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Metal speciation dynamics in colloidal ligand dispersions. Part 2: Electrochemical lability

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Abstract

We investigate the dynamic nature of metal speciation in colloidal dispersions using a recently proposed theory [J.P. Pinheiro, M. Minor, H.P. Van Leeuwen, Langmuir, 21 (2005) 8635] for complexing ligands that are situated on the surface of the particles. The new approach effectively modifies the finite rates of association/dissociation of the colloidal metal complexes, thus invoking consideration of the two basic dynamic criteria: the association/dissociation kinetics of the volume complexation reaction (the "dynamic" criterion), and the interfacial flux of free metal to a macroscopic surface due to dissociation of complex species (the "lability" criterion). We demonstrate that the conventional approach for homogeneous systems that assume a smeared-out ligand distribution, overestimates both the dynamics and the lability of metal complexes when applied to colloidal ligands. It is also shown that the increase of lability with increasing particle radius, as expected for a homogeneous solution, is moderated for spherical microelectrodes and practically eliminated for planar electrodes.
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Keywords: Metal speciation; Colloidal ligands; Lability; Dynamic; Diffusion controlled reactions

1. Introduction

An accurate conceptual framework for metal speciation is necessary to understand the interaction between the different metal species and their reactivity, mobility and bioavailability. In aquatic systems, metal ions are typically distributed over a variety of complexes with dissolved ligands and dispersed particles, spanning a range of sizes, stabilities and labilities [2]. Natural aquatic systems are practically never at equilibrium, thus meaningful interpretation of metal speciation typically requires knowledge of dynamic aspects, i.e., 3-D kinetic features of the interconversion of metal complex species in the bulk solution, together with their relationship with the transport phenom-

ena associated with the selective consumption, usually of the free metal ion, at an interface. Electrochemical techniques have been extensively applied to the study of metal speciation in aquatic systems [3], with the advantage that the mathematical description of the metal fate often is largely similar for an electrode and a natural interface. Among these techniques, the various voltammetric stripping techniques are favored due to their low detection limit, and potential to supply detailed information about the dynamic nature of the system [3–7].

Until recently, the dynamic theories did not take into proper account the nature of colloidal ligands in aquatic systems. Often the ligand distribution was simply taken as homogeneous over the solution volume [8–12], whereas in colloidal systems the ligands are localized within the geometry of the particles. We have proposed a dynamic metal speciation theory which considers ligands that are localized on the surface colloidal particles. This theory

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Nomenclature

a (m) radius of the colloidal particle

C_i (mol m^{-3}) coarse-grained concentration of species i

$C_i(r,t)$ (mol m^{-3}) coarse-grained concentration of the species i at distance r from the consuming surface at time t

C_i^* (mol m^{-3}) coarse-grained concentration of species i in the bulk

C_T^* (mol m^{-3}) total metal coarse-grained concentration in the bulk

c_p (m^{-3}) particle number concentration in the volume V

D_i (m^2 s^{-1}) diffusion coefficient of the species i in solution

d (m) thickness of the ligand layer in the colloidal particle

$J^*(t)$ (mol m^{-2} s^{-1}) time dependent overall metal flux into the electrode

K (mol^{-1} m^3) complexation constant

K' effective complexation constant ($=Kc_{L,T}$)

k_a (mol^{-1} m^3 s^{-1}) formation rate constant of the complex ML ($=k_{-w}K_{os}$)

k_a' (s^{-1}) effective formation rate constant of ML ($= k_a'c_{L,T}$)

k_a^* (mol^{-1} m^3 s^{-1}) generalized formation rate constant of the complex ML

k_d (s^{-1}) dissociation rate constant of the complex ML

k_d^* (s^{-1}) generalized dissociation rate constant of the complex ML

K_{os} (mol^{-1} m^3) stability constant for outer-sphere complexes

k_{-w} (s^{-1}) water loss rate constant

r_0 (m) radius of the electrode

t_z (s) time for a microelectrode to reach steady-state within z percent

z_i valence of the species i

Greek symbols

ε ratio of the diffusion coefficients of bound and free metal

Λ Lability parameter in the transient flux

δ (m) thickness of the diffusion layer of the consuming surface

ξ dynamic parameter in steady-state flux

κ_a^* non-dimensional association constant

μ (m) reaction layer thickness

---

correctly predicts the formation/dissociation rate constants that were shown to differ by several orders of magnitude from those for the homogeneous solution with the same total amount of ligands [1]. The difference between colloidal dispersions and homogeneous systems appeared to be due to an evolution from a chemically controlled release of the metal to a diffusion controlled one, and derives from the differences in spatial ligand distribution. The objective of this work is to apply the new theoretical approach in reconsidering the dynamic nature and lability of colloidal metal complexes, and to compare these features to those for homogeneous solutions.

2. Theory

Let us consider the scheme of a metal ion M which can: (i) associate with a ligand L to form an electroinactive complex ML, and (ii) be reduced to the metal atom, M^0, at an electrode:

$$M + L \underset{k_a}{\overset{k_d}{\leftrightarrows}} ML$$
$$ne^- \downarrow\uparrow \tag{1}$$
$$M^0,$$

where k_a and k_d are the rate constants of complex formation and dissociation, respectively. Under conditions of diffusion controlled mass transport, the flux of M towards the interface can be found by solving the pertaining conservation equations for the different species

$$\partial c_i / \partial t = D_i \nabla^2 c_i \pm (k_d c_{ML} - k_a c_M c_L), \tag{2}$$

under proper initial and boundary conditions. Here, $i = $ M, L or ML and the sign of the final term is + for $i = $ M or L and − for ML. The final term in Eq. (2) is the chemical source term due to the association and dissociation of complex species. Around the electrode, a diffusion layer develops which may grow continuously or reach a steady-state value, depending on the size/shape of the collecting surface and the hydrodynamic conditions. Conductive transport is negligible due to the high background electrolyte concentration used in electrochemical experiments.

