

Voltammetric lability of metal complexes at spherical microelectrodes with various radii.

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Abstract:

The size of a microelectrode can have a dramatic impact on the relative importance of the diffusional and kinetic contributions to the voltammetric current of an electroactive metal ion in a complexing medium. Decreasing the radius enhances the diffusional contribution and, as a consequence, the complex system tends to move away from labile behaviour (where an equilibrium relationship holds). Therefore, sufficiently small microelectrodes (either or not combined with short measuring times) should be able to directly sense free metal concentration for not too fast association/dissociation kinetics. The particular case of steady state spherical (or hemispherical) diffusion under ligand excess (pseudo-first order kinetics) is solved analytically. The ensuing lability criterion is shown to be in accordance with a geometrical derivation based on an analysis of the

random walk of the free metal ions produced by dissociation of the complex. It is shown that, for a generated metal ion, the probability of reaching the microelectrode surface can be quite different from the planar case. Alternatively, the classical reaction layer concept can be used in the derivation of the lability criterion for spherical geometry as it is shown in this work. All treatments quantitatively show how the lability of metal complexes is reduced with decreasing the dimension of the microelectrode.

Keywords: microelectrode, lability, kinetic current, speciation, steady state, reaction layer, CE scheme, pseudo first order, homogeneous complexation.

Introduction

The dynamic speciation of metals, i.e. the distribution and association/dissociation kinetics of their species, largely governs properties such as reactivities and bioavailabilities in complex systems. It is therefore not surprising that sensitive non-equilibrium techniques, such as voltammetry, are taking a prominent position in this field [1-4]. Voltammetric techniques are generally well-defined in terms of geometrical conditions and operational time-scale. Kinetic qualifications like "labile" and "inert" have an inherently sound theoretical definition, based on comparing limiting fluxes controlled by finite rates of dissociation of complex species to the limiting diffusional fluxes of these species [2]. Results obtained in the voltammetric analysis of the metal-ligand complexation (such as heavy metals in environmental samples) will be equally indispensable in the interpretation of metal uptake from complex media by microorganisms [5-10].

Microelectrodes are defined by dimensions which do not largely exceed the thickness of the operational diffusion layer [11]. Their use is widespread due to several reasons, such as no need of supporting electrolyte, low ohmic drop, attainability of steady state, etc. [12-15]. Due to their geometrical characteristics, the relative importance of the diffusional and kinetic contributions in the mass transport towards a spherical microelectrode can be quite different from the planar case and, thus, the lability of the system will be altered [16,17]. In a first orientational study [18], lability criteria have been worked out by considering two cases i) a spherical diffusion layer and a linear reaction layer and ii) spherical diffusion and reaction layers. This treatment only considered the inequalities involved in lability criteria and was oversimplified in not specifying the metal ion's probabilities of reaching the microelectrode surface from a spherical reaction layer.

Hence, it seems timely to analyse the situation for the microelectrode on a more rigorous level, by studying the properties of the continuity equations describing the evolution of the system (with neither convection nor migration) and extracting the information about the impact of decreasing the electrode dimensions (section 1). In the case of ligand excess (pseudo-first order kinetics) and steady state, the rigorous analytical solution (section 2, with details in the Appendix) for the normalised current is worked out (assuming that no finite volume effects arise from possible saturation inside the sphere [19]). This result leads to a lability criterion (section 2.2.1), which can also be confirmed by an intuitive derivation (section 2.2.2) based on the random walk of metal ions produced by dissociation of complexes close to the electrode surface. Finally (section 2.2.3), the validity of the reaction layer concept in the derivation of the lability criterion for spherical geometry is critically analysed.

1.- General mathematical formulation .

Let us consider an electroactive metal ion M



which is complexed by a ligand L to yield an electroinactive complex ML, according to the homogeneous reaction:



If we assume that the only relevant mode of transport towards the spherical or hemispherical electrode of radius r_0 is diffusion, the continuity equations for the species are:

$$\frac{\partial c_M(r,t)}{\partial t} = D_M \left(\frac{\partial^2 c_M(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_M(r,t)}{\partial r} \right) + k_d c_{ML}(r,t) - k_a c_M(r,t) c_L(r,t) \quad (3)$$

$$\frac{\partial c_L(r,t)}{\partial t} = D_L \left(\frac{\partial^2 c_L(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_L(r,t)}{\partial r} \right) + k_d c_{ML}(r,t) - k_a c_M(r,t) c_L(r,t) \quad (4)$$

and

$$\frac{\partial c_{ML}(r,t)}{\partial t} = D_{ML} \left(\frac{\partial^2 c_{ML}(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_{ML}(r,t)}{\partial r} \right) - k_d c_{ML}(r,t) + k_a c_M(r,t) c_L(r,t) \quad (5)$$

The assumption $D_L = D_{ML}$, usual in metal-macromolecular complexation, is not necessary in this work.

Among the boundary conditions we have those for semi-infinite diffusion, prescribing given bulk values at infinite r . Thus, far away from the electrode surface or at $t=0$, the bulk concentrations are related by the equilibrium constant:

$$K = \frac{k_a}{k_d} = \frac{c_{ML}^*}{c_M^* c_L^*} \quad (6)$$

Boundary conditions at the electrode surface arising from the electroinactivity of complex and ligand are

$$\left(\frac{\partial c_{ML}}{\partial r} \right)_{r=r_0} = \left(\frac{\partial c_L}{\partial r} \right)_{r=r_0} = 0 \quad \forall t = 0 \quad (7)$$

For the sake of simplicity, we only consider here limiting flux conditions

$$c_M(r_0, t) = 0 \quad \forall t \geq 0 \quad (8)$$

and the response function is the limiting current:

$$I = nFAD_M \left(\frac{\partial c_M}{\partial r} \right)_{r=r_0} \quad (9)$$

In general, the question of lability concerns the competing relevance of diffusion and complexation kinetics. We now address the question of the impact of the electrode radius r_0 on the lability.

Let us consider any of the continuity equations (3)-(5), such as the one corresponding to the metal ion, and introduce the change of variable

$$\rho \equiv \frac{r}{r_0} \quad (10)$$

Omitting the independent variables for simplicity, the equation reads:

$$\frac{\partial c_M}{\partial t} = \frac{D_M}{r_0^2} \left(\frac{\partial^2 c_M}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial c_M}{\partial \rho} \right) + k_d c_{ML} - k_a c_M c_L \quad (11)$$

where one can recognise that the diffusion coefficient now combines with r_0^2 . This shows that the magnitude of the diffusion terms in the continuity equation increases

when r_0 decreases, whereas the kinetic contribution remains without direct r_0 -dependence (as expected from a volume process). This is consistent with the well known fact that microelectrodes, due to the enhancement of diffusion transport, are particularly useful in tracing fast kinetic processes that become rate limiting under suitable conditions [20]. We conclude that decreasing r_0 increases the diffusive flux and thus tends to decrease the observed lability of a metal complex in its voltammetric response.

