Metal Flux and Dynamic Speciation at (Bio)interfaces. Part I: Critical Evaluation and Compilation of Physicochemical Parameters for Complexes with Simple Ligands and Fulvic/Humic Substances

JACQUES BUFFLE,* ZESHI ZHANG, AND KONSTANTIN STARTCHEV

Analytical and Biophysical Environmental Chemistry (CABE), University of Geneva, Sciences II, 30 quai E. Ansermet, CH-1211 Geneva 4

In the computation of metal flux in aquatic systems, at consuming surfaces like organism membranes, diffusion processes of metal ions, ligands, and complex species, as well as the kinetic and thermodynamic aspects of their chemical interactions, must be considered. The properties of many natural ligands, however, are complicated (formation of successive complexes for simple ligands, polyelectrolytic properties and chemical heterogeneity for macromolecular ligands, large size distribution and fractal structure for suspended aggregates). These properties should be properly modeled to get the correct values of the chemical rate constants and diffusion coefficients required for flux computations. The selection of the most appropriate models and parameter values is far from straightforward. This series of papers discusses the various models and compiles the parameters needed for the three most important types of complexants found in aquatic systems: the small, simple ligands, the fulvic and humic compounds, and the colloidal “particles” or aggregates. In particular, new approaches are presented to compute the rate constants of metal complex formation, with both fulvics/humics and particles/aggregates. The method to include the site distribution of fulvics/humics and the size distribution of particles/aggregates in metal flux computation at consuming interfaces is also discussed in detail. These models and parameters are discussed critically and presented in the same framework, for the computation of metal flux in presence of any of the above complexants or mixtures. Such parameters, largely spread in the literature, are gathered here and selected specifically for environmental applications. The focus in Part I of the series is on simple ligands and fulvic/humic compounds. Part II deals with particulate and aggregate complexants.

1. Introduction

Most biogeochemical environmental processes are dynamic in nature, and their modeling requires the combination of hydrodynamic processes, diffusive transport, and chemical kinetics (1). In aquatic systems (water, sediment, soil), the vital or toxic role of a metal depends not only on its equilibrium distribution between numerous metal complexes but also on the lability of these complexes (2), that is, on complexion rates, as well as on the diffusion coefficients of metal, ligand, and complexes (3–5). Until now, most of the models used for predictions on bioavailability and ecotoxicity, particularly, the biotic ligand model (5, 6) and the free-ion activity model (3, 5, 7), were based on the assumptions that all chemical reactions in the medium external to organism are at equilibrium and that the free-metal ion bulk concentration controls the metal uptake. With such models, metal fluxes are readily obtained by computing the equilibrium metal species distribution with one of the numerous corresponding computer codes (e.g., MINTEQ (8), WHAM (9), and PHREEQC (10)).

It has been clearly shown, however, (5, 11–14) that in a number of cases, particularly, under conditions close to those of natural systems such as microorganism starvation (15), the dynamic processes, such as diffusion in solution or chemical kinetics, may become the limiting factors for bio-uptake and that modeling of these dynamic processes is required. In practice, however, this is rarely included in the interpretation of experimental speciation and bioavailability data (13, 16, 17), mainly for two reasons.

(1) Although the mathematical bases required to compute the metal flux at a consuming interface have been described both in presence of a single ligand (18–20) and in mixtures of ligands (21–23), they assume that all ligands are present in excess compared to metal. This condition is not always fulfilled in natural systems, for example, for complexation with fulvics whose complexing capacity of the strongest sites is very low (24, 25). Importantly, no user-friendly code, for such computations, was accessible until now. Only recently, two such codes (FLUXY (26) and MHEDYN (27)) have been reported.

(2) The parameter values required for such calculations are not readily available. It is well-known that the selection of thermodynamic constants for equilibrium models is sometimes difficult, in particular, for complexes with fulvics or suspended particles. It is even more so for dynamic parameters (diffusion and rate constants) because of the lack of availability of reliable experimental data. It will be shown in Parts I and II of this series that theoretical estimation of their values is possible. It requires the use of appropriate models, as well as additional information on the complexant properties, such as the size distribution of particulate aggregate complexes, the structure of aggregates, or the site
distribution and electrostatic properties of fulvic and humic substances.

Another complication is that environmental systems contain many complexants with quite different properties (28). They can be divided into three categories: (a) The small ligands, typically, have molar masses of $\geq 300$ Dalton (e.g., OH\(^-\), CO\(_3\)\(^2-\), amino acids, citrate, etc.) and form $1/n$ successive complexes, which are described by conventional coordination chemistry; hereafter, they are referred to as "simple ligands". (b) The organic macromolecules, often chemically heterogeneous with polyelectrolytic properties, in particular fulvic and humics, form $1/1$ metal complexes with their complexing sites and exhibit a wide distribution spectrum of equilibrium and rate constants. In addition, they usually bear an overall electric field which markedly influences metal complexation. The homo- or heteroaggregates of these macromolecules are included in category c. (c) The natural "particles" are more often aggregates of various types of solids or polymeric compounds. Their binding properties can also be modeled via the formation of $1/1$ metal complexes in the presence of an electric field. Their size distribution, however, is usually much broader (several orders of magnitudes) than those in category a or b, which significantly influences their diffusive transport. In addition, metal diffusion inside the aggregate may also affect the overall kinetics of metal–aggregate interaction. Putting all these effects into one homogeneous code to compute and compare the contribution of each of the metal species to the metal flux at a consuming interface is not straightforward.

The purpose of this series of papers is to provide the required information for metal flux computation at a consuming interface, such as a bioanalogical dynamic sensor (2, 29) or the plasma membrane of a microorganism (e.g., 5), in the presence of any type of complexant or their mixture. Compilations of selected available parameter values and the appropriate physicochemical theories required to compute these values when experimental data is unavailable are included. The dynamic constants considered are shown in Figure 1, for the case of only one ligand, L, and two complexes, ML and ML\(_2\), for the sake of clarity. However, the concepts discussed below are applicable to systems containing a wide range of ligands with broadly varying dynamic properties. The possible interactions between complexants, in particular aggregation processes, are not considered here (see Part II for more discussion). The effect of electrical migration on metal transport is also not considered here because the focus of the papers is on the flux of trace metals, that is, those with typical total concentrations of $\leq 10^{-6}$ mol dm\(^{-3}\). Electrical migration effects are negligible (18) when the ionic strength is at least 100 times larger than the metal species of interest, which is the case for most trace metals in natural waters.