2.1. Association/dissociation reactions in colloidal dispersions

For low molar mass ligands, k_a is generally consistent with a mechanism in which formation of an outer-sphere complex between the metal and the ligand, with an electrostatically defined stability constant (K_{os}), is followed by a rate-limiting removal of water from the inner coordination sphere of the metal (k_{-w}), commonly known as the Eigen mechanism [13]. In colloidal ligand systems, the concentrations of ligand and bound metal are constrained by the particle geometry. Consequently, the reaction of M with L is subject to diffusion limitations that are different from those in a homogeneous ligand solution. In our recent theory [1], we considered the case where the complexing ligands are localized in a thin shell of thickness d around a spherical particle of radius a. To mathematically define the discontinuous

local concentrations, the conservation equations were reformulated in terms of average, "coarse-grained" concentrations (C_i). An analytical solution was obtained under the following approximations:

- Donnan potentials and double layer effects inside the ligand domain are insignificant;
- there is sufficient excess of ligand over metal, such that the coarse-grained ligand concentration is constant;
- the thickness of the diffusion layer adjacent to the electrode is much larger than the radius of the colloidal particles;
- the ligand layer is much thinner than the particle radius ($d/a \ll 1$), and
- the solution is sufficiently diluted such that individual diffusion layers around neighboring particles do not overlap.

Under these approximations the problem can be written in terms of an equation formally identical to Eq. (2) with modified association and dissociation rate constants k_a^* and k_d^*, defined by:

$$k_a^{*\prime} = k_a^\prime / \left(1 + k_a^\prime \left(4\pi a D_M c_p \right)^{-1} \right) \tag{3a}$$

$$k_d^* = k_d / \left(1 + k_a^\prime \left(4\pi a D_M c_p \right)^{-1} \right) \tag{3b}$$

where D_M is the diffusion coefficient of the metal and c_p is the particle number density. For conditions of excess of ligand, $k_a^{*\prime}$ is defined as:

$$k_a^{*\prime} = k_a^* C_L \quad \text{and} \quad K^\prime = k_a^{*\prime}/k_d^* = K C_L \tag{4}$$

where K is the stability constant of ML, which is assumed to be the same as for the homogeneous solution [1]. The term $k_a^\prime \left(4\pi a D_M c_p \right)^{-1}$ in Eq. (3) can be interpreted as the

ratio of two characteristic times (τ_d/τ_a) which compares the residence time and the mean life time of a free metal ion in the shell layer [1]. The differences between k_d^* and k_d, and k_a^* and k_a, are mainly due to evolution of a chemically controlled reaction (for a homogeneous solution), into a diffusion controlled one (for a colloidal ligand dispersion), as resulting from differences in spatial ligand distribution.

2.2. Dynamic speciation in colloidal ligand systems

Analogous to concepts applied to homogeneous solutions [13], colloidal complex systems are considered dynamic if equilibrium is fully maintained on the relevant time scale and static in the opposite case:

$$k_a^{*\prime}t, k_d^*t \gg 1 \quad \text{dynamic}, \tag{5a}$$

$$k_a^{*\prime}t, k_d^*t \ll 1 \quad \text{static}. \tag{5b}$$

We emphasize that these conditions refer to the volume properties of the system. The expressions for the rate constants effective in colloidal dispersions, $k_a^{*\prime}$ and k_d^*, are given by Eq. (3) which presents two noteworthy limiting cases (Fig. 1):

- *the kinetic limit*, corresponding to the situation, where $\tau_d/\tau_a \ll 1$, and $k_a^{*\prime}$ and k_d^* are equal to $k_a^\prime$ and k_d. This occurs for metals with relatively low formation rate constants (low k_{-w}) and/or systems with small particles.
- *the diffusive limit* with $\tau_d/\tau_a \gg 1$, meaning that the free metal ion frequently reassociates within the same particle, i.e., the rate of reassociation of the metal is much larger than the rate of diffusion away from the particle. This latter diffusion process then becomes the rate-limiting step. This occurs for metals with relatively high k_{-w}
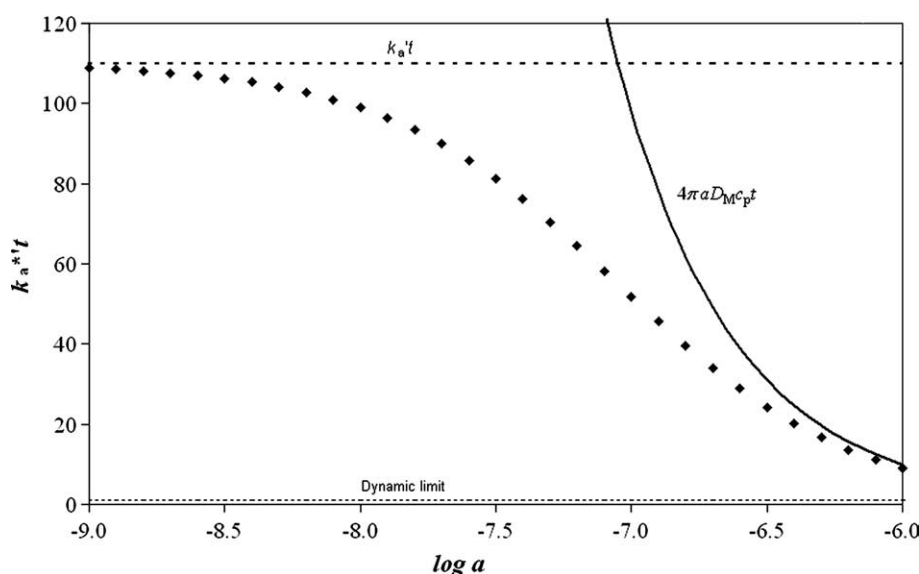

Fig. 1. $k_a^{*\prime}t$ variation with particle radius, a (in m), for cadmium (II) (◆) calculated using Eq. (3a), and the diffusion (full line) and kinetic (dotted line) limits in the presence of 10^{-1} mol m^{-3} binding sites and ionic strength 0.01 M. Other parameters: $t = 0.1$ s, $D_{Cd} = 7.00 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Cd)} = 3 \times 10^8$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$).

values and/or sufficiently large colloidal particles. Note that at this limit $k_a^{*'}$ and k_d^{*} become $4\pi a D_M c_p$ and $4\pi a D_M c_p/K'$, respectively, i.e., depending on the diffusion parameters while being independent of the association rate constant (k_a).