The reasoning can be extended to other microelectrodes, such as the inlaid microdisc, ring or band electrodes. In any case, diffusion is enhanced by the small dimension of the electrode (given by some characteristic length) and lability is lower than in the planar case. As explained at the end of section 2.2.1 these facts might be experimentally exploited to directly determine the bulk concentration of free metal ion.

2.- A particular case: Steady state under excess ligand conditions at a (hemi)spherical electrode.

2.1 Analytical solution

In order to work out a lability criterion for a particularly simple case, we recall that one of the reasons for using microelectrodes lies in their ability for reaching steady state within a reasonable time. Thus, we tackle now the steady state case, which is, of course, simpler than the transient. Consider further that the ligand concentration is so large with respect to the amount of M that its concentration is not altered from the bulk value (ligand excess conditions):

$$c_L(r) \approx c_L^* \quad \forall r \quad (12)$$

Then the equilibrium concentrations of metal ion and complex are linearly related by the effective complexation constant K' :

$$c_{ML}(r) = Kc_L^* c_M(r) = K'c_M(r) \quad (13)$$

We define the non-dimensional (limiting) current as

$$\phi \equiv \frac{I(c_L^* \neq 0)}{I(c_L^* = 0)} = \frac{r_0}{c_{T,M}^*} \left(\frac{\partial c_M}{\partial r} \right)_{r=r_0} \quad (14)$$

i.e. the ratio between the current corresponding to the system given in eqn. (9) and the current for the same system without ligand,

$$I(c_L^* = 0) = nFAD_M \frac{c_{T,M}^*}{r_0} \quad (15)$$

(same amount of total metal $c_{T,M}^*$, spherical steady state), being A the electrode area ($4\pi r_0^2$ in the spherical case and half this value for a hemispherical electrode mounted on a planar insulating surface).

As shown in appendix, the normalised current ϕ for any kinetic constants can be expressed as:

$$\phi = \frac{1}{1 + K'} \left(1 + \frac{\varepsilon K' \sqrt{\kappa_a}}{\sqrt{\varepsilon K' (1 + \varepsilon K') + \sqrt{\kappa_a}}} \right) \quad (16)$$

where the ratio of diffusion coefficients (D_{ML}/D_M) is denoted as ε and κ_a is the non-dimensional (association) kinetic constant given by:

$$\kappa_a \equiv \frac{k_a c_L^* r_0^2}{D_M} \quad (17)$$

The normalised current for the limiting case of (fully) labile complexation ($\kappa_a \rightarrow \infty$) is

$$\phi_{labile} = \frac{1 + \varepsilon K'}{1 + K'} \quad (18)$$

while, for inert complexes ($\kappa_a \rightarrow 0$) we have

$$\phi_{inert} = \frac{1}{1 + K'} \quad (19)$$

Fig 1 shows the behaviour of the non-dimensional current ϕ versus the radius (which can be seen as the experimental control for κ_a) for a set of 3 hypothetical systems sharing common values of ε , K' and D_M but with different k_d -values. The hypothetical systems could be 3 different metals (if their D_M -values were similar enough) with a common ligand, but also the same metal with convenient amounts of 3 different ligands ($K' = k_a c_L^* / k_d$). For all cases, the normalised current increases monotonously with the radius from a minimum value (corresponding to the inert case where ϕ is given by (19)) up to the asymptotic value (corresponding to the labile case of eqn (18)). As seen in Fig 1, the transition from inert to labile depends both on r_0 and on the k_d value. Thus, for the system with the highest k_d (more "intrinsically" labile, dotted upper line), the current is practically not affected by kinetics limitations for $r_0 > 100 \mu\text{m}$, while for the system with the lowest k_d (continuous lowest line), the kinetic limitations on the current are still noticeable at $r_0 = 10 \text{ mm}$.

For purposes of comparison, it is convenient to introduce a parameter ξ (ranging from 0 to 1) which could be called "degree of lability":

$$\xi \equiv \frac{\phi_{kinetic} - \phi_{inert}}{\phi_{labile} - \phi_{inert}} = \frac{I_{kinetic}(c_L^* \neq 0) - I_{inert}(c_L^* \neq 0)}{I_{labile}(c_L^* \neq 0) - I_{inert}(c_L^* \neq 0)} \quad (20)$$

By using the analytical solution (16), one obtains

$$\xi = \frac{\sqrt{k_a}}{\sqrt{\varepsilon K'(1 + \varepsilon K')} + \sqrt{k_a}} \quad (21)$$

Fig 2 shows ξ for different electrode radii, with parameters typical for Ni^{2+} complexation [18,21]. It can be seen that at huge electrode radii, say 1 cm (which would require an impractical time to reach steady state), the lability degree ξ is practically unity, indicating a labile behaviour. On the other hand, for electrode radii less than 10 μm , ξ is less than 5%.

The more labile is a system the larger is the depletion of c_{ML} close to the electrode surface. In fact, via substitution in the analytical solution for the normalised complex profile (A-13), it can be seen that

$$\frac{c_{\text{ML}}(r = r_0)}{c_{\text{ML}}^*} = 1 - \xi \quad (22)$$

Thus the degree of lability can be seen as an indicator of the lability via the concentration of complex at the electrode surface. If the lability is high, $c_{\text{ML}}(r=r_0)$ is close to zero (see lowest curve in Fig 3). When the system is practically inert, $c_{\text{ML}}(r = r_0) \approx c_{\text{ML}}^*$ (see continuous upper curve in Fig 3).

At this point it is useful to emphasize that if a system is not labile at steady state (due, for instance, to the use of a very small microelectrode), then it is certainly not labile during the transient preceding this steady state.

2.2 Lability criteria

2.2.1 Analytical derivation of a lability criterion

One could set an arbitrary border-line between predominantly labile systems and predominantly inert systems at $\xi=1/2$. This would imply that the first category obeys:

$$\xi = \frac{\sqrt{\kappa_a}}{\sqrt{\varepsilon K'(1 + \varepsilon K')} + \sqrt{\kappa_a}} > \frac{1}{2} \quad (23)$$

which can be written as

$$\kappa_a > \varepsilon K'(1 + \varepsilon K') \quad (24)$$

or, in terms of the radius,

$$r_0 > \sqrt{\frac{D_{ML} K'(1 + \varepsilon K')}{k_a c_L^*}} \quad (25)$$

So, according to this general lability criterion, the radius of the microelectrode has to overcome a minimum value for steady state currents at a (hemi)spherical electrode to be labile. The same conclusion could also be reached from eqn. (23), noticing that, due to $\sqrt{\kappa_a} \propto r_0$, the lability degree ξ increases monotonically with increasing r_0 . In any case, it is clear that under the conditions mentioned, the lability of a system only decreases with decreasing radius.

