Evaluation of the Koutecký-Koryta approximation for voltammetric currents generated by metal complex systems with various labilities

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Abstract

The voltammetric response of metal complex systems with various labilities is analyzed by rigorous numerical simulation with the Finite Element Method of the time-dependent concentration profiles of the different species. The ensuing exact fluxes and the corresponding currents are compared to those derived from the Koutecky-Koryta (KK) approximation which assumes a discontinuous transition in the concentration profiles from non-labile to labile behavior. The results indicate a relatively far-reaching correctness of the KK approximation in the complete kinetic range from non-labile to labile complexes, as long as the kinetic flux is computed from the effective concentration of the complex in the reaction layer. Some approximate analytical expressions for this concentration are provided. The KK approximation is shown to be applicable for any metal-to-ligand ratio, provided that the thickness of the reaction layer is expressed in terms of the ligand concentration at the electrode surface.
Keywords:
Homogeneous complexation; Finite Element Method; Reaction layer; Lability; Planar electrode; Concentration profiles

Introduction
Over the nineties there has been a substantial growth of interest in dynamic metal speciation, which not only covers the equilibrium distribution of the different metal species but also the kinetic characteristics of their interconversion [1-3]. Kinetically defined categories of behavior of metal complexes range from inert to dynamic, the latter comprising various degrees of lability. The different notions have been defined on the basis of the voltammetric response of systems with electroinactive complex species and electroactive uncomplexed hydrated metal ions [4-7].

The case of inert complexes is rather trivial because such complexes do not contribute at all to the metal ion reduction process. The voltammetric response is then identical to that of the mere free metal ion. The distinction between labile and non-labile complexes is much more subtle since both of them refer to systems with relatively high rates of conversion of complex species into free metal ions. Labile complexes are characterized by such high rates of dissociation/re-association that, on any relevant spatial scale, full equilibrium between complexed and free metal is maintained. Consequently, interfacial processes involving the free metal (e.g. electrochemical reduction) are then limited by coupled diffusion of complex and free metal. Non-labile complexes represent the other extreme within the dynamic range where the effective rate of dissociation is much lower than that of the diffusive supply. In that case, the rate of dissociation (a volume reaction) determines the contribution of the complex to the interfacial metal ion flux.
The distinction between labile, non-labile and inert complexes is of great importance in the practice of metal speciation [1,8]. For a given total metal concentration, the interfacial fluxes for the three types of complexes may differ drastically. The intermediate case of partially labile (quasi-labile) complexes [4] is rather involved because of the simultaneous significance of the association/dissociation rates of the volume complexation reaction and the diffusional terms in the leading conservation equations. The problem was already tackled by Brdička, Koutecký and other members of the Czechoslovak School [9-14] and this resulted in a rather comprehensive analysis of the so-called kinetic currents. Within this frame, Koutecký and Koryta [14-16] came up with an apparently useful approximation, based on the spatial separation of the depletion layer into non-labile and labile regimes. The borderline between the two regimes would be located at the boundary of the reaction layer, situated at a distance $x = \mu$ from the surface. For $x$ smaller than $\mu$, i.e. within the reaction layer, the contribution from the complex is considered to be purely kinetic, whereas for $x > \mu$, the kinetics are supposed to be infinitely fast and the complex contributes merely via the coupled diffusion with free metal. This discontinuous approach, which we shall denote as the Koutecký-Koryta (KK) approximation, is extremely simple and might provide a practically attractive method for dealing with the partially-labile regime.

This paper aims at a rigorous analysis of the partially-labile situation via numerical simulation of the concentration profiles of the different metal species under various kinetic conditions (see Appendix for computational details on the numerical procedure). This will enable us to deduce the exact fluxes of the different species at any point in space and time which can then be compared to the fluxes derived from the KK approach. The results precisely define the range of validity of the KK approximation.
**General**

We consider the common case of an electroactive metal ion \( M \) (reducible to \( M^0 \)) in the presence of a ligand \( L \) with which it may form the electroinactive complex \( ML \)

\[
\begin{align*}
M^0 & \quad \pm n \, e^- \\
\downarrow & \\
M + L & \quad \xrightarrow{k_a} \quad ML \\
& \quad \xrightarrow{k_d} \\
\end{align*}
\]

The quotient \( k_a/k_d \) of the rate constants defines the stability constant \( K \) of the complex.

The ratio \( Q \) is defined as

\[
Q = \frac{c_{ML}}{c_M c_L}
\]

which equals \( K \) if equilibrium (1) is attained.