In Fig. 1, we depict the change in $k_a^{*'}t$ as caused by variation of the particle radius, a. We note that changing a at a constant overall ligand concentration C_L, requires a corresponding variation of particle number (c_p). The figure shows the transition from the kinetic limit to the decreasing diffusion limit with increasing particle radius. The magnitude of the difference between k_a and k_a^{*} may be several orders of magnitude, hence complexes with colloidal ligands will become less dynamic, or even static with increased particle radius.

2.3. Metal transport towards an electrode

To estimate the magnitude of the contribution from dissociating complexes to the flux of metal towards the electrode, it is necessary to compare the macroscopic diffusive and kinetic fluxes. The limit where the complexed metal fully contributes to the flux is the *labile* case, whereas the case of limiting complex dissociation is the *non-labile* case [14].

In order to obtain the solution of the generic Eq. (2) for a particular system, we must apply the relevant geometrical constraints and boundary conditions. Here we shall consider a system with:

- a spherical electrode, with radius r_0;
- semi-infinite diffusion, and negligible bulk depletion;
- excess ligand condition (as before);
- fully reversible reduction of M–M^0;
- limiting flux conditions, $c_M = 0$ for $r = r_0$, which can be approximated by $C_M = 0$ for $r = r_0$ as long as the colloidal dispersion is sufficiently diluted such that individual diffusion layers around neighboring particles do not overlap [1];
- electroinactive complex species (($\partial C_i/\partial x) = 0$ at r_0 for i = ML, L) and
- far away from the electrode surface or at $t = 0$ the bulk concentrations are related by the equilibrium constant.

Using these constraints Eq. (2) reduces to:

$$\frac{\partial C_i(r,t)}{\partial t} = D_i\left(\frac{\partial^2 C_i(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_i(r,t)}{\partial t}\right) \pm (k_d^* C_{ML}(r,t) - k_a^{*'} C_M(r,t)) \qquad (6)$$

where i = M or ML and the sign of the final term is + for i = M and − for ML. The overall metal flux at the electrode surface is then:

$$J^*(t) = D_M(\partial C_M(0,t)/\partial r) \qquad (7)$$

A generic solution to this equation includes transient elements and steady-state elements. These figure in the expression of the diffusion layer thickness as $\delta(t)$ and r_0,

respectively, where $\delta(t)$ in the planar case equals $(\pi D_M t)^{1/2}$. This blend of transient and quasi steady-state elements by and large renders an analytical solution impossible. For the transient limit with $(\pi D_M t)^{1/2}$ well below r_0, a solution in the Laplace domain was presented, either without [15] or with [16,17] allowance for different diffusion coefficients of M and ML. An analytical solution could only be obtained for dynamic systems ($k_a^{*'}t, k_d^* t \gg 1$). The steady-state flux limit, $(\pi D_M t)^{1/2} \gg r_0$, is best approximated by a spherical microelectrode, and for this case an analytical solution was derived by Galceran et al. [18]. Here we will pursue our analysis of the colloidal ligand system for the two limiting cases of Eq. (2) for which analytical solutions are available, i.e, the steady-state approximation ($\partial C_M/\partial t = 0$) (microelectrode), and the transient case for dynamic systems.

2.4. Steady-state limit

Small disk or spherical microelectrodes have been gaining importance in trace metal studies due to their unique properties, such as a decreased ohmic potential drop, enhanced mass transport and the fast establishment of a steady-state signal [19]. However, the assumption of steady-state imposes a rather strong restriction on the microelectrode radius. According to Zoski et al. [20] the time interval to reach steady-state (t_z) within a deviation of z percent is given by $t_z = r_0^2/(\pi D(z/100)^2)$. Applying this expression for a 5% deviation from steady-state flux and a 5 μm radius electrode (smallest microelectrode commercially available) it would take 3.2 s to reach steady-state. Therefore, even for microelectrodes, neglecting the transient term should be considered with due care.

The universal solution of Eq. (6) for steady-state ($\partial C_M/\partial t = 0$) as presented by Galceran et al. [18] is:

$$J^* = \frac{D_M C_T^*(1+K')^{-1}}{r_0}\left(1 + \frac{\varepsilon K'\left(\kappa_a^{*'}\right)^{1/2}}{(\varepsilon K'(1+\varepsilon K'))^{1/2} + \left(\kappa_a^{*'}\right)^{1/2}}\right) \qquad (8)$$

where $C_T^* = C_M^* + C_{ML}^*$, $\varepsilon = D_{ML}/D_M$ and $\kappa_a^{*'}$ is the dimensionless association constant given by:

$$\kappa_a^{*'} = k_a^{*'} r_0^2/D_M = (r_0/\mu)^2. \qquad (9)$$

Analysis of Eq. (8) reveals that the kinetic information is contained in the parameter denoted by Galceran et al. [18] as the "degree of lability", ξ:

$$\xi = \frac{\left(\kappa_a^{*'}\right)^{1/2}}{(\varepsilon K'(1+\varepsilon K'))^{1/2} + \left(\kappa_a^{*'}\right)^{1/2}} \qquad (10)$$

which actually incorporates features of both dynamics and lability. Let us consider the various limiting cases. The static limit occurs for $\kappa_a^{*'} \to 0$, implying that $\xi \to 0$ and the flux reduces to the flux of free metal:

$$J^* = D_M C_M^*/r_0 \qquad (11)$$

The fully labile situation arises when:

$$\kappa_a^{*\prime}/\varepsilon K'(1 + \varepsilon K') \gg 1, \tag{12}$$

which implies that ξ approaches 1. At this limit, the flux becomes independent of the kinetic parameters and is proportional to total metal:

$$J^* = \overline{D}C_T^*/r_0, \tag{13}$$

where $\overline{D}$ is the well-known mean diffusion coefficient of M and ML [21]:

$$\overline{D} = (1 + \varepsilon K')/(1 + K')D_M, \tag{14}$$

which holds under conditions of effectively complete preservation of the ML $\leftrightarrows$ M equilibrium over the diffusion layer.

