Ligand Mixture Effects in Metal Complex Lability

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The degree of lability of a given metal complex species is modified in the presence of a mixture of ligands. This modification is a consequence of the coupling of the association and dissociation processes of all of the complexes according to the competitive complexation reaction scheme. We show that, because of the mixture effect, the lability of a given complex usually increases when another more labile complex is added into the system, while it decreases upon addition of a less labile one. Typically, complexes tend to adapt to the global lability of the mixture. A quantitative evaluation of these effects for diffusion-limited conditions in a finite domain by rigorous numerical simulation in a system with two complexes indicates that the lability degree of a complex can change by more than 100% with respect to that in the single ligand system. The impact of the mixture effect on the metal flux depends at least on two main factors: the respective abundance of the metal species and the particular values of their lability degrees. Dominant complexes (i.e., those most abundant when these complexes have equal diffusion coefficients) undergo smaller changes in their own lability degree, but these changes have the greater impact on the overall metal flux. Partially labile complexes are more easily influenced by the mixture than labile or inert ones. Some mixture effects can be qualitatively predicted by an analytical expression for the lability index derived using the reaction layer approximation. For a mixture of many complexes, the change in the lability degree of a complex due to the mixture effect can be understood as a combination of the changes due to all of the complexes present.

1. Introduction

The metal flux toward a consuming interface, for example, an analytical sensor or an accumulating organism in an aquatic ecosystem, results from the coupled diffusion and kinetics of interconversion between M and its various species in the medium, for example, complexes with ligands, particles, colloids, and so forth.[1−4] The prediction of the process that controls the metal flux[5−8] is embodied in the concept of lability.[9] A system is labile when the mass transport process to the surface is the limiting one, so that the kinetics of the complex association/dissociation processes are, in comparison, fast enough to reach quasi equilibrium conditions at any relevant spatial scale and time scale of the experiment At the other limit, a system is denoted as nonlabile when the dissociation processes limit the metal flux. Lability is influenced by a range of factors including the kinetics of the complexation processes, the transport phenomena present in the system, the size of the sensor, the processes at the surface leading to consumption of the target species, and the mixture of ligands present in the system. A broad range of situations have been properly analyzed in the older (see for instance refs 10 and 11) and recent literature of the subject,[6,12,13] including planar[14] or spherical sensing surfaces, different stoichiometric relationships between metal and ligand, colloidal ligands, transient or steady-state situations, and so forth.

A quantitative evaluation of the contribution of the complexes to the metal flux for a general partially labile case requires the rigorous solution of a system of transport and reaction equations. Some cases have been analyzed with rigorous numerical simulation, while (rigorous or approximate) analytical expressions have been worked out for techniques that reach steady-state.[6−8,15,16] Parameters have been defined to quantify the lability of a given metal complex and its consequent contribution to the metal flux at a consuming interface. The lability index, $\mathscr{L}$, compares the hypothetical maximum kinetic and diffusive fluxes of metal complex species; the criterion for lability is $\mathscr{L} \gg 1$.[7,12,16] The lability degree, ξ, represents the percentage of the complex contribution to the metal flux with respect to its maximum contribution obtained when the kinetics of the complexation processes are fast enough to reach equilibrium conditions at any time and relevant spatial position ($0 \leq \xi \leq 1$).[3,6−8,15−18] This parameter can be defined for the global system, on the basis of the contribution of all complexes, but it can also be applied to individual complex species leading to a particular lability degree for each complex.

Although a mixture of ligands is the common situation encountered by a metal in a natural medium, very few papers[19−21] have given some consideration to the effect of the mixture, that is, the change in the lability degree of a complex in a mixture with respect to the lability degree of the same complex in a single ligand system with the same total ligand concentration.

In the present paper, we quantify the mixture effect in a system with one metal and two or more ligands by applying a general rigorous formulation. Moreover, the results obtained identify some simple rules for qualitative prediction of this effect in a general mixture. Both a rigorous mathematical framework and the reaction layer approximation[22] are used in the development of the theory which applies to steady-state analytical

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techniques such as permeation liquid membrane (PLM),[23] diffusion gradients in thin film gels (DGT),[24,25] or stripping chronopotentiometry at scanned deposition potential, (SSCP).[26,27] These techniques are used in situ or in the laboratory for the measurement of the availability of metals and for the prediction of the metal bio-uptake by micro-organisms and algae.

2. Lability Degree

Let us consider in solution a mixture of h independent ligands $^1\mathrm{L}$, $^2\mathrm{L}$, ..., $^h\mathrm{L}$, which can bind a metal ion M according to equation

$$\mathrm{M} + {}^i\mathrm{L} \underset{k_{\mathrm{d},i}}{\overset{k_{\mathrm{a},i}}{\rightleftharpoons}} \mathrm{M}^i\mathrm{L} \qquad i = 1, 2, ..., h \tag{1}$$

where K_i, $k_{\mathrm{a},i}$ and $k_{\mathrm{d},i}$ are, respectively, the equilibrium and the association and dissociation kinetic constants for the complexation of M by $^i\mathrm{L}$. A complete list of symbols is gathered in Appendix C. Let us also assume that each ligand is present in the system in a great excess with respect to the metal so that $c_{^i\mathrm{L}}(x) = c^*_{^i\mathrm{L}}$. The corresponding equilibrium conditions are

$$K'_i \equiv K_i c^*_{^i\mathrm{L}} = \frac{k_{\mathrm{a},i} c^*_{^i\mathrm{L}}}{k_{\mathrm{d},i}} = \frac{k'_{\mathrm{a},i}}{k_{\mathrm{d},i}} = \frac{c^*_{\mathrm{M}^i\mathrm{L}}}{c^*_{\mathrm{M}}} \tag{2}$$

where $K'_i = K_i c^*_{^i\mathrm{L}}$, $k'_{\mathrm{a},i} = k_{\mathrm{a},i} c^*_{^i\mathrm{L}}$.

The lability degree, ξ, is defined as[6]

$$\xi \equiv \frac{J_{\mathrm{M}} - J_{\mathrm{free}}}{J_{\mathrm{labile}} - J_{\mathrm{free}}} \tag{3}$$

where J_{M} stands for the actual metal flux crossing the limiting surface $x = 0$, J_{free} is the metal flux arising in the system if all complexes are inert, and J_{labile} is the metal flux arising in the system if all of the complexes are labile.

Thus, ξ defines the fraction of the actual contribution of the complexes to the metal flux ($J_{\mathrm{M}} - J_{\mathrm{free}}$) with respect to their maximum contribution that would arise when the system is labile, that is, when equilibrium conditions between the metal and each ligand are reached at any relevant spatial position and time of the experiment ($J_{\mathrm{labile}} - J_{\mathrm{free}}$). Thus, $\xi \approx 1$ for a labile system, and $\xi \approx 0$ for a non-labile or inert one.

