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Impact of Ligand Protonation on Higher-Order Metal Complexation Kinetics in Aqueous Systems

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The impact of ligand protonation on the complexation kinetics of higher-order complexes is quantitatively described. The theory is formulated on the basis of the usual situation for metal complex formation in aqueous systems in which the exchange of water for the ligand in the inner coordination sphere is rate-determining (Eigen mechanism). We derive expressions for the general case of lability of ML_n species that account for the contributions from all outer-sphere complexes to the rate of complex formation. For dynamic complexes, dissociation of ML is usually the rate-determining step in the overall process $ML_n \rightarrow M$. Under such conditions, it is the role of ligand protonation in the step $ML \rightarrow M$ that is relevant for the kinetic flux. 1:2 complexes of Cd(II) with pyridine-2,6-dicarboxylic acid fall into this category, and their lability at a microelectrode is reasonably well predicted by the differentiated approach. For non-dynamic systems, the kinetic flux arising from dissociation of higher-order complexes contributes to the rate-determining step. In this case, the weighted contribution of protonated and unprotonated outer-sphere complexes in all contributing dissociation reactions must be taken into account. The kinetic flux arising from the dissociation of 1:2 complexes of Ni(II) with bicine at a conventional electrode was quite well described by this combined approach. The results establish the generic role of ligand protonation within the overall framework of metal complexation kinetics in which complexes may be dynamic to an extent that depends on the operational time scale of the measurement technique.

1. Introduction

Understanding of the dynamic features of metal complexes is fundamental to elucidating the significance of metal speciation for processes in environmental and biological systems. Establishment of a rigorous dynamic interpretation framework requires consideration of the effective time scale of these processes and the relevant rate parameters for the species interconversion reactions. In aqueous systems, many complex formation reactions follow the Eigen mechanism,[1,2] i.e., the rapid formation of an outer-sphere complex between the hydrated metal ion, M, and the ligand, L, followed by a slow, rate-limiting dehydration step. In recent years there have been significant advances in the understanding of metal speciation dynamics. Parameters used to quantify lability compare the relative magnitudes of the kinetic, J_{kin}, and diffusive, J_{dif}, fluxes of the complex system. The theoretical basis is developed for the interpretation of data furnished by dynamic analytical techniques[3] and for the relationship between speciation and bioavailability,[4] including aspects such as the size of the consuming interface,[5] multi-ligand complexes, ML_n,[6−8] protonated inner-sphere complexes, and the effect of mixtures of complexants.[9−14]

Until recently, the role of ligand protonation on metal complexation kinetics had not been explicitly considered. The first detailed treatment of the topic for 1:1 ML inner-sphere complexes[15] derived expressions for the lability of metal complexes with protonated and unprotonated ligand species being involved in the formation of the precursor outer-sphere complex. The theoretical framework needs to be extended to describe the significance of ligand protonation for metal speciation dynamics in more involved cases. In the present work we tackle the case of ML_n complexes for which the dissociation to free M involves a sequence of dissociation steps. Quantification of the overall interfacial flux of M requires consideration of all equilibria and pertaining association/dissociation rate constants. Under the simplifying condition of involvement of only the free ligand, it is generally found that the dissociation of ML to M is the kinetically limiting step in the overall process $ML_n \rightarrow M$.[6−8] Here we elaborate on the theory for metal speciation dynamics in ML_n systems by taking into account the involvement of protonated forms of the ligand. Expressions are developed for steady-state diffusion-limited mass transport, under conditions of excess ligand. The concepts are illustrated by experimental data for dynamic and non-dynamic systems.

2. Experimental Methods

2.1. Apparatus. An Ecochemie μAutolab potentiostat was used in conjunction with a Metrohm 663 VA stand. The electrometer input impedance of this instrument is >100 GΩ. The working electrode was a mercury-coated iridium microelectrode (prepared according to reported protocols;[16,17] the radius of a hemispherical droplet was ca. 6×10^{-6} m), or a conventional mercury drop electrode (surface area, $A = 5.2 \times 10^{-7}$ m^2). The auxiliary electrode was glassy carbon, and the reference electrode was Ag|AgCl|KCl(sat) encased in a 0.1 mol dm^{-3} KNO_3 jacket. Measurements were performed at 20 °C. Stripping chronopotentiometry (SCP) measurements were per-

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formed with a stripping current of 5×10^{-11} A at the microelectrode, and 2×10^{-9} A at the conventional electrode, corresponding to conditions of complete depletion in each case.[17,18] The deposition potentials used were −0.95 V for Cd(II) and −1.41 V for Ni(II).

2.2. Reagents. All solutions were prepared with distilled, deionized water from a Milli-Q Gradient system (resistivity >18 MΩ cm). Cd(II) solutions were prepared by dilution of a commercial certified standard from Aldrich. KNO_3 solutions were prepared from solid KNO_3 (BDH, AnalaR). Pyridine-2,6-dicarboxylic acid (PDCA) was from Fluka (purum) and *N*,*N*-bis(2-hydroxyethyl)glycine (bicine) was from Fluka (ultra, ≥99.5%). Cd(II)−PDCA solutions in the pH range 3.7−5.1 were buffered with 5×10^{-3} mol dm^{-3} acetic acid (Prolabo, Rectapur)/sodium acetate (Janssen Chimica, pure), and buffering at pH 6.0 was effected with 0.01 mol dm^{-3} (2-(*N*-morpholino)-ethanesulfonic acid (MES, Fluka, MicroSelect, ≥99.5%). Acetate and MES have low affinity for Cd(II), and, in the presence of PDCA, there is negligible complexation by the buffer components: for acetate, the stability constants for Cd(II) complexation are $\log K_1 = 1.26$, $\log K_2 = 0.74$, and $\log K_3 = 0.70$,[19] and no binding of Cd(II) by MES was observed up to buffer concentrations of 0.1 mol dm^{-3}.[20] Ni(II)−bicine solutions in the pH range 7.0−7.8 were buffered with Na_2HPO_4 (Fluka, MicroSelect, >99.0%)/KH_2PO_4 (Fluka, puriss p.a., >99.5%), and solutions at pH 8.3 were buffered with 2-amino-2-hydroxymethyl-1,3-propanediol (Tris buffer, Fluka, BioChemika, >99.0%). Phosphate and Tris have low affinity for Ni(II), and, in the presence of bicine, there is negligible complexation by the buffer components: for phosphate $\log K_1 = 3.26$ and $\log K(\mathrm{Ni{+}HL}) = 2.08$.;[21,22] for Tris, $\log K_1 = 2.63$ and $\log K_2 = 1.69$.[23] Solutions were initially purged with oxygen-free nitrogen (<0.1 ppm), then a nitrogen blanket was maintained during measurements.

2.3. Choice of Metal−Ligand System. A suitable metal complex to illustrate the concepts presented herein must have a lability that matches the kinetic window of the analytical technique in order to measure kinetically controlled responses. To simplify computations of K^{os}, it is desirable to have a ligand with a well-defined spatial distribution of point charges; however, most simple ligands form complexes that are too labile to be suitable test systems. Furthermore, the pH windows for ligand deprotonation and for the formation of ML and ML_2 must overlap sufficiently so that the role of the various protonated ligand species in the rate-determining step can be discerned. For our present purposes, we wanted to exclude more involved systems such as those with inner-sphere MHL complexes. Selected examples of multidentate ligands with nitrogen and oxygen binding sites were found to fulfill our requirements.