The non-labile limit corresponds to the situation where $\kappa_a^{*\prime}$ is well below $\varepsilon K'(1 + \varepsilon K')$, where the flux becomes [18]

$$J^* = \frac{D_M C_M^*}{r_0}\left(1 + (\kappa_a^*)^{1/2}\right) = D_M C_M^*(1/r_0 + 1/\mu). \tag{15}$$

The term $1/\mu$ corresponds to the "kinetic current" derived by reaction layer theory [22]. The factor $(D_M/k_a^{*\prime})^{1/2}$ is the thickness of the classical reaction layer (μ) in the classical treatment. Within the present context, reaction layers are physically meaningful only if their thickness is well below that of the diffusion layer (r_0). It is easily shown [14] that violation of this condition comes to leaving the dynamic regime.

Fig. 2 shows the evolution of ξ with particle radius, a, for both colloidal ligand dispersions and the analogous homogeneous ligand solution for lead, cadmium and cobalt, with given values of K and C_L. Increasing the particle radius implies a decrease of D_{ML} (calculated using Stokes–Einstein equation for hard spheres) and a decrease of c_p if the value of C_L is kept constant whilst increasing a. We note that to correctly compare the colloidal ligand dispersion with the analogous homogeneous solution their diffusion coefficients (D_{ML}) must be equal. This implies that in the homogeneous solution we consider the ligands to be homogeneously distributed over the solution volume with mobility equal to that of the colloidal ligands in the dispersion. Up to now it was accepted for the homogeneous ligand solution, that a decrease in D_{ML} implied an increase in lability [17]. However, for colloidal ligand dispersions in which $k_a^{*\prime}$ is not fully kinetically controlled ($k_a^{*\prime} < k_a'$), $\kappa_a^{*\prime}$ decreases with increasing radius rendering the relation between ξ and a more involved than previously assumed. The effect of the variation of radius on $\kappa_a^{*\prime}$ is much more important for metals with high k_{-w} (lead, cadmium, mercury, copper) than for metals with lower k_{-w}, e.g., cobalt and nickel. For the latter category, $k_a^{*\prime}$ approaches k_a' for almost the whole range of values of a, as shown in Figs. 2 and 3. Fig. 2 shows that the overall effect of increasing a for the colloidal dispersion is still an increase of lability, although much less pronounced than for the analogous homogeneous ligand solution. This means that the dependency of ε on the radius is of a higher order than that of $\kappa_a^{*\prime}$, thus producing a dampening effect on the extent of increase of lability. Fig. 3, illustrates the variation of the overall flux and the limiting diffusive and kinetic fluxes with a for lead and cobalt using the same parameters as for Fig. 2. It is clear that the decrease in maximum diffusive flux (fully labile situation) with radius is much stronger than the decrease of the kinetic flux, thus underscoring the previous conclusion. Fig. 3 also illustrates, a very important detail which is that the total maximum diffusive plus kinetic flux approaches that of the free metal, reflecting the decrease in both mobility and dynamic nature of the complexes with increasing particle radius.