If diffusion towards a stationary planar electrode is the sole transport mechanism, the conservation equations for \( M \), \( ML \) and \( L \) read

\[
\frac{\partial c_i(x,t)}{\partial t} = D_i \frac{\partial^2 c_i(x,t)}{\partial x^2} \pm k_d \left( c_{ML} - K c_M c_L \right)
\]

with the plus sign for \( i=M \) or \( L \) and the minus sign for \( i=ML \).

The usual initial and boundary conditions are

\[
t = 0, \ x \geq 0 \quad \frac{c_{ML}}{c_M c_L} = \frac{c_{ML}^*}{c_M^* c_L^*}
\]
\begin{equation}
t > 0, \quad x \rightarrow \infty \quad c_i = c_i^* \quad i = M, L, ML
\end{equation}

where \( t \) is time, \( x \) the distance from the electrode surface and \( c_i^* \) the bulk concentration of \( i \).

In case of a sufficiently large excess of ligand \( L \) the association reaction is pseudo first-order and we define

\begin{equation}
K c_i^* = K' = \frac{c_{ML}^*}{c_M^*}
\end{equation}

\begin{equation}
k_a c_i^* = k_a'
\end{equation}

Chronoamperometric limiting current conditions are defined by

\begin{equation}
t \geq 0, \quad x = 0 \quad \begin{cases}
  c_M = 0 \\
  \partial c_{ML} / \partial x = 0
\end{cases}
\end{equation}

which completes the formulation of the problem.

Complex systems are divided into static (or inert) and dynamic categories. The distinction is based on the values of the effective chemical rate constants \( k_d \) and \( k_a' \), relative to the effective time scale \( t \). According to the official definitions [6], and in full agreement with the restrictions of the classical treatments [14], both non-labile and labile complex systems are subject to the condition

\begin{equation}
k_d t \quad , \quad k_a' t \quad >> 1
\end{equation}

The physical meaning is that the conversion of \( M \) into \( ML \) and vice versa is fast on the time scale considered, and the corresponding regime has been denoted as 'dynamic' [5].

It is important to bear in mind that fulfillment of condition (7) does not imply that
equilibrium (1) is maintained on every relevant spatial scale contained in an experiment on time-scale $t$. The condition is concerned with the volume complexation reaction (1) and its fulfillment does not warrant the maintenance of equilibrium in an interfacial process of consumption of free metal ions. This feature actually forms the heart of the mere existence of the so-called reaction layer where the dissociation of ML is not fast enough to 'follow' the depletion of M. The reaction layer is defined by its thickness $\mu$

\[ \mu = \left( \frac{D_M}{k_a} \right)^{1/2} = \left( \frac{D_M}{(k_a c_{L}^*)} \right)^{1/2} \]  

(8)

**Concentration profiles and fluxes of M and ML**

A. The non-labile regime

By various definitions, non-lability is related to the rate of dissociation of the complex being so slow that depletion of ML is negligible even in the immediate vicinity of the electrode surface. Thus it is characterized by the combination of the conditions (7) and

\[ c_{ML}^{\phi} / c_{ML}^* \approx 1 \]  

(9)

where $c_{ML}^{\phi}$ denotes concentration in the reaction layer.

The flux of free metal, generated in the reaction layer adjacent to the electrode surface is then simply given by

\[ J_{kin} = k_d c_{ML}^* \mu \]  

(10)

Typical concentration profiles of M and ML in the non-labile regime are given by Fig. 1. Needless to add that $Q/K$ significantly deviates from 1 only for $x < \mu$. 

26/02/02
In case of a sufficient excess of ML over M ($c_{T,L}^* > c_{T,M}^*$, $K' \gg 1$, $c_{T,L}^*$ and $c_{T,M}^*$ labelling the total ligand and total metal bulk concentrations respectively), the complex is able to maintain an approximately constant $c_M$ ($c_M \approx c_M^*$) from the bulk down to $x \approx \mu$. The limitations of the free metal ion "buffering capacity" of ML only shows up at distances less than $\mu$ where the diffusive depletion of M is faster than the replenishing by dissociation of ML. The non-labile regime, characterized by Fig. 1, is the limiting case where the flux of M is governed by the dissociation of ML in the reaction layer. Since, unlike the diffusion layer thickness $\delta_M \equiv \sqrt{\pi D_M t}$, $\mu$ is not a function of time, the apparent steady state flux may be formulated as diffusional flux of M within the reaction layer:

$$J_M = D_M c_M^* / \mu = k_d c_{ML}^* \mu$$

which is immediately verified using (5) and the definition of $\mu$, eqn. (8).

Conceptually, the non-labile regime is of a special nature: on the one hand it requires high rate constants $k_d$ and $k'_d$ to fulfill condition (7) so that $\mu << \delta_M$, and on the other hand $k_d$ must be so low that depletion of ML inside the reaction layer with thickness $\mu$ is not appreciable. It is this potentially conflicting set of requirements that has given rise to the differentiated definition of the notion of lability [19,20].

