

# Concentration profiles as lability indicators for electrochemical systems containing metal complexes

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Electrochemical processes, involving mass transport of chemically interacting metal complexes and ligands, are considered using the quantitative model based on the second Fick's law equations supplemented with kinetic terms. Concentration profiles obtained at different diffusion and kinetic parameters are used for the characterization of system lability. When chemical steps are fast enough and the interrelation between concentrations of species is specified by stability constants of metal complexes, all complexes in the system might be treated as electrically active species yielding the respective partial currents. In the case of the systems with limited lability, certain deviations from the equilibrium distribution of species is observed in the diffusion layer. The reaction layer concept is analysed and consideration is given to the feasibility of an idealized mass transport model in the electroanalysis.

**Keywords:** metal complexes, lability, electroreduction, chemical steps, reaction layer

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## INTRODUCTION

Chemical interactions between different species are typical of the electrochemical reduction of metal complexes that usually proceeds via a mechanism involving chemical and electrochemical steps (see [1] and references therein). To obtain kinetic parameters of the charge transfer process, the surface concentrations of electrically active complexes (EAC) are required, which can be obtained when the regularities of the mass transport of chemically interacting species are formulated. In solving this problem, there are certain difficulties, the complexity of which depends on the lability of the system.

Formulation of the lability criteria is based on comparing the limiting fluxes controlled by finite rates of the dissociation of complex species to the limiting diffusional fluxes of these species [2]. As a result, this criterion depends on many parameters including diffusion coefficients, the rate constants of chemical steps, the thickness of diffusion and reaction layers, the size of micro-electrodes, etc. [2–11].

The most rigorous criteria are obtained when the preceding chemical reaction is of the first (or pseudo-first) order. The simplest example could be the process  $X \rightarrow O + n e \rightarrow R$  representing the chemical/electrochemical or CE mechanism. This also applies to the theoretical relationships in the linear potential sweep (LPS) theory [12–14]. Analytical expressions for current peaks and their potentials, as well as for the reaction layer thickness, were obtained for the CE mechanism presented above.

However, the most real systems are significantly richer in chemical interactions. Therefore, in assessing the lability of such systems, it is sometimes necessary to take simplifications, the reliability of which cannot always be controlled. In this issue to some extent the analysis of adequate theoretical models that reflect typical properties of real systems can help. It seems quite possible that some assumptions and concepts, used in the simplest cases, might be also acceptable for more complex systems. To substantiate their acceptability and to determine the area of their suitable application, a special analysis is required. The main results arising from such approach are the subject of the present communication.

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## SIMULATION DETAILS

For the numerical evaluation of concentrations, the  $\delta$ -thick diffusion layer was divided into  $n$  intervals of the length  $\Delta x = \delta/n$ . Equilibrium concentrations were used as initial conditions. The iterative evaluation of the concentration,  $c_j(x)$ , was performed using the backward Euler method with the step in time  $\Delta t$ . The stability and accuracy of solution was improved using the conditions:  $\Delta t \leq 0.1/\max(w_{\pm 1}/c_j)$  and  $\Delta t \leq \Delta x^2/(3D)$ , where  $w_{\pm 1}$  and  $D$  were reaction rates and an effective diffusion coefficient, which come from kinetic and diffusive terms, respectively (see below).

## RESULTS AND DISCUSSION

### Model of mass transport

Let us consider the system containing the complexes  $ML_j^{n+}$  ( $j \in [0, N]$ ) and the ligand species L that is capable of forming coordination bonds with  $M^{n+}$  ions. We also assume, for simplicity, that the ligand L is uncharged. Chemical reactions that occur both in the bulk of solution and in the  $\delta$ -thick diffusion layer can be presented in a general form as follows:



The rates of direct and reverse chemical reactions, given by Eq. 1 ( $w_j$  and  $w_{-j}$ , respectively), may be expressed by the relationships

$$w_j = k_j[ML_{j-1}^{n+}][L], \quad (2)$$

$$w_{-j} = k_{-j}[ML_j^{n+}], \quad (3)$$

where  $k_j$  and  $k_{-j}$  are the respective rate constants and the symbol  $[X]$  means the concentration of X species.

