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On the application of Koutecky–Levich analysis to electrochemical processes involving metal complexes. 1. Theoretical background

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The applicability of the Koutecky–Levich (KL) approach for the processes occurring in the systems of labile metal complexes is considered. According to the analysis of simulated RDE voltammograms, the use of classical KL relationships is possible if the predominant complexes are involved in the charge transfer process. In the opposite case, corrections to the initial voltametric data, taking into account the surface distribution of complexes and ligands, are required. The rationale and methodology for correction functions are presented. Inaccuracies in the estimation of kinetic and diffusion characteristics arising from ignoring the peculiarities of mass transfer of chemically interacting particles are analysed.

Keywords: RDE voltammetry, Koutecky–Levich analysis, metal complexes

INTRODUCTION

RDE voltammetry is still one of the most widely used methods for the study of electrochemical processes. Due to the significantly developed theoretical concepts of convective diffusion of reactants to the uniformly accessible surface of the rotating disc electrode, as well as progress in the improvement of measuring equipment, that technique was continuously extended to more complex electrochemical reactions coupled by different chemical and electrochemical steps.

Among the various modifications of the RDE voltammetry the Koutecky–Levich (KL) approach should be mentioned. This method is based on the analysis of reciprocal current density $1/i$ vs reciprocal square root of rotation velocity $1/\sqrt{\omega}$ plotted at different constant potentials E. The KL-approach was originally invented for a single-stage electron transfer with mixed transport-kinetic control [1] and enabled to elucidate both the mass transport parameters, such as the diffusion coefficient D, and the kinetic parameters, such as the standard rate constant k^0 and charge transfer coefficient α. Further developments concern more complex multistage mechanisms involving various combinations of chemical and charge transfer steps. A review of studies performed before the beginning of the present century has shown [2] that the quantitative analysis can be simplified using the reaction layer approach. Certain mathematical relations were obtained in the case of the simplest mechanisms involving single monomolecular chemical steps [3–5].

The richness of different stages is characteristic of complex systems containing coordination compounds of metals and ligands. Their number can be counted in tens, so attempts to perform any more

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general analysis of such objects remains unpromising. This seems to be one of the reasons why KL-analysis has not been more widely used in the reduction of metal complexes, although the RDE voltammetry was often applied. Perhaps the expected results were not obtained due to the insufficient consideration of the specifics of complex systems. Hence, the use of KL analysis requires consideration of its applicability to the object of study since failure to comply with this requirement may lead to various confusions and errors. In this context, we attempt to fill this gap and contribute to the problem to the best of our ability. In our opinion, the use of the model of mass transfer of chemically interacting species [6] expands the possibilities of applying KL-analysis to labile complex systems without limiting the number of chemical stages accompanying charge transfer. The theoretical analysis of RDE voltammograms simulated for the irreversible reduction of metal complexes in labile systems is presented in this communication.

BASIC MODEL

As mentioned above, the conventional Koutecky–Levich approach deals with a simple redox process

$$\mathrm{O} + n\,\mathrm{e} \rightarrow \mathrm{R}, \tag{1}$$

controlled by diffusion and charge transfer. The following equation, valid at sufficiently high cathodic overvoltage η,

$$1/i = 1/i_\mathrm{K} + 1/i_\mathrm{d} = 1/i_\mathrm{K} + 1/(k\sqrt{\omega}\,c_\mathrm{O}), \tag{2}$$

with

$$k = 0.62\,nFD^{2/3}\nu^{-1/6}, \tag{3}$$

has been derived for the quantitative description of RDE voltammograms [1]. It served as a basis for analysing the linear dependencies of $1/i$ on $1/\sqrt{\omega}$ obtained at constant electrode potentials E and different rotating velocities ω.

Following this classical research [1], let us consider in a similar way the charge transfer

$$\mathrm{ML}_\mathrm{p}^{\mathrm{n}+} + n\,\mathrm{e} \rightarrow \mathrm{M} + p\,\mathrm{L}, \tag{4}$$

involving the electrically active complex (EAC) $\mathrm{ML}_\mathrm{p}^{\mathrm{n}+}$, which is part of a more complex system formed by the interaction of metal ions $\mathrm{M}^{\mathrm{n}+}$ with the ligand L. Assume that the process (4) is controlled by diffusion and charge transfer and proceeds in the labile system where chemical steps are sufficiently rapid and do not affect the rate of the total electrochemical process. Then the Butler–Volmer kinetic equation is acceptable:

$$i = i_0\{([\mathrm{L}]_\mathrm{s} / [\mathrm{L}]_\mathrm{b}) \exp(\alpha_\mathrm{a} f\eta) -$$

$$- ([\mathrm{ML}_\mathrm{p}{}^{\mathrm{n}+}]_\mathrm{s} / [\mathrm{ML}_\mathrm{p}{}^{\mathrm{n}+}])_\mathrm{b} \exp(-\alpha_\mathrm{c} f\eta)\}. \tag{5}$$