When steady-state diffusion toward a stationary planar surface is the only relevant transport mechanism in the finite domain, the maximum contribution of the complexes to the metal flux is simply the addition of the purely diffusive flux of all complexes, and the global lability degree of the system under diffusion-limited conditions becomes

$$\xi = \frac{J_{\mathrm{M}} - J_{\mathrm{free}}}{J_{\mathrm{labile}} - J_{\mathrm{free}}} = \frac{J_{\mathrm{M}} - D_{\mathrm{M}} c^*_{\mathrm{M}}/g}{\sum_{i=1}^{h} D_{\mathrm{M}^i\mathrm{L}} c^*_{\mathrm{M}^i\mathrm{L}}/g} \tag{4}$$

where g indicates the thickness of the diffusion domain. Since

$$J_{\mathrm{M}} = D_{\mathrm{M}} \frac{c^*_{\mathrm{M}}}{g} + \sum_{i=1}^{h} \left[D_{\mathrm{M}^i\mathrm{L}} \frac{c^*_{\mathrm{M}^i\mathrm{L}}}{g} \left(1 - \frac{c^0_{\mathrm{M}^i\mathrm{L}}}{c^*_{\mathrm{M}^i\mathrm{L}}} \right) \right] = J_{\mathrm{free}} + \sum_{i=1}^{h} J_{\mathrm{complex},\mathrm{M}^i\mathrm{L}} = J_{\mathrm{free}} + \sum_{i=1}^{h} \xi_i J_{\mathrm{dif},i} \tag{5}$$

each term of the summation at the right-hand side of eq 5 represents the contribution of each complex to the metal flux. We can also define a specific lability degree for a given complex $\mathrm{M}^i\mathrm{L}$ following eq 46 in ref 15, which, for the particular case of diffusion-limited conditions dealt with here, becomes

$$\xi_i = 1 - \frac{c^0_{\mathrm{M}^i\mathrm{L}}}{c^*_{\mathrm{M}^i\mathrm{L}}} \tag{6}$$

where $c^0_{\mathrm{M}^i\mathrm{L}}$ denotes the concentration of $\mathrm{M}^i\mathrm{L}$ at the surface, $x = 0$. In terms of ξ_i, eq 4 can be rewritten as

$$\xi = \frac{\sum_{i=1}^{h} \epsilon_i K'_i \xi_i}{\sum_{i=1}^{h} \epsilon_i K'_i} = \sum_{i=1}^{h} \frac{J_{\mathrm{dif},i}}{\sum_{j=1}^{h} J_{\mathrm{dif},j}} \xi_i \tag{7}$$

where $\epsilon_i = D_{\mathrm{M}^i\mathrm{L}}/D_{\mathrm{M}}$ and $J_{\mathrm{dif},i} = D_{\mathrm{M}^i\mathrm{L}} c^*_{\mathrm{M}^i\mathrm{L}}/g$.

Thus, the global lability degree is a weighted average of the lability degrees for each of the different complexes present in the mixture with weighting factors dependent on the particular diffusion coefficients and on the respective species abundances in the bulk solution, that is, on the fraction of the maximum diffusive flux of $\mathrm{M}^i\mathrm{L}$, $J_{\mathrm{dif},i}$, over the total maximum diffusive flux of all complexes.

Obviously, the rigorous computation of ξ_i requires knowledge of $c^0_{\mathrm{M}^i\mathrm{L}}$ which follows from the solution of the system of differential equations corresponding to the transport and reaction processes in the mixture. This has to be done numerically for a general mixture case (see Appendix A), although there are explicit analytical solutions for simple cases.[15,16]

For instance, in a single ligand system, when the complex is the predominant metal species, $\epsilon_i K'_i \gg 1$ and $g \gg \mu_i^\infty$ (μ_i^∞ is the effective reaction layer thickness for planar semiinfinite diffusion, $\mu_i^\infty = \sqrt{D_{\mathrm{M}}/k'_{\mathrm{a},i}}$); it has been shown that the lability degree of the complex $\mathrm{M}^i\mathrm{L}$, ξ_i, under diffusion-limited conditions, is approximately given by[7]

$$\xi_i \approx \frac{g}{g + \epsilon_i K'_i \mu_i^\infty} = \frac{g}{g + \epsilon_i K_i \sqrt{D_{\mathrm{M}}/k_{\mathrm{a},i}}\, c^{*1/2}_{^i\mathrm{L}}} \tag{8}$$

Results of the rigorous numerical computation of ξ_i for different systems, as indicated in Appendix A, will be used in the present work to analyze the characteristics of each system

3. Lability Index in a Mixture of Ligands by Means of the Reaction Layer Approximation

We invoke the reaction layer approximation to obtain analytical expressions to predict the behavior of mixtures. The reaction layer was introduced by Brdicka and Wiesner (see ref 28, p 346 for a good introduction) as a way to analytically evaluate the limiting electrochemical current in systems with kinetic complexes. It is based on the division of the diffusion domain thickness into a nonlabile and a labile region, separated by the boundary of the reaction layer with thickness μ.[22] Within the reaction layer, the system is nonlabile, and there is a constant complex concentration; that is, the kinetic flux due to dissociation of ML equals the diffusive flux toward the reaction layer boundary.

The lability index ($\mathscr{L}$)[18,29] compares the maximum kinetic and diffusion fluxes of a given complex

$$\mathscr{L} = \frac{J_{\mathrm{kin}}}{J_{\mathrm{dif}}} \tag{9}$$

where J_{kin} is the hypothetical maximum contribution of the complex to the metal flux in the absence of the diffusion limitation for the complex and J_{dif} is the maximum diffusive flux due to the complex. The criterion for lability is thus $\mathscr{L} \gg 1$. In seeking an approximation for $\mathscr{L}$ for a selected complex in the mixture, we assume that all complexes, except the one selected for analysis, can be classified either as fully labile or as nonlabile. For the sake of simplicity, and without any loss of generality as it only means a reordering of the labels of the complexes in the mixture, we will assign an index in the range 1 to m to the labile complexes in the mixture and an index in the range $m + 1$ to $h - 1$ to the nonlabile ones. The index h is kept for the complex whose lability is being assessed via the reaction layer approximation. As indicated in Appendix B, by extending and adapting the reaction layer approximation to the present case,[7,16] the reaction layer thickness for a given complex h, $\mu^{\infty}_{\mathrm{mix},h}$, derived by assuming that complexes with index $m + 1$ to h have a flat concentration profile (equal to the bulk complex concentration), becomes (see eqs B4 and B5)

$$\mu^{\infty}_{\mathrm{mix},h} = \left(\frac{1 + \sum_{i=1}^{m} \epsilon_i K'_i}{\sum_{i=m+1}^{h} \frac{1}{(\mu_i^{\infty})^2}} \right)^{1/2} \tag{10}$$

The hypothetical metal flux due to a given species $\mathrm{M}^h\mathrm{L}$ in the absence of the diffusion limitation, $J_{\mathrm{kin},h}$, is then

$$J_{\mathrm{kin},h} = k_{\mathrm{d},h} c^{*}_{\mathrm{M}^h\mathrm{L}} \mu^{\infty}_{\mathrm{mix},h} \tag{11}$$

The lability index compares this hypothetical maximum flux with the hypothetical maximum flux in the absence of reaction limitations $J_{\mathrm{dif},h}$ and can be written as

$$\mathscr{L}_h = \frac{J_{\mathrm{kin},h}}{J_{\mathrm{dif},h}} = \frac{k_{\mathrm{d},h} \mu^{\infty}_{\mathrm{mix},h} g}{D_{\mathrm{M}^h\mathrm{L}}} = \frac{k_{\mathrm{d},h} g}{D_{\mathrm{M}^h\mathrm{L}}} \left(\frac{1 + \sum_{i=1}^{m} \epsilon_i K'_i}{\sum_{i=m+1}^{h} \frac{1}{(\mu_i^{\infty})^2}} \right)^{1/2} \tag{12}$$

As a practical rule, in order not to have to exchange indices, one just needs to include the analyzed complex (whose lability index we desire) in the denominator of the previous equation.