2.3.1. Pyridine-2,6-dicarboxylic Acid (PDCA), $C_5H_3N(COOH)_2$. The ligand protonation constants are[24,25] $\log K_1 = 4.53$, $\log K_2 = 1.87$, and $\log K_3 = 0.5$. For Cd(II)−PDCA, the stability constants measured at 0.1 M ionic strength and 25 °C have been reported as $\log K_1 = 5.31$, 6.51, 6.75, and 5.7 (refs 26−29, respectively) and $\log K_2 = 4.26$, 4.4, and 4.3 (refs 27−29, respectively).

2.3.2. N,N-bis(2-hydroxyethyl)glycine (Bicine) $(HOCH_2CH_2)_2NCH_2COOH$. The ligand protonation constants are[30] $\log K_1 = 8.39$ and $\log K_2 = 1.78$. For Ni(II)−bicine, the stability constants as measured in 0.1 M electrolyte, 20−25 °C, are reported as $\log K_1 = 6.42$, 5.21, 6.5, and 7.7 (refs 30−33, respectively) and $\log K_2 = 4.32$ and 5.0 (refs 30 and 33, respectively). In the inner-sphere complex, the nitrogen and carboxyl group coordinate to the metal, and the hydroxyl groups remain protonated.[34]

3. Theory

We consider a successive reaction sequence in which unprotonated inner-sphere complexes (ML, ML_2, ... ML_n) are formed in a pH range with both L^- and HL in solution, and both protonated and unprotonated outer-sphere complexes are formed in each step. In the present treatment, the equilibrium concentration of protonated inner-sphere complexes is considered negligible, i.e., upon formation they are rapidly deprotonated. Since all of the proton exchange reactions are fast, the treatment of more involved protonated schemes remains straightforward. The first step is the formation of ML:

$$\begin{tikzcd}
 & +\,\mathrm{HL} \arrow[r, shift left, "K^{\mathrm{os}}_{\mathrm{MHL}}"] \arrow[dd, shift right, <-] \arrow[dd, shift left] & \mathrm{M(H_2O)_6{\cdot}HL^{2+}} \arrow[l, shift left] \arrow[r, "k_{\mathrm{w1}}"] \arrow[dd, shift right, <-] \arrow[dd, shift left] & \mathrm{M(H_2O)_5HL^{2+}} \arrow[dd, shift right] \arrow[dd, shift left, <-, "\text{(fast)}"'] \\
\mathrm{M(H_2O)_6^{2+}} & & & \\
 & +\,\mathrm{L^-} \arrow[r, shift left, "K^{\mathrm{os}}_{\mathrm{ML}}"] & \mathrm{M(H_2O)_6{\cdot}L^{1+}} \arrow[l, shift left] \arrow[r, "k_{\mathrm{w1}}"] & \mathrm{M(H_2O)_5L^{+}}
\end{tikzcd} \tag{1}$$

and so forth up to the formation of ML_n ($n \geq 2$):

$$\begin{tikzcd}
 & +\,\mathrm{HL} \arrow[r, shift left, "K^{\mathrm{os}}_{\mathrm{ML}_i\cdot\mathrm{HL}}"] \arrow[dd, shift right, <-] \arrow[dd, shift left] & \mathrm{M(H_2O)}_{6-i}\mathrm{L}_i{\cdot}\mathrm{HL}^{2-i} \arrow[l, shift left] \arrow[r, "k_{\mathrm{w}i}"] \arrow[dd, shift right, <-] \arrow[dd, shift left] & \mathrm{M(H_2O)}_{5-i}\mathrm{HL}_{i+1}^{2-i} \arrow[dd, shift right] \arrow[dd, shift left, <-, "\text{(fast)}"'] \\
\mathrm{M(H_2O)}_{6-i}\mathrm{L}_i^{2-i} & & & \\
 & +\,\mathrm{L^-} \arrow[r, shift left, "K^{\mathrm{os}}_{\mathrm{ML}_i\cdot\mathrm{L}}"] & \mathrm{M(H_2O)}_{6-i}\mathrm{L}_i{\cdot}\mathrm{L}^{1-i} \arrow[l, shift left] \arrow[r, "k_{\mathrm{w}i}"] & \mathrm{M(H_2O)}_{5-i}\mathrm{L}_{i+1}^{1-i}
\end{tikzcd} \tag{2}$$

where $1 \leq i \leq n$, k_{w} is the rate constant of water removal (s^{-1}), and K^{os} is the stability constant for the outer-sphere complex (dm^3 mol^{-1}). For a volume reaction, maintenance of equilibrium is derived from the pertaining reaction rate constants and the relative time scale. Under conditions of sufficient excess ligand over metal, the association reaction is quasi-monomolecular with rate constant $k'_{\mathrm{a}} = k_{\mathrm{a}}c_{\mathrm{L}}$. A system that is sufficiently dynamic to maintain volume equilibrium within a time scale, t, obeys the following double condition:[35]

$$k'_{\mathrm{a}n}t,\ k_{\mathrm{d}n}t \gg 1 \tag{3}$$

At the other extreme, a static system is defined by

$$k'_{\mathrm{a}n}t,\ k_{\mathrm{d}n}t \ll 1 \tag{4}$$

while systems for which

$$k'_{\mathrm{a}n}t,\ k_{\mathrm{d}n}t \approx 1 \tag{5}$$

are denoted as kinetic.

In the stepwise formation of ML_n, it is generally found that the order of stability follows

$$K_1 > K_2 > \ldots K_n \tag{6}$$

Generally the rate of removal of the second water of hydration is faster than that of the first,[6] i.e.,

$$k_{\mathrm{w2}} > k_{\mathrm{w1}} \tag{7}$$

In addition to differences in k_{w} values, the stability of the various outer-sphere complexes involved must also be considered. In eqs 1 and 2, the K^{os} for the outer-sphere complex involving the free ligand will generally not be the same as that for the protonated ligand and, for a given degree of ligand protonation, K^{os} for the complex involving two ligand molecules will generally be lower than that for the complex that contains only one. Thus, in general, upon going from the first to the second step, the stability of the precursor outer-sphere complex will decrease somewhat, but the rate of water removal will increase so that the resulting change in k_a will be small (cf. eq 8).

As a first approximation, neglecting details of K^{os}, the rate of association for the first step, is less than that for the second:

$$k_{a1} < k_{a2} \tag{8}$$

Thus for a dynamic ML system, obeying eq 3, certainly $k'_{a2}t \gg 1$. Also, eq 6 shows that $k_{d2}/k_{d1} > k_{a2}/k_{a1}$, which, combined with eq 8, gives

$$k_{d2} > k_{d1} \tag{9}$$

and hence even more easily than for ML is

$$k'_{a2}t,\ k'_{d2}t \gg 1 \tag{10}$$

i.e., if equilibrium between M and ML is dynamic, then even more so is that between ML and ML_2. In general, we can say that, as long as $K_n < K_{n-1}$ (eq 6), $ML_n \leftrightarrow ML_{n-1}$ is more dynamic than $ML_{n-1} \leftrightarrow ML_{n-2}$.