Here $f = nF/RT$, i_0 is the exchange current density, α_a and α_c are anodic and cathodic charge transfer coefficients, and η is the overvoltage. Subscripts *s* and *b* denote surface and bulk concentrations, respectively. Here and hereafter, cathodic η and i, including the limiting current density i_d, are considered negative. At sufficiently high cathodic polarisation, the anodic component of Eq. (5) can be neglected. Then

$$i = -\,i_0\,([\mathrm{ML}_\mathrm{p}^{\mathrm{n}+}]_\mathrm{s} / [\mathrm{ML}_\mathrm{p}^{\mathrm{n}+}]_\mathrm{b}) \exp(-\alpha_\mathrm{c} f\eta). \tag{6}$$

According to Ref. [6], mass transfer regularities established for simple redox processes can be also applied to labile complex systems, if the concentration of the reactant O is treated as the total metal concentration c_M. Then, the relation

$$i = i_\mathrm{d}\,(1 - c_{\mathrm{M,s}} / c_{\mathrm{M,b}}) \tag{7}$$

is valid for RDE voltammograms where the limiting current density i_d is given by

$$i_\mathrm{d} = -k\sqrt{\omega}\,c_{\mathrm{M,b}}, \tag{8}$$

with k specified by Eq. (3).

We point to the fundamental difference in the quantitative description of processes (1) and (4). In the case of the redox process, the kinetic and mass transport expressions contain concentration terms referring to the same species, i.e. to the reactant O. Conversely, in the case of the reduction of complexes, the relation between current and potential, Eq. (6), is determined by the EAC concentration, while the current density in Eq. (7) is expressed through the total metal concentration. Considering the relations between $[\mathrm{ML}_\mathrm{p}^{\mathrm{n}+}]_\mathrm{s}$ and $c_{\mathrm{M,s}}$

as functions of i and performing the transformations, which we omit here, we obtain the modified Koutecky–Levich equation adapted for the reduction of metal complexes:

$$F(i)/i = 1/i_K + F(i)/i_d = 1/i_K + F(i)/(k\sqrt{\omega}\, c_{M,b}). \quad (9)$$

Here, i_K is the kinetic current density, expressed by

$$i_K = -\, i_0 \exp(-\alpha_c f\eta). \quad (10)$$

It represents the current that would flow under the kinetic limitation in the absence of any mass-transfer effects. The function

$$F(i) = ([\mathrm{ML}_p^{n+}]_s / [\mathrm{ML}_p^{n+}]_b) / (1 - i/i_d) \quad (11)$$

accounts for the specifics of the complex system pointed out above. $F(i)$ can be calculated using data on the distribution of species at the electrode surface. Provided that $c_{M,s}$ varies with i according to Eq. (7) while the total concentration of the electrochemically inert ligand remains constant ($c_{L,s} = c_{L,b}$), these data can be obtained using material balance equations, written for c_M and c_L, and combined with expressions for the corresponding stability constants β [6].

Simulation procedures

It is of interest to quantify the differences between the classical and modified KL approaches and find out what miscalculations could occur if the specifics of complex systems is ignored. Two systems containing uncharged ligand L, free ions (solvatocomplexes) M^+ and complexes ML^+, ML_2^+ with log $\beta_1 = 7$ and log $\beta_2 = 12$ were chosen for digital analysis: system *A* with an excess of ligand ($c_M = 0.01$ M, $c_L = 0.04$ M) and ligand-deficient system *B* with $c_M = 0.01$ M and $c_L = 0.015$ M. In both cases, the non-dominant monoligand complex ML^+ was chosen as the electrically active species. The rate of the charge transfer process (4) with $p = 1$ and $n = 1$ was simulated by Eq. (5). Kinetic and diffusion parameters were specified as follows: $i_0 = 0.01$ or 1 mA cm^{-2}, $\alpha_c = 0.3$ ($\alpha_a = 1 - \alpha_c$) and $D = 7 \times 10^{-6}$ cm^2 s^{-1}. Each voltammogram was obtained at the specified thickness of diffusion layer δ, which depends on the rotating velocity ω according to the relation

