

## Theoretical aspects of dynamic metal speciation with electrochemical techniques

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### Abstract

Understanding the reaction-diffusion processes of metal species is essential for an adequate description and control of metal availability. Electroanalytical techniques are well suited to probe dynamic speciation in aqueous systems, because transport and reaction influence the current. This short review hinges on the quantification of the contribution of complexes to the resulting flux via the lability degree, while highlighting extensions and other approaches. The reaction scheme is the Chemical Electrochemical (CE) mechanism, but special emphasis is focussed in mixtures of ligands given their relevance in natural waters. Despite the intensive theoretical work devoted to dynamic speciation, there is still a need of further progress, especially regarding heterogeneous ligands, nanoparticles, etc. Rigorous numerical solutions are progressively more accessible. Analytical contributions are usually restricted to limiting cases, but greatly facilitate the physicochemical interpretation of complex systems.

**Keywords:** reaction-diffusion, electroanalytical techniques, analytical expressions, physical interpretation, chemodynamics, steady state

## 1. Introduction

Metals are essential for a normal metabolic functioning, for plant growth and for animal and human health. In excess, they become toxic, but its deficiency is also the source of many diseases.

Not only total concentrations, but also speciation, solubility and mobility, determine both, the nutritive and toxic properties of these elements [1]. Kinetic interconversions and transport processes influence most electroanalytical data, especially in natural media [2]. This focus (away from equilibrium) has been termed dynamic speciation [3]. (Bio)availability is determined by the flux that crosses the internalization surface. It is generally assumed that only the free metal can cross the cell membranes. However, the flux is supported by many metal species which, by dissociation, buffer the metal consumption. The influence of each species is determined by the relative time scales of the processes impinging on the metal resupply. Only when the internalization process is the rate limiting step, is the uptake flux proportional to the free metal concentration in the solution as stated in the Free Ion Activity Model (FIAM) or the Biotic Ligand Model (BLM) [4;5].

Electroanalytical techniques are well suited to study dynamic metal speciation [6-10]. The consumption of a metal on an electrode surface mimics the consumption at a biological surface. Due to the metal depletion, all solution equilibria shift to adapt to the new free metal concentration profile. The knowledge of the species and the extend by which they contribute to the metal supply will increase our understanding of the functioning of natural media. In other fields, this knowledge is helpful for the interpretation of fluxes crossing interphases or membranes [11;12], electrochemical sensors [2], adsorption to resins [13-15], the impact of additives in electroplating[16], etc.

Here we will review the theoretical framework developed to describe metal availability measured with electroanalytical techniques with special emphasis on the concept of lability degree, which evolved from the pioneering work on speciation based on the lability criteria [17].

## **2. The model: Mathematical formulation**

A general formulation of the problem starts from the continuity equation for each species, including the transport phenomena and the chemical reactions relevant to the studied case, in the pertaining geometry and physical domain. The reaction terms imply non-linearity and coupling of the resulting system of differential equations of second order. In general, the system has to be solved by numerical simulation (e.g. using finite differences or finite elements). When the number of species increases, the computational time increases and iterative procedures based on the linearization of the resulting system are especially helpful [13;15;18;19]. Due to the complexity of the general problem and with the aim of reaching approximate analytical expressions, most of the work has been done under reasonable limiting conditions. Common assumptions are steady state, diffusion limited conditions (e.g. corresponding to the application of a sufficiently negative potential at the electrode surface), excess of ligand and one-dimensional geometry (planar or spherical). Most of the metals of interest appear in environmental media at trace concentrations while ligands are orders of magnitude more abundant; so excess of ligand is a reasonable approximation in many cases. This assumption linearizes the system of equations and it is a general requirement for the derivation of approximate analytical expressions. Typically, ligands are involved in acid base equilibria and, often, only one of these species reacts with the ligand appreciably [18;20]. Depending on pH, the concentration of this ligand can even be smaller than that of the metal, but the excess of ligand assumption can still be a good approximation for

those systems where acid base equilibria effectively buffer the ligand concentration. In addition to simple ligands, natural media contain macromolecular ligands with different functional groups. The affinity for the metal is, then, dependent on the metal-to-ligand ratio, a phenomenon called heterogeneity [21;22].

