data from indirect speciation methods. The simulations include postulated metal/NOM complexation reactions [e.g., Eq. (17)] as well as acid/base reactions for NOM obtained through optimization of potentiometric titration data as given in Table 2. Due to complexity of NOM interactions with metals, the ultimate goal is to obtain a model with the least number of complexation reactions required to appropriately describe metal-NOM binding under the experimental conditions studied. Using mass balance and mass action constraints imposed by the chemical equilibrium model, the values of binding constants for the postulated metal/NOM reactions are obtained through optimization of metal/ligand complexation data. For example, for a Co(II)/Leonardite humic acid (LHA) system (Figure 3), Westall et al. (1995) postulated 2 monodentate complexation reactions between Co(II) and the model ligands L_2 (pK_a 6) and L_3 (pK_a 8) forming the species CoL_2^+ and CoL_3^+ . Their model required 8 fitting parameters to describe interactions of the proton and Co(II) with LHA, including 6 parameters for the acid/base reactions of LHA and 2 for the Co-LHA binding reactions (Table 2). Similarly, in a complexation study with U(VI)/humic

acid, Murphy et al. (1999) determined monodentate reactions between the uranyl ion (UO_2^{2+}) and the model ligands L_1 (pK_a 4) and L_2 (pK_a 6) forming the species UO_2L_2^+ and UO_2L_3^+ . However, in their model, the total number of fitting parameters required to describe proton and U(VI) interactions with humic acid was 9, including 7 parameters for acid/base reactions of humic acid and 2 for U(VI)-humic acid interactions. For a Pu(IV)-alginate system, Kantar and Honeyman (2005) found that metals may also complex with organic ligands in a mixture of 1:2 and 1:3 metal/ligand stoichiometry other than a simple 1:1 stoichiometry. The chemical modeling results given by Westall et al. (1995), Murphy et al. (1999) and Kantar and Honeyman (2005) indicate that the binding of metals by NOM occurs on specific sites, mostly associated with carboxylic groups, and the type of species formed highly depends on the chemical conditions (e.g., concentration, pH) studied, as was the case observed in the study by Dong et al. (1999). The stability constants determined using the discrete ligand approach can effectively be used in speciation models to more accurately describe metal ion behavior in environmental systems containing NOM (Figure 4). The metal-ligand complexes dominate over a wide pH range in the speciation diagram.

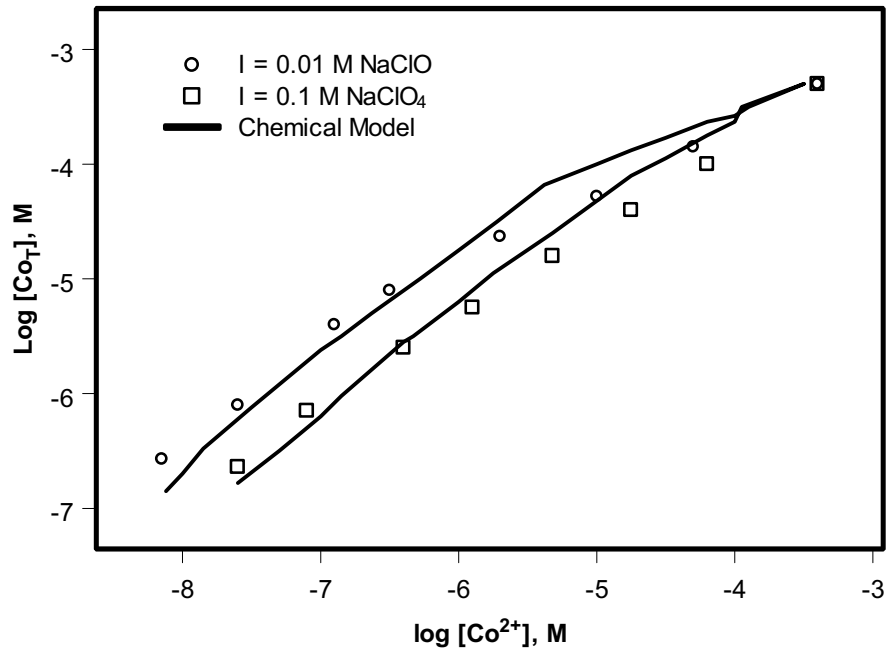


Figure 3. Co^{2+} binding to LHA at constant $\text{pH} = 6.7$ at 2 NaClO_4 concentrations. LHA concentration was about 50 mg carbon/l isolated in dialysis tubing, and the total $\text{Co}(\text{II})$ concentration ranged from 200 to 500 μM in the tubing. Modeled with the 4 discrete-site spectrum model; reactions and constants listed in Table 2 (Westall et al.(1995)).