For complexes so strong that $\varepsilon K' \gg 1$, the general lability criterion (24) simplifies to

$$\kappa_a > (\varepsilon K')^2 \quad (26)$$

(see ref. [22,23] for the similar simplification in the planar case).

After elementary algebraic re-shuffling we obtain, from (26), the following lability criterion:

$$\frac{k_d r_0}{D_{ML}} \sqrt{\frac{D_M}{k_a c_L^*}} > 1 \quad (27)$$

which is just equivalent to expression 13 in reference [18]. Eqn (27) can also be written as a condition for the radius (which could be seen as the experimentally controllable parameter):

$$r_0 > \frac{D_{ML}}{\sqrt{D_M}} \frac{\sqrt{k_a c_L^*}}{k_d} \quad (28)$$

Let us consider some numerical examples, beginning with a system with slow kinetics. With parameters corresponding to Ni^{2+} complexation taken from figure 4 in ref [18] (used for Fig 2), we can expect (according to eqn. (28)) lability only for radii of the electrode larger than 0.32 mm, which indicates that the system is never labile within the practical microelectrode range. Now, we can compare this with an example of a system with fast kinetics. Parameters suggested for Pb^{2+} [18,21] are $k_a=10^{10} \text{ M}^{-1}\text{s}^{-1}$ and $D_M=10^{-9} \text{ m}^2\text{s}^{-1}$. If the parameters for the ligand are $D_{ML}=10^{-10} \text{ m}^2\text{s}^{-1}$ and $c_L^* = 10^{-5} \text{ M}$, application of eqn. (28) predicts that the behaviour of the system can be considered labile for $r_0 > 0.1 \mu\text{m}$.

An experimental exploitation of the results given so far is suggested by eqn. (28): the manipulation of the radius (or the characteristic length of a generic microelectrode) should allow the approximation towards the inert limit. Indeed, a system with not too fast association and dissociation kinetics could be rendered practically inert by using a sufficiently small microelectrode (whichever its geometry and regardless of the fulfilment of the excess ligand conditions, according to the results of section 1). Plots of normalised current against radius would eventually converge towards a flat region (similar to that shown in Fig 1) for sufficiently small microelectrodes. Under these conditions, the current is just due to the free metal concentration and the microelectrode

could act as a direct free metal ion sensor. Among the application of such detection, one can point out the building up of binding curves for heterogeneous ligands.

2.2.2 A random walk derivation of a lability criterion

In order to get a physical picture of the reason why lability always decreases with the electrode radius, we perform here an intuitive derivation of the lability criterion based on the elementary motion of the metal ions close to the microelectrode [24-28]. The key idea is that the number of metal ions that actually reach the surface is substantially lower than in the planar case of a macroscopic electrode.

Let A be a point in the solution, situated at a distance R of the centre of the electrode (point O in Fig 4). Let N be the number of particles (free metal ions) present in a infinitesimally small volume around A at a given instant (considered as "initial", when the free metal ions have been just generated and are about to move). We assume:

i) Each of the N particles moves the same distance Δr (mean free path) from A, during its life time $\Delta t_M = \frac{1}{k_a c_L^*}$. Later on, this distance will be computed from the random

walk (or random flight) movement via the Einstein-Smoluchowski relationship

$$\Delta r = \sqrt{6 D_M \Delta t_M} \quad (29)$$

ii) Due to the absence of any privileged direction during the movement, when Δt_M has elapsed, the N particles (originally in A) would (if none of the particles had hit the electrode surface) scatter homogeneously on the surface of the sphere with centre in A and radius Δr (this "diffusion sphere" is shown in Fig 4 in light grey).

iii) The mean number of particles that hit the electrode surface is counted as if the "trajectories" of the particles leaving A were straight lines (radii from the "diffusion sphere" with centre in A). Those radii intercepting the electrode surface are considered to represent the trajectories of particles hitting the electrode surface.

From the previous hypotheses, it follows that the fraction of particles hitting the electrode surface is proportional to the area of the projection or "shadow" of the electrode surface on the "diffusion sphere". This area (in Fig 4, see dotted arc on the "diffusion sphere" drawn in light grey) is generated by those particles that move away from A following a radius and are intercepted by the electrode surface (dark grey upper circle). Notice that in Fig 4 the 2-D dotted arc is the section of the "shadowed" casket (3-D, not drawn), whose area is the relevant one. Then, the fraction of particles hitting the electrode surface (or probability of hit p_{hit}), can be computed as a ratio of areas:

$$P_{hit} = \frac{\text{"shadowed" casket area}}{\text{diffusion sphere area}} \quad (30)$$

Depending on the relationship between R , Δr and r_0 , two cases arise. The first case, which could be called "small shielding case" arises when no radius of the "diffusion sphere" pointing to the shadowed casket area is tangent to the electrode surface and is depicted in Fig 4. For this case, elementary geometrical reasonings lead to:

$$P_{hit, small\ shielding} = \frac{1}{2} - \frac{R}{4\Delta r} + \frac{(r_0^2 - \Delta r^2)}{4R\Delta r} \quad \text{for} \quad \Delta r^2 + r_0^2 < R^2 \quad (31)$$

The second case, depicted in Fig 5, could be called "large shielding". The projection of the electrode surface on the "diffusion sphere" includes all the radius in between the extreme cases of tangent radii. For this case:

$$P_{hit,large\ shielding} = \frac{1}{2} \left[1 - \sqrt{1 - \frac{r_0^2}{R^2}} \right] \quad \text{for} \quad \Delta r^2 + r_0^2 \geq R^2 \quad (32)$$

where no dependence on Δr appears, as p_{hit} is just related to the solid angle with which the whole electrode is seen from A. In particular, if A lies just on the electrode surface, 1/2 of the particles would hit the electrode, as expected for planar diffusion. But, when A moves away from the electrode surface the probability of the particles hitting the electrode decreases as some of them follow radii not intercepting its surface. These results answer the key question: due to the spherical diffusion not all the particles (nor just 1/2 of them) at a given $R < \Delta r + r_0$ hit the electrode surface, but there is a functional dependence involving R , Δr and r_0 .