For a complex $\mathrm{M}^h\mathrm{L}$, the lability criterion is

$$\mathscr{L}_h \gg 1 \tag{13}$$

For the particular case of only one complex being present in the system, the summations in eq 12 disappear, and $\mathscr{L}_h$ reduces to $\mathscr{L}_h = g/(\epsilon_h K'_h \mu^{\infty}_{\mathrm{mix},h})$, a value that is equal to that given by eq 8 whenever $g \ll \epsilon_h K'_h \mu^{\infty}_{\mathrm{mix},h}$.

When only one complex is present in the system, $\mathscr{L}_h$ is a good approximation to ξ_h for low lability degrees since, in this instance, the concentration of $\mathrm{M}^h\mathrm{L}$ in the reaction layer is close to $c^{*}_{\mathrm{M}^h\mathrm{L}}$, the value assumed in the derivation of eq 10 while $\mathscr{L}_h \gg \xi_h$ as $\mathrm{M}^h\mathrm{L}$ becomes more labile. In a general mixture, the use of $\mathscr{L}_h$ (computed with eq 12) instead of ξ_h might imply difficult choices, since we do not know a priori which are the labile and nonlabile complexes of the mixture. Furthermore, it requires a limiting behavior to be ascribed to all of the complexes: complexes are assumed to be either labile or nonlabile in the derivation of eq 10. This limiting behavior of all complexes can hardly be realistic in a general mixture. Despite these limitations, eq 12 can be used to identify interesting features of the behavior of a complex in a mixture. We would highlight that eq 12 predicts that the lability of a given complex depends on the composition of the mixture in the following way: an increase in the concentration of the labile complex (numerator of eq 12) results in an increase in the lability of the nonlabile complex, $\mathscr{L}_h$, while an increase in the concentration of the *nonlabile* complexes leads to a *decrease* in the lability of the rest of complexes. We could say, thus, that a complex tends to adapt to the global lability character of the mixture. Said otherwise, the system is essentially "kinetically buffered".

4. Mixture Effects in a System with Two Ligands

Following the order of increasing complexity, let us analyze, first, a mixture of two ligands. As we focus our interest on complexes in an aquatic medium, we will assume Eigen and Tamm's mechanism[30,31] so that the kinetic association constant for a given metal is independent of the nature of the ligand, that is, $k_{\mathrm{a},1} = k_{\mathrm{a},2}$; therefore, we assume that the ligands share a common value for the stability constant of the respective outer-sphere complex with the metal (a common charge of the ligands and a fixed ionic strength are required).

4.1. Dependence of ξ_i on the Composition. Figure 1 plots the rigorous global lability degree (ξ) as well as the lability degree of each complex in the mixture (ξ_1 and ξ_2) as a function of the mixture composition which is modified by adding $^1\mathrm{L}$, the ligand of the less labile complex, or $^2\mathrm{L}$, in panels a and b, respectively. In each panel, the concentration of the non-added ligand is kept constant. To highlight the effect of the addition of one complex on the lability degree of the other, we scan a suitable range of concentrations, $c^{*}_{^1\mathrm{L}} < c^{*}_{^2\mathrm{L}}$, so that both complexes are partially labile. Notice in Figure 1a that the lability degree of $\mathrm{M}^1\mathrm{L}$, ξ_1, decreases as $c^{*}_{^1\mathrm{L}}$ increases: this behavior is expected, since an increase in $c^{*}_{^1\mathrm{L}}$ increases the association rate of $\mathrm{M}^1\mathrm{L}$, and consequently, the steady-state situation reached will favor the formation of this complex. On the other hand, ξ_2 also decreases with increasing $c^{*}_{^1\mathrm{L}}$; that is, the addition of the ligand of the less labile complex, $^1\mathrm{L}$, decreases the lability degree of $\mathrm{M}^2\mathrm{L}$. This finding is a specific feature of the mixture and indicates that the lability degree of a given complex in a mixture is dependent not only on the concentration of the directly involved ligand, but also on the concentrations of the other ligands present. We highlight the impact of this result on the concept of lability: lability is, thus, not an intrinsic property of a complex but a property of the medium as well as of the measurement system itself.[6] Notice that eq 12 could be used to justify the decrease of ξ_2 seen in Figure 1a, since the increase of $c^{*}_{^1\mathrm{L}}$ increases the denominator and so decreases $\mathscr{L}_2$. However, in the derivation of eq 12, we did not set a clear limit on when a complex can be considered as labile, and thus included in the denominator of eq 12, or as inert, and thus included in the numerator. So, the application of eq 12 for intermediate cases could be cumbersome and accordingly, we highlight that eq 12 only applies to limiting cases.

Figure 1b depicts the situation for the addition of the more labile ligand, $^2\mathrm{L}$, which leads to an increase in the lability degree of $\mathrm{M}^1\mathrm{L}$. This effect can also be justified by eq 12, since the