The major parameters needed for flux computations are the following (Figure 1; see section 2.1 for more discussion): the diffusion coefficients, $D$, of each species, the rate constants for complex formation, $k_\text{f}$, and dissociation, $k_\text{d}$, of the complex ML, $K_\text{f}^\infty$ and $K_\text{d}^\infty$ = acid–base equilibrium constants of L, $D_\text{av}$ = average diffusion coefficient of L, LH, and LH\(_2\) (section 2.1 for discussion).

![FIGURE 1. Schematic representation of reaction–diffusion processes of successive metal complexes ML\(_n\) at a consuming interface. $D_i$ = diffusion coefficient of species $i$, $K_i$, $k_{i\text{f}}$, $k_{i\text{d}}$ = equilibrium constant, formation, and dissociation rate constants of the complex ML, $K_\text{f}^\infty$ and $K_\text{d}^\infty$ = acid–base equilibrium constants of L. $D_\text{av}$ = average diffusion coefficient of L, LH, and LH\(_2\) (section 2.1 for discussion).](image)

### 2. Dynamic Parameters for Simple Complexes

#### 2.1. Diffusion Coefficients

Listings of the best values of diffusion coefficients are given for (i) free hydrated metal ions in water (Table S1a), (ii) inorganic ligands and some organic ligands (Tables S1b and S2a–c), and (iii) specific metal complexes (Table S3). The values reported for self-diffusion of metal complexes are scarce. The criteria of selection for parameters of Tables S1 and S2 are explained below and in section A1 of the SI. One can make the following comments on the reported values:

When possible, values of diffusion coefficients at infinite dilution are given in Tables S1–S3 and are applicable for most natural waters. Usually, the deviation of a diffusion coefficient, $D$, from its infinite dilution value is less than a few percent when the total salt concentration is lower than 0.1 M. This difference is mainly the result of the changes in the solution viscosity, $\eta$, and can be corrected for by assuming an inverse relationship between $D$ and $\eta$, as in the Stokes–Einstein equation (18, 31).

The effect of temperature on a diffusion coefficient is expressed by its temperature coefficient (in percent per kelvin): $100(dD/D)/dT$. For most inorganic ions (18), values of 2.78–2.99%/K are obtained. Similar values are found for small organic molecules such as amino acids (2.2–2.3%/K, Table S2b).

A few values of diffusion coefficients for peptides are given in Table S2c. A comparison of $D$ values of compounds having similar molar masses, $M_\text{m}$, for example, EDTA (Table S2a) and leucylglycylglycine (Table S2c), suggests that in this size range, branched and linear molecules have comparable $D$ values. The relationship between $D$ and $M_\text{m}$,
for macromolecules in the range of 200–10^5 Daltons is discussed in detail in (32). In particular, in this range, most macromolecules have spherical conformation, and plots of experimental values of log D versus log M_m show (28) that the following semiempirical relationship can be used at 25 °C with good accuracy (with D in m^2/s and M_m in Daltons)

\[ D = 2.84 \times 10^{-9} M_m^{1/3} \]  

(1)

D values for several polysaccharides having M_m values in the range of 10^3–10^5 Daltons are reported in the literature (33).

D values for specific metal complexes (Table S3) are not easily available and should be often estimated. The very small ligands (e.g., inorganic anions) replace water molecules in the inner hydration shell of the metal ion. The net difference between the D values of the hydrated metal and the complex, may be then rather small, and they can be assumed to be equal, as an acceptable approximation. Note, however, that when the hydration shell is completely replaced by small hydrophobic anions like Cl\(^-\) when the hydration shell is completely replaced by small hydrophobic anions like Cl\(^-\) (HgCl\(_2\), in Table S3), the diffusion coefficient of the complex may become significantly greater than that of the hydrated ion. As the ligand size increases, the D value of the complex tends toward that of the ligand. This seems to be true when M_m is greater than ~300 Da.

Because many ligands may exist in several protonated forms, the computation of the transport and reaction of all these species may become prohibitively computer-time-consuming. In such cases, it is useful to consider (i) the diffusion coefficients of the free ligand, L, and its protonated forms, LH\(_i\), (i = 1–h) to be equal, unless conformation changes occur during protonation, and (ii) L and all its protonated forms to be at equilibrium because the proton exchange reaction is usually fast. Under these conditions, they can be treated as an entity, with regards to their reactions with M and their diffusion processes (Figure 1), having a concentration denoted as [LH\(_i\)] = [L] + \(\sum_{i=1}^{h} [LH\(_i\)]\), and an average diffusion coefficient, \(\overline{D}\), given by (1B)

\[ \overline{D} = D_L \frac{1}{\alpha_{L(H)}} + \sum_{i=1}^{h} \frac{D_{LH\(_i\)}}{\alpha_{LH\(_i\)}} \]  

(2)

where

\[ \alpha_{L(H)} = \frac{[LH\(_i\)]}{[L]} = 1 + \sum_{i=1}^{h} \beta_{LH\(_i\)} \]  

(3)

\(\beta_{LH\(_i\)}\) is the \(i^{th}\) cumulative acid–base constant, and \(D_L\) and \(D_{LH\(_i\)}\) are the diffusion coefficients of the corresponding species. As mentioned above, \(\overline{D} = D_L\) when the diffusion coefficients of all the protonated species are equal to \(D_L\). In the opposite case, for \(\overline{D}\) to be constant in the bulk solution and in the diffusion layer (Figure 1), the medium should be sufficiently well pH-buffered for \(\alpha_{L(H)}\) to also be constant. In aquatic systems, this condition usually holds when M is a trace metal; if not, diffusion of H\(^+\) and OH\(^-\) have to be taken into account.

2.2. Selection of Thermodynamic and Conditional Stability Constants. M forms successive complexes, ML, ML\(_2\), ..., ML\(_n\), with most simple ligands. Their equilibrium constants can be expressed either as stepwise, \(K_{n,ML}^{\text{un}}\), or cumulative constants, \(\rho_{n,ML}^{\text{ML}}\),

\[ K_{n,ML}^{\text{un}} = \frac{[ML_n]}{[ML_{n-1}][L]} \]  

\[ \rho_{n,ML}^{\text{ML}} = \frac{[ML_n]}{[M][L]^n} \]  

(4)

(5)

A detailed discussion of the thermodynamic properties of these complexes is out of the scope of this paper. The selection of stability constant values is not straightforward, despite the availability of numerous compilations (34–36). For example, the values of log K registered in the databases of common codes, for calculation of metal species distribution (e.g., MINTEQ and MINEQL) are not always the most correct ones and should be checked carefully. Because the ratio of the association rate constant, \(k_a\), to the corresponding stability constant, \(K\), of a complex is often used for evaluation of its dissociation rate constant, \(k_d\), the errors on both \(k_a\) and \(K\) may affect \(k_d\) and should be minimized.