B. The labile regime
Labile systems obey condition (7), and have such high $k_d$ values that depletion of ML is practically complete. Thus they are characterized by kinetic fluxes that largely outweigh the diffusive fluxes $J_{\text{diff}}$:
This condition has been discussed at length in the literature [21]. The corresponding typical profiles of M and ML are given by fig. 2. In agreement with the fulfillment of condition (7), meaning that \( \mu << \delta \), the labile situation is characterized by 
\[ \frac{c_{ML}^0}{c_{ML}^*} \rightarrow 0, \]
where superscript zero indicates the volume concentration at \( x = 0 \).

Equilibrium between M and ML is essentially maintained to such an extent that the overall metal flux at the surface is given by the coupled diffusion of M and ML. Thus, if their diffusion coefficients are different, the flux is proportional to the weighted mean diffusion coefficient 
\[ \bar{D} = \frac{c_M^*}{c_{T,M}} D_M + \frac{c_{ML}^*}{c_{T,M}} D_{ML} \]
and the total concentration of the free and labile metal species [22].

C. The partially-labile regime

The transition between labile and non-labile regimes is characterized by intermediate values of 
\[ \frac{c_{ML}^0}{c_{ML}^*} \]
which corresponds to \( J_{kin}/J_{dif} \) being of order unity

\[ J_{kin}/J_{dif} \approx 1 \] (13)

The simulation reveals that approaching the electrode from the bulk solution, there is a certain region with depletion of M, together with a metal flux low enough to be “followed” by the complex so that equilibrium is maintained. This is the region where kinetics can be considered infinitely fast in the Koutecký-Koryta approximation. Closer to the electrode surface, the metal flux increases and for \( x < \mu \), the rate of
dissociation of ML becomes limiting. The concentration of ML tends to an approximately constant, $c_{ML}^\phi$, to reach the prescribed zero slope at the surface (see (6)). Fig. 3 illustrates this and the corresponding explosion of the disequilibration factor $Q/K$ towards smaller $x$ in the reaction layer region. The effective current is then due to the diffusion of the free metal arising from complex dissociation (the incoming flux of free metal to the reaction layer is negligible for sufficiently large $K'$) and the kinetic flux approaches

$$J_{kin} = k_d c_{ML}^\phi \mu$$

(14)

by extension of the Koutecký-Koryta approximation to the partially-labile regime.

In order to check the results of this expression, Fig 4 plots (i) the current, as represented by the metal flux at the electrode surface $J_M^0 = D_M \left( \frac{\partial c_M}{\partial x} \right)_{x=0}$, (ii) the kinetic contribution to this flux, $J_{kin} = k_d c_{ML}^\phi \mu$, (iii) the flux of complex arriving at the reaction layer, $J_{ML}^\mu = D_{ML} \left( \frac{\partial c_{ML}}{\partial x} \right)_{x=\mu}$, and (iv) $c_{ML}^0 / c_{ML}^\ast$, for increasing values of the dissociation rate constant. In the whole range of $k_d$ values in the figure, the system is dynamic ($k'_a t, k_d t > 1$). The reaction layer thickness $\mu$, as derived from $k_a$ and $c_L^\ast$, is constant for all the points of the figure; this implies that the stability constant varies inversely with $k_d$.

For $k_d < 10^2$ s$^{-1}$, $J_M^0$ is almost zero, since there is no noticeable dissociation and almost no free metal in bulk solution (we are in excess ligand conditions and $K' >> 1$). As $k_d$ increases, the metal flux increases up to a plateau ($10^4$ s$^{-1}$ $< k_d < 10^6$ s$^{-1}$) where the labile
regime is reached as is recognized in the figure since $c_{\text{ML}}^0/c_{\text{ML}}^* \rightarrow 0$. In this plateau, the current is sensitive only to the equilibrium speciation, being $J_M^0$ proportional to $Dc_{\text{T,M}}^*$.

A further increase of $k_d$ leads to a new increase in $J_M^0$ since the equilibrium is shifted towards free metal as the stability constant $K = k_a/k_d$ decreases ($\varepsilon K'$ no longer larger compared to unity). For $k_d$ high enough ($K' << 1$), a new plateau of $J_M^0$ is reached corresponding to the simple case of only free metal being present.