Let us now derive the kinetic flux J_{kin} from the hitting probabilities just found. For simplicity, we assume a uniform c_{ML}^* for all spatial points (this will overestimate J_{kin} in a labile case as seen in see Fig 3). The number of moles n_{hit} of kinetically generated M crossing the electrode surface per unit of time can, then, be computed as:

$$n_{hit} = k_d c_{ML}^* \left[\int_{r_0}^{\sqrt{\Delta r^2 + r_0^2}} P_{hit,large\ shielding} 4\pi R^2 dR + \int_{\sqrt{\Delta r^2 + r_0^2}}^{r_0 + \Delta r} P_{hit,small\ shielding} 4\pi R^2 dR \right] \quad (33)$$

Using expressions (31) and (32) for the probability and integrating, we find

$$n_{hit} = k_d c_{ML}^* \pi r_0^2 \Delta r \quad (34)$$

Thus, the kinetic flux can be computed as:

$$J_{kin} = \frac{n_{hit}}{4\pi r_0^2} = \frac{1}{4} \Delta r k_d c_{ML}^* \quad (35)$$

which indicates that the kinetic flux is independent of r_0 . Notice that the expression

$$n_{hit} = k_d c_{ML}^* \frac{4\pi}{3} [(r_0 + \Delta r)^3 - r_0^3] \text{ cannot be used, except for the case } \Delta r \ll r_0.$$

On the other hand, the diffusional flux

$$J_{dif} = \frac{D_{ML} c_{ML}^*}{r_0} \quad (36)$$

clearly increases monotonically with decreasing r_0 .

The lability condition could be formulated by imposing [2,23,29] a higher kinetic flux (J_{kin}) than diffusional one (J_{dif}). Using eqn (29) for Δr with $\Delta t_M = \frac{1}{k_a c_L^*}$ in the

expression of J_{kin} (35), the result is

$$r_0 > \frac{4}{\sqrt{6}} \frac{D_{ML}}{\sqrt{D_M}} \frac{\sqrt{k_a c_L^*}}{k_d} \quad (37)$$

which only differs from the analytically found expression (28) by a numerical coefficient close to unity. The criterion again indicates that decreasing r_0 always diminishes lability.

2.2.3. Derivation of the lability criterion using the reaction layer concept

As in some derivations of lability criteria the reaction layer concept has been used, let us revisit now this issue. Several definitions of reaction layer [30-33] have been given. In this work, we adhere to the operational concept of reaction layer, based on the decomposition of the total current into a "free metal contribution (inert)" and a "kinetic current", which can be expressed in terms of fluxes as:

$$J_{total} = J_{inert} + J_{kin} \quad (38)$$

The thickness of the reaction layer μ is a kinetic parameter [34-39], defined such that:

$$J_{kin} = c_{ML}^* k_d \mu \quad (39)$$

In steady state spherical diffusion, the results from random walk analysis in section 2.2.2 support the interpretation of μ as the mean distance travelled by the free metal ion during its life time Δt_M [27,32]: it suffices to compare eqns (35) and (39) while neglecting numeric factors (close to 1) . Thus, the reaction layer can be physically understood as the region from where the electroactive species generated due to the complex dissociation is able to contribute to the current [34].

The computation of μ for steady-state spherical diffusion can be done, for the simplest case, following the procedure used in planar diffusion [33] with the appropriate corrections. The key difference is that the spherical geometry can maintain a steady state for c_M based on diffusion alone ($J_{inert} = D_M c_M^* / r_0$), while the planar cannot (i.e. in planar geometry all the current is a kinetic current as $J_{inert}=0$ in steady state for semi-infinite diffusion as the sole transport mode). For simplicity, we use excess of ligand and a uniform c_{ML}^* for all spatial points (as done for the random walk derivation of the lability criterion). Solving equation (3) for c_M with $c_L(r) \approx c_L^*$ and $c_{ML}(r) \approx c_{ML}^*$ under steady state conditions ($\partial c_M / \partial t = 0$), we obtain

$$c_M = c_M^* \left(1 - \frac{r_0}{r} e^{-\sqrt{\frac{k_a c_L^*}{D_M}}(r-r_0)} \right) \quad (40)$$

from which the flux can be computed as:

$$J_{total} = D_M \left(\frac{\partial c_M}{\partial r} \right)_{r=r_0} = D_M c_M^* \left(\frac{1}{r_0} + \sqrt{\frac{k_a c_L^*}{D_M}} \right) \quad (41)$$

Now we can identify the terms corresponding to the contribution due to pure spherical diffusion of c_M and the kinetic contribution due to the dissociation of c_{ML} along the reaction layer (J_{kin}):

$$J_{total} = \frac{D_M c_M^*}{r_0} + D_M c_M^* \sqrt{\frac{k_a c_L^*}{D_M}} = J_{inert} + c_{ML}^* k_d \sqrt{\frac{D_M}{k_a c_L^*}} = J_{inert} + J_{kin} \quad (42)$$

By comparison with the operational definition (39), we find that the thickness of the diffusion layer for steady state spherical diffusion coupled with a first order homogeneous reaction is

$$\mu = \sqrt{\frac{D_M}{k_a c_L^*}} \quad (43)$$

in coincidence with the same well-known result [32,33] for planar symmetry, excess ligand and $\varepsilon K' > 1$. This value for μ , combined with the diffusional flux expression (36), has been successfully used [18] in the derivation of the lability criterion (28) (found from the analytical solution for the current). However, it must be pointed out that in steady state spherical diffusion, regardless of the relative sizes of μ and r_0 , the kinetic flux must be computed combining eqns (39) and (43).

Conclusions

From inspection of the continuity equations of the metal-ligand system in spherical geometry, it has been concluded that diffusion towards the microelectrode is enhanced when the electrode radius r_0 decreases, while the kinetic terms are unaltered. Thus, a decrease in r_0 favours the kinetic contribution and tends to reduce the lability of the metal complex system. This result can also be applied to microelectrodes other than the spherical or hemispherical ones, on which the discussion has been focused. For not too fast kinetics of complexation, the free metal ion concentration might be directly sensed

using sufficiently small microelectrodes from normalised currents at a flat region in the plot ϕ vs r_0 .