The second Fick's law supplemented by kinetic terms should be written for all mobile species. To express the kinetic terms, it is necessary to take into account that  $ML_j^{n+}$  complexes take part in two chemical steps. When one of them is given by Eq. 1, the next step,  $ML_j^{n+} + L \rightleftharpoons ML_{j+1}^{n+}$ , is characterized by rates  $w_{j+1}$  and  $w_{-(j+1)}$ . Then, the differential equations describing a linear diffusion of metal-containing species take the following form:

$$\frac{\partial[ML_j^{n+}]}{\partial t} = D \frac{\partial^2[ML_j^{n+}]}{\partial x^2} w_j - w_{-j} - (w_{j+1} - w_{-(j+1)}). \quad (4)$$

In contrast with metal complexes, the ligand L takes part in all chemical steps and the differential equation for this species assumes the form:

$$\frac{\partial[L]}{\partial t} = D \frac{\partial^2[L]}{\partial x^2} + \sum_{j=1}^N (w_{-j} - w_j). \quad (5)$$

In the above records, the kinetic terms ( $w_j$  or  $w_{-j}$ ) are equal to zero at  $j < 1$  and  $j > N$ . Besides, the same effective diffusion coefficient  $D$  is attributed to all species. A substantiation of the latter approach has been given by Kačena and Matoušek [15]. The effective  $D$  depends on the individual diffusion coefficients of complex species and their molar fraction in the solution [6, 8, 16].

The set of  $(N+2)$  differential equations has a characteristic feature. A linear combination of equations written for metal-containing species yields a simple relationship

$$\frac{\partial c_M}{\partial t} = D \frac{\partial^2 c_M}{\partial x^2}, \quad (6)$$

containing no kinetic terms. Here  $c_M$  is a total metal concentration, which is determined as a sum of concentrations of metal-containing species, i. e.

$$c_M = \sum_{j=0}^N [ML_j^{n+}]. \quad (7)$$

A similar expression

$$\frac{\partial c_L}{\partial t} = D \frac{\partial^2 c_L}{\partial x^2} \quad (8)$$

is also obtained for the total ligand concentration:

$$c_L = \sum_{j=0}^N j[ML_j^{n+}] + [L]. \quad (9)$$

The usage of simple relationships Eqs. 6 and 8 is very tempting, since the solutions of such equations supplemented with the corresponding initial and boundary conditions have been well-expounded in literature. However, no information concerning individual components of the system follows from these equations. Therefore, to obtain such data, it is necessary to formulate extra interrelations between their concentrations.

In this connection, the labile systems may be considered as a limiting case. Further, we shall designate the systems with extremely high  $k$  values as "ideally labile" (IL systems). Since the chemical reactions in these systems proceed with "a sufficiently high" rate, the relations between concentrations might be determined on the basis of material balance equations, similar to Eqs. 7 and 9 and involving step-wise,  $K_j$ , or cumulative,  $\beta_j$ , stability constants of complexes defined as

$$K_j = \frac{k_j}{k_{-j}} = \frac{[ML_j^{n+}]}{[ML_{j-1}^{n+}][L]}, \quad (10)$$

$$\beta_j = \frac{[ML_j^{n+}]}{[M^{n+}][L]^j}. \quad (11)$$

On using such an approach, the problem becomes simpler and requires Eqs. 6 and 8 to be solved with appropriate initial and boundary conditions.

The initial condition of the system (at  $t = 0$ ) is commonly treated as an equilibrium state with constant (bulk) concentrations of species over the whole area of the system. The same is valid for the respective boundary conditions at  $x \geq \delta$ , since the electrochemical process, that starts at  $t > 0$ , gives rise to the formation of certain concentration gradients only within the diffusion layer (at  $0 < x < \delta$ ). Another boundary condition follows from the first Fick's law and correlates the flux of the electrically active complex (EAC) with the current density ( $i$ ) applied. Since Eq. 7 deals with the total metal concentration, there is no necessity to preset which species is the EAC taking part in the respective charge transfer processes. In any case