It should be noticed that $J_{\text{kin}}$, defined as (14) in the extension of the Koutecký-Koryta approximation to the partially-labile regime, is a good approximation for $J_M^0$ in all the $k_d$ range up to the labile situation. This result deserves some comments:

i) A reaction layer with local disequilibration is present in all the cases, even under labile conditions. As it has been noticed, the condition of lability expressed in terms of bulk properties, eqn. (12), does not imply fulfillment of local equilibrium at any spatial point and time. Actually, the diffusive flux of the metal increases approaching the electrode while $J_{\text{kin}}$ decreases since it depends not only on $k_d$ but also on the local concentration $c_{\text{ML}}^\phi$. This last dependence evidences that under labile conditions, the inequality $J_{\text{kin}} > J_{\text{diff}}$ with $J_{\text{kin}}$ defined for $c_{\text{ML}}^\phi$, cannot be maintained for $x < \mu$ since $J_{\text{kin}}$ and $c_{\text{ML}}^\phi$ tend to zero.

ii) Although $J_{\text{kin}}$ as defined by (14) is a good approximation for $J_M^0$, there is no true steady state since $J_{\text{kin}} > J_{\text{ML}}^\mu$. Due to this inequality, a time dependent $c_{\text{ML}}^\phi$ arises, and for fixed $t$, $c_{\text{ML}}^\phi$ decreases as $k_d$ increases. Fig. 4 clearly shows that the decrease of $c_{\text{ML}}^0/c_{\text{ML}}^*$ towards zero is correlated with the disparity of $J_{\text{ML}}^\mu$ and $J_{\text{kin}}$. 

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Given the simplicity and accuracy of $J_{kin}$ it is interesting to work out an approximate analytical expression for $c_{ML}^\phi$ in order to obtain a simple expression for the metal flux and for the current. Through the analytical resolution of the system (3-6) [23] under ligand excess conditions (flat profile for $c_1(x,t)$), we can obtain $c_{ML}^0$ which can be used as a good approximation for $c_{ML}^\phi$:

$$c_{ML}^\phi = \frac{c_{T,M}^* D_M}{(D_M D_{ML} (k_a + k_d))^{3/2}} \left( D_M k_d \sqrt{D_M D_{ML} (k_a' + k_d)} + D_{ML} k_a' \sqrt{D_M D_{ML} (k_a' + k_d)} \right)$$

which, for large values of the argument of erfc (e.g. high $k_d$-values), can be approximated by

$$c_{ML}^\phi = \frac{c_{T,M}^* k_c}{k_d \sqrt{k_a' + k_d}} \left( \frac{D_M}{D_{ML} (k_a' + k_d)} \right)$$

Per60.14 (16)

whereas for small values of the argument of erfc (e.g. low $k_d$-values), (15) reduces to

$$c_{ML}^\phi = \frac{c_{T,M}^* (D_M k_a' + D_{ML} k_d)}{D_{ML} (k_a' + k_d)} \left( 1 - \frac{2k_a (D_{ML} k_a' + D_M k_d)}{D_M k_a'} \sqrt{\frac{D_a}{D_{ML} (k_a' + k_d)}} \right)$$

Per60.14 (17)

Expressions (16) and (17) are plotted in dotted lines in fig. 4 showing a good agreement with $c_{ML}^\phi$ in both limiting kinetic regimes, but both of them differing from the exact results at intermediate values of $c_{ML}^\phi$.

D. The Koutecký-Koryta approximation for a quasi-labile system with any ligand to metal ratio

This section examines the applicability of the Koutecký-Koryta approximation under non-excess ligand conditions. Fig. 5 is analogous to Fig. 4 but for a system with total...
metal concentration exceeding that of the total ligand concentration. At the lowest $k_d$-values, $J_M^0$ starts with a non zero constant value which reflects the flux of the exceeding free metal in bulk solution. As there is no significant dissociation of complex, the behavior of the system approaches that of an inert system with a metal profile extending up to $x = \delta_M$ (see fig. 6). Increasing $k_d$, $J_M^0$ increases due to the contribution of the complex dissociation, but now, as Fig. 5 shows, $J_{\text{kin}}$ is not a good approximation for the kinetic contribution to $J_M^0$. In order to elucidate this, normalized profiles of the species for $k_d = 5 \cdot 10^2 \text{ s}^{-1}$ are displayed in Fig. 7 (notice the logarithmic scale in abscissas). Basically, the metal concentration coincides with that of Fig. 6 with a concentration profile extending up to $\delta_M$. Due to the high value of the stability constant involved with this $k_d$-value ($K = k_d / k_d = 2 \cdot 10^3 \text{ mol}^{-1} \text{ m}^3$) the depletion of the metal does not appreciably affect the profile of the complex. In fact this case is similar to that of an infinite stability constant for which the ligand concentration is zero in bulk conditions, metal and complex becoming unrestricted with respect to the equilibrium condition [24].