Protonation/deprotonation reactions are very fast on time scales of metal complex formation/dissociation. Thus it is the equilibrium concentrations of the various protonated/deprotonated species in eqs 1 and 2 that are pertinent for metal complexation kinetics. On the level of the Eigen scheme, the rate constant for loss of a water molecule from the inner hydration sphere is practically unaffected by the presence or absence of a proton in the complexing molecule, L. This reasoning applies to the removal of both the first and any subsequent water molecule, i.e., in eq 1 the value of k_{w1} for $M(H_2O)_6{\cdot}HL^{2+}$ is taken to be the same as that for $M(H_2O)_6{\cdot}L^+$, and in eq 2 k_{wi} for $M(H_2O)_{6-i}L_i{\cdot}HL^{2-i}$ is taken to be the same as that for $M(H_2O)_{6-i}L_i{\cdot}L^{1-i}$. However, the removal of the second water molecule from the inner hydration sphere of M is generally faster than that of the first one, and so forth, i.e., $k_{w1} < k_{w2} < k_{w3}$,... This follows from coordination chemical reasoning: a H_2O molecule will be bound more weakly in $M(H_2O)_5L$ than it is in $M(H_2O)_6$ because L is the stronger ligand.[6] The degree to which k_{w2} exceeds k_{w1} depends on the nature of the metal ion and the ligand involved. For example, for Ni(II) complexes, both the electron-donating ability of the ligand and its structural arrangement in the outer-sphere complex play a role in determining the rate of removal of further water molecules.[36,37] Others have reported that, for Ni(II), k_{w2} increases with increasing number of nitrogens coordinated to M.[38,39] Similar effects have been observed for Co(II).[40,41]

3.1. Flux of Free M. The total rate of inner-sphere ML complex formation, following eqs 1 and 2, is given by

$$R_a = k_{w1}c_{M(H_2O)_6{\cdot}HL} + k_{w1}c_{M(H_2O)_6{\cdot}L} = k_{w1}K^{os}_{M{\cdot}HL}c_Mc_{HL} + k_{w1}K^{os}_{M{\cdot}L}c_Mc_L \tag{11}$$

Here we consider the case of an interfacial process involving consumption of the species M. We introduce the concept of a reaction layer[42] to describe the contribution of electroinactive complex species to the flux of free M toward the interface. The reaction layer is a thin layer adjacent to the consuming interface, within which the dissociation of metal complex species is significant for the flux of M. The thickness of this layer is determined by the lifetime, τ_M, of free M and its corresponding mean diffusional displacement. This concept is the basis for formulation of lability parameters[43] and the notion of kinetic currents.[42] In the case of L and HL, both species contribute to the thickness of the reaction layer of ML, μ_{ML}, to an extent weighted by their respective K^{os} values, and the lifetime of free M, τ_M, is given by

$$\frac{1}{\tau_M} = k_{aML}c_L + k_{aMHL}c_{HL} = k_{w1}K^{os}_{M{\cdot}L}c_L + k_{w1}K^{os}_{M{\cdot}HL}\frac{c_H}{K_{a1}}c_L \tag{12}$$

where all concentrations refer to bulk values.

Equation 12 can be conveniently written as

$$\frac{1}{\tau_M} = k_{w1}\left[K^{os}_{M{\cdot}L} + \frac{K^{os}_{M{\cdot}HL}}{K_{a1}}c_H\right]c_L \tag{13}$$

We define

$$K_1^{os'} = K^{os}_{M{\cdot}L} + \frac{K^{os}_{M{\cdot}HL}}{K_{a1}}c_H \tag{14}$$

thus

$$\frac{1}{\tau_M} = k_{w1}K_1^{os'}c_L = k'_{a1} \tag{15}$$

The reaction layer thickness follows as[15]

$$\mu_{ML} = \left(\frac{D_M}{k_{aML}c_L + k_{aMHL}c_{HL}}\right)^{1/2} \tag{16}$$

The purely kinetic flux for ML → M corresponds to the flux only determined by the dissociation rate, i.e., under conditions where concentration polarization is negligible (c is bulk c), and is given by

$$J_{kinML} = k_{d1}c_{ML}\mu_{ML} \tag{17}$$

and

$$\log J_{kinML} = \log k_{d1}c_{ML}D_M^{1/2} - \frac{1}{2}\log[k_{aML}c_L + k_{aMHL}c_{HL}] \tag{18}$$

Similarly, for the second step in the successive complexation scheme, the total rate of inner-sphere ML_2 formation is

$$R_a = k_{w2}c_{M(H_2O)_5L{\cdot}HL} + k_{w2}c_{M(H_2O)_5L{\cdot}L} = k_{w2}K^{os}_{ML{\cdot}HL}c_{M(H_2O)_5L}c_{HL} + k_{w2}K^{os}_{ML{\cdot}L}c_{M(H_2O)_5L}c_L \tag{19}$$

In this step, the relevant parameter is the lifetime of ML, τ_{ML}, as governed by the rate of association with L to ML_2 and the rate of dissociation of ML:

$$\frac{1}{\tau_{ML}} = k_{w2}K^{os}_{ML{\cdot}L}c_L + k_{w2}K^{os}_{ML{\cdot}HL}c_{HL} + k_{d1} = k_{w2}K_2^{os'} + k_{d1} = k'_{a2} + k_{d1} \tag{20}$$

with the reaction layer thickness given by

$$\mu_{ML_2} = \left(\frac{D_M}{k_{aML_2}c_L + k_{aMHL_2}c_{HL} + k_{d1}}\right)^{1/2} \tag{21}$$

For the usual case in which the dissociation of ML is the slow(er) step, k_{d1} is relatively small, and consequently τ_{ML} is predominantly determined by $k'_{a2}t$. However, if dissociation of ML is very fast, then τ_{ML} will be determined by k_{d1}. The kinetic flux for $ML_2 \rightarrow ML$ follows as

$$J_{\mathrm{kinML}_2} = k_{\mathrm{d}2} c_{\mathrm{ML}_2} \mu_{\mathrm{ML}_2} \tag{22}$$

Continuing in the same vein for ML_3 and so forth yields

$$k'_{\mathrm{a}n} = k_{\mathrm{w}n} K_n^{os'} c_{\mathrm{L}} \tag{23}$$

Together with the K_{ML_n} values, eq 23 can be converted into the corresponding series $k_{\mathrm{d}n}$, which is a useful guide in the sequential dissociation of ML_n to M:

$$\mathrm{ML}_n \xrightarrow{k_{\mathrm{d}n}} \mathrm{ML}_{n-1} \cdots \mathrm{ML}_2 \xrightarrow{k_{\mathrm{d}2}} \mathrm{ML} \xrightarrow{k_{\mathrm{d}1}} \mathrm{M} \tag{24}$$

Apart from cases with special chelating effects, we generally find that $k_{\mathrm{d}n} > k_{n-1} > ... k_{\mathrm{d}2} > k_{\mathrm{d}1}$ (eq 9). Thus, in first-order kinetic approximation, as long as $k_{\mathrm{d}1}$ is relatively small (see above), τ_{M} and μ are counted on the basis of eq 12. The presence of higher-order complexes ML_2, ML_3, ... ML_n is manifest via the dependence of the degree of lability on the ligand concentration (see below).

The overall rate of formation of M from ML_n is dominated by the rate of the slower step in the sequence (eq 24). More exactly, the overall kinetic flux arising from the various dissociation reactions is given by

$$\frac{1}{J_{\mathrm{kin}}} = \sum_{i=1}^{n} \frac{1}{J_{\mathrm{kinML}_i}} \tag{25}$$

For dynamic systems, previous work on the lability of ML_n complexes (which did not consider different protonated forms of the ligand)[8] formulated an analytical solution for the steady-state diffusion of M with a sequential scheme that quantifies the contribution from the dissociation of all of the complex species to the metal flux through the degree of lability, ξ.

