

## LABILITY OF COMPLEXES IN STEADY STATE FINITE PLANAR DIFFUSION

José Salvador<sup>a\*</sup>, Jaume Puy<sup>a</sup>, Joan Cecília<sup>b</sup> and Josep Galceran<sup>a</sup>

<sup>a</sup>*Departament de Química,* <sup>b</sup>*Departament de Matemàtica, Universitat de Lleida, Rovira Roure 191, 25198, Lleida, Spain*

\* Corresponding author. e-mail address: salvador@quimica.udl.es

### 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,  $\xi$ , aimed at quantifying rigorously the contribution of the complexes to the metal flux. The differences between the lability degree,  $\xi$ , 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.

**KEYWORDS:** Speciation, Trace metal analysis, Bioavailability; Lability

## **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, polysaccharides, 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 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



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

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

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

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

$$D_{\text{ML}} \frac{d^2 c_{\text{ML}}}{dx^2} + k'_a c_{\text{M}} - k_d c_{\text{ML}} = 0 \quad (4)$$

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

Denoting

$$\varepsilon = D_{\text{ML}}/D_{\text{M}} \quad (5)$$

and introducing a new variable

$$z = \frac{x}{\sqrt{D_{\text{M}}}} \quad (6)$$

the system of equations (3)-(4) becomes

$$\frac{d^2 c_{\text{M}}}{dz^2} = k'_a c_{\text{M}} - k_d c_{\text{ML}} \quad (7)$$

$$\frac{d^2 c_{\text{ML}}}{dz^2} = \frac{k_d}{\varepsilon} c_{\text{ML}} - \frac{k'_a}{\varepsilon} c_{\text{M}} \quad (8)$$

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

$$z = 0 \quad c_{\text{M}} = 0; \left( \frac{dc_{\text{ML}}}{dz} \right)_{z=0} = 0 \quad (9)$$

$$z = z^* = \frac{g}{\sqrt{D_{\text{M}}}} \quad c_{\text{M}} = c_{\text{M}}^*; \quad c_{\text{ML}} = c_{\text{ML}}^* \quad (10)$$

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:

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

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

where

$$n = \frac{k_d}{\varepsilon} + k_a' = \frac{k_d (1 + \varepsilon K')}{\varepsilon} \quad (13)$$

Eqns. (11) and (12) indicate that the steady-state metal and complex concentration profiles are not linear for the general kinetic case under excess ligand conditions.

The metal flux at  $x=0$  can simply be calculated from the gradient of the free-metal concentration profile, given in (11), as

$$J_M = D_M \left( \frac{dc_M}{dx} \right)_{x=0} = \sqrt{D_M} \left( \frac{dc_M}{dz} \right)_{z=0} = \frac{\sqrt{D_M} c_M^* (1 + \varepsilon K')}{z^* + \frac{\varepsilon K'}{\sqrt{n_1}} \tanh[\sqrt{n_1} z^*]} \quad (14)$$

*Fully labile system*

The fully labile case merits some specific comments. When  $k_d \rightarrow \infty$  ( $k_a' = K' k_d$ ), we have  $n \rightarrow \infty$ , as Eqn. (13) shows. Taking into account that  $\tanh$  tends to a constant for an increasing argument,  $c_M(z)/c_M^*$  and  $c_{ML}(z)/c_{ML}^*$  given in (11) and (12) become

$$\frac{c_M(x)}{c_M^*} = \frac{c_{ML}(x)}{c_{ML}^*} = \frac{x}{g} \quad (15)$$

which means that equilibrium conditions at any spatial point are reached and that the steady state metal and complex concentration profiles of a labile system in excess of ligand conditions are linear.

Likewise, applying the same limit,  $k_d \rightarrow \infty$  ( $k_a' = K' k_d$ ), the metal flux given by (14) reduces to

$$J_M = J_{\text{labile}} = \frac{D_M c_M^* (1 + \varepsilon K')}{g} = D_M \frac{c_M^*}{g} + D_{ML} \frac{c_{ML}^*}{g} \quad (16)$$

Eqn. (16) indicates that in a labile system, the metal flux is only limited by diffusion and that, under steady state conditions, the diffusion of the total metal towards the limiting surface is just the addition of the independent maximum diffusion of the free metal and of the complex. Recalling the expressions for the metal and complex concentration profiles given in (15), Eqn. (16) can be rewritten as

$$J_M = J_{\text{labile}} = D_M \left( \frac{dc_M}{dx} \right)_{x=0} + D_{ML} \left( \frac{dc_{ML}}{dx} \right)_{x=0} \quad (17)$$

Notice that (16) and (17) have been obtained as the limit  $k_d \rightarrow \infty$  of (14), which yields the metal flux in the general kinetic formulation of the problem. It is worth highlighting

that although the general problem states  $\left(\frac{dc_{ML}(x)}{dx}\right)_{x=0} = 0$ , as indicated in (9), after the

limit  $k_d \rightarrow \infty$ , the gradient of  $c_{ML}$  at  $x=0$  is not null,  $\left(\frac{dc_{ML}(x)}{dx}\right)_{x=0} \neq 0$  (see (15)), and

$J_M$  defined as  $J_M = \left(\frac{dc_M(x)}{dx}\right)_{x=0}$  for the general kinetic case becomes

$$J_M = D_M \left(\frac{dc_M(x)}{dx}\right)_{x=0} + D_{ML} \left(\frac{dc_{ML}(x)}{dx}\right)_{x=0}, \text{ with the second term differing from zero.}$$

This analytical result here obtained supports the use of (17) for the metal flux in direct mathematical formulations of fully labile systems [29-32].

#### 4.- Lability of the complex

Let us obtain the contribution of the complex to the metal flux, which we label  $J_{\text{complex}}$

[12]. It can be obtained by just subtracting from the metal flux ( $J_M$ ) the term that corresponds to the diffusional transport of the free M present in the system,  $J_{\text{free}}$ , totally uncoupled from complexation. Thus,

$$J_{\text{complex}} = J_M - J_{\text{free}} \tag{18}$$

where for the particular conditions of the present system (diffusion in a finite domain),

$$J_{\text{free}} = D_M \frac{c_M^*}{g} \tag{19}$$

The maximum contribution of the complex arises when the system is labile. Thus, in order to quantify the contribution of the complex to the metal flux, we can define a

lability degree,  $\xi$ , as the fraction of the present contribution with respect to the maximum contribution of the complex to the metal flux [5,12,33,34]:

$$\xi = \frac{J_M - J_{\text{free}}}{J_{\text{labile}} - J_{\text{free}}} \quad (20)$$

Recalling the expression of  $J_{\text{labile}}$  given in Eqn. (16),  $\xi$  rewrites as

$$\xi = \frac{J_M - D_M \frac{c_M^*}{g}}{D_{\text{ML}} \frac{c_{\text{ML}}^*}{g}} = \frac{J_{\text{complex}}}{J_{\text{dif,ML}}} \quad (21)$$

The denominator of Eq. (21) indicates that the maximum contribution of the complexes to the metal flux is independent of the kinetics of complexation, but is limited by diffusion. This is just the situation in labile systems.