$$i = -nFD \left. \frac{\partial c_M}{\partial x} \right|_{x=0} . \quad (12)$$

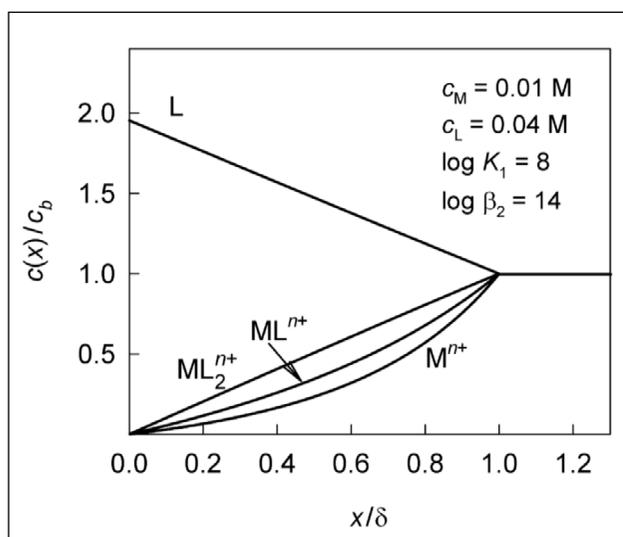
Since the ligand is supposed to be electrochemically inert,

$$\left. \frac{\partial c_L}{\partial x} \right|_{x=0} = 0. \quad (13)$$

The latter condition does not mean that  $[L]$  is also constant; the certain gradient of free ligand  $L$  follows from the material balance expressed by Eq. 9.

### Behaviour of ideally labile systems

An example of concentration profiles obtained at the steady-state conditions ( $\partial c/\partial t = 0$ ) for an ideally labile system is presented in Fig. 1. When the limiting cathodic current density,



**Fig. 1.** Steady-state concentration profiles obtained for the IL system at the limiting current density  $i_d$ . Concentrations of indicated species,  $c(x)$ , are normalized with respect to the respective bulk concentrations

$i_d$ , is applied, surface concentrations of metal-containing species approach zero. Strictly speaking, none of concentration profiles is linear, though the total  $c_M$  varies linearly with the distance  $x$ .

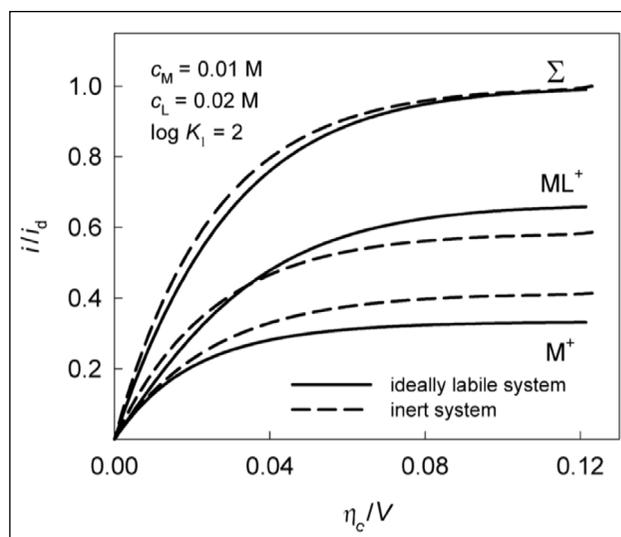
The characteristic feature of the results obtained is that the certain concentration gradients of all metal-containing species arise at the electrode surface. By analogy with Eq. 12, this means that all metal-containing species take part in the electrochemical process producing their own partial currents,  $i_j$ . These quantities can be easily obtained with the respectively modified Eq. 12 using the concentration profiles simulated at different total current densities provided that  $i = \sum i_j$ . Reversible voltammograms obtained for a very simple model system containing  $M^+$ ,  $ML^+$  and  $L$  species are depicted by solid lines in Fig. 2. Cathodic overvoltage, taken as positive ( $\eta_c = |\eta|$ ), was calculated with  $n = 1$  and  $T = 293$  K using the well-known modification of the Nernst equation

$$\eta = \frac{RT}{nF} \ln \frac{[M^+]_s}{[M^+]_b}, \quad (14)$$

where subscripts  $s$  and  $b$  denote the surface ( $x = 0$ ) and bulk concentrations, respectively. For comparison, similar data concerning the inert system are shown by dashed lines. In the latter case, the aforementioned chemical steps are ignored and both charge processes



are assumed to proceed independently of one another. Then the limiting current densities are proportional to the bulk



**Fig. 2.** Reversible steady-state voltammograms simulated for IL (solid lines) and inert (dashed lines) systems. The overall curves are designated by symbol  $\Sigma$ . The partial currents are arranged below with indication of the respective EAC

concentrations of EAC that is a contrast with the labile system, where, due to the release of ligand at the electrode surface, some extra quantity of  $ML^+$  is generated and, as a consequence, the limiting current of  $ML^+$  reduction is higher.