3.2. Degree of Lability. For an interfacial process in which M is consumed, the overall flux of M toward the consuming interface results from the coupled diffusion and kinetics of interconversion between M and its various species in the complex system. Lability parameters have been defined to describe the ability of a dynamic system to maintain equilibrium in the presence of an ongoing interfacial process involving conversion of M, i.e., to quantify the contribution of the complex to the metal flux toward an interface. The lability index, $\mathcal{L}$, is the ratio of the limiting kinetic and diffusive fluxes of metal complex species; the criterion for lability is $\mathcal{L} \gg 1$.[3] The *degree* of lability, ξ, expresses the indirect contribution of the complex ($J_{\mathrm{complex}} - J_{\mathrm{free}}$)[8] to the eventual metal flux, J_{kin}, normalized with respect to its maximum purely diffusion-controlled, contribution, J_{dif}.[5,44] A system attains full lability for ξ approaching 1. The link between $\mathcal{L}$ and ξ is clarified below. Experimentally, ξ is measured as the ratio of the flux-based analytical signal for the kinetically controlled ML_n system as compared to that for the equivalent labile case (each corrected for any free metal present), i.e.,

$$\xi = \frac{X_{\mathrm{ML,kin}} - X_{\mathrm{free\ M}}}{X_{\mathrm{ML,lab}} - X_{\mathrm{free\ M}}} \tag{26}$$

where X is a method-dependent *flux*-related response (e.g., current in voltammetry, τ in SCP, accumulated amount in steady-state diffusive gradients in thin films (DGTs), etc.), $X_{\mathrm{ML,kin}}$ is the analytical signal for the kinetically controlled ML system, $X_{\mathrm{free\ M}}$ is the signal due to free metal only in the ML system, and $X_{\mathrm{ML,lab}}$ is the signal for the fully labile ML case. The value of $X_{\mathrm{free\ M}}$ is computed from the pertaining equilibrium constants, and that of $X_{\mathrm{ML,lab}}$ for systems with $D_{\mathrm{ML}} = D_{\mathrm{M}}$, is taken as the signal for a solution containing metal only, at the same total concentration as in the ML system.

All metal complex species contribute to the diffusive flux, and accordingly J_{dif} is given by

$$J_{\mathrm{dif}} = \sum_i J_{\mathrm{ML}_i} = \sum_i D_{\mathrm{ML}_i} c_{\mathrm{ML}_i} \left[\frac{1}{\delta} + \frac{1}{r_0}\right] \tag{27}$$

For a macroscopic electrode with $r_0 \gg \delta$, the spherical term with $1/r_0$ vanishes, whereas, for a microelectrode with $r_0 \ll \delta$, the radial diffusion term governs the flux.[45] The macroscopic case is more involved when there are differences in the D_i values, since δ then becomes a function of all c_{ML_i} and D_{ML_i}. For transparency, we here continue with the microelectrode case.

The kinetic flux, J_{kin}, is derived from reaction layer theory (eq 17). In the general case, ML may or may not be in equilibrium with complexes of higher stoichiometry. On the level of the Koutecký–Koryta approximation,[42,46,47] the gradients of the various complex species ML_n–... –ML_2–ML in the reaction layer are predominantly governed by the kinetically most stable one, and thus are negligibly small. For a 1:1 inner-sphere complex ML, it has been shown that, under steady-state transport conditions, ξ is given by[5]

$$\xi = \frac{{\kappa_{\mathrm{a}}}^{1/2}}{[\epsilon K'(1 + \epsilon K')]^{1/2} + {\kappa_{\mathrm{a}}}^{1/2}} \tag{28}$$

where κ_{a} is the nondimensional association kinetic constant, as elaborated below. For successive inner-sphere metal complexes ML_n, the degree of lability for the system is a weighted average of the degrees of lability of all of the complexes, with weighting factors given by the respective fraction of the corresponding bulk concentration over the bulk concentration of total bound metal. For a system containing ML_i, and for equal diffusion coefficients of the different complexes, i.e., $\epsilon_i = \epsilon$, it follows from eq 28 that ξ_i is given by

$$\xi_i = \frac{{\kappa_{\mathrm{a}_i}}^{1/2}}{[\epsilon \prod_{j=1}^{i} K'_j (1 + \epsilon \prod_{j=1}^{i} K'_j)]^{1/2} + {\kappa_{\mathrm{a}_i}}^{1/2}} \tag{29}$$

with $K'_j = K_j c_{\mathrm{L}}$. The $\prod_{j=1}^{i} K'_j$ represents the concentration ratio between ML_i and M, and the κ_{a_i} term takes into account the contribution from the various protonated ligand species:[15]

$$\kappa_{\mathrm{a}_i} = \frac{(k_{\mathrm{aML}_i} c_{\mathrm{L}} + k_{\mathrm{aMHL}_i} c_{\mathrm{HL}}) {r_0}^2}{D_{\mathrm{M}}} \tag{30}$$

which incorporates the reaction layer since $\mu = (D_{\mathrm{M}}/k_{\mathrm{a}}^{\mathrm{eff}})^{1/2}$.

For complexes that are sufficiently strong to satisfy $\epsilon \prod_{j=1}^{i} K'_j \gg 1$, i.e., $c_{\mathrm{complex}} \gg c_{\mathrm{freeM}}$, eq 29 for a given metal complex reduces to

$$\xi_i \rightarrow \frac{{\kappa_{\mathrm{a}_i}}^{1/2}}{\epsilon \prod_{j=1}^{i} K'_j + {\kappa_{\mathrm{a}_i}}^{1/2}} \tag{31}$$

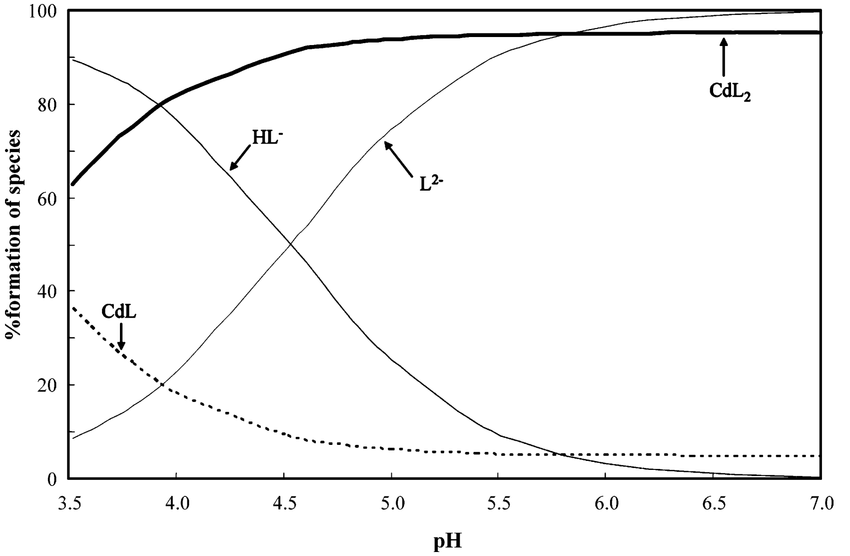

Figure 1. Equilibrium species distribution in bulk solution for Cd(II)−PDCA as a function of pH. The percentage formation of species is with respect to the total metal concentration for CdL^+ and CdL_2, and with respect to total ligand concentration for HL^- and L^{2-}. Calculated for $c_{L,t} = 1 \times 10^{-3}$ mol dm^{-3}, $K(H+L) = 10^{4.53}$ dm^3 mol^{-1}, $K(H+HL) = 10^{1.87}$ dm^3 mol^{-1}, $K(Cd+L) = 10^{5.7}$ dm^3 mol^{-1}, and $K(CdL+L) = 10^{4.3}$ dm^3 mol^{-1}. The concentration of free Cd^{2+} and of H_2L is negligible over the pH range shown.

and the considered step in the complexation scheme attains lability, $\xi \rightarrow 1$, for

$$\kappa_{a_i}^{1/2} \gg \epsilon \prod_{j=1}^{i} K'_j \tag{32}$$

Inequality 32 boils down to the conventional lability criterion,[43] e.g., because ξ is related to the lability index, $\mathscr{L}$, via $\mathscr{L} = \kappa_{a_i}^{1/2}/\epsilon\prod_{j=1}^{i}K'_j$.