Attention should be paid particularly to the following aspects: (i) The value of \(k_a\) is closely linked to a given reaction mechanism. Thus, to compute \(k_a\) from \(K = k_a/K\), values of \(k_a\) and \(K\) for the same reaction are required (see section 2.3 for examples). (ii) When several log K values are reported for the same reaction, the recommended selection procedure is to plot these values as a function of \(1/k\) (with \(k = \text{ionic strength}\)) at the temperature of interest. The value of log K at zero ionic strength, the ionic strength correction parameters, and the standard deviations on these parameters can be obtained from polynomial fittings of such plots. These data are listed in Table S4 for a few bivalent metal–inorganic anion complexes particularly relevant to aquatic chemistry. When required, corrections for temperature can be made from the enthalpy of formation of the complex (e.g., \(\Delta H = 37 \text{ for theory and tables of values}\)). The above approach to select a stability constant is also applicable to acid–base constants.

As discussed in section 2.1, the protonation/deprotonation reactions of ligands are usually very fast compared to metal fluxes and can be considered to be always at equilibrium. Under these conditions, it is convenient to express the metal complex equilibria in terms of conditional stability constants at the pH of interest. For instance, for the complex ML\(_n\), the relation between the thermodynamic stability constant \(\beta_{n,ML}\) and the corresponding conditional constant, \(\rho_{n,ML}^{\text{ML}}\), is given by

\[ \rho_{n,ML}^{\text{ML}} = \frac{[ML_n]}{[M][L]^n} = \frac{[ML_n]}{[M][L]^n} = \frac{\beta_{n,ML}}{\alpha_{L(H)}} \]  

(6)

where [LH\(_i\)] is the total concentration of protonated and unprotonated forms of L and \(\alpha_{L(H)}\) is the degree of protonation of L (eq 3).

2.3. Association Rate Constants of 1/1 ML Complexes with Unprotonated Simple Ligands. The important steps in the formation of the complex ML by reaction of M and L are depicted in eq 7

\[ M + L \rightarrow \frac{k_{s,ML}}{k_w} (M,L) \rightarrow \frac{k_{s,ML}}{k_w} ML \]  

(7)

\(k_{s,ML}\) and \(k_w\) are the rate constants for the formation/ dissociation of the outer-sphere complex (ML), whereas \(k_{s,ML}\) and \(k_w\) are the intrinsic rate constants for the formation/ dissociation of the inner-sphere complex ML. In the classical Eigen–Wilkins mechanism (38), the formation of the outer-sphere complexes is supposed to be so fast that the corresponding equilibrium is always reached. The rate-limiting step of complex formation is assumed to be the elimination of a water molecule from the inner hydration shell of the metal ion, represented by \(k_w\). The corresponding pseudo-first-order rate constant (often denoted by \(k_{s,ML} = k_w\)) depends only on the nature of M and the solvent (here, water). The best values of \(k_{s,ML}\) as well as ranges of reported values, are given in Table S5 for a number of metal ions. As can be seen, the uncertainties on these data are often significant, and it is one of the major limitations in the
accuracy of flux computations. The dissociation rate constant \( k_d \) depends on ML bond energy and can be evaluated as discussed below.

It must be pointed out that in aquatic environmental systems, both M and L concentrations may be very low. For example, the concentrations of the free forms of trace metals and strong ligands may be \(< 10^{-9} \text{ M} \) (sometimes by a few orders of magnitude). In addition, a number of natural ligands are supramolecular (see below). Their small diffusion coefficients and highly negative electric charge lead to lower \( k_d \) and \( k_a \) values. Under such conditions, the formation/dissociation of the outer-sphere complex by diffusion of M and L may become the rate-limiting step in eq 7, as discussed below.

A general expression, for the effective rate constants for the formation and dissociation of ML, can be derived by application of the stationary-state approximation (39) to (M,L) in eq 7, that is, the assumption that its concentration is independent of time

\[
\frac{d[(M,L)]}{dt} = k_a^{in}[(M)] + k_d^{in}[(ML)] - k_a^{out}[(ML)] - k_d^{out}[(M,L)] = 0 \quad (8)
\]

By combining the \([M,L]\) obtained from eq 8 with the formation rate of the inner-sphere complex ML, \( \frac{d[ML]}{dt} = k_d^{in}[(ML)] - k_a^{in}[(M,L)] \), one gets

\[
\frac{d[ML]}{dt} = \frac{k_a^{in}k_d^{out}}{k_a^{in} + k_d^{out}}[(M)] - \frac{k_a^{out}k_d^{in}}{k_a^{out} + k_d^{in}}[ML] \quad (9)
\]

which shows that the effective association and dissociation rate constants are

\[
k_a^{MS} = \frac{k_a^{in}k_d^{out}}{k_a^{in} + k_d^{out}} \quad (10)
\]

and

\[
k_d^{MS} = \frac{k_a^{out}k_d^{in}}{k_a^{out} + k_d^{in}} \quad (11)
\]

where the superscript MS refers to the complex of M with the site S of the ligand L (a notation used also for fulvic and particulate complexants). \( k_a^{MS} \) can be readily computed from eqs 10, 15, and 16 with \( k_a^{in} \approx k_a^{out} \).

**Relationship with the Classical Eigen–Wilkins Mechanism.** In the classical Eigen–Wilkins mechanism, the outer-sphere complex is assumed to be at equilibrium with M and L. This implies (eq 10) that \( k_a^{in} \approx k_a^{out} \), hence

\[
k_a^{MS} = k_a^{in}k_d^{out} \quad (12)
\]

where \( k_a^{in} = k_a^{out} \) is the stability constant of (M,L) and is given by the Fuoss equation (39–41)

\[
K_a^{in} = \frac{4\pi N_Aa^3}{3} \alpha^3 \exp(-U(a)/kT) \quad (13)
\]

\( N_A \) (mol\(^{-1} \)) is the Avogadro number, and the units of \( K_a^{in} \) are cubic meters per mole if SI units are used for the other parameters; \( a \) is the distance of closest approach of M and L and can be taken as the sum of the radii of M and L, when L is a simple inorganic anion (see below for other cases). \( a = 5 \times 10^{-8} \) m is usually the accepted value. For simple ligands, \( U(a) \) is the Coulombic energy between M and L, corrected for the ionic screening described by the Debye–Hückel term (39, 41, 42)

\[
U(a) = \frac{2z_Mz_Le^2}{4\pi\varepsilon_0a}(1 - \frac{\kappa a}{1 + \kappa a}) \quad (14)
\]

where \( z_M \) and \( z_L \) are the charge numbers of M and L, respectively, \( \kappa \) is the reciprocal Debye length in the electrolyte solution, defined by \( \kappa = \sqrt{2N_Ae^2/\varepsilon_0k_BT} \), \( k_B \) is the Boltzmann constant (J K\(^{-1} \)), \( e \) is the charge of an electron (C), \( \varepsilon_0 \) is the vacuum permittivity (8.854 \times 10^{-12} \text{ F m}^{-1} \), and \( \varepsilon \) is the relative permittivity of water (78.54 at 25°C). The ionic strength, \( I \), is expressed in moles per cubic meter.