Although steady state is not achieved in all electroanalytical techniques, it is a reasonable approximation -at least in some stage- of the usually applied techniques to measure chemical availability in aqueous solutions. Indeed, speciation in a natural water with direct techniques is hindered by the induced adsorption of complexes at the electrode surface and by the low total metal concentration. Usually, a preconcentration step is required along which steady state typically is a good approximation. A steady-state treatment of the deposition stage can be applicable to the multiple variants of Anodic Stripping Voltammetry (and their gatherings in Pseudo Polarography [23]) or to the diffusion-limited stage of the 2-pulses variant of AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) [24]. SSCP (Scanned Stripping ChronoPotentiometry) has been widely used due to the low influence of electrodic adsorption [25-30]. If SSCP accumulation time is long enough (120 s), this step can be described (for sufficiently negative deposition potentials) as an accumulation under steady-state conditions in a diffusion domain dependent on the stirring rate. When not using microelectrodes, Nernst diffusion layer concept assumes that there is a layer close to the electrode surface (the diffusive boundary layer, whose thickness is  $\delta$ ) where there is no convection and transport takes place solely by diffusion. The second stage in SSCP quantifies the amount of metal accumulated in the first stage, which results from the contributions of free metal cation and the metal complexes according to their lability degree ( $\xi$ ), as described below.

### 3. Lability degree

The lability degree [31],  $\xi$ , indicates the fraction of the current contribution of the complex(es) to the metal flux ( $J$ ) with respect to the fully labile case, i. e., the maximum contribution that could be reached if dissociation of the complex was fast enough to reach equilibrium with the metal at all the relevant spatial positions and times:

$$\xi \equiv \frac{J - J_{\text{free}}}{J_{\text{labile}} - J_{\text{free}}} \quad (1)$$

where  $J_{\text{free}}$  and  $J_{\text{labile}}$  stand, respectively, for the flux due to the free metal concentration and the total flux in a fully labile system. When  $J_{\text{free}}$  is negligible,  $\xi$  is easily measured since it is just a normalized flux [32].

Consider the simplest system with only one complex



where  $k_{\text{a}}$  and  $k_{\text{d}}$  are the association and dissociation rate constants, respectively.

The fluxes, under steady state, excess of ligand, boundary conditions corresponding to perfect sink at the electrode surface and bulk concentration at infinite (spherical case) or at a given  $\delta$  (planar case) are

$$J_{\text{free}} = D_{\text{M}} \frac{c_{\text{M}}^*}{\delta} \quad (3)$$

$$J_{\text{labile}} = D_{\text{M}} \frac{c_{\text{M}}^*}{\delta} + D_{\text{ML}} \frac{c_{\text{ML}}^*}{\delta} \quad (4)$$

where  $\delta$  coincides with the radius of the electrode  $r_0$  for (hemi)spherical geometry.  $D_j$  and  $c_j^*$  are the diffusion coefficient and bulk concentration of species  $j$ , respectively,

In spherical geometry [31], the solution of the reaction-diffusion system leads to

$$\xi = \frac{\sqrt{\frac{k'_a r_0^2}{D_M}}}{\sqrt{\varepsilon K' (1 + \varepsilon K')} + \sqrt{\frac{k'_a r_0^2}{D_M}}} \quad (5)$$

where  $k'_a \equiv k_a c_L^*$ ,  $K' \equiv K c_L^* = \frac{k_a}{k_d} c_L^*$  and  $\varepsilon \equiv \frac{D_{ML}}{D_M}$ ,