By means of Eqn. (14), Eqn. (21) rewrites:

$$\xi = \frac{z^* - \tanh[\sqrt{n}z^*]/\sqrt{n}}{z^* + \varepsilon K' \tanh[\sqrt{n}z^*]/\sqrt{n}} \quad (22)$$

where  $n$  has been defined in (13). In terms of the degree of lability, the system tends to be labile as  $\xi$  becomes close to 1. Notice that Eqn. (22) predicts rigorously the percentage with which the complex contributes to the metal flux (with respect to its maximum contribution) once the kinetic constants and the spatial dimensions of the sensor are known. However, the evaluation of the metal flux requires both the lability degree and the mobility of the system embedded in  $J_{\text{free}}$  and  $J_{\text{dif,ML}}$

$$J_M = J_{\text{free}} + \xi J_{\text{dif,ML}} \quad (23)$$

As some *in situ* speciation techniques like PLM or DGT allow working with sensors of different thickness of the sensing layer, Eqn. (21) can also be used to determine the

thickness of the diffusion layer of the sensor for a given percentage of the kinetic contribution of the complex. In this way we can exclude the contribution of the complex or include it in the sensor answer (see section 9 below).

The degree of lability can also be easily related with the characteristics of the complex concentration profile. Eqn. (A-8), which corresponds to the integration of the addition of Eqn (7) and Eqn (8) multiplied by  $\varepsilon$ , can be written as

$$c_M(z) + \varepsilon c_{ML}(z) = \varepsilon c_{ML}^0 + \left[ c_M^* + \varepsilon (c_{ML}^* - c_{ML}^0) \right] \frac{z}{z^*} \quad (24)$$

where  $c_{ML}^0$  labels the complex concentration at the electrode surface (where “electrode” denotes, in general, the active surface where M disappears). Recalling that

$\left( \frac{dc_{ML}}{dz} \right)_{z=0} = 0$ , the derivative of (24) becomes

$$\left[ \frac{d}{dz} [c_M(z) + \varepsilon c_{ML}(z)] \right]_{z=0} = \left( \frac{dc_M}{dz} \right)_{z=0} = \frac{c_M^* + \varepsilon (c_{ML}^* - c_{ML}^0)}{z^*} \quad (25)$$

and the metal flux,

$$J_M = \frac{D_M c_M^* (1 + \varepsilon K' \xi)}{g} = D_M \frac{c_M^*}{g} + D_{ML} \frac{c_{ML}^*}{g} \left( 1 - \frac{c_{ML}^0}{c_{ML}^*} \right) \quad (26)$$

The first term of the r. h. s. of Eqn. (26) can be identified with the metal flux when only metal, at a concentration given by  $c_M^*$ , is present in the system. It is denoted as  $J_{\text{free}}$ .

The second term indicates the increase of the flux due to the presence of complex species which is denoted as  $J_{\text{complex}}$ . Using (26) in (21),

$$\xi \equiv \left( 1 - \frac{c_{ML}^0}{c_{ML}^*} \right) \quad (27)$$

a result previously obtained in the context of the spherical diffusion [12]

## 5.- Limiting cases

### 5.1.- The limiting case $\varepsilon K' \gg 1$ and $g \gg \mu^\infty$

A very intuitive description of the diffusion-reaction process relies upon the concept of reaction layer that will be developed in the next section. For planar or spherical semi-infinite diffusion, the thickness of the reaction layer (which we label  $\mu^\infty$  in this work) can be shown to be [12,35]:

$$\mu^\infty = \sqrt{\frac{D_M}{k_a'}} \quad (28)$$

In most configurations,  $g$  will be much larger than  $\mu^\infty$  (for instance, in ref. [20], the thickness of the gel layer of the DGT device was varied from 0.16 mm to 2 mm while a typical  $\mu^\infty$  is of the order of  $\mu\text{m}$ ).

Furthermore, we are mainly interested in cases where the contribution of the complex is large, this implying  $\varepsilon K' \gg 1$ . Otherwise the metal flux would not appreciably differ from  $J_{\text{free}}$ , as can be deduced from eqn. (26). So, one can approximate  $n \approx k_a'$  and

$\sqrt{n} \approx \frac{\sqrt{D_M}}{\mu^\infty}$ . Using both approximations,  $\tanh[\sqrt{n}z^*] \approx 1$ . Thus, from eqn. (14), we

obtain an approximation for the flux:

$$J_M \approx \frac{D_M c_M^* (1 + \varepsilon K')}{g + \varepsilon K' \mu^\infty} \quad (29)$$

Substitution of this expression into (21), yields a very simple expression for the lability degree

$$\xi \approx \frac{g}{g + \varepsilon K' \mu^\infty} \quad (30)$$

With the additional condition  $g \ll \varepsilon K' \mu^\infty$ , Eqn. (30) becomes

$$\xi \approx \frac{k_d g}{\varepsilon k_a^{1/2} D_M^{1/2}} \quad (31)$$

which reverts to the well known Davison condition [7,36] whenever  $\varepsilon=1$ . Recall that the set of conditions for a rigorous use of the Davison condition in the present case are:  $\varepsilon K' \gg 1$ ,  $g \ll \varepsilon K' \mu^\infty$  (more restrictive) and  $g \gg \mu^N$ .

### 5.2.- Immobile complex, $D_{ML} = 0$

The case of an immobile complex,  $D_{ML} = 0$ , also deserves specific mention, because it could be a good approach when macromolecular ligands are present or in cases where a layer with complexing sites in its structure is covering the limiting surface: sensors coated with a gel layer, biofilms, etc.. In steady state, when a metal is complexed to a immobile ligand, we have  $\varepsilon = 0$ ,  $n \rightarrow \infty$ , and  $J_M$ ,  $c_M(z)/c_M^*$  and  $c_{ML}(z)/c_{ML}^*$  given respectively by (14), (11) and (12) reduce to (15) and to

$$J_M = \frac{D_M c_M^*}{g} = J_{\text{labile}} = J_{\text{free}} \quad (32)$$

Thus, we are facing a case where the profiles and the metal flux indicate that we are in labile conditions, independently of the kinetic constants value since: *i*) the concentration profiles of M and ML are related everywhere by the equilibrium constant  $K'$ , as deduced from (15) or alternatively by cancelling the diffusion term in (4); *ii*)  $c_M$  and  $c_{ML}$  drop to zero at the electrode surface; and *iii*)  $J_M$  reduces to  $J_{\text{labile}}$ . However, this

$J_M$ -value also coincides with  $J_{\text{free}}$ , in agreement with the fact that the maximum diffusive flux of ML, which equals the maximum kinetic contribution, drops to zero for immobile complexes.

The result presented above indicates that in steady state conditions, the presence of complexing sites in the gel layer does not modify the flux respect to the absence of this complexing sites. The situation would be different in the transient regime since then the presence of complexing sites in the gel layer: i) increases the metal flux since these sites act as a reservoir of M which is released as the metal concentration profile goes into the gel layer, ii) increases the time to reach steady state conditions.

#### **6.- The reaction layer approximation and the lability criterion**

The reaction layer approximation was historically introduced to compute the kinetic currents in systems with excess of ligand. When the complex is the relevant metal species ( $K' > 1$ ), metal consumption at a limiting surface is supplied by chemical dissociation in a quasi-steady state situation (after a time  $t > \frac{1}{k_a}$ ) while the complex concentration remains almost unchanged. Mathematically, the reaction layer approximation relies on assuming steady-state conditions and a flat complex concentration profile. In this way, the diffusion equation for the metal becomes uncoupled from the transport equation of ML and can be easily solved giving rise to an approximation for the metal flux.