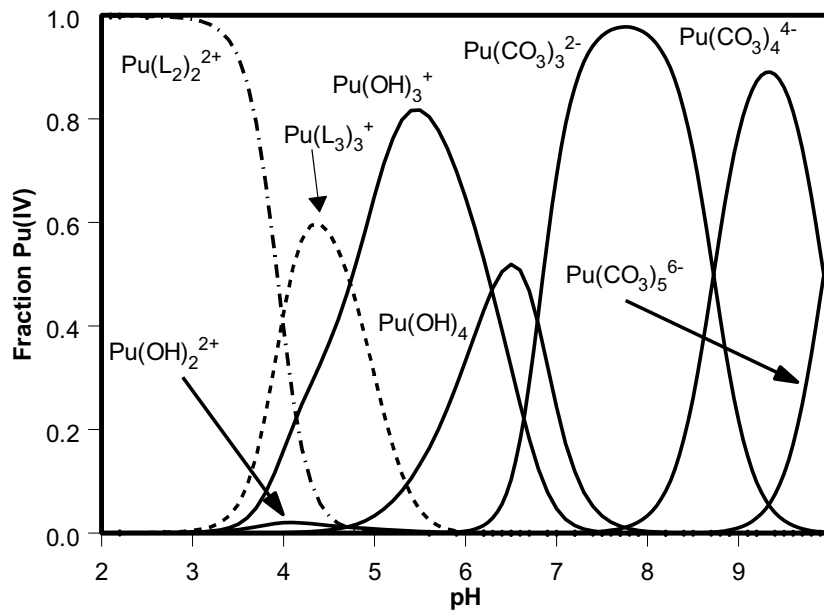


Figure 4. Pu(IV) speciation in the presence of alginic acid (Kantar and Honeyman, 2005), as a function of pH. Pu complexation by alginic acid was evaluated using the discrete ligand approach. The conditional stability constants ($\text{Log } K$) for the formation of $\text{Pu}(\text{L}_2)_2^{2+}$ and $\text{Pu}(\text{L}_3)_3^+$ complexes are 9.457 ± 0.274 and 10.559 ± 0.664 at $I = 0 \text{ M}$, respectively. ($P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$; $\text{Pu}(\text{IV})_T = 2 \times 10^{-11} \text{ M}$; alginic acid = 500 mg/l).

Conclusion

The goals of this study were to 1) provide information on current modeling approaches used for determination of stability constants for metal-NOM complexes, and 2) aid researchers in transitioning from graphical means of data interpretation to more modern computer-based computational methods. We have used Schubert's method to analyze Co(II)/fulvic acid binding since it provides a useful benchmark for comparison with non-traditional techniques. One of the benefits of using Schubert's method is that it can effectively be used as a tool to provide information on reaction stoichiometries and average stability constants over the whole NOM. However, complexation reactions involving NOM are heterogeneous in nature and occur on specific surface sites found in NOM. Chemical models (e.g., the discrete ligand approach) can be viewed as a better approximation to reality compared to non-chemical models, although the actual structure of NOM is not fully known. The discrete ligand approach, in which complex organic matter is represented as an assembly of monoprotic acids with arbitrarily assigned pK_a values, allows direct examination of the interaction of individual acid groups with metal ions. The discrete ligand approach can be applied under a wide

range of experimental conditions to estimate stability constants for metal-NOM. For example, within the framework of the discrete ligand approach, all of the potential mononuclear and polynuclear metal and organic species can be considered, whereas Schubert's method is only applicable for metal-ligand species that are mononuclear with respect to either organic ligand or metal ion. Although the discrete ligand approach requires more fitting parameters (i.e. usually more than 5) compared to Schubert's approach, it provides a means of capturing the complexation behavior of metals with specific sites in a framework suitable for use in equilibrium speciation models under variable chemical conditions. Conversely, the application of non-chemical models (e.g., Schubert-type data) in this vein is problematic. Finally, the discrete ligand approach, in conjunction with surface complexation models (SCM), can be effectively used to more accurately describe metal-ion sorption and transport in the presence of NOM in the subsurface environment. For example, Lenhart and Honeyman (1999) successfully simulated the effects of NOM on U(VI) sorption onto hematite in the presence of NOM by linking the discrete ligand, non-electrostatic approach for NOM with the triple layer surface complexation model.

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