Close to the electrode (for $x$ decreasing below $10^{-5} \text{ m}$, in Fig. 7), the ligand concentration starts to increase. This forces $c_M$ to approach zero in order to fulfil the equilibrium condition, as the value of $Q/K$ close to unity indicates. Clearly, this is not a kinetic effect but an equilibrium one. Due to the high value of the stability constant involved, the increase of $c_L$ takes place when the local total metal profile falls below the local total ligand concentration. This condition is fulfilled for $x$ less than the position of the intersection of the metal and ligand concentration profiles. Below this distance, all the metal tends to be complexed due to the high value of the stability constant...
involved. The profile of the complex is then that of the total metal concentration, and, as the total ligand concentration is constant, a decrease of \( c_{ML} \) implies a corresponding increase of \( c_L \). The position of the intersection point and the pertaining concentrations (\( c_M \) and \( c_L \)) increases as \( k_d \) increases. The higher \( k_d \), the more depleted the concentration profile of ML (\( k_d \rightarrow \infty \) - labile conditions- the complex concentration starts from zero at the electrode surface) and the steeper the concentration profile of the ligand.

As can be seen in Fig 7, the position \( x = \mu \) does not coincide with the boundary of the disequilibrium layer which confirms that the kinetic contribution defined as \( J_{kin} = k_d c_M^0 \mu \) does not equal \( J_M^0 \). In fact this is expected since the life time of the free metal before reassociation depends on \( c_L \) and the \( c_L \)-value close to the electrode is far away from the bulk \( c_L \)-value. So, we should redefine \( \mu \) using the \( c_L \)-value in the reaction layer, \( c_L^0 \):

\[
\mu^0 = \left( \frac{D_M}{k_d c_L^0} \right)^{1/2}
\]  

(18)

which leads to quite a good agreement with the effective layer of disequilibrium as can be seen in Fig. 7. Likewise, the kinetic contribution must also be redefined as

\[
J_{kin} = k_d c_M^0 \mu^0
\]  

(19)

\( J_{kin} \), defined as (19), is also plotted in figure 5. It is a good approximation for \( J_M^0 \) in the range where there is a non-negligible contribution of the dissociation to the metal flux. However, \( J_{kin} \) is not a good approximation for the kinetic contribution at low \( k_d \)-values when \( J_M^0 \) tends to the inert value (as indicated in Fig. 5). In fact, this result is not
surprising since expression (19) has been suggested as direct extension of the kinetic contribution in the case with excess of ligand and $K' >> 1$. Under these conditions, $J_{kin}$ equals the total flux and tends to zero for low $k_d$-values. This limiting value of $J_{kin}$ does not apply for the non-excess ligand case since the metal flux tends to the inert flux. This free metal contribution is not included in (19) and is responsible for the disparity between $J_M^0$ and $J_{kin}$ defined as (19) for low $k_d$-values. On the other hand, excess ligand conditions hold close to the electrode surface for a $k_d$-value greater than $10^2$ s$^{-1}$ in fig. 5 (see also fig. 7) justifying the agreement between (19) and $J_M^0$ in the kinetic range.

Finally it is interesting to examine the concentration profiles close to the electrode surface for a $k_d$-value corresponding to the non-labile range. Fig. 8 shows the concentration profiles of Fig. 6 magnified up to distances of the order of the reaction layer thickness. At distances of the order of $\mu^\phi$, the metal profile intersects with that of the ligand. However, the plateau of the profile of M observed for $x$ below $x = 10^{-5}$ m in fig. 7, does not appear and $\mu^\phi$ differs from the thickness of the effective disequilibration layer. In fact, the metal concentration profile is not affected by the intersection with the profile of the ligand, $J_M^0$ being determined by $\delta_M$ and very different from $J_{kin}$ (see Fig 5). The low $c_M$ in the intersection point compared to that at a higher $k_d$, renders the shift of the complexation equilibrium ineffective. Hence the depletion plateau as observed in fig. 7 in the profile of $c_M$ between $x = \mu^\phi$ and $x = 10^{-5}$ m does not occur.
In summary, as can be seen in fig. 5, when \( c_{T,M}^* > c_{T,L}^* \), the Koutecky-Koryta approximation based on the spatial separation of a reaction layer and a labile layer can also be used with the corrections discussed in this section. \( J_M^0 \) can be well approximated by \( J_{\text{kin}} \), defined as (19), in the \( k_d \) range where \( J_{\text{kin}} > D_M c_M^* / \delta_M \) whereas \( D_M c_M^* / \delta_M \) is a good approximation for \( J_M^0 \) in the remaining \( k_d \) range.