$$\delta = 1.61\, D^{1/3}\nu^{1/6}\,\omega^{-1/2}. \quad (12)$$

Simulated RDE voltammograms cover the range of rotation velocity from 450 to 2000 rpm. In the case of an excess of ligand (system *A*) curves have a usual shape with a single plateau of the limiting current. The voltammograms obtained at $i_0 = 0.01$ mA cm^{-2} are given in Fig. 1. At higher exchange current density ($i_0 = 1$ mA cm^{-2}), they have a similar shape, but the overvoltage is noticeably lower, and curves reach the plateau of limiting current at 0.3–0.4 V. In the absence of an excess of ligand (system *B*), the shape of voltammograms becomes more complicated (the inset in Fig. 1). Irregularities in the form of pre-waves, which are observed at lower cathodic polarizations, are sometimes also called limiting currents. Discussions on their nature [6–10] lead to the conclusion that a significant change in the complexation degree occurs at the electrode surface in this region. Despite these differences, the current density in the plateau region obeys Eq. (8) in the case of both systems.

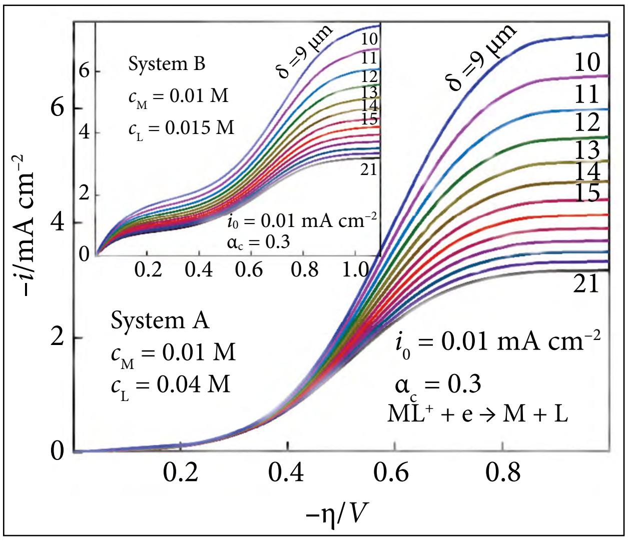

Fig. 1. RDE voltammograms simulated for the charge transfer $ML^+ + e \longrightarrow M + L$ at different intensity of forced convection. The effective thickness of diffusion layer (δ) is indicted at the respective voltammograms

RESULTS AND DISCUSSION

Since the stability constants β_1 and β_2 are markedly different, diligand complexes ML_2^+ prevail in the system *A* with a concentration practically equal to c_M (see the data for $i/i_d = 0$ in Fig. 2). In this case, surface concentrations of ML_2^+ vary almost linearly with i/i_d and, as follows from Eqs. (7) and (11), the function $F(i)$ should be close to 1. This deduction is in line with the data in Fig. 3 presented by a solid line

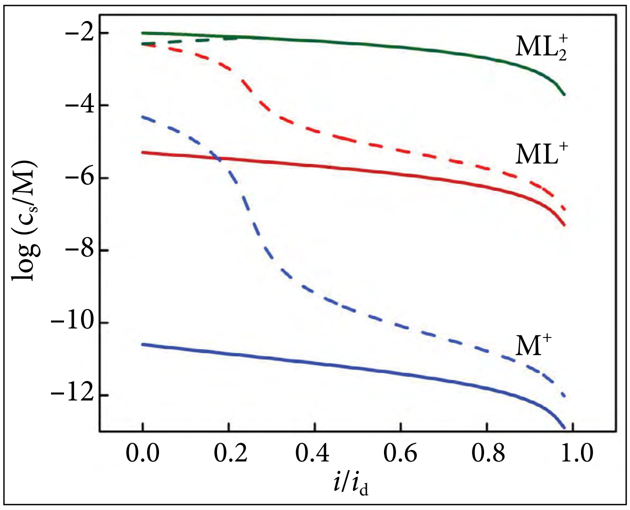

Fig. 2. Variations of surface concentrations with normalized cathodic current density simulated for system *A* (solid lines) and system *B* (dashed lines)

at $p = 2$. Thus, if the predominant complex is electrically active, the classical KL approach needs no corrections. We will not consider this case any further. On the contrary, when the ligand is deficient, the bulk concentrations of ML^+ and ML_2^+ complexes are approximately close (see dashed lines at $i/i_d = 0$ in Fig. 2). Surface concentrations of complex species vary differently with the normalized current density (Fig. 2), and this ultimately affects the shape of the correction functions. In the case of the lack of ligand (system *B*), variations of *F*(*i*) functions are so significant that semi-logarithmic coordinates are required to visualize them (Fig. 3).