The reaction layer approximation has been used to formulate lability criteria, which provide a simple way of determining which is the process limiting the metal flux: either the dissociation of the complex or the supplying of complex from the bulk solution. The maximum ability of the kinetic process to produce metal flux, i. e., the hypothetical

maximum kinetic flux in absence of diffusion limitation for the complex, is evaluated by using the reaction layer approximation and the condition  $c_{ML}(x) = c_{ML}^*$ . The resulting metal flux has been denoted as  $J_{kin}$  in the literature. The maximum supply of complex is the maximum diffusional flux, to which, for transient cases, an extra contribution coming from the decrease of the complex concentration at each volume element of the system has to be added. If  $J_{kin} \gg J_{dif}$ , the transport of complex limits the metal flux available at the active surface and we say that the system is labile. Under the contrary situation,  $J_{kin} \ll J_{dif}$ , we have a metal flux kinetically limited and we say that the system is partially labile or non labile. This comparison is classically assessed by means of the evaluation of the lability parameter  $L$ . Then, the application of the lability criteria corresponds to  $L \gg 1$  for a labile complex and  $L \ll 1$  for a non labile one.

A key parameter in the evaluation of  $J_{kin}$  is the reaction layer thickness,  $\mu$ , whose expression for one complex in planar semi-infinite diffusion was derived by Koutecký and Brdicka [37]. It can be seen that, in planar geometry and semiinfinite diffusion, the

expression  $\mu^\infty = \sqrt{\frac{D_M}{k_a c_L^*}}$  stands for: i) an operational parameter to evaluate  $J_{kin}$  by

means of  $J_{kin} = k_d c_{ML}^* \mu^\infty$  [35], ii) the effective thickness of the disequilibrium layer

[38] since  $J_M = D_M \frac{c_M^*}{\mu^\infty}$  iii) the average distance traveled by the metal ion before

reassociation [39]. When changing the system under consideration (e.g. the reaction scheme, the geometry, etc.) or other conditions, these three concepts do not always coincide in just one mathematical expression and we have to decide which one of the 3 concepts (see page 346 in reference [40]) is the one to be retained as "reaction layer".

We adhere here to the operational definition [12,35], as explained in i), so that the reaction layer thickness is an operational parameter (different for different scenarios)

that yields the hypothetical maximum kinetic flux, i.e. without any limitation due to the diffusion of the complex.

We aim now at providing this parameter and the corresponding lability criterion for one complex that diffuses in a finite domain.

### 6.1.- Expression for the thickness of the reaction layer under finite planar diffusion

Let us consider

$$c_{ML}(x) \approx c_{ML}^*, \quad \forall x \quad (33)$$

despite the fact that the metal concentration drops to zero close to the limiting surface.

Using Eq. (33), we are evaluating the hypothetical metal flux in absence of diffusion limitation of the complex. Eq. (3) becomes

$$\frac{d^2 c_M}{dx^2} = \frac{c_M - c_M^*}{(\mu^\infty)^2} \quad (34)$$

The integration of (34) with the boundary condition given in (9) leads to

$$\left( \frac{dc_M}{dx} \right)_{x=0} = \frac{c_M^*}{\mu^\infty} \coth \left( \frac{g}{\mu^\infty} \right) \quad (35)$$

The operational definition [12,35] of the thickness of the reaction layer,  $\mu$ , is based on splitting the overall flux into two components,

$$J_M = J_{kin} + J_{free} = J_{kin} + \frac{D_M c_M^*}{g} \quad (36)$$

where  $\frac{D_M c_M^*}{g}$  is the steady state metal flux in absence of complex. With this splitting,

$J_{kin}$  will reflect the contribution of the complex to the metal flux. Notice also that this

splitting is not necessary in planar semiinfinite diffusion since the steady state metal flux of the free metal is zero. Writing  $J_{\text{kin}}$  as

$$J_{\text{kin}} = k_d c_{\text{ML}}^* \mu \quad (37)$$

the combination of eqns. (36), (37) and (35), leads to the following expression for  $\mu$

$$\mu = \mu^\infty \left[ \coth \left( \frac{g}{\mu^\infty} \right) - \frac{\mu^\infty}{g} \right] \quad (38)$$

As stated above, we are adhering to an operational definition of  $\mu$  which allows reproducing the metal flux as indicated in (36). Each change of the geometry of the sensor, boundary conditions, presence of other ligands, formation of complexes with other stoichiometric metal to ligand ratios, etc., that modifies the dependencies of  $J_{\text{M}}$  on the characteristic parameters will also modify the expression for  $\mu$ .

Two limiting cases can also be considered. When  $g \gg \mu^\infty$ , Eqn. (38) yields

$$\lim_{g/\mu^\infty \rightarrow \infty} \mu = \mu^\infty = \sqrt{\frac{D_{\text{M}}}{k_a}} \quad (39)$$

which is the well-known Koryta expression (28) for semiinfinite diffusion.

In the opposite limiting case of thin enough diffusion layers,  $g \ll \mu^\infty$ , using the asymptotic expansion of the hyperbolic cotangent for small arguments, one obtains:

$$\lim_{g/\mu^\infty \rightarrow 0} \mu = 0 \quad (40)$$

and further substitution into (37) leads to

$$\lim_{g/\mu^\infty \rightarrow 0} J_{\text{kin}} = 0 \quad (41)$$

which means that all systems tend to be inert for thin enough diffusion layers.

Using (38), the lability parameter reads

$$L = \frac{J_{\text{kin}}}{J_{\text{dif}}} = \frac{k_d \mu}{D_{\text{ML}}} g = \frac{1}{\varepsilon K'} \left[ g \frac{k_a'^{1/2}}{D_M^{1/2}} \coth \left( g \frac{k_a'^{1/2}}{D_M^{1/2}} \right) - 1 \right] \quad (42)$$

and the lability criterion becomes

$$L \gg 1 \quad (43)$$

for a labile system.

For the usual case of  $g \gg \mu^{\text{N}}$ , Eqn. (42) reduces to

$$L = \frac{g}{\varepsilon K' \mu^\infty} = \frac{k_a'^{1/2} g}{\varepsilon K' D_M^{1/2}} \quad (44)$$

which coincides with the lability parameter reported by Jansen et al. [36]. The derivation of the lability parameter by Jansen et al. was obtained via substitution of  $t$  with  $g^2/\bar{D}$  (where  $\bar{D}$  means the average diffusion coefficient of M and ML) in the lability parameter obtained for planar semiinfinite diffusion and, as found in eqn. 44, this is a good approximation for the present case whenever  $g \gg \mu^{\text{N}}$ .