**Conclusions**

The Finite Element Method is suitable for the computation of the time-dependent concentration profiles of the different species in the voltammetric response of metal complex systems with various labilities. The obtained profiles can be analyzed in order to understand the behavior of the system. The corresponding fluxes are compared to the fluxes derived from the Koutecky-Koryta (KK) approximation which is based on a simplified infinitely sharp transition from non-labile to labile behavior at the boundary of the reaction layer. The comparison shows a relatively far-reaching correctness of the KK approximation in the complete kinetic range of complexes with varying labilities, as long as the kinetic flux is computed from the effective concentration of the complex in the reaction layer \( c_{ML}^* \) (see eqn. (14)). This concentration is of great importance for the voltammetric response of the system and it can be defined by the approximate analytical expressions (16) and (17). The analysis confirms that close to the electrode surface there is a disequilibration layer (where \( Q \neq K \)) with a thickness of that of the reaction layer, even in the case of labile complexes.

The KK approximation (see eqn. (19)) is shown to be applicable for any metal-to-ligand ratio in the complex system, provided that the thickness of the reaction layer is expressed in terms of the local ligand concentration at the electrode surface (eqn. 18). In this case, however, the KK expression is a good approximation for the metal flux only...
in the kinetic range under conditions where the contribution of the dissociation of the complex to the metal flux is significant.

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**Appendix**

Linear systems (i.e. excess of ligand) can be dealt with analytically [11,25,26], but non-linear homogeneous reaction-diffusion problems require numerical approaches [27] such as the Galerkin Finite Element Method (GFEM) [28-30]. Indeed, despite the domain is -in principle- infinite, the concentration profiles significantly differ from bulk values just in a small region close to the electrode. A few nodal points can be unevenly placed in this region so that high accuracy can be obtained in the GFEM solution of the spatial dependence of the problem with low computational cost.

We use the following transformations and simplifications:

1.- Nondimensional concentrations are defined as

\[ \hat{c}_i = \frac{c_i}{c_i^*} \quad \text{(A-1)} \]

2.- The space variable is re-scaled using the largest diffusion coefficient:

\[ z = \frac{x}{\sqrt{D_M}} \quad \text{(A-2)} \]

3.- The differential equations are linearized by using the auxiliary variable

\[ r(z,t) = k_d \left( c_{ML}^* \hat{c}_{ML}(z,t) - K \cdot c_M^* \cdot \hat{c}_M(z,t) \cdot c_L^* \cdot \hat{c}_L(z,t) \right) \quad \text{(A-3)} \]
4.- By solving a combination of the continuity equations (3) for L and ML with the equality of diffusion coefficients $D_L = D_{ML}$, we have

$$c_L + c_{ML} = \hat{c}_{T,L}^*$$ \hspace{1cm} XXX(A-4)

Then, eqns. (3)-(4) can be written as

$$\frac{\partial \hat{c}_M}{\partial t} = \frac{\partial^2 \hat{c}_M}{\partial z^2} + \frac{1}{c_M} r$$ \hspace{1cm} NormcM XXX(A-5)

$$\frac{\partial \hat{c}_L}{\partial t} = \varepsilon \frac{\partial^2 \hat{c}_L}{\partial z^2} + \frac{1}{c_L^*} r$$ \hspace{1cm} NormcL XXX(A-6)

$$r - k_d \left( c_{T,L}^* - \hat{c}_L^* \hat{c}_L^* - K \hat{c}_M^* \hat{c}_L^* \hat{c}_L^* \right) = 0$$ \hspace{1cm} Kinetic XXX(A-7)

where $\varepsilon \equiv D_{ML} / D_M$.

The initial condition is

$$\hat{c}_M(z,0) = \hat{c}_L(z,0) = 1$$ \hspace{1cm} XXX(A-8)

The boundary conditions become:

$$\hat{c}_M(\infty,t) = \hat{c}_L(\infty,t) = 1, \hspace{0.5cm} \hat{c}_M(0,t) = \frac{\partial \hat{c}_L}{\partial z} \bigg|_{z=0} = 0$$ \hspace{1cm} XXX(A-9)

Linear piecewise interpolation functions have been used in the discretized weak formulation of the problem. Let $(z_1, z_2, \ldots, z_N)$ be the vector of spatial grid points, with $z_N$ large enough so that the differences between local and bulk concentrations are negligible. Using
\[ c_i(t) = (\hat{c}_i(z_1, t), ..., \hat{c}_i(z_N, t)), \ i = M, L \]

\[ \bar{r}(t) = (r(z_1, t), ..., r(z_N, t)) \]

\[ p(t) = \left. \frac{\partial \hat{c}_M}{\partial z} \right|_{z=0} \]

one can write XXX(A-5) and XXX(A-6) as a system of ordinary differential equations in the time variable:

\[
A \cdot \ddot{c}_M(t) + B \cdot \dot{c}_M(t) + \begin{pmatrix} p(t) \\ \vdots \\ 0 \end{pmatrix} - \frac{1}{c_M} A \cdot \ddot{r}(t) = 0 \]