It can be seen even intuitively that some results obtained for IL systems are in a certain contradiction with reality. The most objectionable feature of this model consists in the fact that the electrochemical activity of complexes is associated with their stability, since the shape of concentration profiles and partial currents depend mainly on  $K_f$ . Certainly, thermodynamics allows us to treat any metal-containing species as a possible EAC, since the same equilibrium potential should be attributed to any charge transfer process, Eqs. 15 or 16. However, there is a lot of experimental data (see, e. g. [17]) testifying that the EAC is liable to contain less ligand particles than the more stable complex predominating in the solution. The removal of ligands from its inner coordination sphere promotes adsorption and a decline in the potential barrier of electron transfer. Thus, kinetic factors, and the activation energy, first of all, should be responsible for the electrochemical activity of complexes. Special methods have been suggested and successfully applied for establishing the EAC composition [1, 17]. At the same time, the model of the IL system leaves no freedom in choosing the EAC. Therefore, alternatives free from such limitations should be considered.

### Systems of limited lability

Rates of chemical reactions vary within a wide region of magnitude. Due to diffusion limitations, the rate constant of bimolecular reaction cannot exceed  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [18]; therefore this value can be used as an upper limit of  $k_f$ . Reactions whose half-times are less than 10 s are considered fast [19]; then the rate constant for monomolecular reaction should exceed  $0.1 \text{ s}^{-1}$ . In accordance with the reaction rate, metal complexes are sometimes classified as labile and inert, but it is not possible to draw a sharp boundary line between the two groups since other parameters mentioned above should be considered.

The rate of complex formation depends on various factors, such as the nature of the bond, the constitution of the electronic shells of the central metal atom, stereochemistry of the complex, etc. [19]. It has been suggested [20] that the rate constant for ligand penetration is characteristic of the metal ion alone. However, exceptions are possible for chelating reactions in which steric effects, such as chelate ring formation, can reduce the overall complexation rate. Unfortunately, kinetic data are incomparably weaker than vast databases of stability constants. We were able to find some more exhaustive data on the formation of Cu(II)-amino acid complexes [20–22]. It was found that the release of a water molecule from the inner hydration sphere of the metal ion is the rate-determining step. Forward rate constants for glycine and  $\alpha$ -alanine were found to be of the same order of magnitude ( $10^8$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), but those

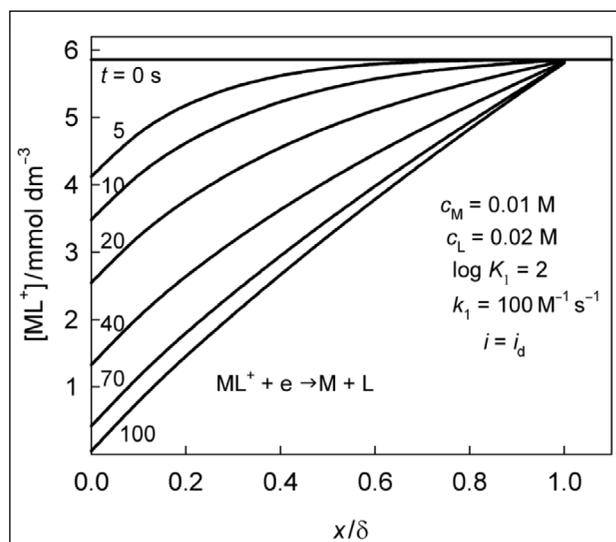
for  $\beta$ -alanine are substantially smaller ( $10^6$ – $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). This effect was interpreted on the basis of ring closure as the rate-determining step. It was supposed that the five-membered chelate ring undergoes transformation into a six-membered configuration.