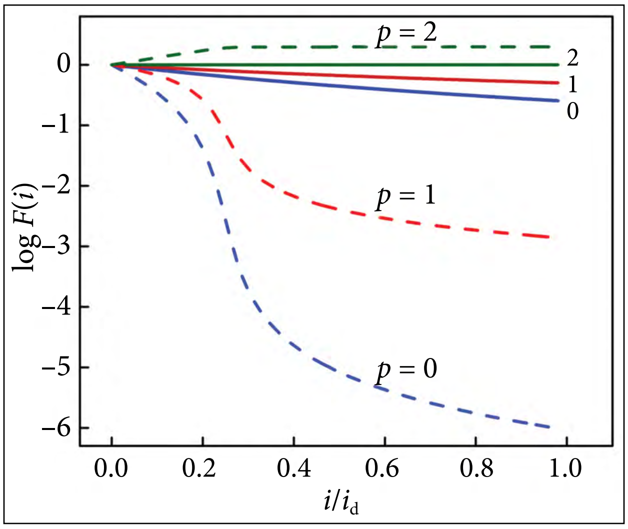

Fig. 3. Functions *F*(*i*) vs normalized cathodic current density obtained for different EAC: M^+ ($p = 0$), ML^+ ($p = 1$) and ML_2^+ ($p = 2$). Simulation for system *A* (solid lines) and system *B* (dashed lines)

With the current values taken at the same η, one can construct KL plots consistent with Eqs. (2) or (9). In both cases, linear dependencies are observed (Fig. 4), but their parameters (the intercept and the slope) are different. Slopes of non-corrected plots (dashed lines in Fig. 4) depend on the electrode potential while the application of correction functions *F*(*i*) (solid lines) leads to parallel dependencies with slopes, which are constant at all η. The differences in both approaches decrease with increasing overvoltage. In our opinion, this feature might serve as a criterion allowing us to judge the adequacy of the considered mechanism and to choose the approach for analysis. Note that KL plots with potential-dependent slopes are possible for some multistep mechanisms [2]; in particular, such behaviour was observed for electrode processes involving Fe(II) complexes with EDTA and phenanthroline [11].

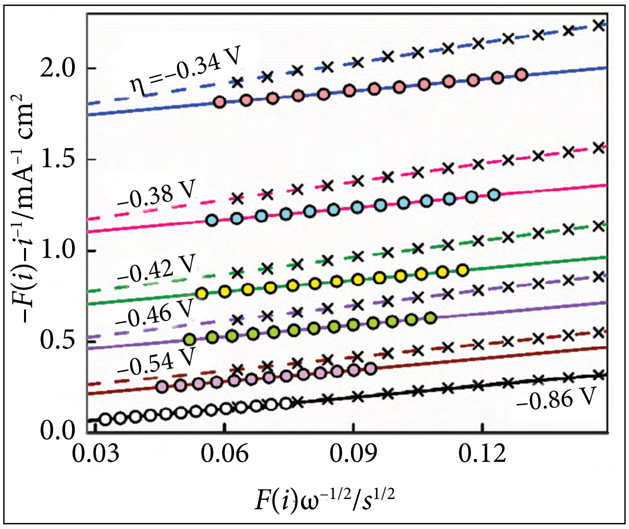

Fig. 4. Comparison of KL plots obtained at different cathodic overvoltages by Eq. (1) (crosses, dashed lines) and by Eq. (9) (circles, solid lines). $i_0 = 0.01$ mA cm^{-2}

Since KL slopes are sometimes applied to estimate the values of diffusion coefficients, we checked what results can be obtained by using Eq. (2) within the frameworks of the classical and modified KL approaches. The results obtained show (Fig. 5) that the introduction of the *F*(*i*) function is highly desirable, because in the absence of this correction you get markedly distorted *D* values. This seems to be the case with the unsound (reduced by ~3 times) *D* values of some Cu(II)-amino acid complexes [12] obtained, as reported, from KL plots.