MatrixcM XXX(A-13)

\[
A \cdot \ddot{c}_L(t) + \varepsilon \cdot B \cdot \dot{c}_L(t) - \frac{1}{c_L} A \cdot \ddot{r}(t) = 0 \]

MatrixcL XXX(A-14)

where \( A \) and \( B \) are

\[
A = \begin{pmatrix}
\frac{h_1}{3} & \frac{h_1}{6} & 0 & \ldots & 0 & 0 \\
\frac{h_i}{6} & \frac{h_i + h_2}{6} & \frac{h_2}{6} & \ldots & 0 & 0 \\
\frac{h_2}{6} & \frac{h_2 + h_3}{6} & \frac{h_3}{6} & \ldots & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & \frac{h_{N-2} + h_{N-1}}{3} & \frac{h_{N-1}}{6} \\
0 & 0 & 0 & \ldots & \frac{h_{N-1}}{6} & \frac{h_{N-1} + h_N}{3}
\end{pmatrix}
\]

XXX(A-15)
\[
B = \begin{pmatrix}
\frac{1}{h_1} & -\frac{1}{h_1} & 0 & \cdots & 0 & 0 \\
-\frac{1}{h_1} & \frac{1}{h_1} + \frac{1}{h_2} & -\frac{1}{h_2} & 0 & \cdots & 0 \\
0 & \frac{1}{h_2} & \frac{1}{h_2} + \frac{1}{h_3} & \cdots & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & \frac{1}{h_{N-2}} + \frac{1}{h_{N-1}} & -\frac{1}{h_{N-1}} \\
0 & 0 & 0 & \cdots & \frac{1}{h_{N-1}} + \frac{1}{h_N} & \frac{1}{h_N} \\
\end{pmatrix}
\]

XXX(A-16)

with \( h_i = z_{i+1} - z_i \).

The Inverse-Euler Finite Difference method (to ensure stability of the calculations and avoid spurious oscillation of the solution) is applied to the resulting system (eqn. XXX(A-7), XXX(A-13) and XXX(A-14)), thus transforming the original coupled set of ordinary differential equations into a non linear algebraic system:

\[
\left( \frac{1}{\Delta t} A + B \right) \cdot \hat{c}_M(t + \Delta t) + \begin{pmatrix} p(t + \Delta t) \\
0 \\
\vdots \\
0 \end{pmatrix} - \frac{1}{c_M} A \cdot \bar{r}(t + \Delta t) - \frac{1}{\Delta t} A \hat{c}_M(t) = 0 \quad \text{XXX(A-17)}
\]

\[
\left( \frac{1}{\Delta t} A + \varepsilon B \right) \cdot \hat{c}_L(t + \Delta t) - \frac{1}{c_L} A \cdot \bar{r}(t + \Delta t) - \frac{1}{\Delta t} A \hat{c}_L(t) = 0 \quad \text{XXX(A-18)}
\]

\[
r_i(t + \Delta t) - k_d \left( c_{T,L}^* - c_L^* \hat{c}_L(z_i, t + \Delta t) + K c_M^* \hat{c}_M(z_i, t + \Delta t) \hat{c}_L(z_i, t + \Delta t) \right) = 0 \quad \text{XXX(A-19)}
\]

with \( \hat{c}_M(z_i, t + \Delta t) = 0 \), due to the boundary condition (6). This system is iteratively solved with a Newton-like method, modified in order to avoid loss of convergence [31].
One of the main advantages of the GFEM method is the use of arbitrary unequal spatial grids. In this case, a spatial grid with ca. 50 nodes has been used. The distances (in units of \( z \)) between nodes increase going from the electrode surface to the bulk solution (at some 10 units). The typical distances taken are: 10\(^{-5}\) units (8 nodes), 2 \( \cdot 10^{-5} \) units (4 nodes), 8 \( \cdot 10^{-5} \) units (1 node) and then the distances double until they reach around 10\(^{-1}\) units.

Values of the concentrations at each spatial position and time \( t \) are used as a first trial in the iterative solution of the algebraic resulting system at the next time interval, \( t + \Delta t \). The time interval used is \( \Delta t = 10^{-4} \) s.