Up to now our focus has been the particle radius and the corresponding D_{ML} (or ε). Nevertheless there are other
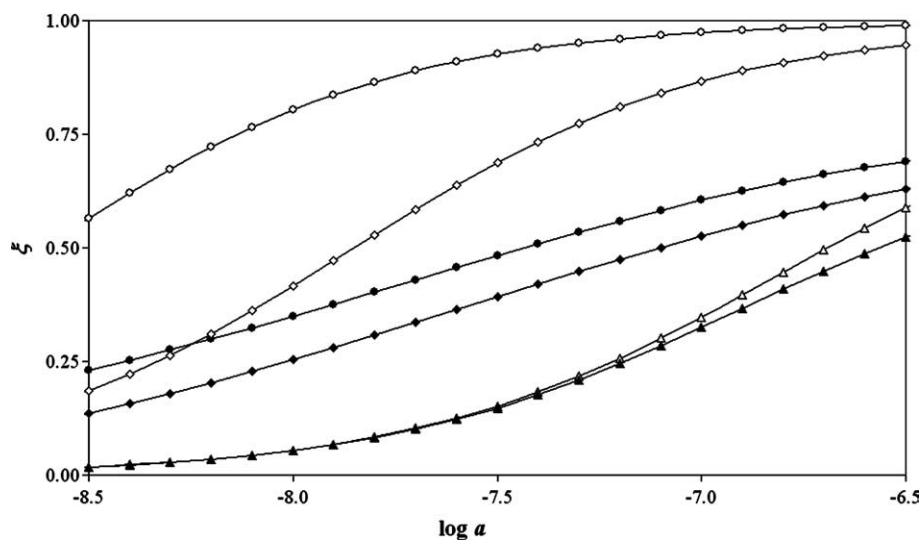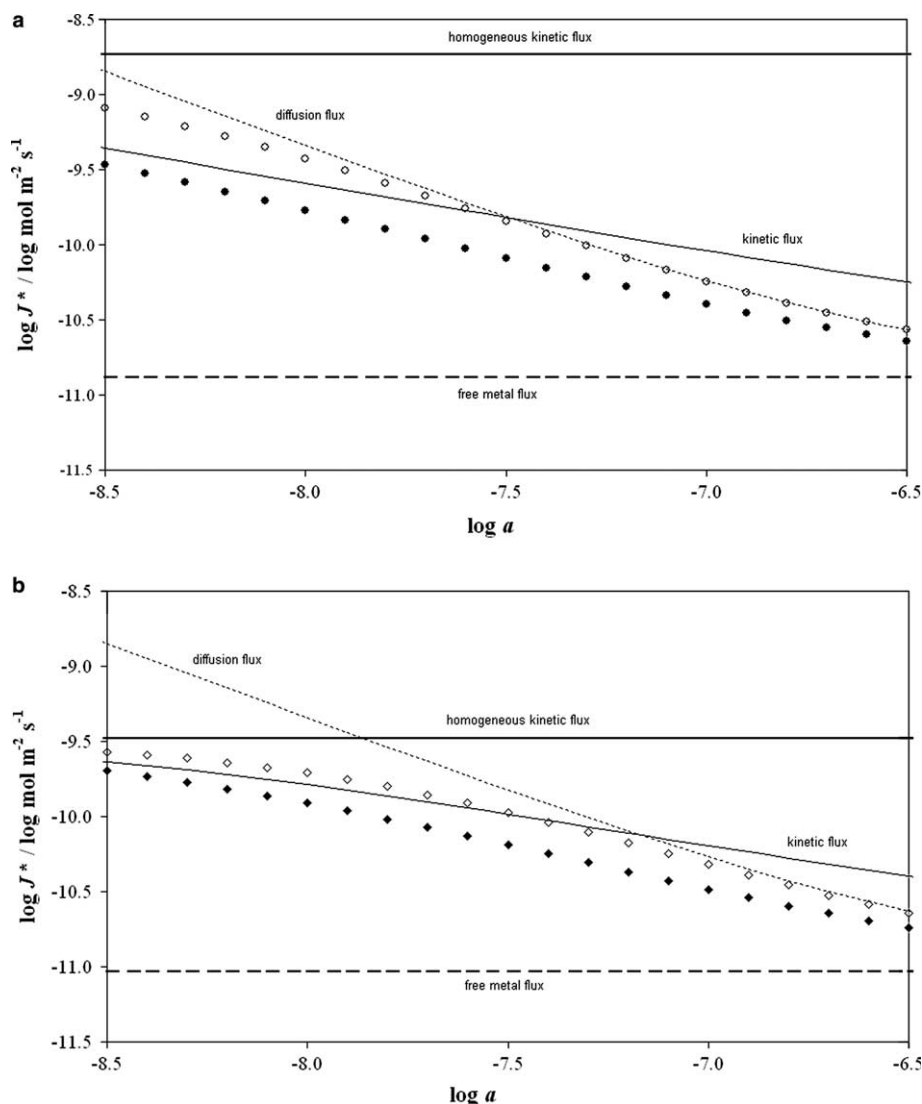

Fig. 2. Variation of ξ with particle radius, a (in m), for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for lead (II) ($\bigcirc$), cadmium (II) ($\diamond$) and cobalt(II) ($\triangle$) calculated using Eq. (10), in the presence of $C_L = 3 \times 10^{-2}$ mol m^{-3} binding sites and ionic strength 0.01 M. Other parameters: $K = 5 \times 10^7$ M^{-1}, $D_{Pb} = 9.9 \times 10^{-10}$ m^2 s^{-1}, $D_{Cd} = 7.0 \times 10^{-10}$ m^2 s^{-1}, $D_{Co} = 7.0 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Pb)} = 7 \times 10^9$ s^{-1}, $k_{-w(Cd)} = 3 \times 10^8$ s^{-1}, $k_{-w(Co)} = 2 \times 10^6$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$).

Fig. 3. Variation of log J^* with particle radius, a (in m), for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for (a) lead (II) ($\bigcirc$), (b) cadmium (II) ($\triangle$) calculated using Eq. (8), in the presence of $C_L = 3 \times 10^{-2}$ mol m^{-3} binding sites and ionic strength 0.01 M. The thick interrupted line represents the free metal flux (static system) (Eq. (11)), the full line represents the homogeneous kinetic flux (Eq. (15): μ calculated using k_a'), the thin interrupted line represents the maximum diffusive flux (labile) (Eq. (13)) and the thin line represents the kinetic flux (Eq. (15): μ calculated using $k_a^{*\prime}$). Other parameters: $K = 5 \times 10^7$ M^{-1}, $D_{Pb} = 9.9 \times 10^{-10}$ m^2 s^{-1}, $D_{Co} = 7.0 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Pb)} = 7 \times 10^9$ s^{-1}, $k_{-w(Co)} = 2 \times 10^6$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$).

parameters that also impact on the dynamic character of the system, viz. k_a, K (or k_d), C_L, c_p, and the electrode radius [9,11,14]. The influence of K is well studied and we shall not treat it again here. The influence of k_a can be probed by using different metals and was discussed before [1]. On the other hand, the influence of C_L and c_p might be coupled and this raises interesting questions as to the consequences of varying them. Two evident options are the change of particle concentration (c_p and C_L both increase) and variation of pH. The latter option alters the degree of protonation of the binding sites in the colloidal particle, which comes to effectively changing C_L while maintaining c_p constant, a situation that frequently arises in practice. Fig. 4 shows the variation of ξ with C_L for a colloidal ligand dispersion of particles of 100 nm radius