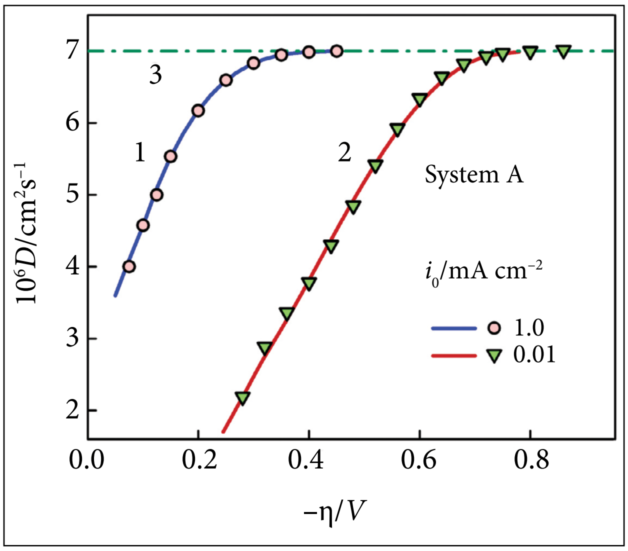

Fig. 5. Diffusion coefficients obtained for system *A* by non-corrected KL approach at the exchange current densities of 1.0 (curve 1) and 0.01 (curve 2) mA cm^{-2}. True *D* values are shown by line 3

Finally, we consider it necessary to check the values of the kinetic parameters by comparing the values of α_c and i_0 obtained from the KL plots with those that were set during the simulation of RDE voltammograms. For this purpose, we used the Tafel analysis of kinetic currents (Fig. 6). As usual, α_c is obtained from the Tafel slope and the extrapolation of log i_K to $\eta = 0$ yields the value of log i_0. It is evident from the data given in Fig. 6 that the non-corrected KL plots approach produce distorted kinetic parameters.

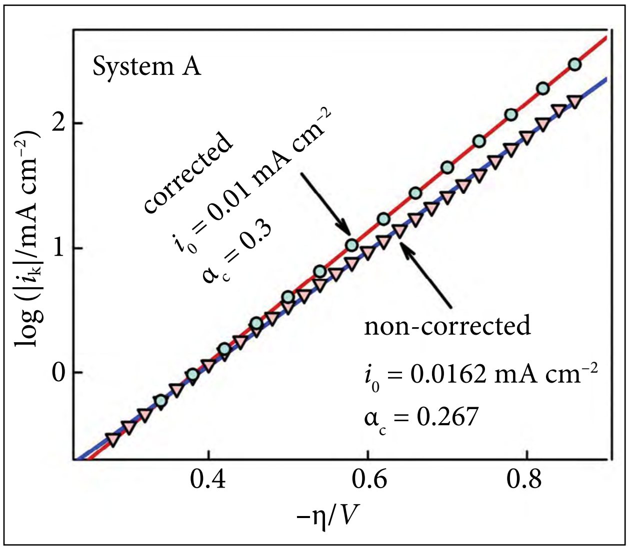

Fig. 6. Tafel plots of kinetic current density at the excess of ligand. Kinetic parameters following from non-corrected (triangles) and corrected (circles) data are presented

The above differences are especially pronounced in the case of ligand deficiency. At first glance, the KL plots obtained for systems *A* and *B* have no significant differences if presented in the usual coordinates (cf. Figs 4 and 7). However, kinetic analysis without making the necessary corrections leads to significant distortions of the set parameters. The kinetic currents obtained should be very sensitive to the reproducibility of the voltammetric characteristics. Since the overvoltage depends very strongly on the current density in the pre-wave region of the RDE voltammogram, even the accuracy of the calculated data may not be sufficient to obtain an acceptable curve (see the inset in Fig. 7).

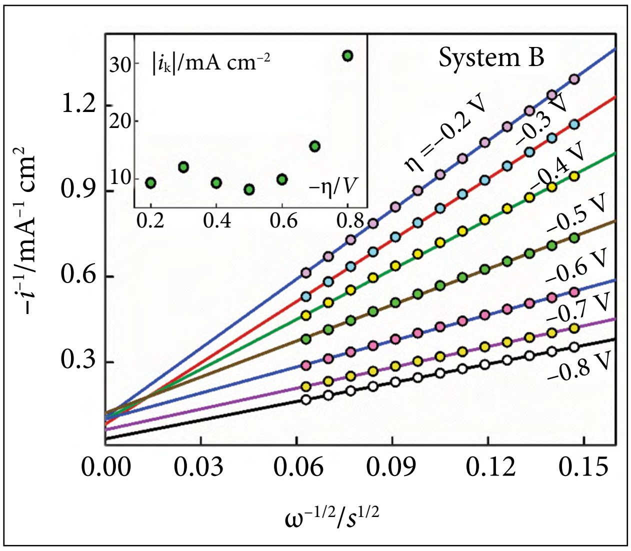

Fig. 7. Non-corrected KL plots obtained at i_0 = 1 mA cm^{-2} for system *B*. Kinetic current densities obtained by Eq. (1) are given in the inset