FIGURES:

![Fig 1: Concentration profiles of \( c_M \) (referred to the left ordinate axis) and \( c_{ML} \) (referred to the right ordinate axis) for a non-labile case. Parameters: \( c_{T,L}^* = 1 \) mol m\(^{-3}\), \( c_{T,M}^* = 0.1 \) mol m\(^{-3}\); \( k_a = 10^8 \) mol\(^{-1}\) m\(^3\) s\(^{-1}\), \( k_d = 10 \) s\(^{-1}\), \( t = 1 \) s, \( D_M = 1.10^{-9} \) m\(^2\) s\(^{-1}\), \( D_{ML} = D_L = 5 \) 10\(^{-9} \) m\(^2\) s\(^{-1}\).](image-url)
Evaluation of Koryta-Koutecky.

$10^{-2}$ m$^2$ s$^{-1}$. Dotted lines correspond to the effective metal profile given by the reaction layer thickness $\mu=3.33 \times 10^{-9}$ m.

**Fig 2:** Concentration profiles of $c_M$ and $c_{ML}$ for a labile case. Parameters: $k_a = 10^8$ mol$^{-1}$ m$^3$s$^{-1}$, $k_d = 10^5$ s$^{-1}$, $K = 10^3$ mol$^{-1}$ m$^3$. Other parameters as in figure 1. The vertical dotted line indicates the thickness of the diffusion layer, $\delta_D = \sqrt{\pi DT}$.

**Fig 3:** Concentration ratios for a labile case. Parameters: $Q$ and $K$. Other parameters as in figure 1.
Fig 3: Concentration profiles of $c_M/c_M^*$ and $c_{ML}/c_{ML}^*$ (referred to the left ordinate axis) and $Q/K$ (referred to the right ordinate axis) for a partially-labile case. Parameters: $k_a = 10^3$ mol$^{-1}$ m$^3$s$^{-1}$, $k_d = 10$ s$^{-1}$. Other parameters as in figure 1. The vertical dotted lines indicate the end of the reaction layer at $x = \mu = 1.05 \times 10^{-6}$ m and the end of the diffusion layer at $x = \delta_c = \sqrt{\pi D \tau} = 1.86 \times 10^{-5}$ m.

Fig 4: Plot of the metal flux at the electrode surface, $J_M^0 = D_M \left( \frac{\partial c_M}{\partial x} \right)_{x=0}$; the kinetic contribution, $J_{kin} = k_d c_{ML}^\phi \mu$; the flux of complex arriving at the reaction layer, $J_{ML}^\mu = D_{ML} \left( \frac{\partial c_{ML}}{\partial x} \right)_{x=\mu}$; and $c_{ML}^0/c_{ML}^*$ for increasing values of the dissociation kinetic constant. Other parameters as in fig. 1.
Fig. 5: Plot of the metal flux at the electrode surface, $J_M^0 = D_M \left( \frac{\partial c_M}{\partial x} \right)_{x=0}$; the kinetic contribution, $J_{kin}$, defined as (14), $J_{kin} = k_d c_M^p \mu$ (continuous line), or defined as (19), $J_{kin} = k_d c_M^p \mu^\phi$ (dotted line); the flux of complex incoming the reaction layer, $J_{ML}^\mu = D_M \left( \frac{\partial c_{ML}}{\partial x} \right)_{x=\mu}$; and $c_{ML}^0/c_{ML}^*$ vs. the dissociation kinetic constant for a non excess ligand system. Parameters are: $c_{t,L}^* = 0.8 \text{ mol m}^{-3}$, $c_{t,M}^* = 1 \text{ mol m}^{-3}$. Other parameters as in fig. 1. The inert flux value $D_M c_M^*/\delta_M$ is also plotted in dashed-dotted line.
Fig 6: Concentration profiles for M (◊), L (□) and ML (*) corresponding to \( k_d = 10 \text{ s}^{-1} \) in fig. 5. Concentrations are referred to the left \( y \)-axis, while \( Q/K \) (marker •) is referred to the right \( y \)-axis. The vertical dotted line indicates \( \delta_M = \sqrt{\pi D_M l} = 5.61 \times 10^{-5} \text{ m}. \)

Notice the explosion of the \( Q/K \) value close to the electrode surface.
Fig 7: Normalized concentration profiles corresponding to $k_d = 500 \text{ s}^{-1}$ of fig. 5. The vertical dotted lines indicate $\mu^a = 1.91 \times 10^{-8} \text{ m}$, $\mu = 7.07 \times 10^{-7} \text{ m}$ and $\delta_M = \sqrt{\pi D_M t} = 5.61 \times 10^{-5} \text{ m}$. Markers as in figure 6.

Fig. 8: Concentration profiles corresponding to $k_d = 10 \text{ s}^{-1}$ of fig. 5. Magnification of fig 6 up to distances from the electrode surface of the order of the reaction layer. The vertical dotted line indicates $\mu^a = 2.13 \times 10^{-7} \text{ m}$, while $\mu = 5.00 \times 10^{-6} \text{ m}$ is not seen in the figure.

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