To account for the rate of chemical interactions, it is necessary to return to the set of Eqs. 4 and 5 containing kinetic terms. The results given below were obtained for “a system of limited lability” (LL system) involving  $M^+$ ,  $ML^+$  and L species using the following set of parameters:  $c_M = 0.01 \text{ M}$ ,  $c_L = 0.02$  or  $0.1 \text{ M}$ ,  $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , and diffusion layer thickness  $\delta = 0.02 \text{ cm}$ . The steady-state limiting current density, obtained by the equation

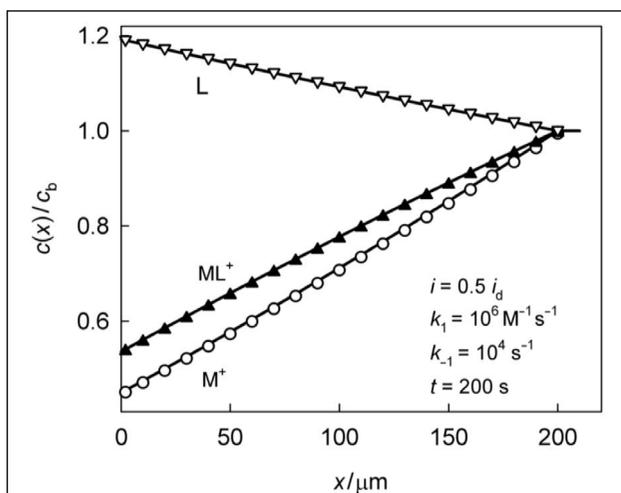
$$i_d = \frac{nFDc_M}{\delta} \quad (17)$$

was equal to  $0.24125 \text{ mA cm}^{-2}$ . The rate constant of complex formation,  $k_f$ , and that of its dissociation,  $k_d$ , varied, but the interrelation between them and stability constants (Eq. 10) was always obeyed.

The dynamics of mass transport can be seen from the data given in Fig. 3. A steady state is actually attained at  $t > 100 \text{ s}$ , when the shift of the diffusion front  $x \sim \sqrt{Dt}$  achieves  $\delta$ . The data obtained for the LL system at sufficiently long times can be compared with the respective steady-state data simulated for the IL system. In so doing, both  $M^{n+}$  and  $ML^{n+}$  were treated as electrically active species and their concentration gradients, obtained for the IL system at  $x = 0$ , were used as boundary conditions for the LL system. At  $k_f > 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , concentration profiles are similar in both systems (Fig. 4). However, we shall see from the following discussion that a certain discrepancy can be observed at lower reaction rates.



**Fig. 3.** Dynamics of EAC ( $ML^+$ ) concentration profiles when the system is perturbed by current step  $i(t) = i_d$

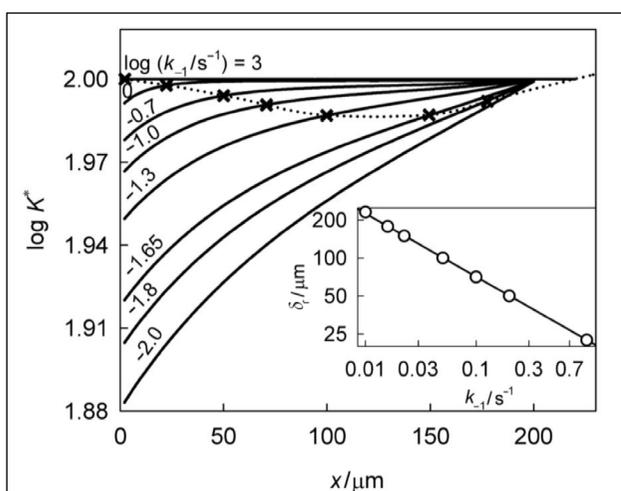


**Fig. 4.** Comparison of normalized steady-state concentration profiles simulated at  $i = 0.5 i_d$  for IL (solid lines) and LL (symbols) systems