Notice that  $J_{\text{kin}}$ , the hypothetical maximum contribution of the complex to the metal flux in absence of diffusion limitation for the complex, differs from  $J_{\text{complex}}$ , the actual contribution of the complex to the metal flux. Only when there is no diffusion limitation, i. e., when the metal flux is limited by the kinetics of the dissociation  $J_{\text{kin}}$  will coincide with  $J_{\text{complex}}$ . Otherwise,  $c_{\text{ML}}^0 < c_{\text{ML}}^*$  and  $J_{\text{kin}} \gg J_{\text{complex}}$ . This is seen in Fig 1 which shows the metal flux  $J_{\text{M}}$  computed from (14) vs. the kinetic dissociation constant of the complex,  $k_d$ . For the data of the figure,  $J_{\text{free}}$  is negligible, so that  $J_{\text{M}}$  and  $J_{\text{complex}}$  converge. Thus, the sigmoidal shape exhibited by the metal flux, depicted

in continuous line, is due to the contribution, by dissociation, of the complex, as indicated by the decrease in the ML concentration at the surface (also plotted in Fig. 1) and the concomitant increase in  $J_M$ .

Fig 1 also depicts  $J_{kin}$  obtained applying (37). As can be seen,  $J_{kin}$  reproduces accurately  $J_M$  for low  $k_d$ -values ( $J_{free}$  is negligible for  $\xi \varepsilon K' \gg 1$ ). However,  $J_{kin} \gg J_M$  when the  $c_{ML}$ -profile diverges from the flat  $c_{ML}^*$ -value, i. e., for the partially labile regime, as expected. The development of the complex concentration profile is just an indication of the incapacity of the diffusion process to keep the bulk complex concentration unaltered at the limiting surface. For this reason, the hypothetical metal flux in absence of diffusion limitation,  $J_{kin}$ , exceeds the actual metal flux. However, with the appropriate changes, we are now going to see that the reaction layer approximation could still be used to approximate the contribution of the complex to the metal flux.

### 6.2.- The partially labile case

For the partially labile case, there is a non-flat concentration profile of ML,  $c_{ML}(x) \neq c_{ML}^*$ ,  $\forall x$ , and Eqns. (33) and (34) are not realistic to approach the contribution of the complex to the metal flux. Previous work [14,15] has shown that the reaction layer approximation can still provide accurate values for the metal flux by using ML concentration at  $x = 0$ . Labelling this value as  $c_{ML}^0$ , we can integrate the differential equation (34) in the range where  $c_{ML}(x)$  is constant and approximately equal to  $c_{ML}(x) = c_{ML}^0$ . This range approximately spans the reaction layer. An implicit final expression for  $\mu$  is thus obtained, but simple algebra indicates that it reduces to

(38) whenever  $\mu < g$ . The complex contribution to the metal flux can then be computed, within the reaction layer approximation, by means of  $J_{kin}^\phi$  which is formally identical to  $J_{kin}$ , but computed by using concentrations at the reaction layer,  $c_{ML}^0$ , instead of the bulk concentrations:

$$J_{kin}^\phi = k_d c_{ML}^0 \mu \quad (45)$$

$J_{kin}^\phi$  is expected to be an accurate approximation of  $J_{complex}$  for all the  $k_d$  range. This is seen in Fig 1, which shows that  $J_{kin}^\phi$  reproduces accurately  $J_M$  (or  $J_{complex}$  as both converge).

The reaction layer can be visualised in Fig. 2. Despite the operational definition of  $\mu$ , we can see that for the data of the figure, it is a region close to the limiting surface characterised by the absence of equilibrium between metal and complex. This is easily recognised by the divergence of the normalised concentration profiles,  $c_{ML}/c_{ML}^*$  and  $c_M/c_M^*$ . Notice then that for the partially labile regime, the system can be spatially divided into a nonlabile and a labile region, separated approximately by the boundary of the reaction layer. This division has been schematically depicted in [41] noting that the kinetic flux due to the dissociation equals the diffusive flux of ML towards the reaction layer.

For data of fig. 2,  $\mu = 5.83 \times 10^{-6}$  m. As  $g = 8 \cdot 10^{-4}$  m, the approach  $g \gg \mu^\infty$  applies and  $\mu$  and  $\mu^\infty$  converge ( $\mu^\infty = 5.87 \times 10^{-6}$  m).

### **7.- Concentration profiles and metal flux**

Let us now analyse the concentration profiles and the transport of metal along the diffusion space. Fig 2 plots M and ML concentration profiles, together with the metal

flux  $J_M(x) = D_M \left( \frac{dc_M}{dx} \right)_x$  at different distances from the electrode surface (i.e. the flux crossing a plane with constant abscissa). As can be seen, neither the metal nor the complex concentration profiles are linear close to the electrode surface. But, for  $x \gg \mu$ , the effective thickness of the reaction layer given by (38), there is almost equilibrium and the normalised metal and complex concentration profiles tend to be linear. Accordingly, the metal flux tends to be constant in agreement with the linear metal concentration profile.

As we are in steady state,  $J_M(x) + J_{ML}(x)$ , where  $J_{ML}(x) = D_{ML} \left( \frac{dc_{ML}}{dx} \right)_x$ , should be constant across planar surfaces defined by constant  $x$ . (This is easily seen by addition and integration of M and ML diffusion equations). Since at  $x=0$  there is no flux of ML, as prescribed by the boundary condition, the decrease in  $J_M(x)$  when  $x$  increases is compensated by an increase in  $J_{ML}(x)$ .

Notice that far enough from the electrode surface ( $x \gg \mu$ ),  $J_M(x)$  and  $J_{ML}(x)$  are related by

$$J_{ML}(x) = \varepsilon K' J_M(x) \quad x \gg \mu \quad (46)$$

indicating the fulfilment of local equilibrium conditions between M and ML at this distance. Moreover, in this region ( $x \gg \mu$ ), there is no net dissociation since there is equilibrium and  $J_M(x)$  is constant, in agreement with the almost linear metal concentration profile. The same is also true for ML, indicating that both species diffuse independently as in the fully labile case. On the other hand, for  $x < \mu$ , there is net dissociation and the incoming  $J_M(x+dx)$  to any volume element is smaller than the

outgoing  $J_M(x)$  flux, the difference between both being just the net dissociation of ML to keep constant the M concentration in the element as required by the steady-state conditions.

**8.- Dependence of the degree of lability on  $c_L^*$  and  $g$ .**

The degree of lability decreases as the ligand concentration increases. In excess of ligand, the complexation process is lineal with an effective association rate constant,  $k_a'$ , dependent on  $c_L^*$ . Additionally, most metal in the system is in the complex form whenever  $\varepsilon K' \gg 1$ . In steady state, an increase of the ligand concentration modifies the balance between the association and dissociation rates, because the former is increased. As a consequence,  $J_{\text{complex}}$  decreases with increasing ligand concentration and the lability degree, which is depicted in Fig. 3, follows the same trend. Notice that the decrease of  $\xi$  follows the dependence  $c_L^{*-1/2}$  for low  $\xi$ -values. This dependence is also exhibited by the approximate expression (44) reported for the lability parameter  $L$ , which is close to  $\xi$  for low  $\xi$ -values, as can be seen in the figure.

The goodness of the simple expression (30), which yields results quite close to the rigorous  $\xi$ -values obtained from (22), is also remarkable. At high enough  $c_L^*$ -values,  $g \ll \varepsilon K' \mu^\infty$  and  $\xi$  reduces to eqn (31) and depends on  $c_L^{*-1/2}$  as indicated above.