**Generalized Expressions for the Rate Constants.** As mentioned above, in environmental applications, eq 10 cannot always be simplified into eq 12 and, therefore, like \( k_a^{in} \) and \( k_d^{in} \), should be known independently. It has been shown theoretically that they can be computed from eqs 15 and 16 (39, 42)

\[
k_a^{in} = \frac{4\pi N_A(D_M + D_L)U(a)/kT}{\exp(U(a)/kT) - 1} \quad (15)
\]

\[
k_d^{in} = \frac{3(D_M + D_L)U(a)/kT}{\exp(U(a)/kT) - 1} \quad (16)
\]

where \( D_M \) and \( D_L \) (in m\(^2\) s\(^{-1} \)) are the diffusion coefficients of M and L and \( k_a^{in} \) and \( k_d^{in} \) are expressed as m\(^3\) mol\(^{-1} \) s\(^{-1} \), respectively; \( a \) (m) is the distance of closest approach, defined above for the simple inorganic ligands. More complicated cases, that is, multidentate ligands, fulvic/humic compounds, and particulate complexants, are discussed below and in Part II of this series. Note that, in both eqs 15 and 16, when \( U(a) \rightarrow 0 \), \( U(a)/kT(\exp(U(a)/kT) - 1) \rightarrow 0 \). In addition, as expected, the ratio of eqs 15 to 16 also leads to eq 13, that is, the expression for \( k_a^{out} \).

Equation 16 shows that in some cases, \( k_a^{out} \) may be small, particularly when the ligand is highly charged and the ionic strength is rather low (i.e., when \( U(a) \) is highly negative), which is frequent in natural systems. \( k_d^{out} \) then is not negligible compared to \( k_d^{in} \) (eq 10), and when \( k_d^{in} \approx k_d^{out} \), eq 10 tends to \( k_a^{MS} = k_a^{in} \). In Figure 2, the values of \( k_a^{in} \) and \( k_a^{out} \), for various metal ions and ligands with \( z_M = -1, -2, \)
or \(-3\), at \(T = 0.01\ M\), are compared. The values of \(k_{\text{d}}\) for the complexes with fulvic acids (§ 3) are also included in Figure 2. Clearly, the classical Eigen mechanism which assumes fast equilibrium for outer-sphere complex formation (\(k_{\text{d}} \ll k_{\text{a}}\)) should be used with caution: it is not rigorously applicable for metals with very high dehydration rate constants (e.g., Pb(II), Hg(II), Cu(I)); Figure 2) for complex formation with either simple ligands or fulvics. In such cases, eqs 15–16 should be used.

Experimentally determined values of \(k_{\text{a}}\) (denoted as \(k_{\text{a}}\), values in Table S6a), as a function of the theoretically calculated values of \(k_{\text{a}}\) (eqs 10, 15, and 16, are plotted in Figure 3a). The validity of this theory, for the determination of \(k_{\text{a}}\), can be estimated from the variability of the points around the straight line of slope 1.0.

### 2.4. Association Rate Constants in Cases of Multiple Metal Coordinations or Protonated Ligands

Formation of 1/1 ML complexes with unprotonated ligands is not the only type of reaction occurring in aquatic systems. Other important processes are briefly discussed below.

**Successive Complex Formation.** In such cases, the relevant association and dissociation rate constants correspond to each individual reaction step

\[
\text{ML}_{n-1} + L \rightarrow \text{ML}_n
\]

whose stability constant is \(K_a = k_{\text{a}}/k_{\text{d}}\). A first estimation of the value of \(k_{\text{a}}\) can be made from eq 10 or 12, where \(U(a)\) is computed from eq 14, by replacing \(2z_M\) by \(2z_M+1\) in addition, \(k_{\text{d}}\) is modified for statistical reasons (74), as follows. The number of exchangeable hydration water molecules of the metal ion (corresponding to the number, \(v\), of free sites), which can be replaced by the coordinating atoms of \(L\), is smaller for \(ML_{n-1}\) than for \(ML_{n-2}\) or \(M\). The probability of \(L\) to react with \(M\) is thus given by \(v/n\), where \(v\) is the maximum number of free sites (e.g., \(n = 6\) for transition metals with octahedral configuration). The dehydration rate constant of these complexes, \(k_{\text{d}}\), is then given by

\[
k_{\text{d}} = k_{\text{d}}/v\frac{v}{v-1}
\]

In many cases, the value of \(k_{\text{a}}\), based on eq 18, however, should be taken as a lower limit of the real value. This is apparent from the plot (Figure 3b) of experimental \(k_{\text{a}}\) (\(k_{\text{aexp}}\)) values versus the values computed theoretically (\(k_{\text{aMS}}\)) from eq 10 with \(k_{\text{dexp}} = k_{\text{d}}\), for a number of ML complexes, with variable \(n\) (see Table S6b for the list of numerical values).

The ligands \(L\) bound to \(M\) in \(ML_{n-1}\) may affect the binding energy of the remaining water molecules in the inner hydration shell of \(M\) (usually the energy decreases), leading to \(k_{\text{d}}\) values greater than those given by eq 18 and, consequently, to \(k_{\text{dexp}}\) values up to 1–2 orders of magnitude greater than \(k_{\text{dMS}}\) (Figure 3b; 38, 39). This effect is the most important with donor ligands such as SCN\(^-\) or CN\(^-\). But for carboxylate ligands, it is weak or negligible. Hydroxo complexes are of special importance: the rate of water loss of a hydrolyzed metal ion can be much larger than that of the free metal ion, in particular, for slowly reacting metals, such as Cr(III), Al(III), and Fe(III), so that their reactions with other ligands may be much faster than those of the free metal ion. This is directly related to the dependence of \(k_{\text{d}}\) on the charge to radius ratio of the metal ion (7 and ref therein). For example, the \(k_{\text{d}}\) values are \(2 \times 10^6\), \(1 \times 10^5\), \(\sim 10^7\), and \(\sim 10^8\) \text{s}^{-1} \text{ for Fe(H}_2\text{O)}_5\text{OH}^+\), Fe(H)\text{O)}_5\text{OH}^2+, Fe(H)_2\text{O)}_6\text{OH}^+, and Fe(HO)_2\text{O)}_4\text{OH}^+, respectively.