Previous work established that, in the most general case, with an arbitrary step as the rate-limiting one, and all preceding steps (i.e., ML_i with $i < n$) as fast, the lability degree for the slowly reacting species is a good approximation for that of the complete system as computed via the rigorous expression[8]

$$\xi = \frac{D_{ML}\sum_{i=1}^{n}\dfrac{c^*_{ML_i}}{r_o}\xi_i}{D_{ML}\sum_{i=1}^{n}\dfrac{c^*_{ML_i}}{r_o}} = \frac{\sum_{i=1}^{n} c^*_{ML_i}\xi_i}{\sum_{i=1}^{n} c^*_{ML_i}} = \frac{\sum_{i=1}^{n}[\xi_i(\prod_{j=1}^{i} K'_j)]}{\sum_{i=1}^{n}[\prod_{j=1}^{i} K'_j]} \tag{33}$$

The elaborations for any arbitrary general case are accounted for in eq 33.

4. Results and Discussion

Here we illustrate the theoretical concepts detailed above by considering the case of ML_2 complexes. In addition to eq 1 we then have

$$\begin{array}{lccccc} & + HL & \xrightleftharpoons{K^{os}_{ML\cdot HL}} & M(H_2O)_5L\cdot HL^+ & \xrightarrow{k_{w2}} & M(H_2O)_4HL_2^+ \\ M(H_2O)_5L^+ & \uparrow\downarrow & & \uparrow\downarrow & & \downarrow\uparrow \text{(fast)} \\ & + L^- & \xrightleftharpoons{K^{os}_{ML\cdot L}} & M(H_2O)_5L\cdot L & \xrightarrow{k_{w2}} & M(H_2O)_4L_2 \end{array} \tag{34}$$

As detailed above, the usual situation will be that $ML \rightarrow M$ is the rate-determining step in the overall dissociation of ML_2 to M. For a dynamic system, the general expressions, eqs 23, 27, and 28, are simplified, for $j = 2$ and with $\epsilon K'_1 K'_2 \gg 1$, to

$$\xi \rightarrow \frac{\kappa_a^{1/2}}{\epsilon K'_1 K'_2 + \kappa_a^{1/2}} \tag{35}$$

where

$$\kappa_a = \frac{(k_{aML}c_L + k_{aMHL}c_{HL})r_0^2}{D_M} \tag{36}$$

Whether or not the dissociation of ML (eq 1) determines the overall rate of the reaction ($ML_2 \rightarrow M$) depends on the relative magnitudes of J_{kinML} and J_{kinML_2}. For the usual case of $J_{kinML_2}/J_{kinML} \gg 1$ (see, e.g., eq 9), all the reactions in eq 34 can be considered to be in rapid equilibrium with those in eq 1, and J_{kinML} is the pertaining parameter to consider in computing the lability of ML_2. Then, ML_2 species act as a buffer for ML because $ML_2 \rightarrow ML$ is much faster than $ML \rightarrow M$. Accordingly J_{dif} for the system is the sum of J_{difML} and J_{difML_2} (eq 27). Equation 35 shows that, for the ML_2 case, ξ is dependent on $c_L^{-3/2}$, i.e., experimental observation of this concentration dependency in a ML_2 system is diagnostic for $ML \rightarrow M$ being the rate-limiting step.[6,7] Below we illustrate and validate our treatment for a dynamic and a non-dynamic system.

4.1. The Cd(II)/PDCA System. The equilibrium species distribution for the Cd(II) complexes and the protonation of the ligand PDCA is shown in Figure 1. This system appears to be suited for identifying the role of protonated ligand species in metal speciation dynamics, i.e., the concentration ratio HL^-/L^{2-} changes significantly over the same pH region where ML_2 is forming.

Analysis of the system in terms of the reaction scheme involving protonated ligand species (eqs 1 and 34) requires calculation of the pertaining K^{os} values. These were computed via the differentiated approach reported previously,[15] and details are given in the Supporting Information. The pertaining values for K^{os} (mol dm^{-3}) for the involved outer-sphere compexes are $M(H_2O)_6\cdot L = 20$, $M(H_2O)_6\cdot HL^+ = 2$, $M(H_2O)_5L\cdot L^{2-} = 0.3$, $M(H_2O)_5L\cdot HL^- = 0.3$. The computed degree of lability for

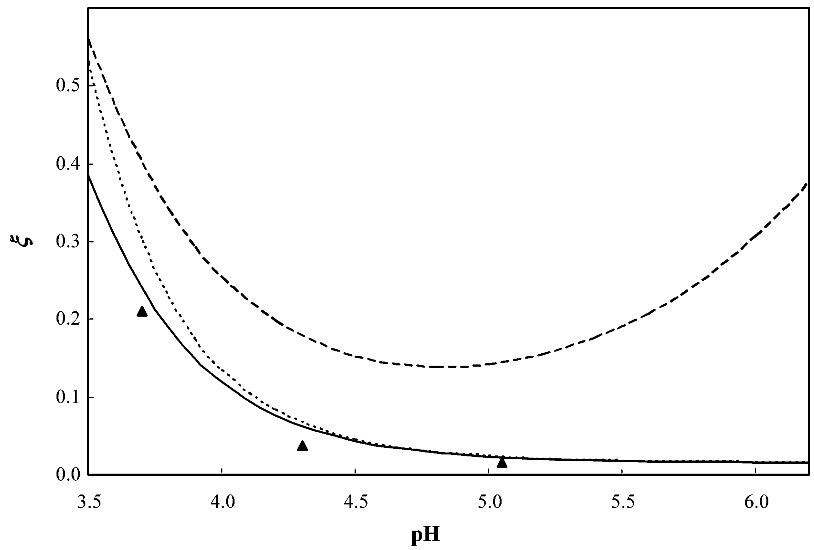

Figure 2. Comparison of the measured (points) and computed (curves) degree of lability, ξ, vs pH for Cd(II) complexes with PDCA at a microelectrode. The solid curve is ξ computed from the overall kinetic flux that considers both $Cd(H_2O)_6{\cdot}L$ and $Cd(H_2O)_6{\cdot}HL^+$ (eq 17); the short dashed curve is that resulting from $Cd(H_2O)_6{\cdot}L$ only ($J_{kin,ML} = k_d c_{ML}(D_M/k_w K^{os}_{M\cdot L} c_L)^{1/2}$); and the long dashed curve is from $Cd(H_2O)_6{\cdot}HL^+$ only ($J_{kin,MHL} = k_d c_{ML}(D_M/k_w K^{os}_{M\cdot HL} c_{HL})^{1/2}$). The curves are computed for the experimental concentrations $c_{Cd,t} = 4 \times 10^{-7}$ mol dm^{-3}, $c_{PDCA,t} = 2.4 \times 10^{-3}$ mol dm^{-3}, $r_0 = 6 \times 10^{-6}$ m, and $k_{w1} = 3.5 \times 10^8$ s^{-1}; other conditions are as in Figure 1.