while, in planar geometry (finite domain) [33],

$$\xi = 1 - \frac{1 + \varepsilon K'}{\varepsilon K' + \frac{\delta}{m} \coth\left(\frac{\delta}{m}\right)} \quad (6)$$

where

$$\frac{1}{m^2} = \frac{1}{\mu^2} \left( \frac{1 + \varepsilon K'}{\varepsilon K'} \right) \quad (7)$$

and

$$\mu = \sqrt{\frac{D_M}{k'_a}} \quad (8)$$

The parameter  $m$  has dimensions of a distance and can be seen as an “effective” thickness of the reaction layer in the solution and  $\mu$  is the reaction layer thickness introduced by Koutecky in planar semi-infinite diffusion [34].

In both geometries  $\xi$  can be identified as

$$\xi = 1 - \frac{c_{ML}^0}{c_{ML}^*} \quad (9)$$

where  $c_{ML}^0$  is the complex concentration at the electrode surface. So, the lability degree is a measure of the fraction of dissociation of the complex at the electrode surface.

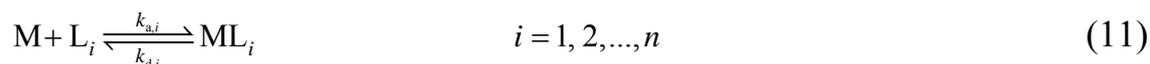
The steady-state metal flux at the electrode surface can be written as

$$J = \frac{D_M c_M^* (1 + \varepsilon K' \xi)}{\delta} = D_M \frac{c_M^*}{\delta} + \xi D_{ML} \frac{c_{ML}^*}{\delta} \quad (10)$$

#### 4. Mixtures

Natural media contain complex mixtures of ligands, some of which are heterogeneous and can be approached as a mixture of ligands sharing a common diffusion coefficient.

Let us, then, consider a mixture of ligands  $L_1, L_2 \dots L_n$ , that can bind -in parallel- to a metal ion M according to the scheme



where subscript  $i$  indicates that the parameters correspond to the complexation process of the ligand  $L_i$ .

Under the previous assumptions, the continuity equations become [35]

$$D_M \nabla^2 c_M + \sum_{i=1}^n k_{d,i} c_{ML_i} - \left( \sum_{i=1}^n k'_{a,i} \right) c_M = 0 \quad (12)$$

$$D_{ML_i} \nabla^2 c_{ML_i} - k_{d,i} c_{ML_i} + k'_{a,i} c_M = 0 \quad i = 1, 2, \dots, n \quad (13)$$

where  $\nabla^2$  stands for the Laplacian operator in the relevant 1-D geometry (planar, spherical or cylindrical) with boundary conditions,

$$\text{electrode surface} \quad c_M = 0; \quad \text{grad}(c_{ML_i}) = 0 \quad \forall i \quad (14)$$

and bulk concentrations at a given finite or infinite distance.

A procedure for the rigorous solution of the system (12)-(13) developed in the literature is based on uncoupling this system using as unknowns the linear combinations of the concentrations that diagonalize the matrix of coefficients that appears when (12)-(13) is written in a matricial form. Explicit analytical expressions for the concentration profile for each species and for the metal flux can be written[35].

##### 4.1 Lability degree of a complex in a mixture

The integration of the equation resulting from the addition of all the diffusion equations (12)-(13), with the corresponding boundary conditions, results [35] into

$$J = D_M \frac{c_M^*}{\delta} + \sum_{i=1}^n D_{ML_i} \frac{c_{ML_i}^*}{\delta} \xi_i \quad (15)$$

where

$$\xi_i \equiv 1 - \frac{c_{ML_i}^0}{c_{ML_i}^*} \quad (16)$$

Eqn. (16) is a generalization of Eqn. (9) for the lability degree of a given complex  $ML_i$  in a mixture. Since  $c_{ML_i}^0$  depends on the solution of the coupled system (12)-(13), the lability degree of a complex is not an intrinsic property of the complex, but dependent on the composition of the system as well as on the size of the sensor [31] and its surrounding diffusive boundary layer.