**Complexes with Organic Chelating Agents.** With a multidentate ligand \(L\), the complex formation mechanism may be quite different from that depicted in eq 7, and experimental data should be preferably used for the association rate constant. In the absence of such data, the approach described in section 2.3 can be employed, provided that the steric effects for complex formation are weak or negligible. The formation of the first coordination bond (i.e., with a first arm of the chelating agent), in this case, is often slower than any other successive bond formation and is, as with the simple ligands,
controlled by the loss of a water molecule from the inner coordination shell of M. Hence, eqs 12 and 13 or 10, 15, and 16 may be used. The approximation made is often reasonable for bidentate ligands (Figure 3a) and sometimes for ligands having higher coordination. The binding of the nth coordinating atom \((n > 1)\) may become the limiting step in the presence of important steric constraints (39), and the overall rate constant is then lower than that obtained from eq 10. For many multidentate ligands, an additional difficulty may arise in the computation of \(U(a)\) because of the presence of several different charges (e.g., \(-\text{NH}_2^+\) and \(-\text{COO}^-\) in amino acids) at different positions. \(U(a)\) then is the sum of all the electrostatic interactions in the complex ML, including the intramolecular interactions between the different charged sites on L. The computation of \(U(a)\) then requires information on the geometrical configurations of L and ML, as discussed in some detail in the literature (43).

**Metal Complexes with Protonated Ligands.** Most ligands may exist in protonated forms. ML then may be formed by two parallel reactions of M, with either L or the protonated ligand HL. When possible, the reaction paths and the corresponding parameters described in the literature should be used. However, it has been shown experimentally (39) that for many simple mono- and bidentate ligands, as well as for a few multidentate ligands, the overall rate of complex formation can be written as \(R = k_3[L]\), where [L] is the free ligand concentration, and \(k_3\) is an overall rate constant which can be written as

\[
k_3 = k_3^L + k_3^{HL} \frac{[H]}{[H]}
\]

where \(k_3^L\) (\(= k_3^{MS}\)) and \(k_3^{HL}\) are the rate constants for the reactions of M with L (M + L → ML) and of M with HL (M + HL → MHL + H), respectively. The experimental values reported in the literature for \(k_3^{HL} (= k_3^{HL})\) are compiled in Table S6a and discussed below.

When kinetic data are unavailable, the overall formation rate constant \(k_o\) can be estimated theoretically by eq 20 (section A4 of the SI)

\[
k_o = k_3^{ML} \frac{K_{os,ML}}{[H]} + K_{os,HL} \frac{K_{os,ML}}{[H]} \frac{1}{1 + K_{os,ML} K_{os,HL}}
\]

where \(k_3^{ML}\) and \(K_{os,ML}\) are the dehydration rate constants of M, for its reactions with L and HL, respectively. It can be assumed that \(k_3^{ML} = k_3^{MS} = k_3^{HL}\). A comparison of eqs 19 and 20 shows that \(k_3^L = k_3^{MS}\) while \(k_3^{HL} = k_3^{HL}\). Thus \(k_3^L\) and \(k_3^{HL}\) mainly differ in their respective values of \(K_{os}\). Since \(z_{HL}\) is less negative than \(z_{L}\), it is expected that \(K_{os,ML} > K_{os,ML}\) (eq 13), but at low pH, the term \(z_{HL}^+ [H]\) may compensate for this lower \(K_{os}\). In general, eq 20 predicts that the ML formation path via (M,HL) predominates when

\[
[H] = K_{os,ML} / K_{os,ML} K_{os,HL} \frac{1}{1 + K_{os,ML} K_{os,HL}}
\]

and because \(K_{os,ML} / K_{os,ML}^{HL}\) is close to 1.0, regardless of the values of \(z_2\) and ionic strength, the inequality (eq 21) simplifies to \([H] \approx 10 / z_{HL}^+\).

Experimentally determined values of \(k_3^{HL}\) and \(k_3^{HL}\) are compared with theoretically computed values (\(k_3^L = k_3^{MS} = k_3^{HL}\)) in Figure 3c, for complexes with a variety of metals and ligands (Table S6a for numerical values). \(k_3^{HL}\) values are close (although slightly lower) to the theoretical ones for a number of complexes. However, for some complexes, often with multidentate ligands, the difference may be up to 4 orders of magnitude. This is true in particular for most aliphatic amino-carboxylates of Ni, for which the \(k_3^{HL}\) values were too small to be measurable (7, 75). A detailed discussion on the effect of protonation of ligands on complex formation/disassociation rate is out of the scope of this paper.

**FIGURE 4.** Distribution of the hydrodynamic radius of Suwanee river fulvic substances in aqueous solution, calculated from diffusion coefficient measured at pH 8.5 and low ionic strength (5−27 mM), using the Stokes−Einstein equation. Techniques used are fluorescence correlation spectroscopy (FCS), flow field flow fractionation (FIFF), and NMR (PG-NMR). The signal is normalized to give an equivalent total signal intensity. The bar histogram corresponds to the thickness distribution of the SWFA adsorbed on mica surfaces, measured by AFM. The figure shows that the SWFA flatten somewhat, but not completely, when they are adsorbed at the surface. Modified from ref 44.

**3. Dynamic Parameters for Metal Complexes with Humic Substances**

This section only deals with fulvics and humics dissolved as isolated molecules, that is, noaggregated with each other or with other colloidal material. Aggregates are treated in part II of this series.

**3.1. Nature of Fulvic and Humic Complexants.** The molecules of fulvic (FS) or humic (HS) substances can be visualized (28, 44–46) as relatively small (\(M_m \approx 1000−2000\) Da, radius \(\approx 1\) nm; see section 3.2.), spherical, rather rigid, branched, highly hydrated macromolecules, bearing a high electric charge density at pH > 5 because of the deprotonated carboxylate sites. Interestingly, the size and molar mass distribution windows of fulvic and humic substances are relatively narrow (Figure 4) under environmental conditions, in the absence of homoaggregation. Two types of complexing sites can be discriminated (28, 47): (i) the major sites, which represent \(\geq 90\%\) of the whole sites, are weak complexing sites, mainly composed of single carboxylate or phenolic groups, and (ii) the minor sites, which comprise \(< 10\%\) of the whole sites, have moderate to very strong complexing strength and a highly variable chemical nature (e.g., salycylate, acetyl-acetone, N- or S-bearing chelating sites; 28, 48, 71). In unpolluted environmental conditions, they play a major role in the complexation of trace metals. The reactions with these sites only are discussed below.