Previously the analysis of the CE mechanism was based on the concept that a thin reaction layer is formed at the electrode surface where a certain non-equilibrium distribution of the system components occurs. In the case of preceding reactions of the first (or pseudo-first) order, the thickness of such layer was estimated by the relationship

$$\delta_r = \sqrt{\frac{D}{k_{-1}}} \quad (18)$$

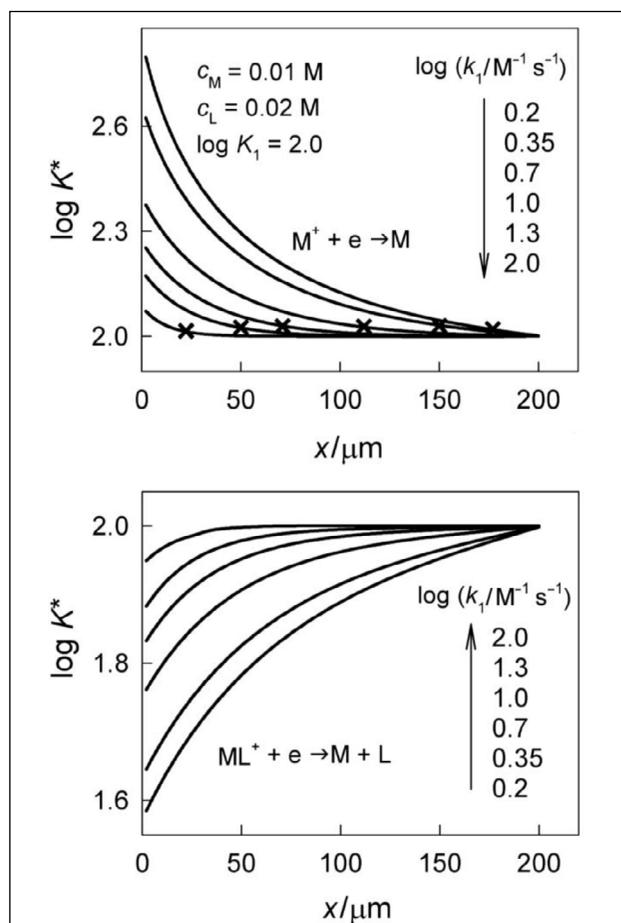
To check whether this concept is suitable in the case of the system under consideration, we calculated effective  $K^*$  values substituting simulated  $c(x)$  functions in Eq. 10. The data obtained at the constant ratio of  $k_1/k_{-1} = 100 \text{ M}^{-1}$  ( $\log K_1 = 2$ ) are shown in Fig. 5. An obvious divergence of  $K^*$



**Fig. 5.** Effective stability constants  $K^*$  as functions of coordinate  $x$ . Both  $M^+$  and  $ML^+$  species are electrochemically active. The thickness of the hypothetical reaction layer,  $\delta_r$ , is marked with crosses. Its dependence on  $k_{-1}$  determined by Eq. 18 is shown in the inset (semi-logarithmic presentation)

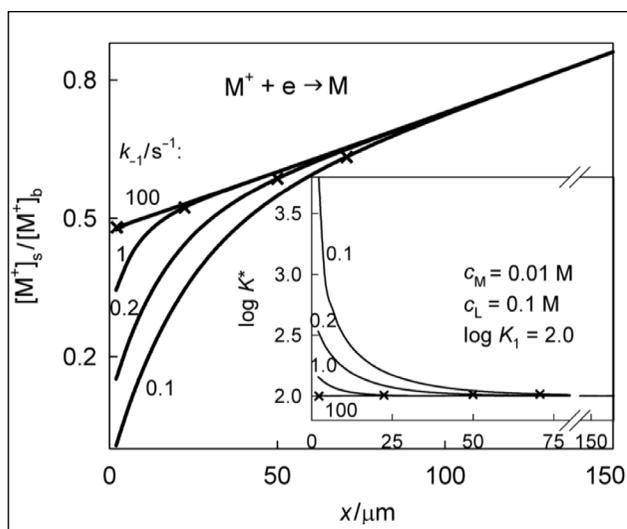
from the specified  $K_1$  quantity should occur in the reaction layer. However, there is no indication that such layer actually exists as a part of the diffusion layer. This conclusion holds true when a sufficient EAC excess is present (Figs. 5 and 6, respectively).

Though the amounts of both species  $M^+$  and  $ML^+$  are of the same order, moderate deviations from the equilibrium, depending on the rate constants, are still observed over the whole diffusion layer, but the concept of reaction layer is not working in this case.