Fig 4 plots the rigorous analytical expression for the metal flux at the electrode surface, Eqn. (14), together with  $J_{\text{complex}}$  (computed as  $J_{\text{complex}} = J_M - J_{\text{free}}$ ) and the lability degree  $\xi$  given by (21) in terms of  $\log g$ . In this figure, we can see the monotonous decrease of  $\xi$  as the diffusion region decreases while, parallel to this decrease,  $J_M$

diverges from  $J_{\text{labile}}$  to approach  $J_{\text{free}}$ . Thus any system is labile for a large enough diffusion domain thickness, while all systems tend to be inert when  $g \ll \mu$ . This result agrees with the behaviour obtained for the short and long time regimes in planar semi-infinite diffusion [10] according to the fact that changing the thickness of the diffusion domain implies a change in the time required to reach steady state.

Notice that in Fig. 4,  $J_{\text{M}}$  increases monotonously as  $g$  decreases. This behaviour is independent of any set of parameters of the system, since  $\frac{dJ_{\text{M}}}{dg}$  is always negative as can be analytically seen by inspection of the derivative of (14).

Interestingly,  $J_{\text{complex}} = J_{\text{M}} - J_{\text{free}}$  shows a maximum in Fig 4. A qualitative understanding of this behaviour can be provided: when the diffusion layer is large enough (for instance,  $g = 10^{-3}\text{m}$  in figure 4), the complex behaves as labile and  $J_{\text{M}}$ ,  $J_{\text{complex}}$  and  $J_{\text{labile}}$  coincide. Decreasing  $g$ , all the fluxes  $J_{\text{M}}$ ,  $J_{\text{complex}}$  and  $J_{\text{labile}}$  increase due to the reduction of the distance from the electrode to the bulk concentrations. However, the increase of both  $J_{\text{M}}$  and  $J_{\text{complex}}$  is not as large as that of  $J_{\text{labile}}$  indicating that the loss of lability of the system has started. A further decrease of  $g$  not only reduces the distance from bulk conditions, but also reduces the lability of the system. The result is that  $J_{\text{complex}}$  decreases (see points for  $\log(g) < -6$  in the figure) while  $J_{\text{M}}$  still shows an increase due to the increase of  $J_{\text{free}}$  also depicted in the figure.

Let us obtain the thickness of the diffusion layer corresponding to this maximum. With  $J_{\text{M}}$  given by (14) and  $J_{\text{free}}$  defined in (19),  $J_{\text{complex}}$  can be written as:

$$J_{\text{complex}} = \frac{\varepsilon \sqrt{D_M} c_{\text{ML}}^* (\sqrt{n} z^* - \tanh[\sqrt{n} z^*])}{z^* (\sqrt{n} z^* + \varepsilon K' \tanh[\sqrt{n} z^*])} \quad (47)$$

Although it can be solved numerically, the derivative of (47) with respect to  $z^*$  equalled to zero has no explicit analytical solution. However, if  $\sqrt{n} z^* \gg 1$  (valid whenever  $\varepsilon K' \gg 1$  and  $g \gg \mu^{\text{N}}$ ), then  $\tanh[\sqrt{n} z^*] \cong 1$  and  $(\text{sech}[\sqrt{n} z^*])^2 \cong 0$ . Under these conditions, the thickness of the diffusion layer that renders  $J_{\text{complex}}$  maximum, denoted as  $g_{\text{max}}$ , becomes

$$g_{\text{max}} = \sqrt{D_M} z_{\text{max},Ap}^* = \sqrt{D_{\text{ML}}} \frac{1 + \sqrt{1 + \varepsilon K'}}{\sqrt{k_d} \sqrt{1 + \varepsilon K'}} \quad (48)$$

Replacing  $g_{\text{max}}$  in (22), the degree of lability of the complex is:

$$\xi \cong \frac{1}{1 + \sqrt{1 + \varepsilon K'}} \quad (49)$$

a value dependent on  $\varepsilon$  and  $K'$ . Notice that  $g_{\text{max}}$  corresponds to the thickness of the diffusion layer more sensitive to the presence of the complex, since the complex contribution to the metal flux in this configuration is maximum. Notice that the degree of lability of the complex is not very high for this thickness of the sensor (recall  $\varepsilon K' > 1$ ) (See Table 1). Although a higher lability degree would be obtained at a greater  $g$ , the absolute complex contribution would be lower, a consequence of the variation of both  $J_M$  and  $J_{\text{free}}$ . Table 1 checks the accuracy of the approximate equation (48) with the rigorous numerical solution of the derivative of (47).

Together with the peaked behaviour of  $J_{\text{complex}}$ , the transition from the labile to the non-labile regime of the complex is evidenced in fig 4 by a shoulder in  $J_M$  which moves  $J_M$  from practically being  $J_{\text{labile}}$  to values close to  $J_{\text{free}}$ . The difference in the abscissa for a fixed ordinate value between  $J_{\text{labile}}$  and  $J_{\text{free}}$  can be found from (16) and (19) as

$$\Delta(\log \delta) = \log(1 + \varepsilon K') \quad (50)$$

which estimates the thickness of the  $J_M$ -shoulder.

## 10.- CONCLUSIONS

The contribution of the complex to the metal flux under diffusion limited conditions in a planar finite domain can be fully analysed for any value of the association/dissociation rate constants. The explicit analytical expression for the metal flux (14) gives rise to a rigorous quantification of the lability degree of the system (eqn.22). We highlight the simple expression (29) for a good approximation of the flux under the usual relevant conditions ( $\varepsilon K' \gg 1$  and  $g \gg \mu^N$ ).

Complementary, the specific lability criterion (42) and the reaction layer thickness (38) for the present system have been worked out within the reaction layer approximation.

The lability degree,  $\xi$ , describes the percentage of the kinetic contribution with respect to the maximum kinetic contribution of the complex to the metal flux, once the concentrations, kinetic constants, diffusion coefficients and spatial dimensions of the sensor are known.

Alternatively, the lability parameter,  $L$ , compares the kinetic flux,  $J_{\text{kin}}$ , a measure of the hypothetical ability of the complexation process to produce metal flux in absence of diffusion limitation of the complex, with the maximum diffusional supply of ML, in

order to determine which is the process limiting the metal flux in the system. If the diffusional supply is limiting we say that the system is labile while the system is partially labile or non labile when the kinetics of dissociation is the limiting process.

The analytical expression reported for the lability degree can also be used to determine the thickness of the diffusion layer of sensors like DGT or PLM, so that we measure a prefixed percentage of the maximum kinetic contribution of the complex. In this way we can select the contribution of the complex in the sensor answer.

Limiting expressions for the fully labile case are obtained from the general kinetic ones. These expressions (see, for instance, eqn. (17)) indicate that the gradient of the complex at the limiting surface is not zero in fully labile conditions in agreement with previous mathematical formulation of the fully labile case in the literature.

The limiting case of immobile complex has also been studied. In steady state conditions, the concentration profiles of M and ML are in equilibrium everywhere, regardless the value of the kinetic constants. However,  $J_M$  coincides with  $J_{\text{free}}$  this indicating that there is no contribution of the complex to the metal flux in steady state conditions, as expected (in steady-state conditions, the maximum complex contribution is just the maximum diffusional flux of the complex which is null in this case). However, immobile complexes contribute to the metal flux in the transient regime and increase the time required to reach steady state.

