Lability of complexes in steady-state finite planar diffusion

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Abstract

The analytical solution of the reaction-diffusion problem of a species forming a complex (with any association and dissociation rate constants) in solution and disappearing at an active planar surface is presented for a finite diffusion region where the system reaches steady state under diffusion limited conditions. This problem arises in a number of fields ranging from electroanalytical techniques or in situ trace metal sensors to biouptake by organisms. The analysis of the solution allows the introduction of the degree of lability, ξ, aimed at quantifying rigorously the contribution of the complexes to the metal flux. The differences between the lability degree, ξ, and the lability parameter, L, used in the statement of lability criteria are shown. A particular expression for the reaction layer thickness and the lability criterion for the set of conditions of this work are also reported. Finally, when the diffusion layer thickness (such as the gel thickness in some DGT set-ups) can be changed, the lability degree enables the tuning of the relevance of the kinetic contribution of the complex to the flux.
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1. Introduction

The understanding of the environmental impact of metal compounds is a subject that has received strong attention in recent years [1–3]. As it has been pointed out, the serious pollution hazard of heavy metals demands reliable analytical techniques able to measure the flux of metal that reaches micro-organisms, algae, plants, and living organisms present in the media [4]. The analysis of this flux is called dynamic speciation since it depends on the time scale and on the kinetic parameters of the undergoing processes, as well as on the spatial scale and geometry of the sensor or micro-organism.

A concept that plays a key role in this issue is lability. It is used to quantify the ability of the complexes to contribute to the metal flux. In fact, in a natural sample, a great number of ligands such as particles, colloids, polysaccha-

rides, proteins, humic and fulvic acids are present. The interaction of the metal with these ligands can reduce the metal flux received by a living organism via reduction of the mobility of the metal or via a kinetic control of the dissociation processes [5,6].

The importance of the lability criteria has been recognised since long time ago. Accordingly, a great effort has been devoted to provide these criteria for different conditions of interest in terms of the parameters that characterise the system [7–15]. In this pursuit, the so-called reaction layer approximation has become a very useful tool. Introduced by Brdicka and Wiesner in the context of the influence of the complex electroinactive species on the electrodic reduction of a free metal ion [16,17], the reaction layer approximation is based on the assumption of steady-state conditions and a constant complex concentration in the system. In this way, the metal transport equation becomes uncoupled from the transport equation for the complex. In the simplest application of the reaction layer approximation, the complex concentration is assumed to be the bulk complex concentration. This approximation

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allows to assess J_{kin}, a characteristic parameter of the system defined as the hypothetical ability of the dissociation process in contributing to the metal flux in absence of diffusion limitation for the complex. The lability criterion is just based on the comparison of this ability of the dissociation process with the ability of maximum supply of complex to the reaction layer, which in steady-state conditions is the maximum diffusional flux of the complex. When J_{kin} is greater than the maximum supply of complex, diffusion is rate limiting and we say that the system is labile; while if J_{kin} is less than the diffusional supply we are in conditions of kinetic control and we say that the system is partially labile or non-labile.

The lability criterion is thus an inequality used to predict if a system is non-labile or labile, but this criterion cannot quantitatively describe the lability degree of the system for partially labile cases.

This paper focuses on systems with planar diffusion in a finite domain. This is the case of relevant techniques deployed "in situ" such as diffusion gradient in thin films (DGT) [18–23] and permeation liquid membrane (PLM) [24–28] which have emerged in the last years as powerful techniques for the dynamic speciation of metals in different compartments of the natural media. As the exposure time of these sensors is usually longer than the effective time of the transient regime, steady-state conditions prevail. Further consideration of excess of ligand conditions allows us to provide analytical solutions for the concentration profiles and the metal flux. It is the aim of this work: (i) to develop analytical expressions for quantifying the contribution of the complexes to the metal flux under the particular conditions used in this work, (ii) to work out a parameter which, on the basis of the rigorous solution, quantifies the degree of lability, (iii) to develop suitable expressions for the reaction layer thickness in order to report the lability criterion for the present case, (iv) to analyse the effect of the change of the thickness of the diffusion layer and provide an analytical expression for the thickness that allows measuring a prefixed percentage of the contribution of the complex to the metal flux.