After making substantial corrections, the modified data can be approximated by parallel straight lines (Fig. 8), which give correct values of diffusion coefficients and the specified kinetic parameters. At the same time, the modified plots have a completely different scale compared to the original curves (cf. Figs 7 and 8). The data for each individual overpotential occupy its own region of values, different from the regions belonging to other η. Besides, the data related to a certain overvoltage are concentrated in a rather restricted range that narrows with decreasing cathodic overvoltage. Because of this, the error of extrapolation of corrected KL plots to the infinite intensity of forced convection increases. To overcome this predicament, more accurate experimental data related to this area are required.

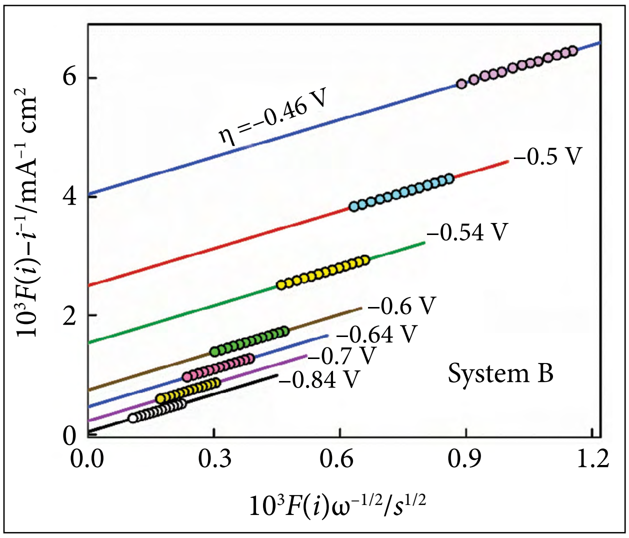

Fig. 8. Corrected KL plots obtained for system *B* at different cathodic overvoltages ($i_0 = 1$ mA cm^{-2})

CONCLUDING REMARKS

The Koutecky–Levich approach was originally invented for a single-stage electron transfer with mixed transport-kinetic control [1]. This method can be extended to processes involving metal complexes, but then several factors that distinguish these electrochemical systems should be considered.

In contrast to the simple redox system, the charge transfer process involves an electrochemically active complex (EAC), which is only a part of the complex system. At the same time, all kinds of complexes and ligands participate in mass transfer. This fact requires to take into account the distribution of these substances at the electrode surface.

Solution of this problem in a general form is possible in the case of labile systems in which chemical interactions are not rate-determining steps. Then an adequate modification of KL analysis based on a posteriori correction of voltammetric data could be employed. However, the calculation of correction functions requires stability constants of complexes as well as understanding the composition of EAC. Although this reduces the power of KL analysis, its value as a supplementary technique remains significant.

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DĖL KOUTECKIO-LEVIČIAUS ANALIZĖS TAIKYMO ELEKTROCHEMINIAMS PROCESAMS, KURIUOSE DALYVAUJA METALŲ KOMPLEKSAI. 1. TEORINĖS NUOSTATOS

Santrauka

Nagrinėjamas Kouteckio-Levičiaus (KL) metodo tinkamumas procesams, vykstantiems labilių metalų kompleksų sistemose. Apskaičiuotų sukamojo diskinio elektrodo voltamperogramų analizė rodo, kad klasikines KL lygtis galima taikyti tada, kai krūvio pernašos procese dalyvauja vyraujantys kompleksai. Priešingu atveju reikalingos pradinių voltamperinių duomenų pataisos, įvertinančios kompleksų ir ligandų susiskirstymą elektrodo paviršiuje. Pateikiamas korekcinių funkcijų pagrindimas ir jų skaičiavimo metodika. Analizuojami kinetikos ir difuzijos charakteristikų įvertinimo netikslumai, atsirandantys, jei chemiškai sąveikaujančių dalelių transporto ypatumai yra ignoruojami.