**Fig. 6.** Effective stability constants  $K^*$  as functions of coordinate  $x$ , simulated at different  $k_1$  values as indicated. The thickness of the hypothetical reaction layer,  $\delta_r$ , is marked with crosses. The case of single EAC:  $M^+$  (top part) or  $ML^+$  (bottom part)

However, the situation changes significantly when  $M^+$  ions are reduced in the solution containing an excess of ligand. In this case, an amount of this EAC is by one order lower than that of  $ML^+$  complexes and the role of electrically inert  $ML^+$  species, as EAC donors, becomes considerable. The conditions that are created in this case are rather similar to those which the concept of reaction layer was suggested for. The reaction layer can be detected from both the concentration profiles (Fig. 7) and  $K^*(x)$  values (Fig. 8). It can be seen from these data that Eq. 18 is a good approximation for the reaction layer thickness.



**Fig. 7.** Normalized concentrations of  $M^+$  species, as functions of coordinate  $x$ , simulated at different  $k_{-1}$  values as indicated. Effective stability constants  $K^*$  as functions of coordinate  $x$  are shown in the inset

It seems likely that the regularities established for a very simple model could serve as a guide to more complex cases. The results obtained for the model system show that at least two parameters, viz. the rate constant,  $k_{-1}$ , and the complexation degree, are responsible for deviations from the equilibrium distribution. This effect is most pronounced at low concentrations of the electrically active complexes that are generated by the preceding reaction. Of course, any preliminary premise on system lability should be validated or disproved by respective simulations.

The above results show that the condition  $k_{-1} > 1 \text{ s}^{-1}$  might serve as a criterion of sufficient lability when the current-step perturbation of the system is applied or the steady-state electrolysis is performed. From this point of view, the aforementioned Cu(II) complexes are referable to labile compounds. This circumstance makes it possible to use the IL model for determining the surface concentrations of species with an acceptable error. On the other hand, the presence of a thin non-equilibrium layer offers the prospect to operate with concentration gradients in compatibility with the active current density.

In the case of other electrode geometry, an account of chemical steps can be performed in the same manner. Differential equations, written for each component that takes part in the mass transport, should be supplemented with the respective kinetic terms. Again, the above-described linear combinations of the differential equations yield the relationships that contain no kinetic terms and operate with the total concentrations of metal and ligand. Because of the non-uniform distribution of diffusional flows, it is likely that the effects of chemical interactions would be also different in various regions of the solution adjacent to an electrode surface. These cases seem to be more complicated and need further investigations.

## CONCLUSIONS

Electrochemical processes, involving mass transport of chemically interacting metal complexes and ligands, are considered using the quantitative model based on the second Fick's law equations supplemented with kinetic terms. The results, obtained with different diffusion and kinetic parameters, show that concentration profiles obtained can be used for the characterization of system lability.

When chemical steps are fast enough and the interrelation between the concentrations of species is specified by stability constants of metal complexes, all complexes in the system show electrical activity and yield the respective partial currents.

In the case of the systems with limited lability, certain deviations from the equilibrium distribution of species is observed in the diffusion layer. In default of the electrically active complex, the reaction layer concept can be applied and used in the electroanalysis.

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### KONCENTRACIJŲ PROFILIAI – METALŲ KOMPLEKSŲ ELEKTROCHEMINIŲ SISTEMŲ LABILUMO INDIKATORIAI

#### *S a n t r a u k a*

Elektrocheminiai procesai, susiję su chemiškai sąveikaujančių metalų kompleksų ir ligandų masės transportu, nagrinėjami remiantis kiekybiniu modeliu, pagrįstu antrojo Fiko dėsnio lygtimis, papildytais kinetiniais nariais. Keičiant įvairias difuzines ir kinetines charakteristikas apskaičiuoti koncentracijų profiliai, kurie naudojami sistemų labilumui charakterizuoti. Kai cheminės stadijos yra pakankamai greitos, o sąryšius tarp komponentų koncentracijų apibrėžia kompleksų stabilumo konstantos, visi sistemos kompleksai rodo elektrocheminį aktyvumą ir sukuria atitinkamas parciales sroves. Jei sistemos labilumas ribotas, pusiausvyrusis dalelių susiskirstymas difuzijos sluoksnyje pasikeičia. Šis reiškinys analizuojamas pasitelkiant reakcijos sluoksnio koncepciją. Aptariamos idealizuoto masės transporto modelio taikymo elektroanalizėje galimybės.