Special attention has been devoted to the behaviour of the system when the thickness of the diffusion domain changes. It is shown that, decreasing the thickness of the diffusion domain, the free metal flux always increases, while the degree of lability of the system decreases, i. e.,  $J_M$  approaches  $J_{\text{labile}}$  for large enough thickness of the diffusion

domain while  $J_M$  approaches  $J_{\text{free}}$  for low enough thickness of the diffusion domain.

In this transition,  $J_M$  develops a shoulder, while  $J_{\text{complex}}$  shows a peaked behaviour.

The thickness of the diffusion domain that renders  $J_{\text{complex}}$  maximum can be obtained from Eqn. (22).

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## APPENDIX A

### **Rigorous solution of the system (7)-(10)**

Let us combine equations (7)-(8) to rewrite this system in terms of new unknown functions,  $y_0$  and  $y_1$ , so that each new equation depends only on one unknown function [33,42]. Following d'Alembert methodology, a general linear combination of (7) and (8) can be written as

$$\frac{d^2(c_M(z) + wc_{ML}(z))}{dz^2} = k'_a \left(1 - \frac{w}{\varepsilon}\right) c_M(z) + k_d \left(\frac{w}{\varepsilon} - 1\right) c_{ML}(z) \quad (\text{A-1})$$

where  $w$  is the weight of  $c_{ML}$  in the combination. Imposing that

$$k_d \left(\frac{w}{\varepsilon} - 1\right) = wk'_a \left(1 - \frac{w}{\varepsilon}\right)$$

and solving for  $w$ , we have

$$\begin{aligned} y_0(z) &= c_M(z) + \varepsilon c_{ML}(z) \\ y_1(z) &= -c_M(z) + \frac{c_{ML}(z)}{K'} \end{aligned} \quad (\text{A-2})$$

In terms of  $y_0$  and  $y_1$ , Eqns. (7)-(8) become

$$\frac{d^2 y_0(z)}{dz^2} = 0 \quad (\text{A-3})$$

$$\frac{d^2 y_1(z)}{dz^2} = n y_1(z) \quad (\text{A-4})$$

with

$$n = \frac{k_d}{\varepsilon} + k'_a = \frac{k_d(1 + \varepsilon K')}{\varepsilon} \quad (\text{A-5})$$

The general solutions of (A-3) and (A-4) are

$$\begin{aligned} y_0(z) &= A_{1,0}z + A_{2,0} \\ y_1(z) &= A_{1,1} \exp(\sqrt{n} z) + A_{2,1} \exp(-\sqrt{n} z) \end{aligned} \quad (\text{A-6})$$

Rewriting the boundary conditions at the bulk solution in terms of  $y_0$  and  $y_1$  we have

$$\begin{aligned} y_0^* &= c_M^* (1 + \varepsilon K') \\ y_1^* &= 0 \end{aligned} \tag{A-7}$$

and their application to (A-6) lead to

$$y_0(z) = c_M^* (1 + \varepsilon K') + T_0 (z - z^*) \tag{A-8}$$

$$y_1(z) = T_1 \sinh \left[ \sqrt{n} (z - z^*) \right] \tag{A-9}$$

where  $T_0$  and  $T_1$  denote the remaining integration constants. These constants can be obtained by imposing the boundary conditions at  $z=0$ . Then,

$$T_0 = \frac{c_M^* (1 + \varepsilon K') \sqrt{n}}{\sqrt{n} z^* + \varepsilon K' \tanh \left[ \sqrt{n} z^* \right]} \tag{A-10}$$

and

$$T_1 = \frac{-c_M^* (1 + \varepsilon K')}{\sqrt{n} z^* \cosh \left[ \sqrt{n} z^* \right] + \varepsilon K' \sinh \left[ \sqrt{n} z^* \right]} \tag{A-11}$$

Replacing these values in (A-8)-(A-9), we have the sought solution (similar to that in ref. [42]), which in terms of the original unknowns can be written as indicated in equations (11) and (12).

APPENDIX B: TABLE OF THE MOST RELEVANT SYMBOLS:

symbol	meaning	eqn.
$c_{ML}^0$	complex concentration at the electrode surface	24
$c_i^*$	bulk concentration of species $i$	2, 10
$D_i$	diffusion coefficient of species $i$	3, 4
$g$	thickness of the diffusion domain	10
$J_{\text{complex}}$	contribution of the complexes to the metal flux	18
$J_{\text{dif}}$	maximum diffusive flux due to complex ML	44
$J_{\text{free}}$	flux if the complexes were inert (i.e. due to free M)	19, 36
$J_{\text{kin}}$	hypothetical maximum kinetic contribution if there was no limitation from the diffusion of the complexes	36, 37, Fig 1, 44
$J_{\text{kin}}^\phi$	approximation to the contribution of complex ML to the metal flux using reaction layer concentrations.	Fig 1, 45
$J_{\text{labile}}$	flux if the complexes were labile	16, 17
$J_M$	total metal flux at $x=0$ , i.e. $J_M(x=0)$	14
$J_M(x)$	metal flux at a given $x$	$J_M(x) = D_M \left( \frac{dc_M}{dx} \right)_x$
$J_{ML}(x)$	flux of complex at a given $x$	$J_{ML}(x) = D_{ML} \left( \frac{dc_{ML}}{dx} \right)_x$

$k_a, k_d$	association and dissociation rate constants	2
$L$	lability parameter comparing $J_{kin}$ and the maximum diffusional flux of the complexes	42
$n$	uncoupling parameter	13, A-5
$z$	new spatial variable	6
$z^*$	bulk position expressed in the variable $z$	10
$\varepsilon$	dimensionless diffusion coefficient for the complex ML	5
$\mu$	diffusion layer thickness in finite diffusion	38
$\mu^\infty$	diffusion layer thickness in semi-infinite diffusion	28
$\xi$	degree of lability	20