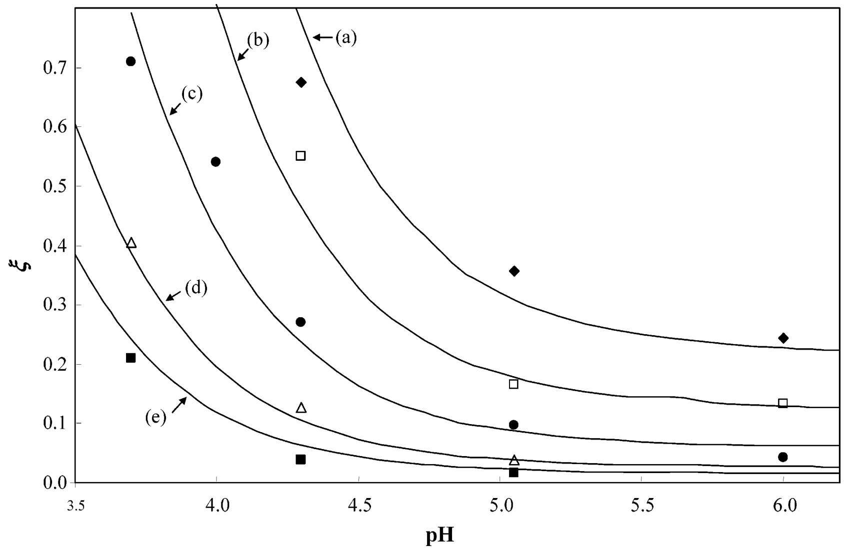

Figure 3. Comparison of the measured (points) and computed (curves) degree of lability, ξ, vs pH for Cd(II) complexes with PDCA at a microelectrode considering the contribution from both protonated and deprotonated outer-sphere complexes to the overall kinetic flux. Data are shown for $c_{Cd,t} = 4 \times 10^{-7}$ mol dm^{-3} and $c_{PDCA,t}$/mol dm^{-3} = (a) 3.9×10^{-4} (◆); (b) 5.8×10^{-4} (□); (c) 9.6×10^{-4} (●); (d) 1.7×10^{-3} (Δ); and (e) 2.4×10^{-3} (■). Other conditions are as in Figures 1 and 2.

Cd(II) complexes with PDCA is compared with measurements at a microelectrode as a function of pH and ligand concentration in Figures 2 and 3. Figure 2 compares measured lability at one ligand concentration with that predicted considering (i) both protonated and unprotonated outer-sphere complexes, (ii) only protonated or (iii) only unprotonated complexes. Figure 3 shows the agreement between the computed values for the combined outer-sphere contribution and that measured as a function of pH for several ligand concentrations. The convincing agreement between measured and computed values over a wide concentration range confirms the consistency of the parameters used. At pH values greater than ca. 4.0, the concentration of L becomes significant, and hence the degree of lability computed on the basis of both HL and L being involved in outer-sphere complexation is approximately the same as that involving only L. For pH values below 4, some differences are discernible, and the L^{2-}-only case predicts slightly greater lability than what is observed. The experimental data are in reasonable agreement with the values predicted on the basis of both HL^- and L^{2-} being involved in outer-sphere complexation. Unfortunately, strong adsorption of the fully protonated ligand[48] (significant at pH 3.7) prevents reliable measurements for lower pH.

Comparison of the computed kinetic and diffusional fluxes shows that $J_{kinML} \ll J_{kinML_2}$. For example, at pH 5, for $c_{L,t} = 2.4 \times 10^{-3}$ mol dm^{-3}, J_{kinML} and J_{kinML_2} are 10^{-9} and 10^{-7} mol m^{-2} s^{-1}, respectively. Thus ML → M is the rate-determining step, and use of J_{kinML} in the computations gives the same result as if the overall J_{kin} is used (eq 25). Note that this is so, even though there is a relatively small difference of ca. 1.5 log units between K_1 and K_2; setting k_{w2} equal to k_{w1} still yields $J_{kinML_2} \gg J_{kinML}$ (by a factor of ca. 10). This result was also found for a wide range of dynamic metal–ligand systems, confirming conclusions from earlier work that had not considered the involvement of protonated forms of the ligand.[6–8]

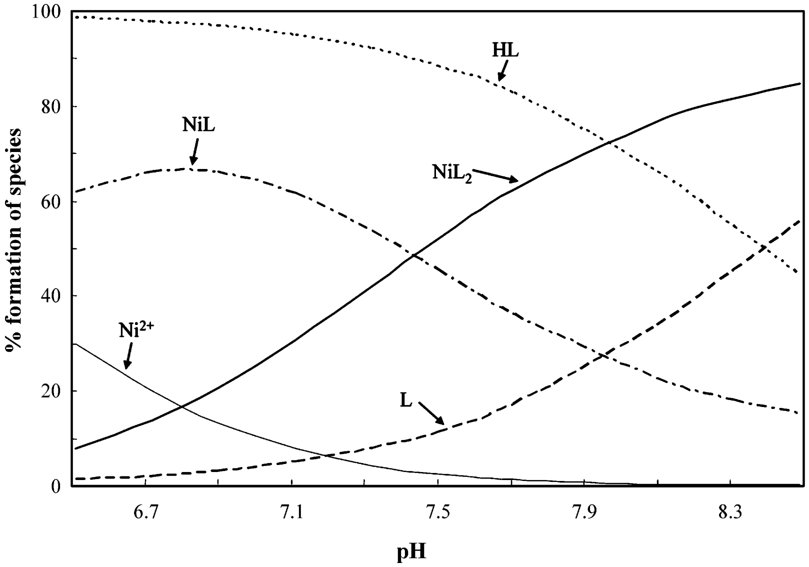

Figure 4. Equilibrium species distribution in bulk solution for Ni(II)−bicine as a function of pH. Calculated for $c_{\mathrm{Ni(II)}} = 4 \times 10^{-7}$ mol dm^{-3}, $c_{\mathrm{L,t}} = 1.0 \times 10^{-3}$ mol dm^{-3}, $K(\mathrm{H+L}) = 10^{8.39}$ dm^3 mol^{-1}, $K(\mathrm{H+HL}) = 10^{1.8}$ dm^3 mol^{-1}, $K(\mathrm{Ni+L}) = 10^{5.2}$ dm^3 mol^{-1}, and $K(\mathrm{NiL+L}) = 10^{4.0}$ dm^3 mol^{-1}.