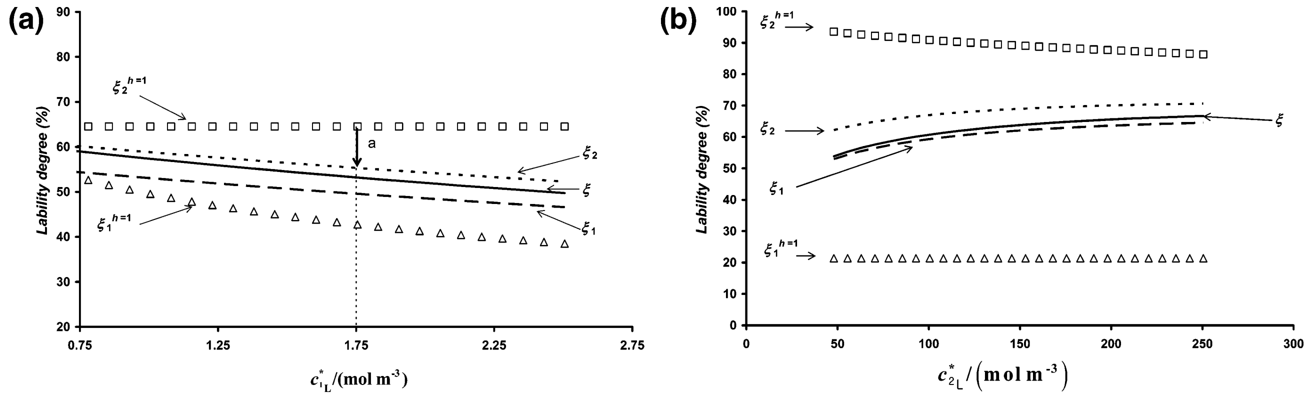

Figure 1. Global lability degree of the system, (ξ, continuous line with no marker), the lability degree of complex M^1L, (ξ_1, long dashed line), and the lability degree of complex M^2L, (ξ_2, short dashed line) in the mixture as functions of the bulk concentration of ligand ^1L. Lability degree $\xi_1^{h=1}$ (Δ) and $\xi_2^{h=1}$ ($\square$) for the single ligand systems at the same total ligand concentration obtained from eq 8. Parameters: $c^*_{T,M} = 0.1$ mol m^{-3}, $D_M = 10^{-9}$ m^2 s^{-1}, $\epsilon_1 = \epsilon_2 = 1$, and $g = 10^{-3}$ m. Case a: $c^*_{^2L} = 30$ mol m^{-3}, $K_1 = 100$ m^3 mol^{-1}, $K_2 = 10$ m^3 mol^{-1}, $k_{a,1} = k_{a,2} = 10$ m^3 mol^{-1} s^{-1} (this combination of parameters leads to practically 20% of the metal as M^1L and 80% as M^2L for the point with abscissa $c^*_{^1L} = 0.75$ mol m^{-3} and 45.5% as M^1L and 54.5% as M^2L for the point with abscissa $c^*_{^1L} = 2.5$ mol m^{-3}). Case b: $c^*_{^1L} = 1.5$ mol m^{-3}, $K_1 = 3000$ m^3 mol^{-1}, $K_2 = 10$ m^3 mol^{-1}, $k_{a,1} = k_{a,2} = 10^3$ m^3 mol^{-1} s^{-1} (this combination of parameters leads to practically 90% of the metal as M^1L and 10% as M^2L for the point with abscissa $c^*_{^2L} = 50$ mol m^{-3} and 64.3% as M^1L and 35.7% as M^2L for the point with abscissa $c^*_{^2L} = 250$ mol m^{-3}). The arrow "a" in panel a indicates the decrease of ξ_2 from the single M+^2L system to the mixture with $c^*_{^1L} = 1.75$ mol m^{-3}.

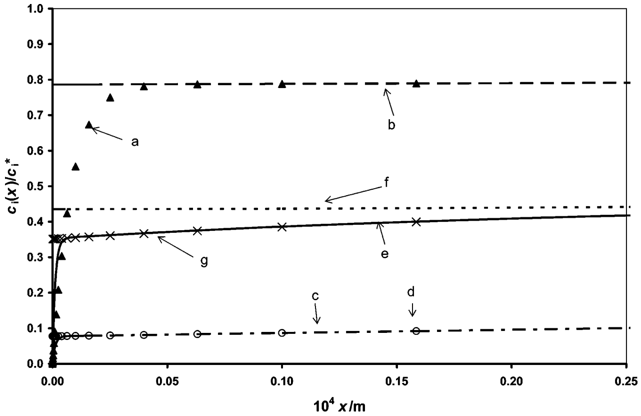

Figure 2. Normalized concentration profiles c_i/c_i^* in different systems. Single ligand ^1L + M system with parameters of Figure 1b for $c^*_{^1L} = 1.5$ mol m^{-3}: curve a (▲) c_M/c^*_M and b (long dashed line) $c_{M^1L}/c^*_{^1L}$. Single ligand ^2L + M system with parameters of Figure 1b and $c^*_{^2L} = 70.5$ mol m^{-3}: curve c (dotted-dashed) c_M/c^*_M and d ○ $c_{M^2L}/c^*_{M^2L}$. Mixture M + ^1L + ^2L system with parameters of Figure 1b and $c^*_{^1L} = 1.5$ mol m^{-3}, $c^*_{^2L} = 70.5$ mol m^{-3}: line e (continuous line) c_M/c^*_M, f (short dashed line) $c_{M^1L}/c^*_{M^1L}$, and g (×) $c_{M^2L}/c^*_{M^2L}$.

increase of $c^*_{^2L}$ increases the numerator in the expression for $\mathcal{L}_1$. However, Figure 1b also shows an increase of ξ_2 when $c^*_{^2L}$ increases. This increase is the opposite of that expected for a single ligand system (see eq 8), and it cannot be justified for the mixture with the simplifying expression, eq 12. This effect can be understood as a decrease of the influence of M^1L, the most abundant complex in the system, on M^2L as $c^*_{M^2L}$ increases.

For the global lability degree, we recall that the behavior of ξ depends not only on the relative values of ξ_1 and ξ_2 but also on the bulk complex concentrations of both complexes (see eq 7). Given this dependence, the magnitude of ξ progressively approaches that of the complex whose concentration increases, giving rise to a decreasing (Figure 1a), increasing (Figure 1b), or nonmonotonous behavior of ξ depending on the respective values of ξ_1 and ξ_2 and on the initial $c^*_{M^1L}$ and $c^*_{M^2L}$ values.

4.2. Lability Degree of a Complex in the Mixture Compared to the Lability Degree in the Single Ligand System. Markers $\square$ and $\triangle$ in Figure 1 denote the lability degree of each complex in a single ligand system, $\xi_i^{h=1}$, at the same ligand concentration as that of this ligand in the mixture. According to eq 8, $\xi_2^{h=1}$ does not change with $c^*_{^1L}$, as clearly seen in Figure 1a. The figure also shows that $\xi_2^{h=1} > \xi_2$ for any amount of ^1L, while $\xi_1^{h=1} < \xi_1$. Actually, a given binary mixture (e.g., the one defined by $c^*_{^1L} = 1.75$ mol m^{-3} in Figure 1a) can be understood as the addition of the corresponding concentration of ^1L (e.g., 1.75 mol m^{-3}) to the single ligand system M + ^2L (e.g., $c^*_{^2L} = 30$ mol m^{-3}) or vice versa. Notice that the mixture effect on ξ_2 (evaluated, for instance, as $|\xi_2^{h=1} - \xi_2|$) increases as $c^*_{^1L}$ increases, and a similar behavior for ξ_1 is found in Figure 1b, where ξ_1 reaches values three times higher than $\xi_1^{h=1}$.

A complementary and intuitive view of the effect of a mixture on the lability degree of a ligand can be obtained by looking at the respective concentration profiles. Figure 2 plots the concentration profiles of the system depicted in Figure 1b for $c^*_{^2L} = 70.5$ mol m^{-3}. In this figure, the normalized profiles of M^1L and M^2L ($c_i(x)/c_i^*$) coincide with that of the metal whenever there is equilibrium, while they diverge from the normalized metal profile, tending to be flat when the dissociation is kinetically limited. As indicated in eq 6, the lability degree is determined by $c^\circ_{M^iL}/c^*_{M^iL}$ and accordingly M^2L is seen to be more labile than M^1L (compare the intercepts of the profiles with $x = 0$) in agreement with the results of Figure 1b. Figure 2 also depicts the profiles for the single ligand systems M + ^1L and M + ^2L at the same bulk ligand and free metal concentration as in the mixture. By comparing these profiles with those of the mixture, we see that the mixture has led to a noticeable decrease in $c^\circ_{M^1L}/c^*_{M^1L}$ and a noticeable increase in $c^\circ_{M^2L}/c^*_{M^2L}$ so that the lability degree of M^1L, the less labile complex, has increased significantly when a more labile complex has been added and vice versa. We can rationalize this behavior by comparison with the metal concentration profile: for the single M + ^2L system, the concentration profile of the metal is, in steady state, the most depleted of the three metal profiles in Figure 2 according to the highest metal flux arising in this almost labile system. Conversely, the metal concentration profile is the less depleted for the single M + ^1L system in accordance with the nonlabile behavior of this complex. In the mixture,