and analogous homogeneous systems; Fig. 5 shows the variation of the overall, limiting diffusive and kinetic fluxes with C_L for the same parameters as for Fig. 4. With increasing C_L, the colloidal system loses lability much faster than the analogous homogeneous solution. From Eq. (3a), it is readily seen that $k_a^{*\prime}$ will tend to the constant diffusion limit, $4\pi a D_M c_p$, whereas the value of K' continues to increase linearly with C_L. For colloidal dispersions the overall effect on the lability criterion (Eq. (12)) is that $\kappa_a^{*\prime}$ remains constant whilst $\varepsilon K'(1 + \varepsilon K')$ grows with $(C_L)^2$. Lability for the colloidal ligand complexes is thus inversely proportional to $(C_L)^2$. For the analogous homogeneous solution κ_a' grows with C_L, hence the lability decreases linearly with C_L. In Fig. 5, the different slopes of the diffusive fluxes for colloidal and analogous homogeneous ligands
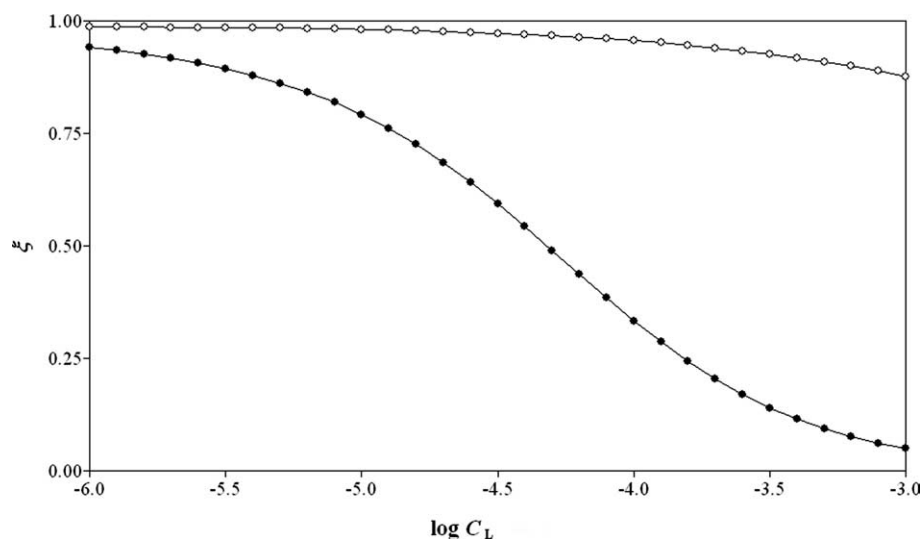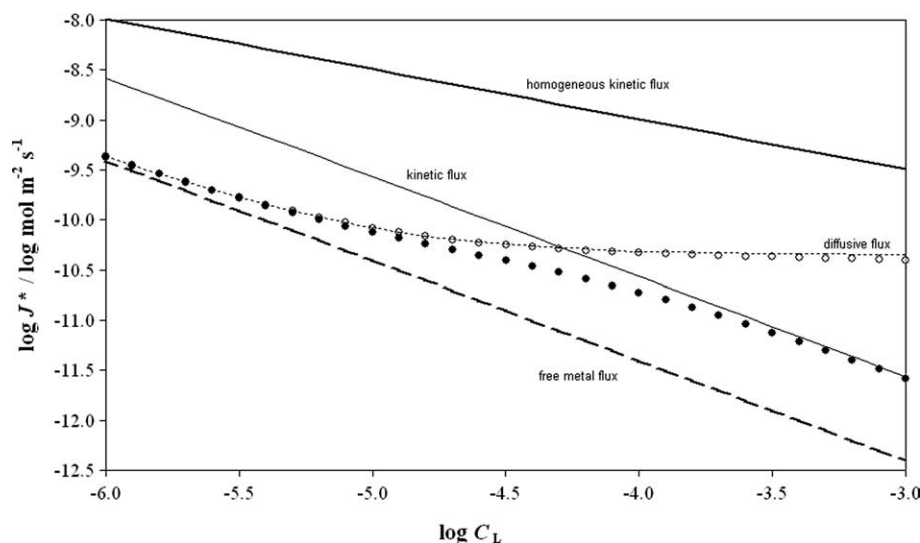
Fig. 4. Variation of ξ with ligand concentration, C_L, for lead (II) for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for particle diameter a of 100 nm ($c_p = 1.1 \times 10^{18}$ m^{-3}) ($\bigcirc$), calculated using Eq. (10). Other parameters: $K = 5 \times 10^7$ M^{-1}, $D_{Pb} = 9.9 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Pb)} = 7 \times 10^9$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$), ionic strength 0.01 M.

Fig. 5. Variation of log J^* with ligand concentration, C_L, for lead (II) for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for a particle of 100 nm diameter ($c_p = 1.1 \times 10^{18}$ m^{-3}) ($\bigcirc$) calculated using Eq. (8). The thick interrupted lines correspond to the free metal flux (static system) (Eq. (11)), the thick line corresponds to the homogeneous kinetic flux (Eq. (15): μ calculated using k_a'), the thin interrupted line corresponds to the maximum diffusive flux (labile) (Eq. (13)) and the thin line corresponds to the homogeneous kinetic flux (Eq. (15): μ calculated using $k_a^{*'}$). Other parameters: $K = 5 \times 10^7$ M^{-1}, $D_{Pb} = 9.9 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Pb)} = 7 \times 10^9$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$), ionic strength 0.01 M.

clearly show the quadratic and linear dependences of the flux on C_L. For constant c_p and decreasing C_L (lower ligand loadings) the colloidal dispersion approaches the behavior of the analogous homogeneous solution as each particle carries less and less ligand sites. This directly results from Eq. (3) where $k_a'(4\pi a D_M c_p)^{-1}$ becomes smaller and thus $k_a^{*'}$ approaches k_a'.

Another relevant situation occurs when we increase the time scale of the electrochemical process to increase the lability of the system. For a microelectrode this is equivalent to increasing the microelectrode radius, but for larger electrodes the steady-state approximation does not hold. On the other hand, it is a well established fact that chang-

ing from a spherical microelectrode to a stationary planar electrode the lability of the system increases [11,23], thus making it interesting to extend our analysis to the transient limit of planar electrodes.