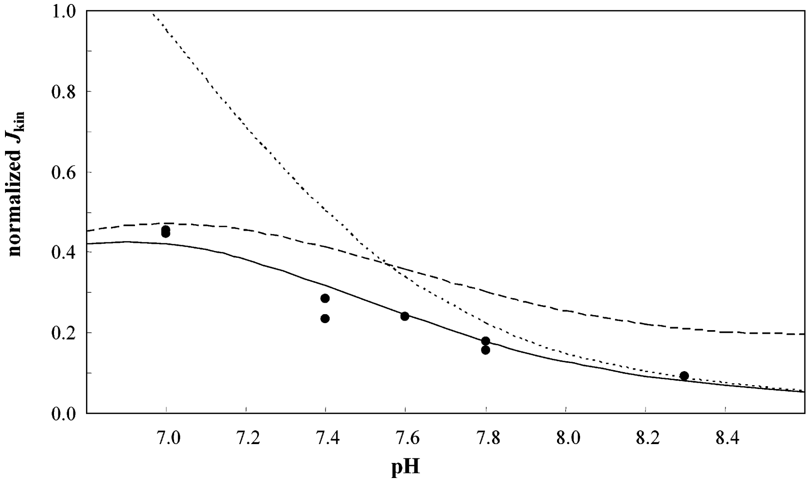

Figure 5. Comparison of the measured (points) and computed (curves) degree of lability, ξ, vs pH for Ni(II) complexes with bicine at a conventional mercury drop electrode. The solid curve is ξ-computed from the overall kinetic flux that considers $\mathrm{Ni(H_2O)_6{\cdot}L}$, $\mathrm{Ni(H_2O)_6{\cdot}HL^+}$, $\mathrm{Ni(H_2O)_5L{\cdot}L}$, and $\mathrm{Ni(H_2O)_5L{\cdot}HL^+}$; the short dashed curve is that resulting from the unprotonated outer-sphere species only, i.e., $\mathrm{Ni(H_2O)_6{\cdot}L}$ and $\mathrm{Ni(H_2O)_5L{\cdot}L}$; and the long dashed curve is from the protonated species only, i.e., $\mathrm{Ni(H_2O)_6{\cdot}HL^+}$ and $\mathrm{Ni(H_2O)_5L{\cdot}HL^+}$. The curves are computed for the experimental concentrations $c_{\mathrm{Ni(II),t}} = 4 \times 10^{-7}$ mol dm^{-3}, $c_{\mathrm{L,t}} = 1.0 \times 10^{-3}$ mol dm^{-3}, $\delta = 2 \times 10^{-4}$ m, $k_{\mathrm{w1}} = 2 \times 10^4$ s^{-1}, and $k_{\mathrm{w2}} = 4 \times 10^4$ s^{-1}. Other conditions are as in Figure 4.

4.2. The Ni(II)/bicine System. It is also of interest to study non-dynamic systems in which the kinetics are characterized by condition 5, implying that the system does not equilibrate on the relevant time scale. For such kinetic systems, the Koutecký−Koryta approximation[42,46,47] no longer holds, and lability considerations are irrelevant. Disequilibration is significant over the complete diffusion layer, so that the uncoupling of dissociation/association kinetics and diffusion is no longer possible. The magnitude of the flux approaches that of the kinetic contribution arising from sequential complex dissociation (eq 25), as long as this remains well below the value of J_{dif}. The non-dynamic case is illustrated by Ni(II) complexes with bicine. While the electrochemical irreversibility of Ni(II) confounds measurement of stability constants,[49] it does not pose any problems for determination of the kinetic behavior of the complexes as long as the accumulation is carried out at sufficiently negative potential. The equilibrium species distribution shows that, over the pH range 6.5−8.5, there is a significant change in the amount of $\mathrm{NiL^+}$ and $\mathrm{NiL_2}$, as well as of HL and $\mathrm{L^-}$ (Figure 4).

The rate of removal of water from the inner hydration sphere of Ni(II) ($k_{\mathrm{w}} \approx \mathrm{O}(10^4)$ s^{-1}) is much lower than that for Cd(II) (which has $k_{\mathrm{w}} \approx \mathrm{O}(10^9)$ s^{-1}).[2] Accordingly, the Ni(II)−bicine system corresponds to the kinetic case, i.e., $k'_{\mathrm{a1}}t$, $k_{\mathrm{d1}}t \approx 1$. This ampholytic ligand is interesting with regard to estimation of the various K^{os} values since the protonated ligand has one positive charge ($\mathrm{NH^+}$) and one negative charge ($\mathrm{COO^-}$) (see Supporting Information for the full computations). The pertaining values for K^{os} (mol dm^{-3}) for the involved outer-sphere complexes are $\mathrm{M(H_2O)_6{\cdot}L^+} = 2.4$, $\mathrm{M(H_2O)_6{\cdot}HL^{2+}} = 0.3$, $\mathrm{M(H_2O)_5L{\cdot}L} = 0.7$, and $\mathrm{M(H_2O)_5L{\cdot}HL^+} = 0.3$.

Figure 5 shows the experimental data and the computed values for the various possible contributions to the flux of M. For clarity, only the overall J_{kin} options are shown (eq 25). The best fit to the experimental data was obtained when both J_{kinML} and $J_{\mathrm{kinML_2}}$ were considered together with the involvement of both HL and L^- in the formation of the pertaining outer-sphere complexes. This means that both k'_{a2} and k_{d1} count in τ_{ML} (see eq 20). Consideration of either J_{kinML} or J_{kinML_2} as the sole kinetic flux significantly overestimates the measured signals. In addition, at low pH, considering the involvement of only L^- overestimates the lifetime of the free M (and the ensuing reaction layer thickness), while, at higher pH, c_{HL} is low, and thus ignoring $M{\cdot}L^{os}$ and $ML{\cdot}L^{os}$ overestimates the lifetime of ML.

4.3. Extension to ML_n Systems with $n > 2$. For the usual relative magnitudes of $K_1 > K_2 > K_3 > ... K_n$, practical cases of dynamic ML_n complexes are expected to follow the situation where the higher-order reactions can be assumed to be in equilibrium with ML. Accordingly, predictions of lability can be made on the basis of ML→M as the rate-determining step. The impact of the differentiated contribution of various protonated ligand species on the complexation kinetics will become less significant as the number of coordinated ligands increases. This is so because, as the number of coordinated ligands increases, the pH range over which the formation of the ML_n species occurs lies to increasingly higher pH values.

5. Conclusions

The impact of ligand protonation on metal complexation kinetics in ML_n systems has been determined on the basis of the Eigen mechanism for aqueous systems. The usual situation for successive complex formation is $K_1 > K_2 > .... K_n$. For dynamic metal−ligand systems, this has the consequence that the kinetic flux for dissociation of $ML_2 \rightarrow ML$ is greater than that for $ML \rightarrow M$, and thus complexes of higher stoichiometry can often be considered to be approximately in equilibrium with ML. For the ML_2 case considered herein, it means that the rate of dissociation of ML_2 can be neglected in the analysis. Consequently, the degree of lability is derived from the rate of dissociation of ML, incorporating the simultaneous effects of both protonated and unprotonated outer-sphere complexes, weighted by their respective stabilities. This was illustrated experimentally for 1:2 complexes of Cd(II) with PDCA.

For the majority of ML_n systems ($n \geq 2$), the differentiated impact of protonated ligand species in the complexation kinetics becomes increasingly insignificant as n increases. That is, use of the reaction layer thickness computed on the basis of the weighted contribution of all the ligand species present gives a result comparable to that for the involvement of either only HL or only L. This is a consequence of the different pH ranges over which metal complexation and ligand deprotonation occur. For a given dynamic system, predictions of lability at any pH are best made on the basis of the weighted contribution approach presented herein; more detailed characterization can then establish if a simpler approximation would suffice.