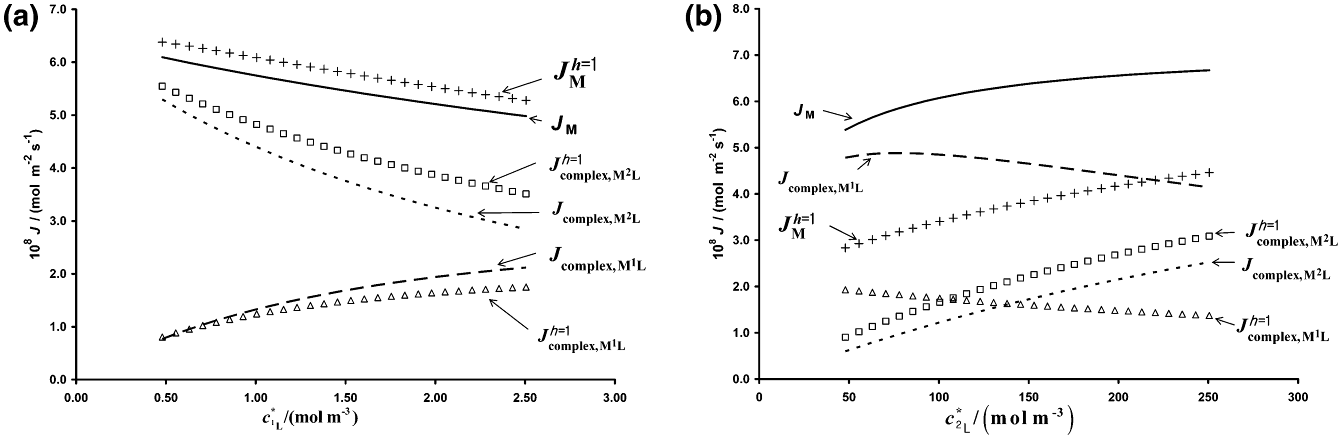

Figure 3. Metal flux, J_M (continuous line), contributions of M^1L and M^2L to the metal flux, and $J_M^{h=1}$ (+) expected in the mixture system when the lability degree of both complexes was $\xi_1^{h=1}$ and $\xi_2^{h=1}$. Parameters: case a, as in Figure 1a; and case b, as in Figure 1b.

the lability degree and the metal concentration profile are in between the values of both single ligand systems. The large depletion of the metal concentration profile in the mixture, in comparison with the single M + ^{1}L system, forces M^1L to a net dissociation over a wider range of the diffusion domain, (notice that the profile of M^1L diverges from that of the corresponding metal profile along a thicker region in the mixture than in the single M + ^{1}L system) thus resulting in a lower $c^o_{M^1L}/c^*_{M^1L}$ and a higher contribution of M^1L to J_M; that is, the lability degree of M^1L has increased when the more labile complex M^2L is present in the system. The increase of the thickness of the reaction layer of M^2L is also predicted by eq 10.

4.3. Impact of the Mixture on the Metal Flux. To assess the impact of the mixture effect on the real metal flux, J_M, we compute the hypothetical metal flux labeled $J_M^{h=1}$ in the mixture assuming that the lability degree of each complex was that corresponding to the single ligand system (with c^*_{iL} and $c^*_{M^iL}$ existing in the real mixture):

$$J_M^{h=1} = J_{free} + D_{M^1L}\frac{c^*_{M^1L}}{g}\xi_1^{h=1} + D_{M^2L}\frac{c^*_{M^2L}}{g}\xi_2^{h=1} \qquad (14)$$

Figure 3a,b shows both fluxes, J_M and $J_M^{h=1}$, for the same systems depicted in Figure 1a,b, respectively, together with the corresponding contributions to the metal flux of both complexes, $J_{complex,i} = D_{M^iL}\ \{c^*_{M^iL}/g\}\xi_i$ and the hypothetical contributions corresponding to the single ligand systems, $J^{h=1}_{complex,i} = D_{M^iL}\{c^*_{M^iL}/g\}\xi_i^{h=1}$.

In addition to consideration of the change in the degree of lability of a particular complex, the mixture effect can be assessed via the difference $J_M^{h=1} - J_M$, which by combination of eqs 5 and 14 can be expressed as

$$J_M^{h=1} - J_M = D_{M^1L}\frac{c^*_{M^1L}}{g}(\xi_1^{h=1} - \xi_1) + D_{M^2L}\frac{c^*_{M^2L}}{g}(\xi_2^{h=1} - \xi_2) = \frac{D_M c^*_M}{g}[\epsilon_1 K'_1(\xi_1^{h=1} - \xi_1) + \epsilon_2 K'_2(\xi_2^{h=1} - \xi_2)] \qquad (15)$$

This expression allows us to define a complex M^iL as "dominant" over another complex M^jL whenever $\epsilon_i K'_i > \epsilon_j K'_j$, because for a similar change in the lability degree, that is, $|\xi_i^{h=1} - \xi_i| \approx |\xi_j^{h=1} - \xi_j|$, the dominant complex will determine the overall change in $J_M^{h=1} - J_M$.

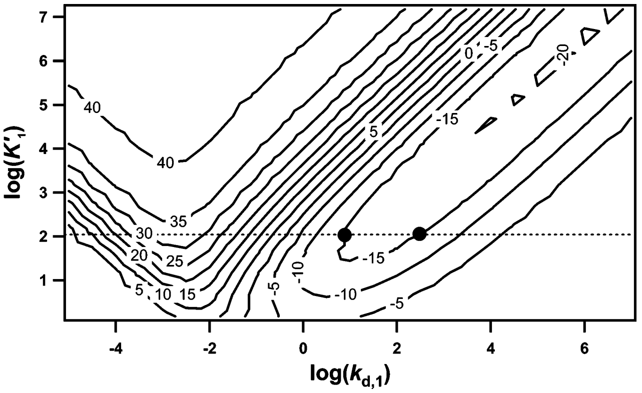

Figure 4. Contour plots of $(J_M^{h=1} - J_M)/J_M$. Parameters: $K_2 = 100K_1$, $K_{d,1} = 10^2 k_{d,2}$, $c^*_{1L} = c^*_{2L} = 1.5$ mol m^{-3}, $\epsilon_1 = \epsilon_2 = 1$, and $g = 10^{-3}$ m with the rest of parameters as in Figure 1a.

Notice that $J_M^{h=1} - J_M$ is dependent on the change in the lability degree, on the respective diffusion coefficients, and on the bulk concentrations of the complexes. To rationalize the difference $J_M^{h=1} - J_M$ in Figure 3a, we recall that the changes of both lability degrees, $(\xi_1^{h=1} - \xi_1)$ and $(\xi_2^{h=1} - \xi_2)$, are quite similar but of opposite sign (see Figure 1a). Thus, M^2L, the more abundant complex in the mixture, dominates the mixture effect on J_M (see eq 15) leading to $J_M^{h=1}$ being higher than J_M. However, the resulting difference $J_M^{h=1} - J_M$ is small because of the buffering by the corresponding cancellation of the effects of each complex. In contrast, for the system depicted in Figure 3b, the highest mixture effect on the lability degrees appears on M^1L (see in Figure 1b that $|\xi_1^{h=1} - \xi_1| > |\xi_2^{h=1} - \xi_2|$), which is also the dominant complex in the mixture ($K'_1 = 4500 > K'_2$). The influence of the mixture on ξ_2 is moderate and, thus, $J^{h=1}_{complex,M^1L} - J_{complex,M^1L}$ is dominant on $J_M^{h=1} - J_M$ which, combined with a mild cancellation effect, leads to J_M overcoming noticeably $J_M^{h=1}$, reaching twice $J_M^{h=1}$ at the leftmost part of Figure 3b.