The site density of major sites is typically (28, 49) 7 mol/1 mg in HS to 10 mol/kg in FS. Combination with the above molar mass yields site densities of 3 of (HS) to 10 (FS) sites per molecule. Since the minor sites represent less than 10% of the major sites, each molecule of FS or HS statistically contains 0 or 1 minor complexing site. Thus, as far as the properties of minor sites are concerned, FS or HS can be visualized as an ensemble of different but similar molecules having (a) the same size (\(r_1 \approx 1\) nm), (b) similar density of carboxylate (3 per HS molecule, 8 per FS molecule) and phenolate groups (4 per HS molecule, 3 per FS molecule), (c) a significant electric charge density resulting from the deprotonation of carboxylate groups in the usual pH range.
which creates an overall electric field over the whole fulvic/humic molecule (50), that is, in a domain significantly larger than the complexing site dimension, and (d) one or no minor site (with moderate or strong complexation affinity) located in the above-mentioned electric field.

In addition, because the chemical nature of the minor sites varies widely, a solution of fulvics or humics can be considered to be an ensemble of \( n \) classes of similar molecules, differing only by the binding energy of their minor complexing sites (the class zero corresponding to the fulvics or humics without minor complexing site). The interactions of \( M \) with FS or HS is then described by a set of reactions between \( M \) and each site type \( n^i, S \), of the mixture of ligands.

\[
M + ^iS \rightleftharpoons M^iS \tag{22}
\]

3.2. Diffusion Coefficient of Humic Compounds and Their Metal Complexes. The amount of data reported on the diffusion coefficients of fulvic and humic substances, in the literature, is rather limited. A few values for the gyration radius or diffusion coefficients have been published (46, 51–54), but they have often been determined using techniques like analytical centrifugation or transmission electron microscopy, which are either prone to artifacts or not sensitive enough to be used in dilute solution, that is, in complete absence of homoaggregation. Only recently developed, sensitive, and reliable techniques (fluorescence correlation spectroscopy, flow field flow fractionation, and atomic force microscopy) could be combined to measure unambiguous values of diffusion coefficients and sizes of fulvic and humic substances as function of pH and ionic strength (44, 55). These data, along with electrophoretic measurements (50), unequivocally showed that fulvic and humic molecules behave as rather rigid spherical molecules and provided a detailed database for diffusion coefficient and hydrodynamic radius \( r_{DS} \) and \( r_{HS} \) for fulvic and humic substances, respectively, for soil-derived aquatic fulvic and humic substances, particularly, those of Suwanee River (Figures S1A and B and S2). As mentioned earlier, all the techniques used showed that the distribution window of \( r_{DS} \) is rather narrow for an environmental macromolecule (Figure 4).

The representativity of these values for fulvics and humics of other aquatic origins has been confirmed from a systematic study of fulvic substances extracted from 18 different water bodies (56). The corresponding variability of diffusion coefficient values was \( \pm 20\% \), with an average value of \( 2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) \( (r_{DS} \approx 1.6 \text{ nm}) \), that is, results were very similar to those obtained for Suwanee river FS. In addition, the data clearly suggest that at the low concentration level found in natural waters (usually \( <20 \text{ mg L}^{-1} \)) and at \( pH \geq 5 \), aquatic FS and HS molecules are little or not at all aggregated with each other.

Very little information, about the diffusion coefficients of metal fulvic and metal humic complexes at natural, low concentrations of fulvics or humics is available in the literature. Values of \( D \approx 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) have been determined by voltammetric techniques for Pb–fulvic complexes (57). As expected, these values are similar to those reported for fulvics and humics alone (Figures S1 and S2) because the radii of hydrated fulvic and humic molecules are at least 10 times bigger than those of the relevant unhydrated metal ions. In addition, because FS and HS are rather rigid molecules, only small conformation changes are expected during the metal complex formation. Consequently, as a good approximation, the diffusion coefficients of the metal–fulvic or metal–humic complexes can be taken to be the same as those of fulvic and humic molecules.

3.3. Association and Dissociation Rate Constants of Metal Fulvic Complexes. For the sake of simplicity, in the following discussion, only the term fulvic will be used, even though the concepts discussed in the rest of section 3 are applicable to both humics and fulvics. First of all, consider the reaction between a metal ion \( M \) and a single type of minor sites \( i \) of the fulvic molecules. Three effects may influence the overall kinetics of reaction (Figure 5): (i) the diffusion of \( M \) and FS toward each other, followed by diffusion of \( M \) inside FS, to form an outer sphere \( (M, S) \) complex with the minor complexing site \( S \), (ii) the electric field inside the FS, which influences the stability and formation/dissociation rates of the outer-sphere complex, and (iii) the kinetics of formation/dissociation of the inner-sphere complex \( M^iS \), which is controlled by the rate of elimination of a water molecule from the inner hydration shell of \( M \), in the complex \( (M, S) \).

In aquatic systems, the concentration of fulvic molecules containing the most strongly binding minor sites might be less than \( 10^{-8} \text{ M} \) and the free \( M \) concentration is often much lower. In addition, fulvics usually bear a strong negative electric field, which slows down the dissociation of the outer-sphere complex. Thus the formation/dissociation rates of the outer-sphere complex may become the rate-limiting step for \( M^iS \) formation (Figure 2), contrary to the assumption made in the classical Eigen mechanism (section 2.3). Hence, the generalized eqs 10, 15, and 16 should be used for computing the effective association rate constant of the complex, rather than eq 12. For the fulvic complexes, the potential energy, \( U(a) \), between \( M \) and \( S \) results from the interaction of the positive charge of \( M \) with the overall electric field of FS. Hence, \( U(a) = z_M e \Psi(a) \), where \( e \) is the elementary electric charge, \( z_M \) the number of charge of the ion \( M \), and \( \Psi(a) \) the electric potential at the distance \( a \) of the site \( S \). Detailed profiles of \( \Psi \) inside the fulvics and humics, as function of \( pH \) and ionic strength, have been reported in the literature (50) and are given in Figure S3. They are average profiles for the ensemble of fulvic (or humic) molecules. In addition, the position of a site \( S \) will vary statistically in the various FS/HS molecules. Thus, there is no one single value of \( U(a) \) for site type \( n^i \), and an average value of \( \Psi \), \( \Psi \), obtained from Figure S3, should be used in preference for the computation of \( k^{on}_S \) and \( k^{off}_S \). The values of \( \Psi \) for various \( pH \) and ionic strength conditions are given in Table 1. They are consistent with other observations of the literature (48, 73).