The analytical solution of the problem for steady state spherical diffusion can be derived for the ligand excess case (see Appendix). An important result is that the normalised current depends only on three parameters: ε , K' and κ_a (see eqn. (A-7)). The latter parameter (given by eqn (17)) is the non-dimensional rate constant and includes r_0^2 as a factor multiplying k_a , thus expressing that in terms of kinetic effects a decrease in r_0 is equivalent to a decrease in k_a . From the analytical expression for the normalised current (see eqn. (16)), a rigorous lability criterion (eqn (24)) is found, which (for large $\varepsilon K'$) is equivalent to the one already previously found in the literature. Practically the same criterion (see eqn. (37)) can also be obtained from an alternative derivation making use of a statistical random walk approach. Such analysis demonstrates that the probability of reaching the electrode surface depends on the position of the metal ion (produced from dissociation of complex) with respect to the electrode surface. For spherical geometry, steady state, excess of ligand, pseudo first order reaction and no complex depletion, the expression for the reaction layer thickness μ (43) is the same as the well-known expression for planar geometry. The reaction layer concept can be used to successfully derive a lability criterion which is essentially the same as that obtained with the analytical solution (27) or the random walk approach (37).

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Appendix: Steady state current for the "kinetic" case under spherical diffusion and ligand excess.

We need to solve the steady state analogues of eqns. (3)-(5) with no-time dependency and the ligand excess condition (12). In fact, the latter condition renders the continuity equation (4) unnecessary and implies the crucial linearisation of the remaining equations (for the bulk concentrations see eqn. (13)).

Apart from (10), we introduce the following dimensionless variables:

$$\theta \equiv \frac{c_M}{c_M^*} \qquad \lambda \equiv \frac{c_{ML}}{c_{ML}^*} \qquad (A-1)$$

where the spatial dependence (such as $\theta(\rho)$) is not explicated.

With these dimensionless variables, eqn. (3) for steady-state can be written:

$$0 = \frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d\theta}{d\rho} \right) + \frac{k_a c_L^* r_0^2}{D_M} (\lambda - \theta) \qquad (A-2)$$

which suggests the introduction of the dimensionless kinetic constant κ_a given by (17).

Summation of eqns.(A-2) and (5) (using the dimensionless variables) cancels out the kinetic terms:

$$0 = \frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d}{d\rho} (\theta + \varepsilon K' \lambda) \right) \qquad (A-3)$$

The boundary conditions are:

$$\rho = 1 \qquad \theta = 0 \qquad \frac{d\lambda}{dx} = 0 \qquad (A-4)$$

$$\rho \rightarrow \infty \qquad \theta = 1 \qquad \lambda = 1 \qquad (A-5)$$

The magnitude sought is ϕ , given by (14), which can be expressed:

$$\phi = \frac{1}{1 + K'} \left(\frac{d\theta}{d\rho} \right)_{\rho=1} \qquad (A-6)$$

From this re-formulation of the problem, it is easy to deduce that the solution depends just on 3 parameters:

$$\phi = \phi(\varepsilon, K', \kappa_a) \quad (\text{A-7})$$

The solution of eqn. (A-3), taking into account the boundary values, is:

$$\theta + \varepsilon K' \lambda = -\frac{1}{\rho} \left(\frac{d\theta}{d\rho} \right)_{\rho=1} + 1 + \varepsilon K' \quad (\text{A-8})$$

Substitution of the expression of λ (isolated from (A-8)) into (A-2), and introduction of the new variable $\omega = \rho\theta$, yields

$$\frac{d^2\omega}{d\rho^2} - \kappa_a \left(\frac{1}{\varepsilon K'} + 1 \right) \omega - \frac{\kappa_a}{\varepsilon K'} \left(\frac{d\theta}{d\rho} \right)_{\rho=1} + \kappa_a \left(\frac{1}{\varepsilon K'} + 1 \right) \rho = 0 \quad (\text{A-9})$$

Its solution, in terms of 2 integrations constants C_1 and C_2 is:

$$\omega = C_1 e^{-\sqrt{\kappa_a \left(\frac{1}{\varepsilon K'} + 1 \right)} \rho} + C_2 e^{\sqrt{\kappa_a \left(\frac{1}{\varepsilon K'} + 1 \right)} \rho} - \frac{1}{1 + \varepsilon K'} \left(\frac{d\theta}{d\rho} \right)_{\rho=0} + \rho \quad (\text{A-10})$$

As θ is bounded, $C_2=0$. The boundary condition $\theta=0$ at $\rho=1$ requires

$$C_1 = \frac{\left(\frac{d\theta}{d\rho} \right)_{\rho=1} - (1 + \varepsilon K')}{(1 + \varepsilon K') e^{-\sqrt{\kappa_a \left(\frac{1}{\varepsilon K'} + 1 \right)}}} \quad (\text{A-11})$$

Computing $\left(\frac{d\theta}{d\rho} \right)_{\rho=1}$ from the newly found solution, one can finally obtain:

$$\left(\frac{d\theta}{d\rho} \right)_{\rho=1} = 1 + \frac{\varepsilon K' \sqrt{\kappa_a}}{\sqrt{\varepsilon K' (1 + \varepsilon K')} + \sqrt{\kappa_a}} \quad (\text{A-12})$$

which, through substitution into (A-6), leads to (16).

The same result can be derived from the work of Oldham [40], imposing zero flux for one of the "interconverting isomers" (see eqn. (18) in ref. [40]) and zero concentration for the other interconverting isomer.

After some algebra, it can also be seen that the normalised profile of complex is:

$$\lambda = 1 - \frac{\sqrt{\kappa_a}}{\rho(\sqrt{\varepsilon K'}(1 + \varepsilon K') + \sqrt{\kappa_a})} - \sqrt{\frac{\varepsilon K'}{1 + \varepsilon K'}} \frac{\left(1 - e^{-(\rho-1)\sqrt{\frac{\kappa_a(1+\varepsilon K')}{\varepsilon K'}}}\right)}{\rho(\sqrt{\varepsilon K'}(1 + \varepsilon K') + \sqrt{\kappa_a})} \quad (\text{A-13})$$

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Figure Captions

Fig 1 : Impact of the rate constants on the lability. Plot of the normalised current (ϕ given by (16)) expected for three systems sharing $\epsilon=0.1$, $K'=10^2$ and $D_M=10^{-9} \text{ m}^2\text{s}^{-1}$ vs. the logarithm of the electrode radius r_0 . Solid line: $k_d=10^{-2} \text{ s}^{-1}$; dashed line: $k_d=1 \text{ s}^{-1}$; dotted line: $k_d=10^2 \text{ s}^{-1}$.