Contour plots of $(J_M^{h=1} - J_M)/J_M$ provide a convenient means to systematically explore the "mixture effect" for the typical range of the kinetic constants and K'_1 values. Contour plots are depicted in Figure 4 for a ratio $k_{d,1} = 100\ k_{d,2}$ and in Figure 5 for $k_{d,1} = 10^4\ k_{d,2}$. Negative values of $(J_M^{h=1} - J_M)/J_M$ appear in the right area of both figures, while positive $(J_M^{h=1} - J_M)/J_M$ values appear mostly in the left. This general trend can be understood by recalling that, in these plots, M^1L is more labile than M^2L and $c^*_{M^2L} > c^*_{M^1L}$ (i.e., M^2L is dominant). Let us

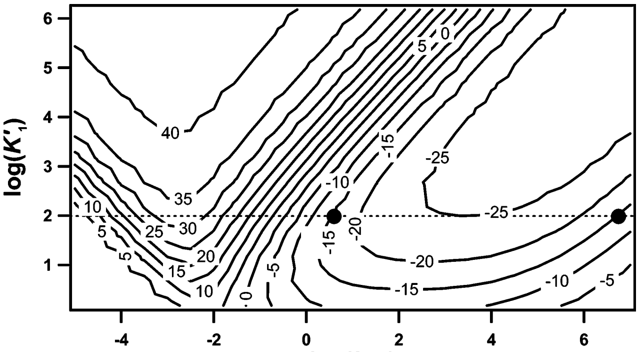

Figure 5. Contour plots of $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$. Parameters: $K_2 = 10^4 K_1$, $k_{\mathrm{d},1} = 10^4 k_{\mathrm{d},2}$, and the rest as in Figure 4.

analyze Figure 4 following the horizontal dashed line at log K_1' = 2. At the rightmost part of this horizontal line (e.g., close to abscissa log $k_{\mathrm{d},1} = 6$), both complexes are labile, the shift of the steady-state position due to the mixture effect is negligible and $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$ tends to zero. On decreasing $k_{\mathrm{d},1}$, $\mathrm{M}^2\mathrm{L}$ tends to be inert, while $\mathrm{M}^1\mathrm{L}$ is still labile, and we observe that $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$ increases (see, for instance, points within the segment between both bullets). This can be explained as follows: the lability degree of $\mathrm{M}^2\mathrm{L}$ in the mixture increases with respect to the value in the single ligand system (because of the presence of another labile complex in the system) and thus $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$ has a negative value. Under these conditions, the change in ξ_2 is significant, while the change in ξ_1 is negligible since $\mathrm{M}^1\mathrm{L}$ is labile. A further decrease of $k_{\mathrm{d},1}$ causes $\mathrm{M}^1\mathrm{L}$ to tend toward nonlability (e.g., around abscissae log $k_{\mathrm{d},1} = -1$). When the effect of $\xi_1 < \xi_1^{h=1}$ is predominant, $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$ changes to a positive value. At the leftmost part of this horizontal line, both complexes are inert and even more so in the mixture than in the respective single ligand systems; thus, $(J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}})/J_{\mathrm{M}}$ decreases because it becomes increasingly difficult for the mixture to change the steady-state dissociation position of each complex.

In Figure 5, the difference between the dissociation kinetic constants of both complexes is higher than in Figure 4, so that, from the transition of $\mathrm{M}^2\mathrm{L}$ to partially labile, up to the transition of $\mathrm{M}^1\mathrm{L}$, we have to move over a larger range of k_{d} values. Graphically, the distance between the bullets in Figure 4 is larger than that in Figure 5.

Summarizing, when both complexes are partially labile with significantly different lability degrees, the mixture effect on both lability degrees is opposite, and the impact on J_{M} is buffered by the corresponding cancellation depending on the particular difference in ξ_i values and on the respective bulk concentrations and mobilities. However, when there is only one predominant factor (only one relevant $\xi_i^{h=1} - \xi_i$, concentration, or mobility) there is almost no cancellation, and the mixture effect on J_{M} reaches maximal values.

5. Increasing the Number of Ligands in the System.

When the number of ligands present in the system increases, the effect of the mixture on one complex can be analyzed in terms of the combined impact of each ligand. Figure 6 shows systems with three ligands; one of them ($\mathrm{M}^1\mathrm{L}$) is almost inert, and the rest are almost labile. As we use Eigen's relationships to assign the kinetic parameters $k_{\mathrm{d},\,j}$ to the different complexes (k_{a} value is common to all of the ligands) and as total ligand concentrations are of the same order of magnitude, the most inert complex ($\mathrm{M}^1\mathrm{L}$) is the most abundant one. Figure 6a considers the addition of the ligand of the less labile complex and shows a concomitant decrease of all of the lability degrees, as expected. Moreover, the lability degree of the almost labile complexes in the mixture are greatly decreased with respect to the values for the single ligand systems. For instance, ξ_3 goes from $\xi_3^{h=1} \approx 100\%$ to $\xi_3 \approx 25\%$ at the rightmost part of the figure. Conversely, a mild mixture effect on ξ_1 is seen in the figure (small difference between ξ_1 and $\xi_1^{h=1}$). This is a consequence of the larger abundance of $\mathrm{M}^1\mathrm{L}$ with respect to $\mathrm{M}^2\mathrm{L}$ and $\mathrm{M}^3\mathrm{L}$. We could say that $\mathrm{M}^1\mathrm{L}$, the dominant complex, determines the metal profile while the other profiles try to adapt to it; that is, $\mathrm{M}^1\mathrm{L}$ acts as a kinetic buffering agent. Accordingly, in spite of a large mixture effect decreasing ξ_2 and ξ_3, the resulting mixture effect on J_{M} is mainly due to the slight increase in lability of $\mathrm{M}^1\mathrm{L}$. This latter effect is mitigated by the fact that both $\xi_2^{h=1} - \xi_2$ and $\xi_3^{h=1} - \xi_3$ (which increase as $c_{^1\mathrm{L}}^*$ increases) are opposite in sign to $\xi_1^{h=1} - \xi_1$. Likewise, Figure 6b considers the addition of the ligand ($^1\mathrm{L}$) of an almost labile complex to a mixture of one nonlabile ($\mathrm{M}^3\mathrm{L}$) and another labile complex ($\mathrm{M}^2\mathrm{L}$). This high lability implies a practically flat $\xi_2^{h=1}$ in Figure 6b as follows from eq 8. Notice that, at a given abscissa value, the differences $\xi_1^{h=1} - \xi_1$ and $\xi_2^{h=1} - \xi_2$ are larger than $\xi_3^{h=1} - \xi_3$, since $\mathrm{M}^3\mathrm{L}$ is highly dominant in the