FIGURES

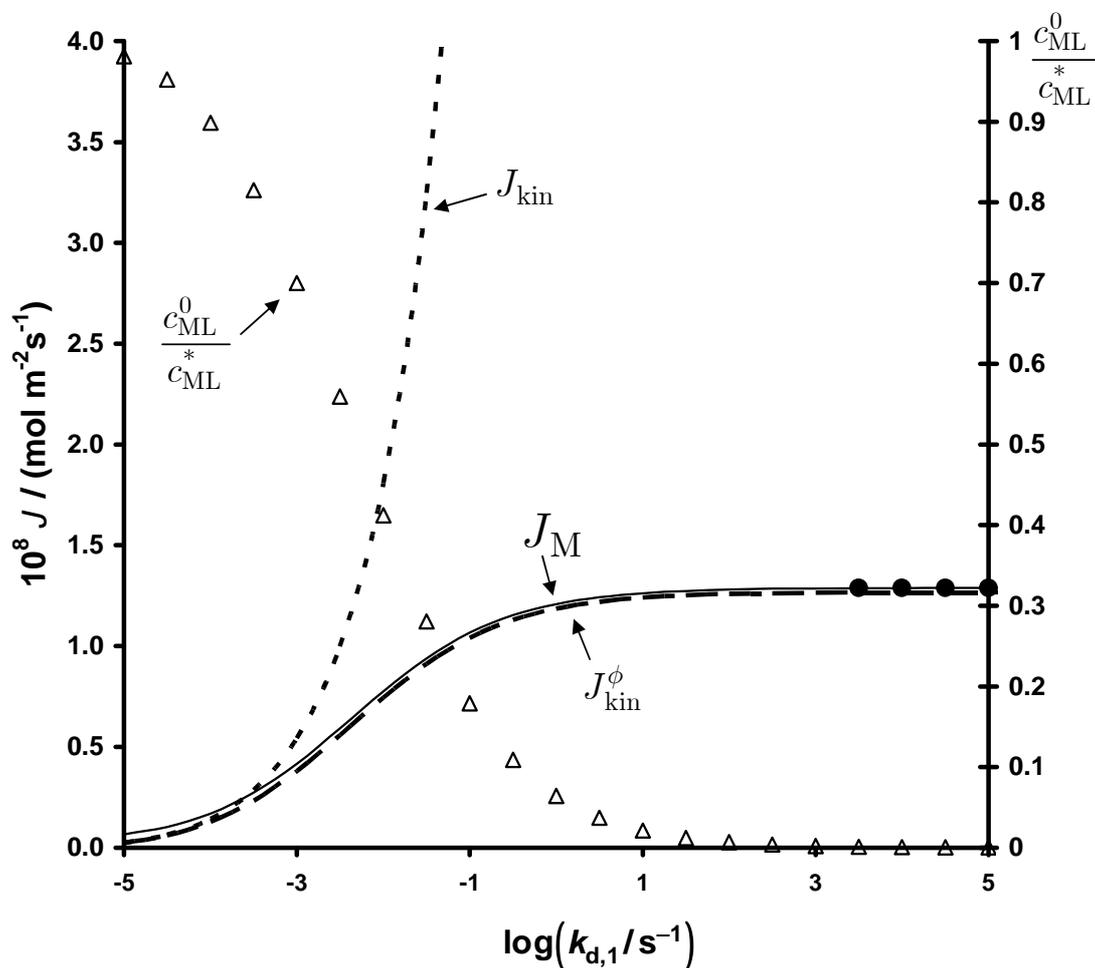


Fig. 1. Metal flux at the electrode surface,  $J_M$  (continuous line), the kinetic flux,  $J_{kin}$  (short dashed line) and  $J_{kin}^\phi$  (long dashed line), referred to the left ordinate axis and  $c_{ML}^0 / c_{ML}^*$  ( $\Delta$ ), referred to the right ordinate axis as functions of the dissociation kinetic constant  $\log(k_d/s^{-1})$ . Parameters:  $c_{T,M}^* = 0.1 \text{ mol m}^{-3}$ ,  $c_{T,L}^* = 3.0 \text{ mol m}^{-3}$ ,  $K=100 \text{ m}^3 \text{ mol}^{-1}$ ,  $g=8 \times 10^{-4} \text{ m}$ ,  $D_M=10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $\varepsilon = 0.1$ . In each point  $k_a$  takes the value required to maintain a fixed  $K$ . The horizontal bullets on the right side indicate the metal flux for the labile case.

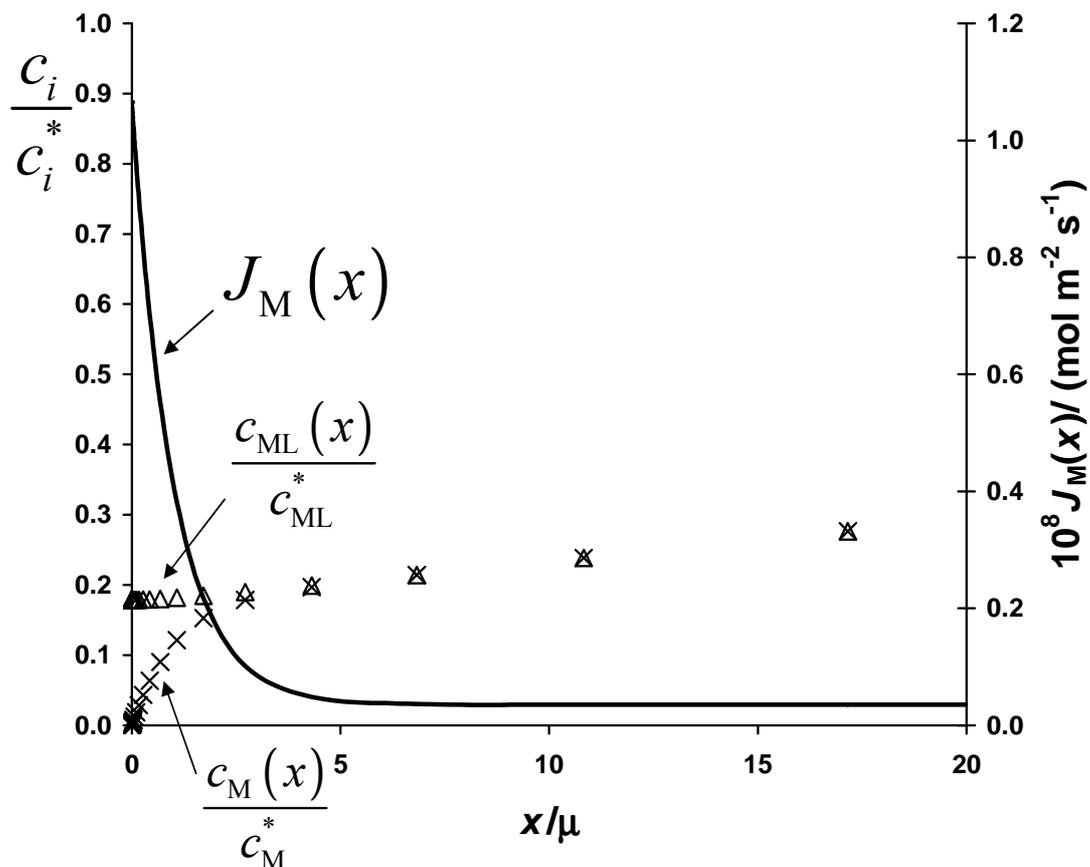


Fig 2. Normalised concentrations profiles,  $c_i/c_i^*$ , of M ( $\times$ ) and ML ( $\Delta$ ) referred to the left ordinate axis and the free metal flux (continuous line) referred to the right ordinate axis as a function of the distance to the electrode surface measured as  $x/\mu$ . Parameters:  $k_d=0.1 \text{ s}^{-1}$ ,  $k_a=10 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1}$ . The rest of parameters as in Fig. 1.