The global lability parameter of the system [36;19] can be derived from (1) as:

$$\xi = \frac{\sum_{i=1}^n \varepsilon_i K_i' \xi_i}{\sum_{i=1}^n \varepsilon_i K_i'} \quad (17)$$

The global lability parameter is, then, a weighted average of the particular lability parameters of the different complexes present in the mixture with weighting factors dependent on the particular diffusion coefficients and on the respective abundances in the bulk solution.

The treatment outlined above has been applied to successive complexes with metal –to–ligand stoichiometric relationship 1:n [37] and to mixtures of parallel and successive complexes. In any case, the lability degree of a complex can be written as in Eqn. (16).

4.2 Mixture Effects. Could the flux in a mixture be predicted with the lability degrees measured in single ligand systems?

4.3 Dependence of  $\xi_i$  on the system composition

The lability degree of a given complex  $i$  in a mixture decreases as its ligand concentration  $c_{L_i}^*$  in the mixture increases (see evolution in Fig 1). This behaviour is parallel to that found in single ligand systems [38] and can be explained by the shift of the steady state towards the formation of this complex. More relevant is that not only  $\xi_i$ , but also the lability degree  $\xi_j$  of a co-existent complex is also modified.  $\xi_j$  increases with increasing  $c_{L_i}^*$  when  $\xi_j^{h=1} < \xi_i^{h=1}$  where  $\xi_k^{h=1}$  labels the lability degree of  $M^k L$  in the single ligand system  $M + {}^kL$ [36]. In other words, the addition of a ligand,  $L_j$ , decreases the lability degree of all the more labile complexes while increases the lability of the less labile ones. A particular case with two ligands is depicted in Fig.1. Notice how the addition of  $L_2$  (which rises the more labile complex concentration) increases the lability of (the more inert)  $ML_1$ .

The dependence of the lability degree on the composition of the system suggests the arising of mixture effects. Let us check whether the actual metal flux in the mixture,  $J$ , differs from the hypothetical metal flux,  $J^{h=1}$ , expected when the lability degree of each complex in the mixture takes the value corresponding to the single ligand system with common  $c_{L_i}^*$  and  $c_{ML_i}^*$  values.

A systematic exploration of the "mixture effect" has been done in [36] and [19]. The main results indicate that when both complexes are labile, the mixture effect is negligible and  $(J^{h=1} - J)/J$  tends to zero. A similar situation arises when both complexes are inert. Important mixture effects can appear when one complex is labile while the other is partially labile. In this case, the addition of the labile ligand mainly increases the lability of the partially labile, since this is the most sensitive to the changes of composition. Accordingly,  $(J^{h=1} - J)/J$  takes negative values since  $J$  is higher than

$J^{h=1}$ . On the contrary, when one complex is inert and the other partially labile, the addition of the inert leads to positive values of  $(J^{h=1} - J)/J$  which can reach 40%. Differences of the order of 20% have been experimentally reported in the system Cd/NTA/citrate [39].

A mechanistic explanation of the mixture effect can be obtained by looking at the concentration profiles in Figure 2. The normalized profile of a complex  $c_{ML_i}/c_{ML_i}^*$  coincides with the normalized metal profile whenever dissociation of this complex reaches equilibrium. Fig. 2 depicts the profiles of M and  $ML_2$  for the mixture with  $ML_1$  of Fig. 1 and for the single ligand system  $M + L_2$  at the same bulk ligand and free metal concentration as in the mixture. Notice that the mixture has led to a noticeable increase in  $c_{ML_2}^0/c_{ML_2}^*$  indicating a decrease of  $\xi_2$  due to the presence of the more inert complex  $ML_1$ . The metal concentration profile of the mixture has also increased as compared to the single  $M+L_2$  system. In this way,  $ML_2$  is less forced to dissociate: notice the reduction of the corresponding reaction layer thickness. This is the reason why  $ML_2$  is less labile in the mixture. When there is a dominant complex, it determines the metal profile and the rest of complexes try to adapt to it, analogous to an acid-base indicator adapting to the pH of the media.