In the non-dynamic case, the coupling between association/dissociation kinetics and diffusion is more intricate. Experimental data for 1:2 complexes of Ni(II) with bicine are best described by an overall J_{kin} that includes the rates of dissociation of both ML and ML_2 as well as the weighted contribution of all the pertaining outer-sphere complexes involving both protonated and deprotonated ligand species.

The theoretical framework provides a good description of the measured flux of M for both the dynamic and the non-dynamic case. The kinetic features of a given system can be reliably predicted on the basis of the most general approach, i.e., by taking into account the rates of dissociation for all the complexes present, together with the weighted contributions from all the protonated and deprotonated outer-sphere complexes involved. In certain cases, within a given operational window, e.g., of pH, approximations may suffice.

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Nomenclature

Symbols and Abbreviations

c, bulk concentration (mol dm^{-3})
δ, diffusion layer thickness (m)
D, diffusion coefficient (m^2 s^{-1})
J, flux (mol m^{-2} s^{-1})
k_a, complex formation rate constant (dm^3 mol^{-1} s^{-1})
k_d, complex dissociation rate constant (s^{-1})
k_w, rate constant for water substitution (s^{-1})
K, stability constant (dm^3 mol^{-1})
$\mathcal{L}$, lability index (dimensionless)
ξ, degree of lability (dimensionless)
μ, reaction layer thickness (m)
PDCA, pyridine-2,6-dicarboxylic acid
r_0, radius of microelectrode (m)

Supporting Information Available: A detailed description of the methodology for computation of the K^{os} values is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 97.
(2) Morel, F. M. M.; Hering, J. G. *Principles and Applications of Aquatic Chemistry*; Wiley: New York, 1993.
(3) van Leeuwen, H. P.; Town, R. M.; Buffle, J.; Cleven, R. F. M. J.; Davison, W.; Puy, J.; van Riemsdijk, W. H.; Sigg, L. *Environ. Sci. Technol.* **2005**, *39*, 8545.
(4) van Leeuwen, H. P. *Environ. Sci. Technol.* **1999**, *33*, 3743.
(5) Galceran, J.; Puy, J.; Salvador, J.; Cecília, J.; van Leeuwen, H. P. *J. Electroanal. Chem.* **2001**, *505*, 85.
(6) Puy, J.; Cecília, J.; Galceran, J.; Town, R. M.; van Leeuwen, H. P. *J. Electroanal. Chem.* **2004**, *571*, 121.
(7) van Leeuwen, H. P.; Town, R. M. *J. Electroanal. Chem.* **2006**, *587*, 148.
(8) Salvador, J.; Puy, J.; Galceran, J.; Cecília, J.; Town, R. M.; van Leeuwen, H. P. *J. Phys. Chem. B* **2006**, *110*, 891.
(9) Turner, D. R.; Whitfield, M. *J. Electroanal. Chem.* **1979**, *103*, 43.
(10) Turner, D. R.; Whitfield, M. *J. Electroanal. Chem.* **1979**, *103*, 61.
(11) Galceran, J.; Puy, J.; Salvador, J.; Cecília, J.; Mas, F.; Garcés, J. L. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5091.
(12) Salvador, J.; Garcés, J. L.; Galceran, J.; Puy, J. *J. Phys. Chem. B* **2006**, *110*, 13661.
(13) Salvador, J.; Garcés, J. L.; Companys, E.; Cecília, J.; Galceran, J.; Puy, J.; Town, R. M. *J. Phys. Chem. A* **2007**, *111*, 4304.
(14) Buffle, J.; Startchev, K.; Galceran, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2844.
(15) van Leeuwen, H. P.; Town, R. M.; Buffle, J. *J. Phys. Chem. A* **2007**, *111*, 2115.
(16) Tercier, M. L.; Parthasarathy, N.; Buffle, J. *Electroanalysis* **1995**, *7*, 55.
(17) van Leeuwen, H. P.; Town, R. M. *J. Electroanal. Chem.* **2002**, *523*, 16.
(18) Town, R. M.; van Leeuwen, H. P. *J. Electroanal. Chem.* **2001**, *509*, 58.
(19) Gerding, P. *Acta Chem. Scand.* **1968**, *22*, 1283.
(20) Soares, H. M. V. M.; Conde, P. C. F. L.; Almeida, A. A. N.; Vasconcelos, M. T. S. D. *Anal. Chim. Acta* **1999**, *394*, 325.
(21) Swiatek, J.; Pawlowski, T. *J. Inorg. Biochem.* **1991**, *44*, 163.
(22) Sigel, H.; Becker, K.; McCormick, D. *Biochem. Biophys. Acta* **1967**, *148*, 655.
(23) Bai, K.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1697.
(24) du Preez, J.; Rohwer, H.; van Brecht, B. J.; Caira, M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 975.
(25) Funahashi, S.; Haraguchi, K.; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349.
(26) Ahmed, I.; El-Roudi, O.; Boraei, A. *J. Chem. Eng. Data* **1996**, *41*, 386.

(27) Evtimova, B.; Scharff, J.; Paris, M. *Bull. Chem. Soc. Fr.* **1969**, 81.

(28) Anderegg, G. *Helv. Chim. Acta* **1960**, *43*, 414.

(29) Suzuki, K.; Yamasaki, K. *Naturwissenschaft* **1957**, *44*, 396.

(30) Krishnamoorthy, C.; Nakon, R. *J. Coord. Chem.* **1991**, *23*, 233.

(31) Azab, H.; Anwar, Z.; Sokar, M. *J. Chem. Eng. Data* **2004**, *49*, 62.

(32) Springer, V.; Karlicek, R.; Majer, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 774.

(33) Jokl, V.; Majer, J.; Mazacova, M. *Chem. Zvesti* **1964**, *18*, 584.

(34) Frost, A. E.; Chaberek, S.; Bicknell, N. J. *J. Am. Chem. Soc.* **1957**, *79*, 2755.

(35) de Jong, H. G.; van Leeuwen, H. P. *J. Electroanal. Chem.* **1987**, *235*, 1.

(36) Margerum, D. W.; Rosen, H. M. *J. Am. Chem. Soc.* **1967**, *89*, 1088.

(37) Hague, D. N.; White, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 1337.

(38) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. *ACS Monogr.* **1978**, *174*, 1.

(39) Hague, D. N.; Kinley, K. *J. Chem. Soc., Dalton Trans.* **1974**, 249.

(40) Hunt, J. P. *Coord. Chem. Rev.* **1971**, *7*, 1.

(41) Hague, D. N.; White, A. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3645.

(42) Heyrovský, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1966.

(43) van Leeuwen, H. P. *Electroanalysis* **2001**, *13*, 826.

(44) Salvador, J.; Puy, J.; Cecília, J.; Galceran, J. *J. Electroanal. Chem.* **2006**, *588*, 303.

(45) Štulík, K.; Amatore, C.; Holub, K.; Marec̆ek, V.; Kutner, W. *Pure Appl. Chem.* **2000**, *72*, 1483.

(46) Koutecký, J.; Koryta, J. *Electrochim. Acta* **1961**, *3*, 318.

(47) Koryta, J.; Dvorak, J.; Kavan, L. *Principles of Electrochemistry*, 2nd ed.; Wiley: Chichester, U.K., 1993.

(48) Buffle, J.; Mota, A. M.; Gonçalves, M. L. S. S. *J. Electroanal. Chem.* **1987**, *223*, 235.

(49) Town, R. M.; Pinheiro, J.-P.; Domingos, R.; van Leeuwen, H. P. *J. Electroanal. Chem.* **2005**, *580*, 57.