Fig 2 : Plot of the "degree of lability" ξ (see eqn (20)) vs. the electrode radius r_0 (notice its logarithmic scale). Data corresponding to Ni^{2+} complexation (see figure 4 in ref [18]): $\epsilon K'=10$, $D_M=10^{-9} \text{ m}^2\text{s}^{-1}$; $k_a=10^5 \text{ M}^{-1}\text{s}^{-1}$ and $c_L^*=10^{-5} \text{ M}$

Fig 3 : Impact of the lability on the normalised profiles of complex ($\lambda \equiv c_{\text{ML}} / c_{\text{ML}}^*$ versus $\rho \equiv r / r_0$) with data as in Fig 2. Continuous upper line: $r_0=10 \mu\text{m}$ (yielding $\xi \approx 0.03$); dashed line: $r_0=0.1 \text{ mm}$ (yielding $\xi \approx 0.23$) and dotted lower curve: $r_0=1 \text{ mm}$ (yielding $\xi \approx 0.75$). Notice the relationship (26) between ξ and the concentration of complex at the electrode surface. λ has been computed analytically using the solution (A-13).

Fig 4 : Schematic representation (in a planar section) of the diffusion of N particles from A towards the electrode surface (upper small circle of radius r_0 , drawn with continuous line). The fraction of particles hitting the electrode surface is assumed to be proportional to the area (shown with "bullets") projected by the electrode on the "diffusion sphere" (large circle of radius Δr drawn with dashed line).

Fig 5 : Case of "large shielding": the electrode surface intercepts a relatively large amount of radii. Same conventions as in Fig 4. A radius of the "diffusion sphere" tangent to the electrode surface is also depicted.