2. Mathematical formulation

Let us consider, in solution, the complexation of a metal M with a ligand L according to the scheme

$$M + L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} ML \tag{1}$$

and let us assume that the ligand is present in the system in a great excess with respect to the metal so that $c_L = c_L^*$ (from now on, c_i^* labels the concentration value of species i at the bulk solution). The corresponding equilibrium conditions then read

$$K' = \frac{k_a'}{k_d} = \frac{c_{ML}^*}{c_M^*} \tag{2}$$

where $K' = Kc_L^*$, $k_a' = k_a c_L^*$ and K, k_a and k_d are respectively the equilibrium constant, and the association and dissociation kinetic constants of the complexation process.

When diffusion towards a stationary planar surface is the only relevant transport mechanism, for steady-state conditions we can write

$$D_M \frac{d^2 c_M}{dx^2} + k_d c_{ML} - k_a' c_M = 0 \tag{3}$$

$$D_{ML} \frac{d^2 c_{ML}}{dx^2} + k_a' c_M - k_d c_{ML} = 0 \tag{4}$$

Notice that in ligand excess conditions, the kinetics of interconversion of M and ML are pseudo first-order and the system (3) and (4) becomes linear.

Denoting

$$\varepsilon = D_{ML}/D_M \tag{5}$$

and introducing a new variable

$$z = \frac{x}{\sqrt{D_M}} \tag{6}$$

the system of Eqs. (3) and (4) becomes

$$\frac{d^2 c_M}{dz^2} = k_a' c_M - k_d c_{ML} \tag{7}$$

$$\frac{d^2 c_{ML}}{dz^2} = \frac{k_d}{\varepsilon} c_{ML} - \frac{k_a'}{\varepsilon} c_M \tag{8}$$

As usual, when the metal is the only one species consumed at the limiting surface, the boundary value problem in diffusion limited conditions is given by

$$z = 0 \quad c_M = 0; \left(\frac{dc_{ML}}{dz}\right)_{z=0} = 0 \tag{9}$$

$$z = z^* = \frac{g}{\sqrt{D_M}} \quad c_M = c_M^*; \ c_{ML} = c_{ML}^* \tag{10}$$

where g is the thickness of the diffusion domain. For instance, in the case of DGT, it would be the thickness of the gel layer, if one can assume that some kind of stirring restores the bulk concentration at the diffusion region edge ($x = g$). As it has been pointed out [13], when g is of the order of the concentration polarisation thickness in the external solution phase, the boundary condition (10) is not suitable.

3. Rigorous solution

The rigorous solution of the system (7)–(10) is outlined in Appendix A. The resulting concentration profiles can be written as:

$$\frac{c_M(z)}{c_M^*} = \frac{z + \frac{\varepsilon K'}{\sqrt{n}} \left[\tanh[\sqrt{n}z^*] + \frac{\sinh[\sqrt{n}(z-z^*)]}{\cosh[\sqrt{n}z^*]} \right]}{z^* + \frac{\varepsilon K'}{\sqrt{n}} \tanh[\sqrt{n}z^*]} \tag{11}$$

$$\frac{c_{ML}(z)}{c_{ML}^*} = \frac{z - \frac{1}{\sqrt{n}} \left[\frac{\sinh[\sqrt{n}(z-z^*)]}{\cosh[\sqrt{n}z^*]} - \varepsilon K' \tanh[\sqrt{n}z^*] \right]}{z^* + \frac{\varepsilon K'}{\sqrt{n}} \tanh[\sqrt{n}z^*]} \tag{12}$$

where