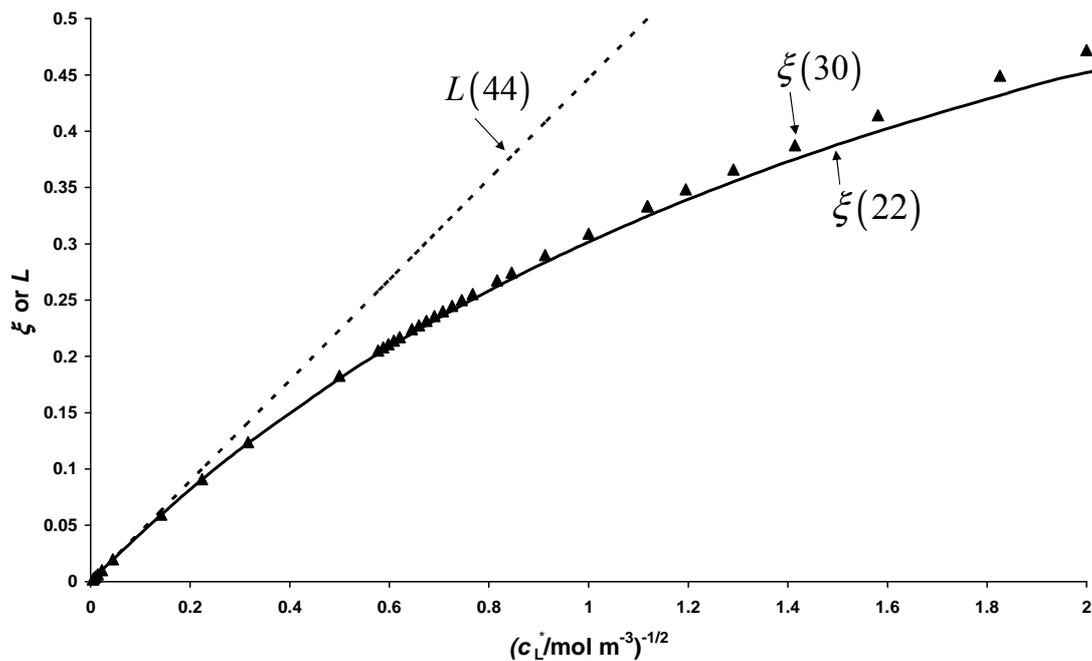


Fig 3. Plot of the lability degree,  $\xi$  vs.  $c_L^{*-1/2}$ . Continuous line:  $\xi$  calculated by means of (22). Marker full triangle, approximated  $\xi$ -value calculated by means of (30). The approximate lability parameter  $L$ , calculated by means of the simple expression (44) that renders  $L$  proportional to  $c_L^{*-1/2}$  is also depicted in dotted line in the figure. Parameters: as in Fig 1. except  $k_d=10^{-2} \text{ s}^{-1}$  and  $k_a=1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $D_M=5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $\varepsilon = 0.8$ .

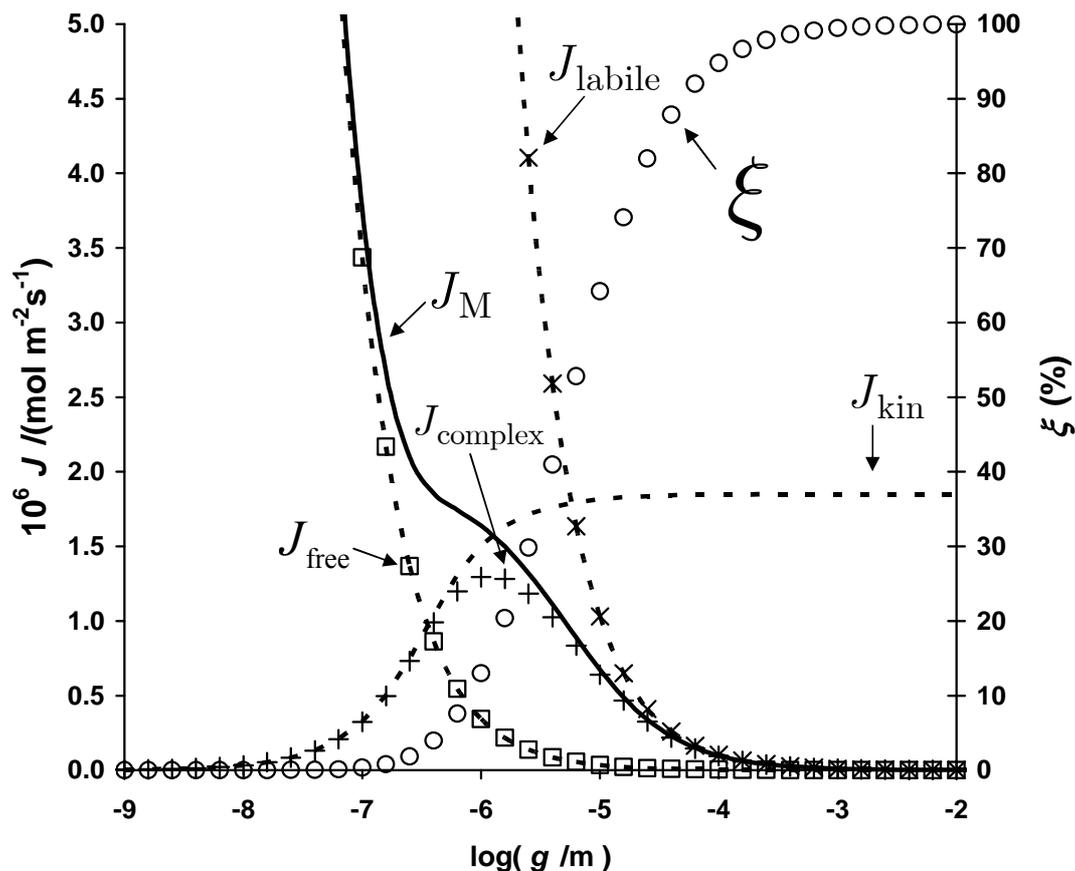


Fig 4. Metal flux at the electrode surface  $J_M$  (continuous line), the complex contribution to the metal flux  $J_{\text{complex}}$  (marker +), the kinetic flux  $J_{\text{kin}}$  (short dashed line),  $J_{\text{labile}}$  (short dashed line with marker  $\times$ ) and  $J_{\text{free}}$  (short dashed line with marker  $\square$ ), referred to the left ordinate axis and the lability degree  $\xi$  of the system (o) (in %) referred to the right ordinate axis as function of  $\log(g/m)$ . Parameters:  $k_d=100 \text{ s}^{-1}$ ,  $k_a=10^4 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

The rest of parameters as in Fig. 1.

Table

$\varepsilon$	$K'$	$k_d$	$\log(g_{\max})$ from (48)	$\log(g_{\max})$ num. solution	$\xi$ (%) as (49)	$\xi$ (%) as (22)
0.1	290.03	$1 \times 10^{-5}$	-1.43	-1.43	15.4	15.4
0.1	290.03	$1 \times 10^{-2}$	-3.93	-3.93	15.4	15.4
0.1	140.07	$1 \times 10^6$	-7.90	-7.90	20.5	20.5
0.01	70.07	$2 \times 10^{-7}$	-1.90	-1.96	43.4	39.1
0.01	70.07	$2 \times 10^{-1}$	-4.90	-4.96	43.4	39.1
0.01	70.07	$2 \times 10^6$	-8.40	-8.46	43.4	39.1

Table 1. Comparison of the thickness of the diffusion domain that renders  $J_{\text{complex}}$  maximum,  $g_{\max}$ , calculated via (48), with the exact one, obtained by numerical solution of the derivative of (47). We also compare the degree of lability at this  $g_{\max}$ , calculated with (22) with the approximate degree of lability calculated with (49). The rest of parameters as in Fig. 1.