2.5. Transient limit

The general solution for the flux towards a stationary planar electrode is available only in the Laplace domain [16], but for our purposes it is sufficient to consider the dynamic case for which an analytical solution is available. De Jong et al. [17] presented the following solution of Eq. (6) for the limiting metal flux at the electrode surface:

$$J^*(t) = \left(D_M k_a^{*\prime}\right)^{1/2} C_T^* \frac{\left(\varepsilon^{-1} + K'\right)^{3/2}}{(1 + K')(K')^{3/2}} \exp\left(\Lambda^2 t\right)\mathrm{erfc}\left(\Lambda t^{1/2}\right),$$

(16)

and

$$\Lambda = \frac{\left(k_a^{*\prime}\right)^{1/2}\varepsilon^{-1/2}(\varepsilon^{-1} + K')}{(1 + K')^{1/2}(K')^{3/2}}.$$

(17)

The lability of the complex species is related to $\Lambda t^{1/2}$ [16]:

$$\begin{aligned} \Lambda t^{1/2} \gg 1 \quad &\text{labile,} \\ \Lambda t^{1/2} \ll 1 \quad &\text{non-labile.} \end{aligned}$$

(18)

In the labile limit, the flux becomes independent of the kinetic parameters:

$$J^*(t) = \overline{D}^{1/2} C_T^* / (\pi t)^{1/2}.$$

(19)

In the non-labile limit and for $\varepsilon K' \gg 1$ [14], exp-$(\Lambda^2 t)\mathrm{erfc}(\Lambda t^{1/2})$ approaches unity, and the flux reduces to that for purely kinetic control:

$$J^*(t) = k_d^* \left(D_M / k_a^{*\prime}\right)^{1/2} C_T^*$$

(20)

Fig. 6, illustrates the evolution of the lability criterion, $\Lambda t^{1/2}$, with the particle radius, a, for both colloidal ligand dispersions and the analogous homogeneous solutions of
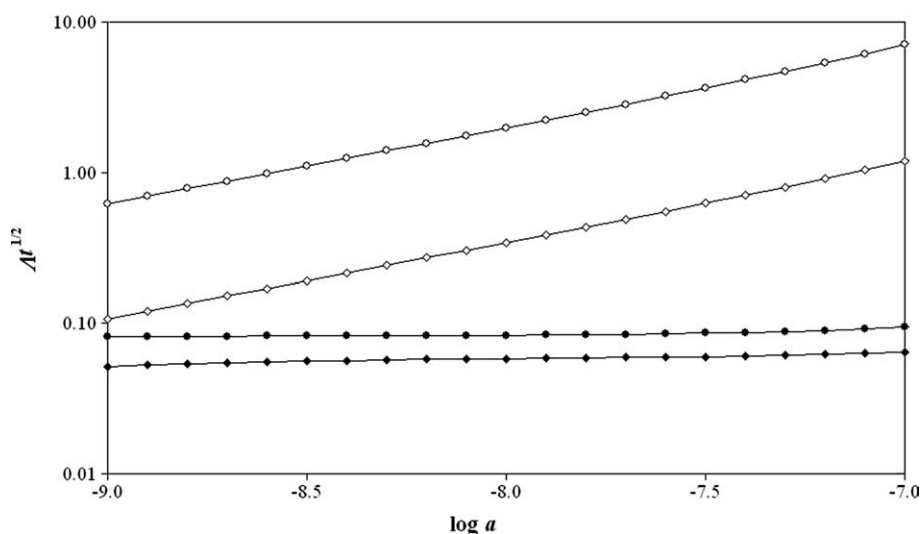

Fig. 6. Variation of $\Lambda t^{1/2}$ with particle radius, a (in m), for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for lead (II) (○) and cadmium (II) (◇) calculated using Eq. (17), in the presence of $C_L = 3 \times 10^{-1}$ mol m^{-3} binding sites and ionic strength 0.01 M. Other parameters: $t = 0.1$ s, $K = 1 \times 10^7$ M^{-1}, $D_{Pb} = 9.9 \times 10^{-10}$ m^2 s^{-1}, $D_{Cd} = 7.0 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Pb)} = 7 \times 10^9$ s^{-1}, $k_{-w(Cd)} = 3 \times 10^8$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$).
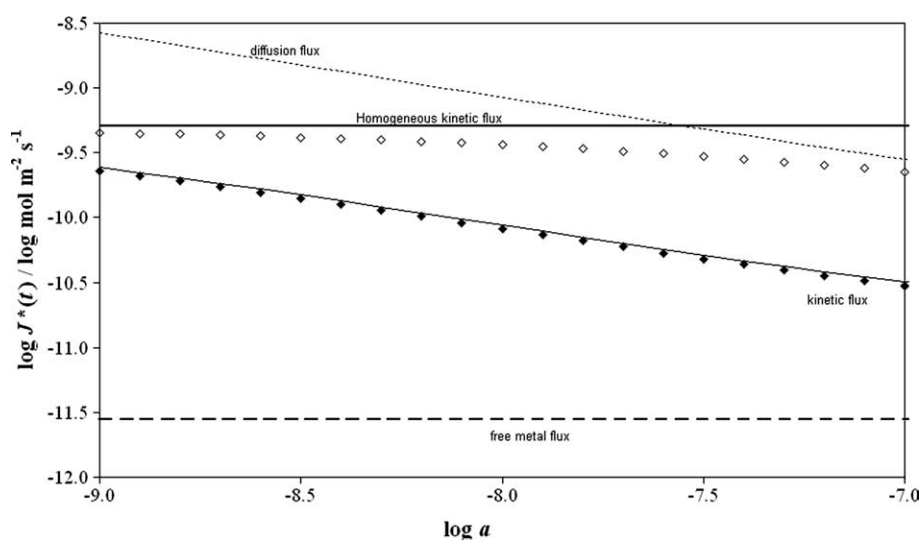