## 5. Extensions and alternatives to this treatment

The lability degree for a specific complex beyond perfect sink conditions ([40-42]) can be extended as:

$$\zeta_i \equiv \frac{1 - \frac{C_{ML_i}^0}{C_M^*}}{1 - \frac{C_M^0}{C_M^*}} \quad (18)$$

which even applies beyond excess-ligand conditions. This lability degree is unaffected by some changes in the coupled flux at the surface (i.e. it reflects the dynamics of the solution)[42;43].

Closed expressions for the lability degree (i.e. not involving concentrations at the surface) can only be derived from analytical solutions, which often are linked to some simplification. For the single ligand system, an approximate analytical expression for the transient current in the CE (Chemical Electrochemical) mechanism [44] without the restriction of excess ligand has been obtained. In excess of ligand with a common diffusion coefficient for all species, the diffusive kinetic steady state approximation allows a simple approximate analytical expression for both planar and spherical geometry (see eqn. 19 in [45]) and any potential applied to the electrode, while recent work tackled other geometries [46;47]. Expressions reported for the currents in the CE mechanism for different diffusion coefficients can also be rewritten to account for the lability degree in these systems [48;49].

A general formulation (in planar geometry) under transient conditions in a general mixture of ligands with any range of diffusion coefficients and without ligand excess conditions was numerically solved by using the Lattice-Boltzmann approach [41]. This numerical strategy is highly general and can tackle problems with any geometry (even irregular 3-D electrodes) and flexible boundary conditions (e.g. Michaelis-Menten for

internalisation [42]), but it requires long computational times. A user friendly program, called MHEDYN, restricted to planar geometry, was developed with this approach. The computational tool was applied to study the complexation of Cu and Pb to some mixtures of simple ligands as well as to a rigorous numerical computation of the contribution of the fulvic acid metal complexes to the flux by considering the fulvic acid as a heterogeneous mixture of ligands with abundances according to a Sips distribution and kinetic constants estimated based on Eigen's mechanism [41;50;51]. A critical compilation of data for simple ligands and heterogeneous complexants was compiled in [52] and [53]. Another computational code, called FLUXY, provides steady-state fluxes under spherical (or planar) geometry and excess of ligand allowing, also, the coupling with a first order internalisation process (e.g. a linearized Michaelis-Menten boundary condition) [40;54]. In FLUXY, the user can choose between the rigorous diagonalization of the system (12)-(13) and approximate analytical expressions for the flux using the reaction layer concept. MHEDYN and FLUXY were applied to describe mixtures of simple and heterogeneous complexants of Pb, Zn and Ni [55]. Applications of these kinetic approaches to electrochemical techniques are still scarce. Work with heterogeneous ligands has mostly concentrated, up to now, on fully labile systems aiming at recovering the distribution of affinities present [56-61].

A further development presented a compact expression for an equivalent or "effective" reaction layer of all the mixture, whose layer thickness was called "composite reaction layer". This produced a very simple expression for the total flux (see Eqn 43 in [62]). Mixture effects have also been predicted with this analytical expression [50;62].

Although a great effort has been devoted in the last years to describe the metal complexes with heterogeneous ligands and natural colloidal soft particles, this issue is still challenging. Intensive work have been devoted to extend the Eigen ideas to these particles [63-66] and compute the corresponding physicochemical parameters with especial emphasis in the particulate character of these ligands, which can lead to diffusion-influenced kinetics of metal association and to electrical effects arising from the charge of these particles, and responsible for the kinetic acceleration of the binding kinetics [67-69].