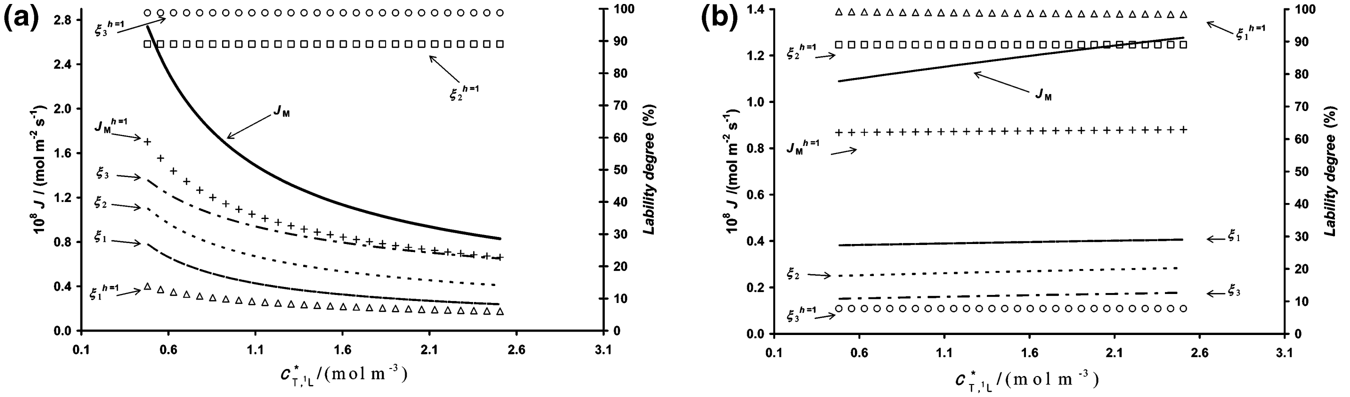

Figure 6. Lability degrees of the complexes $\mathrm{M}^1\mathrm{L}$ (ξ_1, long dashed line), $\mathrm{M}^2\mathrm{L}$ (ξ_2, short dashed line), and $\mathrm{M}^3\mathrm{L}$ (ξ_3, dotted dashed line) together with $\xi_1^{h=1}$ (Δ), $\xi_2^{h=1}$ (□), and $\xi_3^{h=1}$ (○) obtained by means of eq 8 for the single $\mathrm{M}^1\mathrm{L}$, $\mathrm{M}^2\mathrm{L}$, and $\mathrm{M}^3\mathrm{L}$ systems, referred to the right ordinate axis as functions of $c_{\mathrm{T},^1\mathrm{L}}^* = c_{^1\mathrm{L}}^* + c_{\mathrm{M}^1\mathrm{L}}^*$, the total bulk concentration of ligand $^1\mathrm{L}$. Metal flux, J_{M}, in the mixture (continuous line) and metal flux $J_{\mathrm{M}}^{h=1}$ (+) expected in the mixture system when the lability degrees of the complexes were $\xi_1^{h=1}$, $\xi_2^{h=1}$, and $\xi_3^{h=1}$. Both metal fluxes are referred to the left ordinate axis. Parameters: case a, $K_1 = 10^4\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, $K_2 = 10^2\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, $K_3 = 10\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, $k_{\mathrm{a},1} = k_{\mathrm{a},2} = k_{\mathrm{a},3} = 10^3\ \mathrm{m}^3\ \mathrm{mol}^{-1}\mathrm{s}^{-1}$, $c_{\mathrm{T},^2\mathrm{L}}^* = c_{\mathrm{T},^3\mathrm{L}}^* = 1.5\ \mathrm{mol\ m}^{-3}$, $\epsilon_1 = \epsilon_2 = \epsilon_3 = 1$, $g = 10^{-3}$ m, and the rest of parameters as in Figure 1a. Case b: $K_1 = 10\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, $K_2 = 10^2\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, $K_3 = 10^4\ \mathrm{m}^3\ \mathrm{mol}^{-1}$, and the rest of parameters as in case a.

mixture. This predominance justifies that $\xi_3^{h=1} - \xi_3$ determines the negative values of the difference $J_{\mathrm{M}}^{h=1} - J_{\mathrm{M}}$ seen in the figure.

Conclusions

The lability degree, ξ_j, of a given complex depends on the mixture of competing ligands present in the system; that is, ξ_j (and ξ) is a property of the medium composition. A rigorous numerical simulation has been developed to evaluate this effect. Moreover, the reaction layer approximation has been used to derive an approximate analytical expression to understand the effect of the mixture on the lability degree of a given complex.

Typically, the addition of a ligand of a labile complex to the system leads to an increase of the lability degree of the other complexes, while the addition of a nonlabile one leads to a decrease of the lability degree of all of the complexes. These effects are more noticeable for the less abundant complexes and among these, for the partially labile ones.

Results obtained by rigorous numerical simulation are also qualitatively predicted by the analytical expression for the lability index of a complex in a mixture, eq 12, obtained within the framework of the reaction layer approximation.

In a mixture of two ligands, when both complexes show sufficiently different lability degrees, the mixture effect has opposite sign on each complex; that is, each complex tries to adapt to the other. If the concentrations are similar, the mixture effect reaches the highest impact on the metal flux when the effect of only one of the complexes is relevant, so that the cancellation is negligible. This happens when one of the complexes exhibits limiting behavior, that is, labile or nonlabile, while the other is partially labile. When the concentrations are sufficiently different, the less abundant complex greatly modifies its lability degree to adapt to that imposed by the predominant one. Furthermore, it is the impact of the mixture effect on the most abundant complex that determines the resulting influence on the metal flux.

In a mixture of many complexes, the lability degree of a complex can be understood as resulting from its particular lability plus the effects from all other complexes. The largest mixture effects on the lability degree appear for the less abundant and partially labile complexes. When one complex is dominant in the mixture (a complex with the product $D_{\mathrm{M}^i\mathrm{L}}c^*_{\mathrm{M}^i\mathrm{L}}$ much higher than the rest), the mixture effects on this complex determine the behavior of the whole system.

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Appendix A

Mathematical Formulation of the Problem. When diffusion toward a stationary planar surface is the only relevant transport mechanism, for steady-state conditions, we can write

$$D_{\mathrm{M}}\frac{\mathrm{d}^2c_{\mathrm{M}}}{\mathrm{d}x^2} + \sum_{i=1}^{h}k_{\mathrm{d},i}c_{M^i\mathrm{L}} - (\sum_{i=1}^{h}k'_{\mathrm{a},i})c_{\mathrm{M}} = 0 \qquad \text{(A-1)}$$

$$D_{\mathrm{M}^i\mathrm{L}}\frac{\mathrm{d}^2c_{\mathrm{M}^i\mathrm{L}}}{\mathrm{d}x^2} - k_{\mathrm{d},i}c_{\mathrm{M}^i\mathrm{L}} + k'_{\mathrm{a},i}c_{\mathrm{M}} = 0 \qquad i = 1, 2, ..., h \quad \text{(A-2)}$$

with boundary conditions,

$$x = 0 \qquad c_{\mathrm{M}} = 0;$$

$$\left(\frac{dc_{\mathrm{M}^1\mathrm{L}}}{dx}\right)_{x=0} = \left(\frac{dc_{\mathrm{M}^2\mathrm{L}}}{dx}\right)_{x=0} = ... = \left(\frac{dc_{\mathrm{M}^h\mathrm{L}}}{dx}\right)_{x=0} = 0 \quad \text{(A-3)}$$

$$x = g \qquad c_{\mathrm{M}} = c^*_{\mathrm{M}}; \quad c_{\mathrm{M}^1\mathrm{L}} = c^*_{\mathrm{M}^1\mathrm{L}}; ...\ c_{\mathrm{M}^h\mathrm{L}} = c^*_{\mathrm{M}^h\mathrm{L}} \qquad \text{(A-4)}$$

where g indicates the thickness of the diffusion domain of the system. Notice that in ligand excess conditions, the kinetics of interconversion between M and $\mathrm{M}^i\mathrm{L}$ are pseudo-first-order, and the system (A-1) − (A-2) is linear.