Fig. 7. Variation of log $J^*(t)$ with particle radius, a (in m), for an analogous homogeneous solution (open symbols) and colloidal dispersions (full symbols) for cadmium (II) (◇) calculated using Eq. (16), in the presence of $C_L = 3 \times 10^{-1}$ mol m^{-3} binding sites and ionic strength 0.01 M. The thick interrupted lines represents the free metal flux (static system) (Eq. (11)), the thick line represent the homogeneous kinetic flux (Eq. (15): μ calculated using k_a'), the thin interrupted line represents the maximum diffusive flux (labile) (Eq. (13)) and the thin line represents the kinetic flux (Eq. (15): μ calculated using $k_a^{*\prime}$). Other parameters: $t = 0.1$ s, $K = 1 \times 10^7$ M^{-1}, $D_{Cd} = 7.0 \times 10^{-10}$ m^2 s^{-1}, $k_{-w(Cd)} = 3 \times 10^8$ s^{-1}, $k_{os} = 3.66 \times 10^{-3}$ mol^{-1} m^3 ($z_M z_L = -2$).

the same mobility for lead and cadmium, at given K and C_L values. Fig. 7 shows the corresponding variation of overall, limiting diffusive and kinetic fluxes with a for cadmium (II). We note that maintaining C_L constant while increasing a implies a decrease in c_p. From Fig. 6, it can be observed that the lability of the colloidal complexes does not increase with the particle radius, in contrast to the microelectrode case (Fig. 2). This is due to the different dependencies of the diffusional flux on the diffusion coefficient as this varies from power 1 for the microelectrode to power 1/2 for the transient. The point is clearly demonstrated by comparing the slopes of the limiting diffusion fluxes in Figs. 7 and 3. Application of Eq. (16), (valid only in the dynamic regime), to colloidal complexes, requires that the dynamic criterion is satisfied whereas the system becomes more and more static with increasing particle radius and/or C_L.

3. Conclusion

Using a new theory for metal speciation dynamics in colloidal dispersions, with the complexing ligands localized on the surface of the particles, we have demonstrated that the conventional approach of assuming an analogous homogeneous ligand distribution with the same mobility overestimates both the dynamics and the lability of colloidal metal complexes. We have proposed the use of $k_a^{*\prime}$ and k_d^* instead of $k_a^\prime$ and k_d in both the dynamic and the lability criteria in order to obtain a correct interpretation of dynamic metal speciation in colloidal dispersions. The increase of lability with particle radius, as expected for the analogous homogeneous case is toned down at the steady-state flux limit and practically eliminated at the transient flux limit. The difference between these limits lies in the dissimilar dependency of the diffusional flux on the diffusion coefficient which varies from a power 1 dependence in the steady-state to a power 1/2 dependence in the transient regime. With increasing ligand concentration, a colloidal metal complex loses lability much faster than the homogeneous solution counterpart.

Further development of the topic of dynamic metal speciation in colloidal ligand systems will require:

- development of criteria for labile and dynamic behavior in stirred systems where convection is the dominant mode of mass transport,
- collection of experimental evidence in support of the theory, applying various voltammetries and stripping voltammetries, and
- extension of the colloidal dispersion theory to encompass the fact that ligands may be distributed over the complete volume of the particle rather than only over the surface (for example, a gel particle or a humic colloid).

References

[1] J.P. Pinheiro, M. Minor, H.P. Van Leeuwen, Langmuir 21 (2005) 8635.
[2] J. Buffle, Complexation Reactions in Aquatic Systems. An Analytical Approach, Ellis Horwood, Chichester, 1988.
[3] A.M. Mota, M.M. Correia dos Santos, in: A. Tessier, D. Turner (Eds.), Metal Speciation and Bioavailability, John Wiley and Sons, New York, 1995, Chapter 5.
[4] T.M. Florence, G.M. Morrison, J.L. Stauber, Sci. Tot. Env. 125 (1992) 1.
[5] H.P. van Leeuwen, R.M. Town, Environ. Sci. Technol. 37 (2003) 3945.
[6] J.P. Pinheiro, H.P. van Leeuwen, J. Electroanal. Chem. 570 (2004) 69.
[7] G. Capodaglio, G. Scarponi, G. Toscano, C. Barbante, P. Cescon, Fres. J. Anal. Chem. 351 (4–5) (1995) 386.
[8] W. Davison, J. Electroanal. Chem. 87 (1978) 395.
[9] H.P. van Leeuwen, J. Buffle, R. Cleven, Pure Appl. Chem. 61 (1989) 255.
[10] J.P. Pinheiro, A.M. Mota, H.P. van Leeuwen, Coll. Surf. A: Phys. Eng. Aspects 151 (1999) 181.
[11] J. Galceran, J. Puy, J. Salvador, J. Cecilia, H.P. van Leeuwen, J. Electroanal. Chem. 505 (2001) 85.
[12] J. Galceran, J. Puy, J. Salvador, J. Cecilia, F. Mas, J.L. Garces, Phys. Chem. Chem. Phys. 5 (22) (2003) 5091.
[13] F.M.M. Morel, J.G. Hering, Principles and Applications of Aquatic Chemistry, John Wiley, New York, 1993.
[14] H.P. van Leeuwen, Electroanalysis 13 (2001) 826.
[15] J. Koutecký, R. Brdička, Collect. Czech. Chem. Commun. 12 (1947) 337.
[16] H.G. de Jong, K. Holub, H.P. van Leeuwen, J. Electroanal. Chem. 234 (1987) 1.
[17] H.G. de Jong, H.P. van Leeuwen, J. Electroanal. Chem. 234 (1987) 17.
[18] J. Galceran, J. Puy, J. Salvador, J. Cecília, H.P. van Leeuwen, J. Electroanal. Chem. 505 (2001) 85.
[19] K. Stulik, C. Amatore, K. Holub, V. Marecek, W. Kutner, Pure Appl. Chem. 72 (8) (2000) 1483.
[20] C.G. Zoski, A.M. Bond, E.T. Allinson, K.B. Oldham, Anal. Chem. 62 (1990) 37.
[21] V. Kačena, L. Matoušek, Collect. Czech. Chem. Commun. 18 (1953) 294.
[22] J. Heyrovský, J. Kůta, Principles of Polarography, Publishing House of the Czechoslovak Academy of Sciences, Praha Academic Press, New York, 1966.
[23] H.P. van Leeuwen, J.P. Pinheiro, J. Electroanal. Chem. 471 (1999) 55.