Table 1 shows that, at natural \( pH \) and ionic strength, \( \Psi \) is always negative, having an absolute value of \( >30 \text{ mV} \). Under these conditions, the exponential term in the denominators of eqs 15 and 16 becomes much smaller than one and the rate constants are given by
TABLE 1. Average Value of the Potential Difference, ψ, between the Inside and Outside of Fulvic Macromolecules for Various Values of pH and Ionic Strength, I

<table>
<thead>
<tr>
<th>Ionic Strength (mM)</th>
<th>pH 10.7</th>
<th>pH 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-99.6</td>
<td>-40.7</td>
</tr>
<tr>
<td>20</td>
<td>-36.0</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>-32.0</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-32.0</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>-32.0</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>-66.4</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>-59.0</td>
<td></td>
</tr>
</tbody>
</table>

*ψ* values are calculated from Figures S3-1 and S3-2 by integration over the sphere of radius *r*<sub>os</sub>, as mentioned in SI (section B2). The values in the table correspond to experimental measurements under the given conditions. Other values at any pH and ionic strength, in the ranges 4 < *pH* < 11 and 0.005 M < *I* < 0.15 M, can be computed with the following empirical equation, derived in the SI (section B2): ψ = -217.4 + 127.9 *pH* - 28.29 *pH<sup>2</sup> + 2.496 *pH<sup>3</sup> - 0.07685 *pH<sup>4</sup> + 3.159 pH log *I* - 3.864 log *l*.

3.4. Relationship between Kinetic and Thermodynamic Complexation Constants. By substituting the expressions of *k<sub>os</sub>MS* and *k<sub>os</sub>** in **eqs 10 and 11) in eq 25, one gets

\[ k = k_{\text{os}}^{\text{MS}}/k_{\text{os}}^{\text{d}} \]


3.5. Overall Kinetic Properties of Metal–Fulvic Complexes, Based on Their Kinetic and Thermodynamic Complexing Site Distributions. Because the fulvic acids include a large number of different site types, with different dissociation rate constants, *k<sub>os</sub>** in **eq 9), the fulvic site distribution with respect to their *k<sub>os</sub>* values (i.e., the kinetic site distribution) must be considered to compute the overall metal flux. Because the association rate constant is site-independent, the latter distribution is directly related to that based on the stability constants, *K*, which can be obtained as described below. All experimental data show that under most environmental conditions, metal complexation by fulvic minor sites follows the so-called linear Freundlich isotherms (28, 58–61), over several orders of magnitude of [M]

\[ \log [\text{MS}] = \Gamma \log \left( \frac{K^*_F}{1 - T} \right) + \Gamma \log [M] \]

where [MS] is the total bound metal molar concentration at a given value of [M] and [FS] is the concentration of fulvic substances in kg dm<sup>-3</sup>. *K* and *Γ* are constants characteristic of a given metal at the conditions used (see below).
Equation 29 is typically valid for all trace metals when [MS]/(FS) < 0.5 mol/kg (Figure 5A and B, 59–61, 65), that is, for most aquatic systems. This [MS]/(FS) range also corresponds to that of the minor sites of fulvic discussed in section 3.1.

Γ is a dimensionless parameter, linked to the chemical heterogeneity of fulvics, and consequently to their metal complexing buffering capacity, as discussed quantitatively in the literature (62, 67) and section B3 of SI. Its value lies between 0 < Γ < 1 and is often close to 0.5. Γ\textsubscript{o} has units of stability constant, that is, dm\textsuperscript{3} mol\textsuperscript{-1}, but its value depends on units used for [MS]/(FS). Interestingly, both Γ and Γ\textsubscript{o} depend on the nature of the metal ion and conditions (pH, ionic strength), but within experimental errors, they can be considered to be independent of the origin of the fulvic (28, 58, 70; section B3 in SI). It should be mentioned that various models have been proposed to interpret the observed isotherms in terms of metal–fulvic molecular interactions at equilibrium. These models are discussed in detail elsewhere (28, 48, 63–65) and will not be repeated here. It must however be pointed out that the parameters Γ and Γ\textsubscript{o} are model independent because they can be determined directly from the experimental data, whitout making any physicochemical assumption. Γ and Γ\textsubscript{o} data for aquatic fulvic substances are compiled in Table 2.

In the present context, the striking feature is that a Freundlich isotherm (eq 29), for the test metal ion, corresponds to a mathematically well-defined distribution of complexing sites (the so-called Sips distribution; 72), with regards to their thermodynamic stability constant (thermodynamic site distribution). In the linear regime of the isotherm (eq 29), that is, for the minor site types, the corresponding cumulative site distribution is given by

\[ \log \chi = \log(\Phi/\omega) + \Gamma \log \Gamma\textsubscript{o} - \Gamma \log \Gamma K \]  

(30)

By combining eqs 25 and 30, the thermodynamic site distribution can be related to the corresponding kinetic site distribution, that is, the distribution of sites with regards to \( k\textsubscript{o} \).

In eq 30, \( \chi \) is the cumulative mole fraction of sites \( i \), that is, the sum of the mole fractions of all site type \( (\Delta\chi) \), whose equilibirum constants lie between infinity and \( K \). \( \sigma = \sum_{i=1}^{\infty} [S]/(FS) \) is the total density of the sites in the FS in the same units as those of [MS]/(FS), coherent with the value used for \( \Gamma\textsubscript{o} \). It is characteristic for a given type of fulvic substances, regardless of its origin (typically for aquatic soil-derived FS, \( \sigma \approx 6–10 \) mol/kg of FS, that is, \( \sigma \approx 12–20 \) mol/kg of C when (FS) is expressed in terms of its equivalent of dissolved organic carbon (DOC; 28). \( \Phi \) is linked to the Sips distribution function and is given by

\[ \Phi = \left( \frac{\Gamma}{1-\Gamma} \right)^\frac{1}{\Gamma} \sin^\frac{(1-\Gamma)\pi}{\Gamma\pi} \]  

(31)

With a good approximation, \( \log \Phi = -0.17u \) in the range of 0.2 < Γ < 0.8. It must be pointed out that eq 30 has been confirmed by theoretical computations (48, 71), also enabling the appraisal of the chemical nature of a few important complexing sites of the fulvics.