## **6. CONCLUSIONS**

Analytical and computational modelling in dynamic speciation are complementary, and must be checked against experimental results. The lability degree can be a tool to quantify the contribution of the different species to the measured current, but it is not an intrinsic property of the species and depends on the sensor (size, geometry) and the system composition. Accordingly, the accurate determination of true physicochemical parameters (such as association/dissociation rate constants, diffusion coefficients, etc.) remains essential.

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## Figures

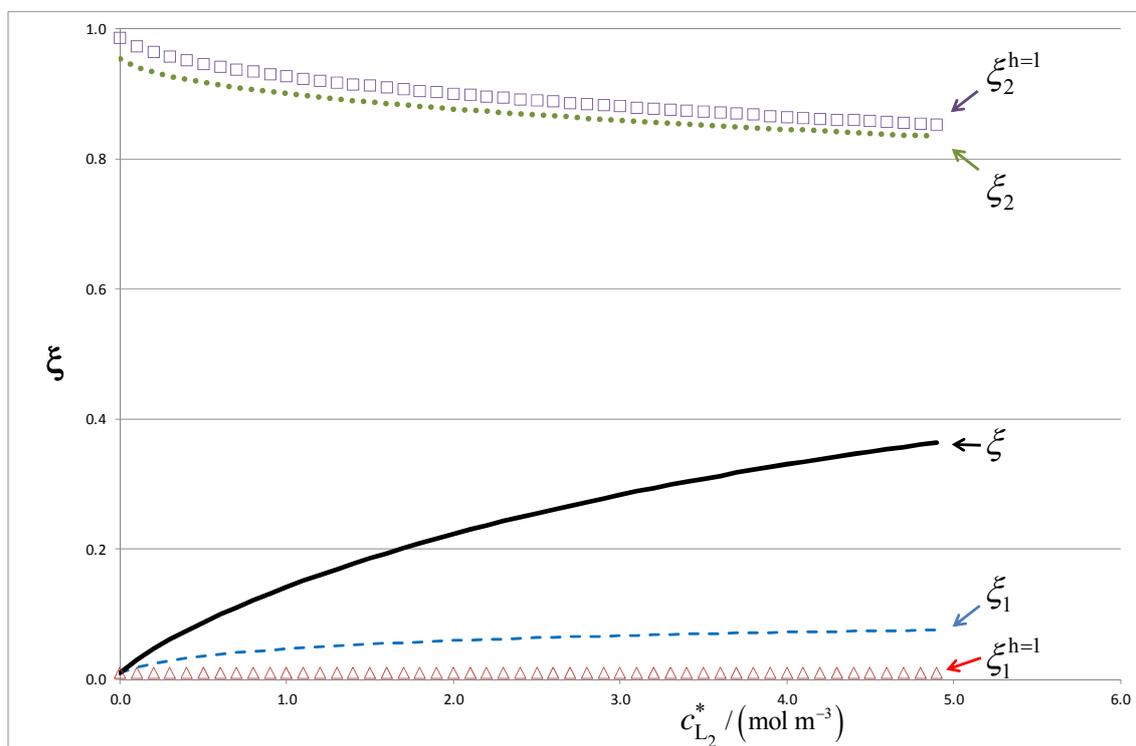


Fig. 1.: Global lability degree of the system, ( $\xi$ , black continuous line), the lability degree of complex  $ML_1$ , ( $\xi_1$ , blue dashed line), and the lability degree of complex  $ML_2$ , ( $\xi_2$  green dotted line) in the mixture as a function of the bulk concentration of ligand  $L_2$ . Lability degree  $\xi_1^{h=1}$  (red triangle marker) and  $\xi_2^{h=1}$  (purple square marker) for the single ligand systems at the same bulk ligand concentration, i. e., corresponding to the systems with only  $ML_1$  or only  $ML_2$  being present. Theoretical expectations (under steady state and semi-infinite diffusion domain) for a mixture NTA+glycine-Cd [39] probed with a spherical electrode of radius  $10 \mu\text{m}$ . Parameters:  $D_M=6.09 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $\varepsilon_1 = \varepsilon_2 = 1$ ,  $c_{L_1}^* = 4 \times 10^{-5} \text{ mol m}^{-3}$ ,  $K_1 = 10^{6.8} \text{ m}^3 \text{ mol}^{-1}$ ,  $K_2 = 10^{1.5} \text{ m}^3 \text{ mol}^{-1}$ ,  $k_{a,1} = k_{a,2} = 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The concentration of metal is immaterial for excess of ligand conditions.