A procedure for the rigorous solution of the system (A-1) − (A-2) is based on the uncoupling of the system of equations.[10,15] As shown previously, this can be done by diagonalizing the matrix and rewriting the system in terms of a new set of unknowns given by the eigenvectors. Details of this procedure have been given in ref 16.

Appendix B

General Expression for the Reaction Layer Thickness in a Mixture System. The reaction layer approximation allows the evaluation of the maximum hypothetical metal flux in absence of diffusion limitation (J_{kin}) by assuming that the complex concentration profile is flat reaching the maximum value, the bulk complex concentration. The solution of the metal diffusion equation under these conditions gives then J_{kin}. Notice that even though $c^0_{\mathrm{ML}} \simeq c^*_{\mathrm{ML}}$ there might be a very large kinetic contribution because $K' \gg 1$ (i.e., $J_{\mathrm{complex,ML}} \gg J_{\mathrm{free}}$).

Let us obtain the reaction layer thickness of a complex $\mathrm{M}^h\mathrm{L}$ when the complexes with ligands 1 to m are labile and the rest are nonlabile. Under these conditions, we assume $c_{\mathrm{M}^i\mathrm{L}} \cong c^*_{\mathrm{M}^i\mathrm{L}}$ for the nonlabile complexes and for $\mathrm{M}^h\mathrm{L}$, while $c_{\mathrm{M}^i\mathrm{L}}(0) = 0$ for the labile ones. Equation A-1 can then be approximated as

$$D_{\mathrm{M}}\frac{\mathrm{d}^2c_{\mathrm{M}}}{\mathrm{d}x^2} + \sum_{i=1}^{m}k_{\mathrm{d},i}c_{\mathrm{M}^i\mathrm{L}} + \sum_{i=m+1}^{h}k_{\mathrm{d},i}c^*_{\mathrm{M}^i\mathrm{L}} - (\sum_{i=1}^{h}k'_{\mathrm{a},i})c_{\mathrm{M}} = 0 \qquad \text{(B-1)}$$

Adding the transport equations for the labile complexes and for the metal, we have

$$(D_{\mathrm{M}} + \sum_{i=1}^{m}D_{\mathrm{M}^i\mathrm{L}}K'_i)\frac{\mathrm{d}^2c_{\mathrm{M}}}{\mathrm{d}x^2} + \sum_{i=m+1}^{h}k_{\mathrm{d},i}c^*_{\mathrm{M}^i\mathrm{L}} - \sum_{i=m+1}^{h}k'_{\mathrm{a},i}c_{\mathrm{M}} = 0 \qquad \text{(B-2)}$$

which can be rewritten, dividing by D_{M} and using eq 2 as

$$(1 + \sum_{i=1}^{m}\epsilon_iK'_i)\frac{\mathrm{d}^2c_{\mathrm{M}}}{\mathrm{d}x^2} + \left(\sum_{i=m+1}^{h}\frac{k_{\mathrm{d},i}}{D_{\mathrm{M}}}K'_i\right)(c^*_{\mathrm{M}} - c_{\mathrm{M}}) = 0 \qquad \text{(B-3)}$$

or

$$\frac{\mathrm{d}^2 c_{\mathrm{M}}}{\mathrm{d}x^2} = \left(\frac{\displaystyle\sum_{i=m+1}^{h} \frac{k_{\mathrm{d},i}}{D_{\mathrm{M}}} K'_i}{1 + \displaystyle\sum_{i=1}^{m} \epsilon_i K'_i} \right) (c_{\mathrm{M}} - c^*_{\mathrm{M}}) \tag{B-4}$$

Parallel to the procedure carried out in previous works,[7,8,16] we express the factor in between brackets in terms of a constant. Thus, we write

$$\frac{\mathrm{d}^2 c_{\mathrm{M}}}{\mathrm{d}x^2} = \frac{c_{\mathrm{M}} - c^*_{\mathrm{M}}}{(\mu^{\infty}_{\mathrm{mix},h})^2} \tag{B-5}$$

We have chosen to label the inverse of the square root of the factor in between brackets as $\mu^{\infty}_{\mathrm{mix},h}$ (see eq 10), because it can be seen that it corresponds to the reaction layer thickness of this system under semi-infinite diffusion (the semi-infinite diffusion is denoted via the superscript ∞). Indeed, the solution of eq B-5 with the conditions of bulk complex concentration and finite diffusion domain leads to a diffusion layer thickness[7,16] specific for finite diffusion which, in the limit of g tending to infinity, reverts to $\mu^{\infty}_{\mathrm{mix},h}$.

Appendix C: Most Relevant Symbols

c_i^0: concentration of species i at the active surface ($x = 0$) (eqs 5 and 6)

c_i^*: bulk concentration of species i (eq 2)

D_i: diffusion coefficient of species i (eq 4)

g: thickness of the diffusion domain (eq 4)

h: number of different ligands (eq 4)

$J_{\mathrm{complex,M}^i\mathrm{L}}$: contribution of the complex $\mathrm{M}^i\mathrm{L}$ to the metal flux in the mixture (eq 5)

$J^{h=1}_{\mathrm{complex,M}^i\mathrm{L}}$: contribution of the complex $\mathrm{M}^i\mathrm{L}$ to the metal flux if this was the only complex in the system (Figure 3 and below eq 14)

$J_{\mathrm{dif},i}$: maximum diffusive flux due to complex $\mathrm{M}^i\mathrm{L}$ (eq 5 and 9)

J_{free}: flux if the complexes were inert (i.e., due to free M; eq 3)

J_{kin}: hypothetical maximum kinetic contribution if there was no limitation from the diffusion of the complexes (eq 9)

J_{labile}: global metal flux arising in the system if all the complexes are labile (eq 3)

J_{M}: actual metal flux crossing the active surface (eq 3)

$J^{h=1}_{\mathrm{M}}$: hypothetical metal flux in the mixture assuming that the lability degree of each complex was that corresponding to the single ligand system (eq 14)

K'_i: dimensionless stability constant of complex $\mathrm{M}^i\mathrm{L}$ for excess ligand conditions (eq 2)

$k_{\mathrm{a},i}$, $k_{\mathrm{d},i}$: association and dissociation rate constants for complexes with ligand ${}^i\mathrm{L}$ (eq 2)

${}^i\mathrm{L}$: ligand with index i (eqs 1 and 2)

$\mathcal{L}$: lability index comparing J_{kin} and the maximum diffusional flux of the complexes (eqs 9 and 12)

ϵ_i: dimensionless diffusion coefficient for the complex $\mathrm{M}^i\mathrm{L}$ (eq 7)

$\mu^{\infty}_{\mathrm{mix},h}$: diffusion layer thickness in semi-infinite diffusion for complex $\mathrm{M}^h\mathrm{L}$ in a mixture with m complexes being labile (eq 10)

μ^{∞}_i: diffusion layer thickness in semi-infinite diffusion $\sqrt{D_{\mathrm{M}}/k'_{\mathrm{a},i}}$ for complex $\mathrm{M}^i\mathrm{L}$ being alone (eq 8)

ξ: global degree of lability (eq 3)

ξ_i: degree of lability of complex $\mathrm{M}^i\mathrm{L}$ in the mixture (eqs 3 and 6)

$\xi_i^{h=1}$: degree of lability of complex $\mathrm{M}^i\mathrm{L}$ if this was the only complex in the system (eq 14)

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