In practice, the kinetic and thermodynamic distributions of the metal–fulvic complexes under specific conditions can thus be computed as follows. The \( \log K \) scale is divided into equal \( \Delta \log K \) intervals. The \( \log \chi^\ast \) couple set, as a whole, is first computed from eqs 30 and 31 and the couples \( (\{S\}, \{K\}) \) are obtained from

\[ \{S\}_i = (\chi^\ast - k^{-1} \chi^\ast) = 0.5 \log(\chi^\ast - k^{-1} \chi^\ast) \]  

(32)

and

\[ \log \chi^\ast = 0.5 \log(\chi^\ast - k^{-1} \chi^\ast) \]  

(33)

From this set of couples, the distributions of \([M\]S and \([S]\) with respect to \(\log K\) are obtained using any computer code (e.g., 8, 10). Flux computations can then be performed by using the expression for \( k\textsubscript{s} \) (section 3.3) and the values of \( k\ast \) corresponding to the above set of \( (\{S\}, \{K\}) \) couples, obtained from eq 25. The following aspects are worth noting:

1. To get the correct site distributions, \( \Delta \log K \) should be small enough so that the discrete distribution is close to the continuous one. The use of very small values, however, may need long computer times for flux computations. \( \Delta \log K \) values between 0.1 and 0.5 (preferably not larger than 0.3) are recommended.

2. The selection of the \( \log K \) range, \( \log K\text{min} \) to \( \log K\text{max} \) (as well as the related \( k\text{s} \) range) should also be made carefully. It should include site types for which, at the test value of \( [MS]/(FS) \) (or \( [M] \)), the \( \chi^\ast K \) values are neither too low (unoccupied sites) nor too high (very strong and inert complexes). For this purpose, eqs 29 and 30 can be linked using the so-called differential equilibrium function, \( K^\ast \), which has a few salient features, as explained in section B3 of the SI. First, it can be readily computed from experimental data using eq 34

\[ K^\ast = (1-\Gamma)/\Gamma[M] \]  

(34)

and by combination of eqs 29 and 34, \( K^\ast \) can be related to the desired value of \([MS]/(FS) \). In addition, it is theoretically well established (62) that \( K^\ast \) is an average of the individual stability constants of all sites, weighted over their concentration and degree of occupation, in such a way that the value of \( K^\ast \) is close to (or equal to, when \( \Gamma = 0.5 \)) that of \( K \) for which \([M\]S = \<[S] \). On a logarithmic scale, it is thus the center of the distribution (section B3 in SI). Finally, it has also been shown that the complexes with \( \log K^\ast \) \( \geq \log K^* + 2 \) are saturated but are present in such low proportions that they do not play a significant role in the overall flux of metal–fulvic complexes (27). Furthermore, the contribution of complexes with \( \log K^\ast \) \( < \log K^* - 2 \) is also small because the corresponding sites are almost unoccupied (section B3 and
discussion of Figure S4 in SI). Thus for computation of thermodynamic distribution, the most useful range of $\log K$ to explore is $\log K_{\text{min}} = \log K - 2 \leq \log K \leq \log K + 2 = \log K_{\text{max}}$. For flux computations, the limiting values of $\log k_d$ of the kinetic distribution can be estimated from the limiting values of $\log K$, although they should only be considered as guidelines. In particular, in some cases, values of $\log k_d$ corresponding to $\log K < \log K^* - 2$ are required (27) because even minute proportions of the very weak but labile complexes may play a significant role in the total flux.

Finally, the selected range of $K$ or $k_d$ should preferably not lie beyond the range of $\log [M]$ for which $\Gamma$ and $K^{no}_n$ have been determined (eq 29). Until now, however, eq 29 has been found to be valid over at least 3–5 orders of magnitude of $\log [M]$, and no limit to its validity has yet been found in the low $[M]$ domain (corresponding to high X values). Thus careful extrapolations of eq 30 is even possible at high $K$ values.

### Symbols

- $a$: distance of closest approach between a metal ion and a complexing site
- $D_X$: diffusion coefficient of species X
- $\bar{D}_L$: average diffusion coefficient of protonated and unprotonated ligand L
- $H$: proton
- $K_{ML}^n$: stepwise equilibrium stability constant of the complex ML
- $K^{os}$: equilibrium stability constant of the outer-sphere complex (ML)
- $K^*$: constant parameter of the Freundlich isotherm (eq 29)
- $k_{-w}$: rate constant for the water loss from the inner shell of an hydrated metal ion
- $k_{d,os}^{n}$, $k_d^{os}$: outer-sphere complex formation/dissociation rate constants of the complex (ML)
- $k_{d,lin}^{n}$, $k_d^{lin}$: inner-sphere complex formation/dissociation rate constants of the complex ML
- $k_{d,MS}^{MS}$, $k_d^{MS}$: effective formation/dissociation rate constant of the complex ML
- $k_{a,ML}^{n}$, $k_d^{n}$: formation/dissociation rate constants of the complex ML from/to ML$^{-n}$
- $k_{a,exp}^{L}$, $k_d^{exp}$: theoretical ($k_{a,exp}^{L} = k_d^{MS}$) and experimental values of ML formation rate constant
- $\lambda_{HL}^{L}$, $\lambda_{HL}^{exp}$: theoretical and experimental values of the rate constant for the reaction $M + HL \rightarrow ML + H$.
- $\lambda_{k,MS}$, $\lambda_{k_d}$: stability constant and dissociation rate constant of the complex $M'S$ formed between $M$ and the fulvic site type $n^i$.

### Literature Cited

4. van Leeuwen, H. P.; Galceran, J. In Physicochemical Kinetics and Transport at Chemical–Biological Surfaces; IUPAC Series on Analytical and Physical Chemistry of Environmental Systems; van Leeuwen, H. P., Koester, W., Eds.; John Wiley: Chichester, U.K., 2004; Vol. 9, Chapter 3.

N. Parthasarathy is greatly acknowledge for helpful discussions. Swiss National Foundation is acknowledged for its support (Grants 20-61871.00 and 200020-101974/1).

### Supporting Information Available

Tables including lists of values for diffusion coefficients for metal ions, inorganic anions, organic ligands, and various metal complexes, stability constants of metal complexes with inorganic ligands, rates of water loss from hydrated metal ions, and experimental rate constants for complex formation, figures including diffusion coefficients of fulvics and humics and their electric potential distribution as function of pH and ionic strength, and concepts including the computation of rate constants of complexes with protonated ligands and that of the complexing site distribution of fulvics and humics, in relation to the physicochemical meaning of the differential equilibrium function. This material is available free of charge via the Internet at http://pubs.acs.org.


Received for review March 22, 2007. Revised manuscript received August 28, 2007. Accepted September 6, 2007.

ES070702P