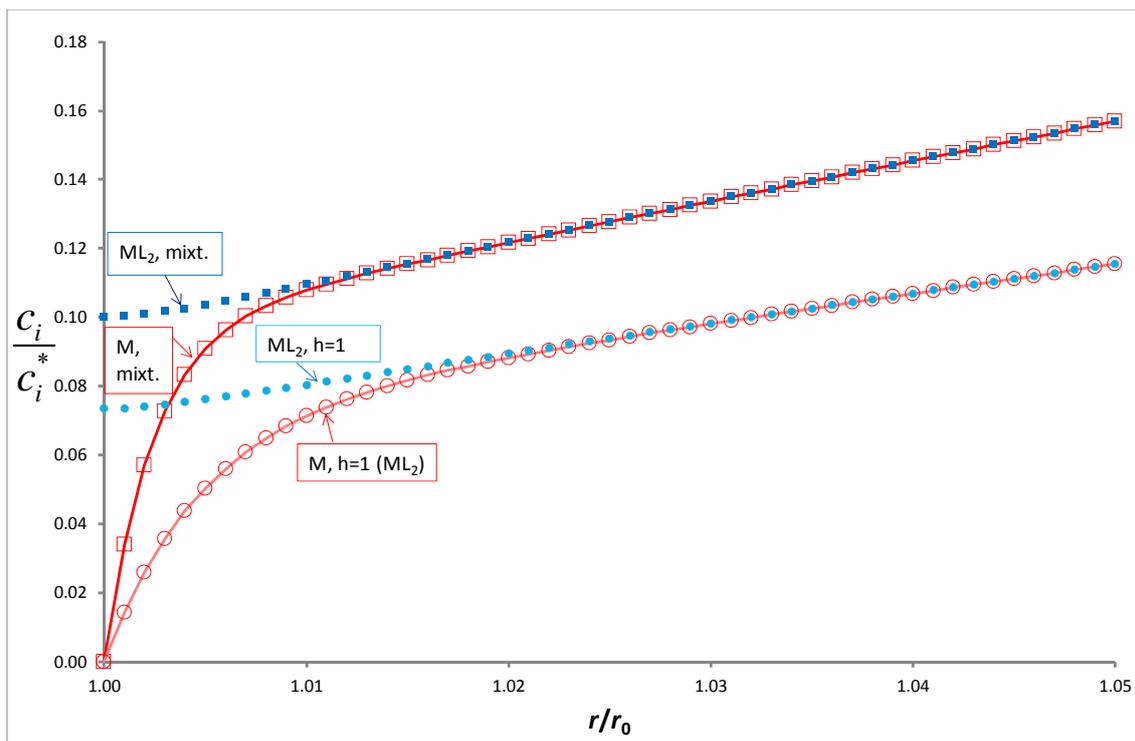


Fig. 2.: Normalized concentration profiles  $\frac{C_i}{C_i^*}$  in different systems related to Fig. 1 with  $c_{L_2}^* = 1 \text{ mol m}^{-3}$ . Red empty squares and blue full squares stand, respectively, for M and  $ML_2$  in the mixture. Light-red empty circles and light-blue full circles stand, respectively, for M and  $ML_2$  in a hypothetical system without  $L_1$  (i.e. consisting of just M and  $L_2$ ). The practically constant (in the region depicted) normalized profile of  $ML_1$  in the mixture (around 0.953) is not shown.

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