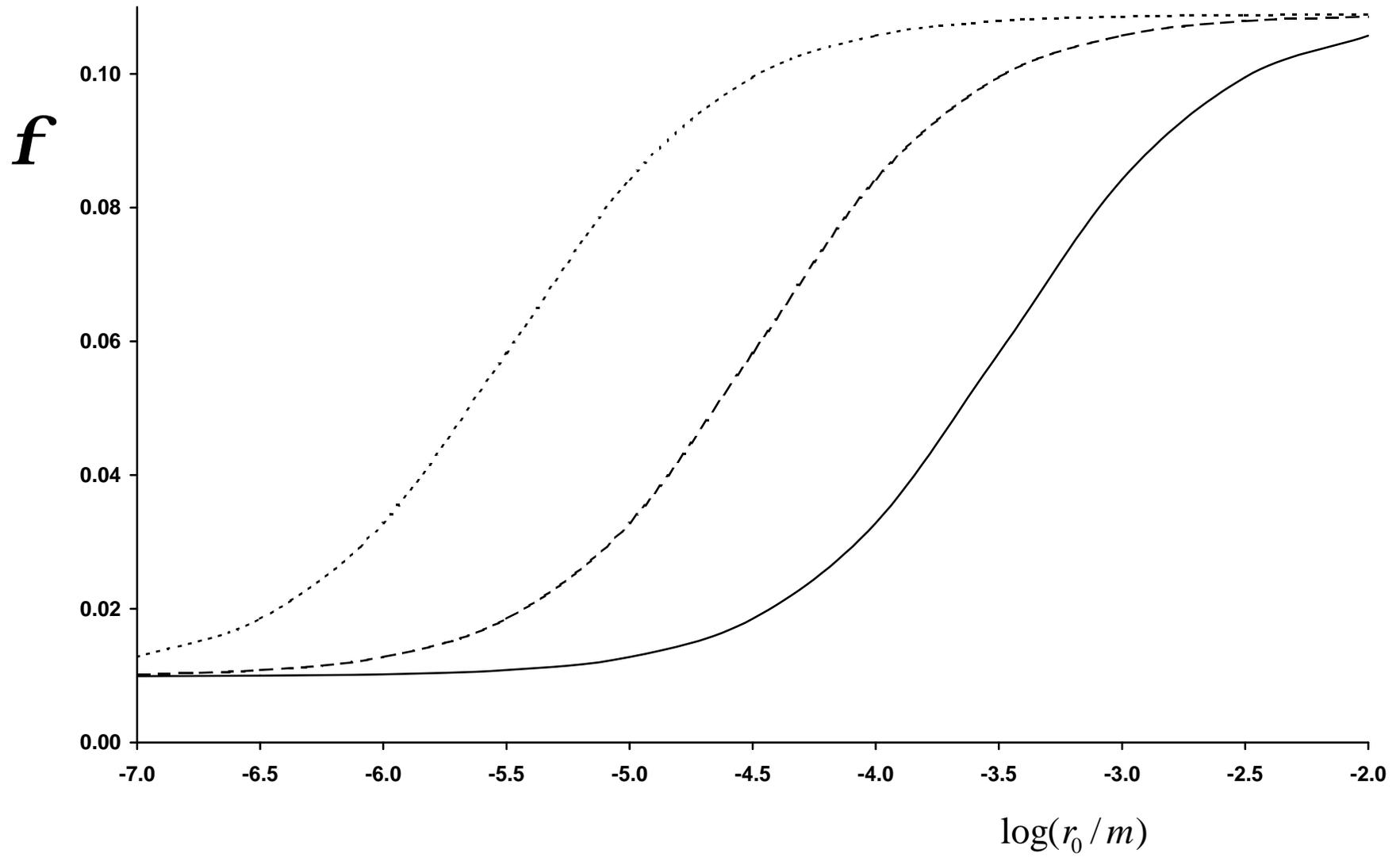


Fig 1

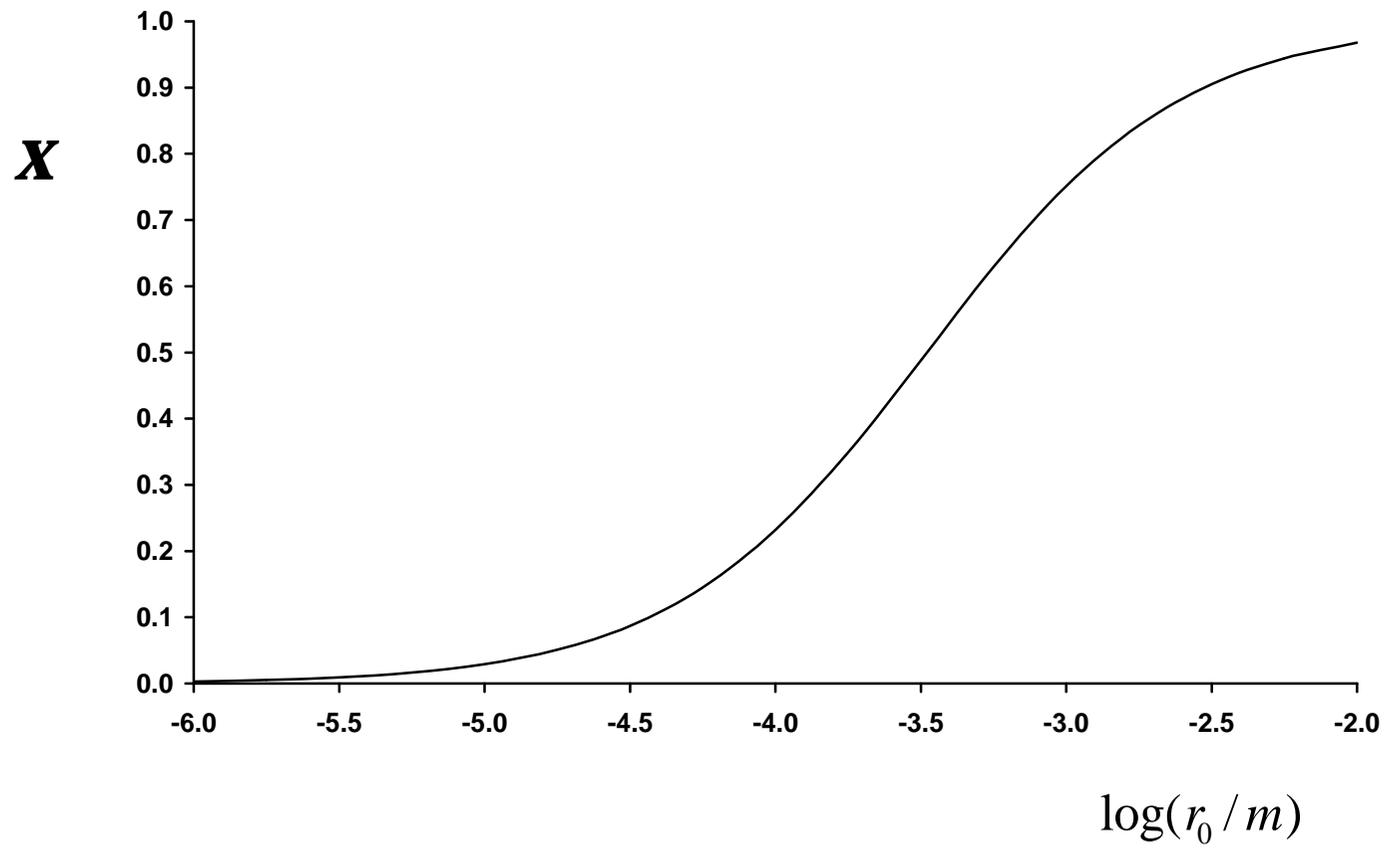


Fig 2

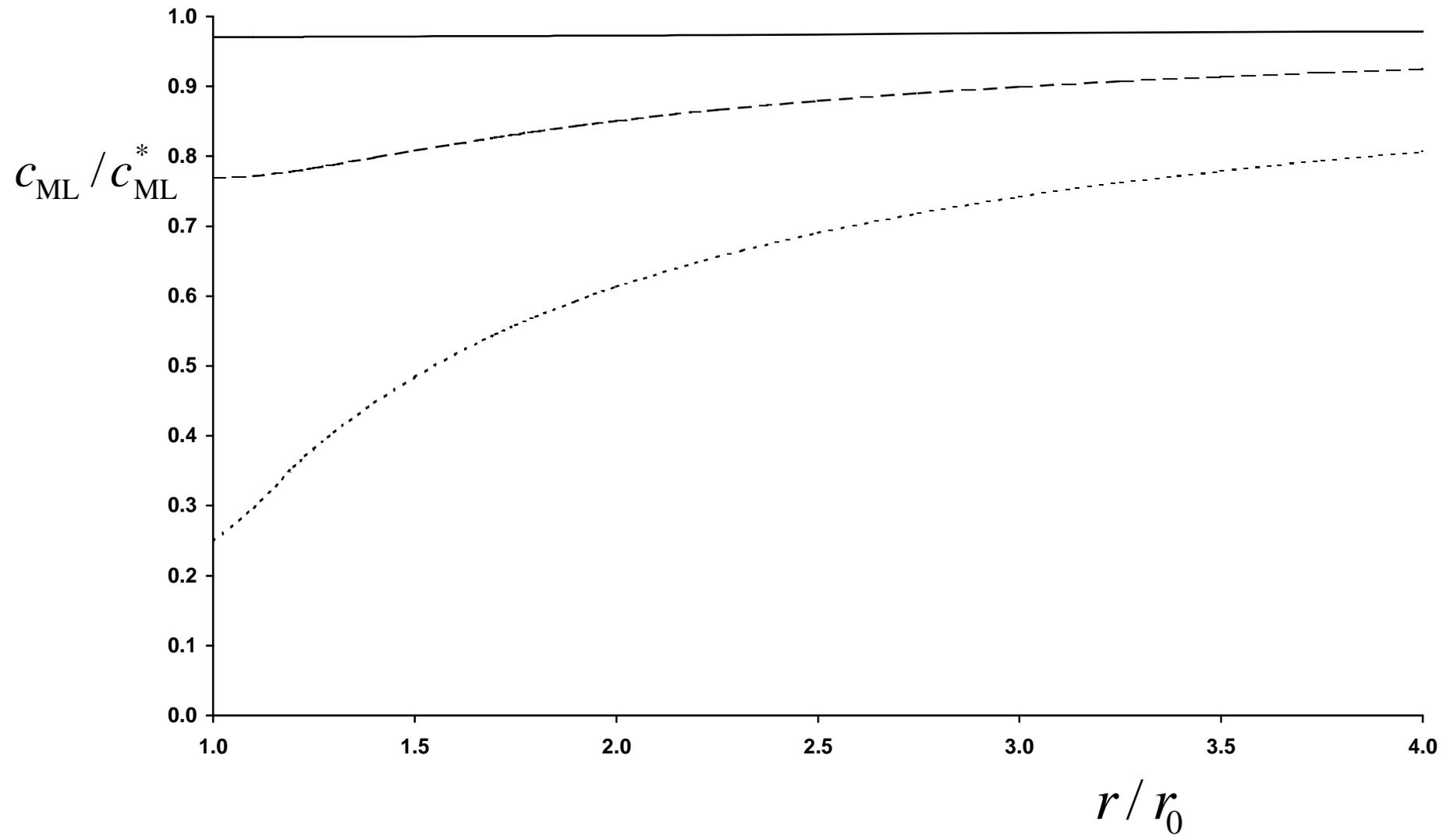


Fig 3

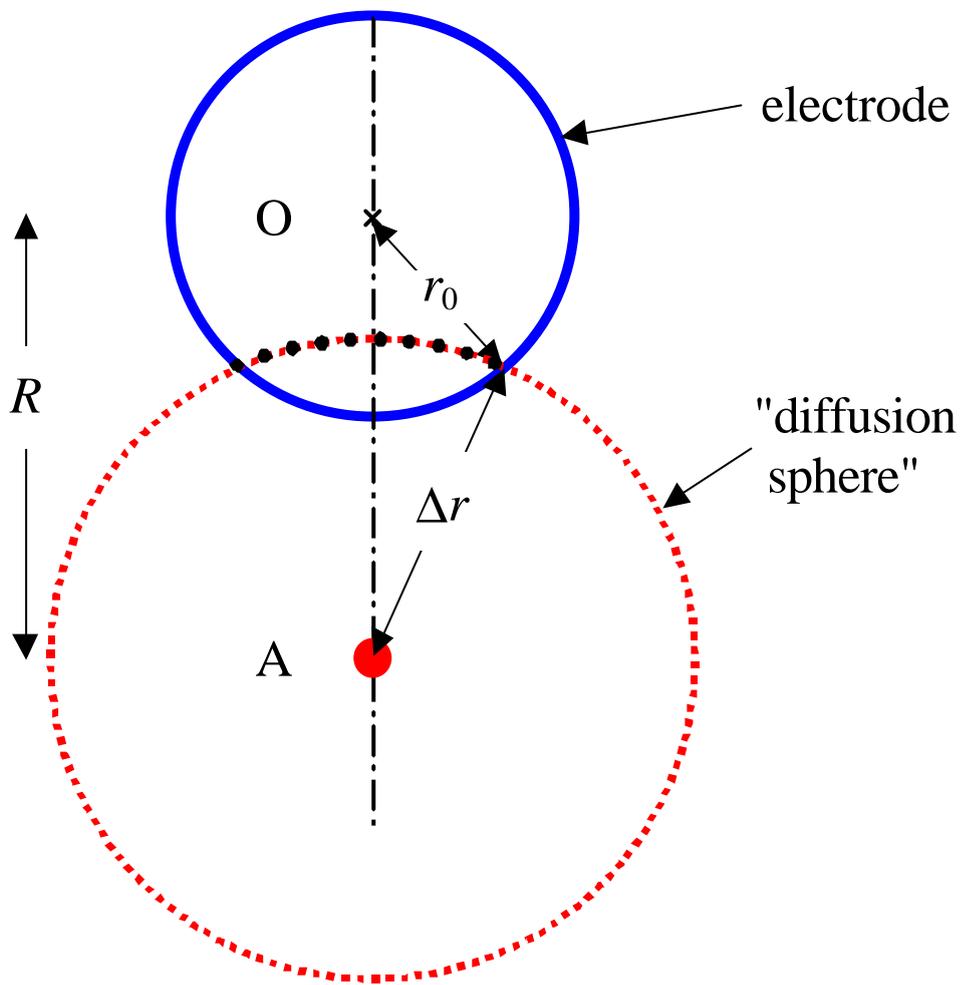


Fig 4

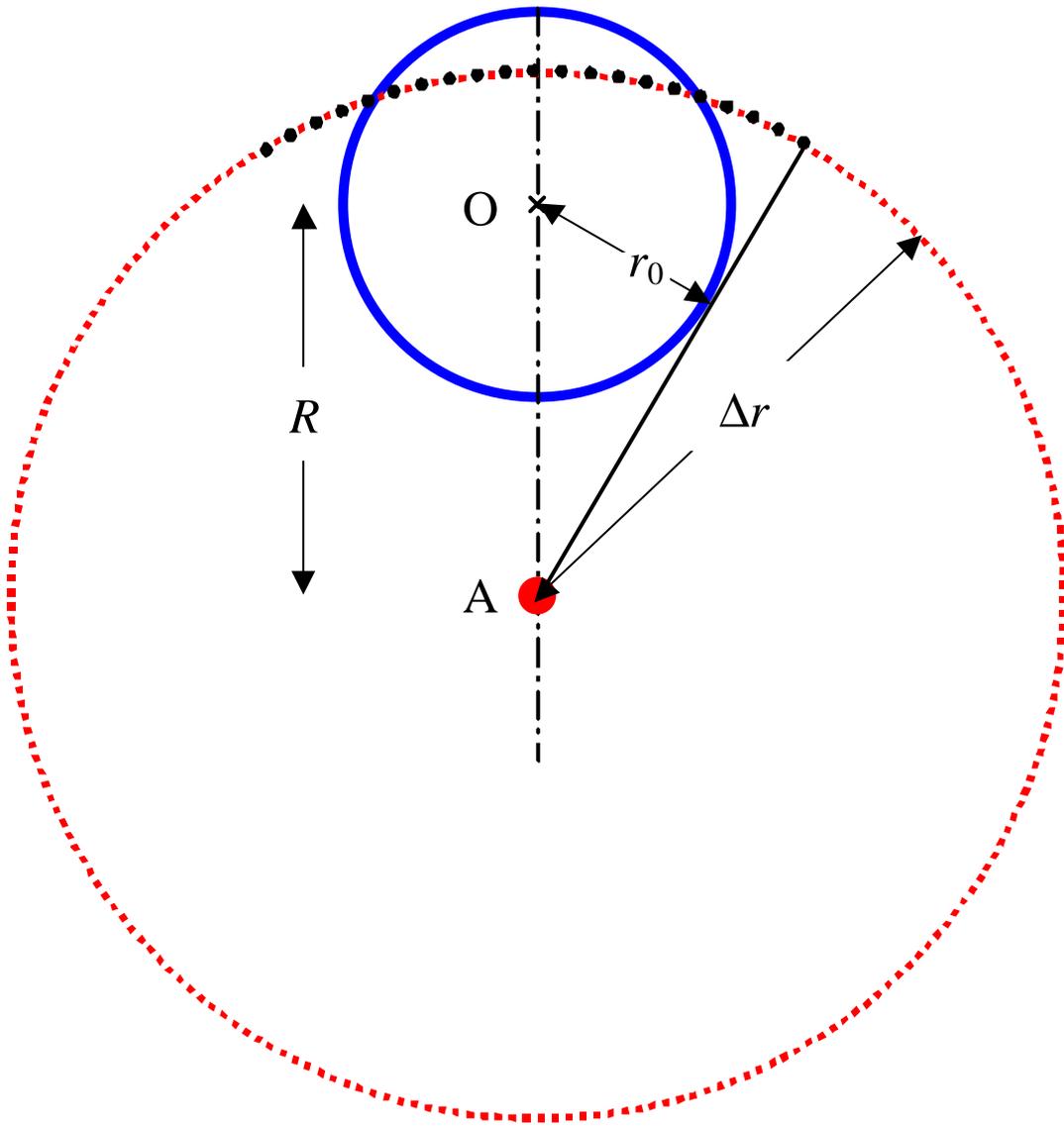


Fig 5