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INFLUENCE OF KINETIC PARAMETERS AND DIFFUSION COEFFICIENTS ON STATIONARY CONCENTRATION OF ELECTROACTIVE AND ELECTROINACTIVE SPECIES IN A MODEL ELECTROCHEMICAL PROCESS WITH A PRECEDING CHEMICAL REACTION

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This work is aimed at studying the influence of kinetic parameters and diffusion coefficients on stationary concentration distribution of electroactive and electroinactive species in a model electrochemical process with a preceding chemical reaction under constant current. We consider a preceding homogeneous first-order chemical reaction with a reversible heterogeneous electrochemical reaction at a planar electrode surface. To elucidate the peculiarities of stationary concentration distribution of electroactive and electroinactive species in a thin stagnant layer attached to a planar electrode surface, the exact solutions of a system of differential equations describing the variations of the concentrations of the participating species with a distance to electrode surface have been analyzed. The cases of equal and unequal diffusion coefficients of species involved in a preceding chemical reaction have been considered. It has been shown that the diffusion coefficients of both reacting species can affect their concentration profiles in a thin stagnant layer attached to electrode surface. The calculations demonstrate that the stationary concentration of electroactive and electroinactive species decreases with an increase of the diffusion coefficients. The influence of the rate constants of a preceding chemical reaction on the stationary concentration is different for electroactive species and electroinactive one. As the rate constants of a preceding chemical reaction are increased, the stationary concentration of electroactive species decreases, whereas the stationary concentration of electroinactive species increases slightly. This is also valid for the case of the stationary surface concentration of electroactive and electroinactive species. The thickness of a thin stagnant layer attached to a planar electrode surface where a change of the concentration of electroactive species takes place, also affects the stationary concentration distributions. The effect of this parameter is especially crucial at low values of a preceding chemical reaction rate constants.

Keywords: *CE mechanism, concentration profile, surface concentration, preceding chemical reaction, Nernst diffusion layer, reaction layer, diffusion coefficient, chemical reaction rate constant, steady-state conditions*

INTRODUCTION

The study of the mass transport of electroactive species from/to bulk of the solution and to/from electrode surface is crucial for the comprehension of heterogeneous charge transfer processes [1–14]. Earlier to investigate transport at micrometric level, the mapping of concentration profiles of redox-active species with excellent accuracy and resolution by using nanometric amperometric probes has been presented in [2]. The effect of natural convection on transport at microdisk electrodes was investigated. Recently, the analysis of the concentration profiles and fluxes in time-dependent 2 D model for transport of species in electrodialysis has been conducted in [3]. Experimentally, a strong effect of natural convection has been revealed in 3D concentration profiles along an electrodialysis channel in [4]. A new approach to control concentration profiles at electroactive biofilm interfaces has been implemented in [5]. Ion specificity in the measured concentration depth profile of ions at the vapor-glycerol interface has been investigated in [6]. New correlations from millimetric to submillimetric interelectrode distances has been obtained in mass transport evolution in microfluidic thin film electrochemical reactors in [7]. A theoretical analysis of the enzyme reaction processes within the multiscale porous biocatalytic electrodes has been done in [8]. The nonlinear mass transfer at the electrodes with reversible homogeneous reactions and the steady-state behavior of pseudo-first-order EC-catalytic mechanism at a rotating disk electrode have been investigated in [9] and [10]. Nonlinear effects of diffusion limitations on the response and sensitivity of amperometric biosensors have been found in [11]. *In situ* SECM study on concentration profiles of electroactive species from corrosion of stainless steel has been carried out in [12].

In this paper, a model electrochemical process with a preceding homogeneous first-order chemical reaction and a reversible heterogeneous electrochemical reaction at a planar electrode surface is considered. In this model process, a reversible heterogeneous charge transfer reaction is fast (Nernstian), and the mass transport of electroactive species is due to diffusion. We will analyze the peculiarities of stationary concentration distributions of electroactive and electroinactive species in a thin stagnant layer attached to a planar electrode surface under constant current. The control parameters of the system will be the diffusion coefficients of the species involved in a preceding chemical reaction and the rate constants of a preceding chemical reaction. It will be found the ranges of these parameters at which the stationary concentration distribution of electroactive species can be influenced by the presence of electroinactive species at most. To our knowledge, this question has not been raised in the literature.

The paper is organized as follows: the second section presents the main equations for a model electrochemical process with a preceding homogeneous first-order chemical reaction in the Nernst diffusion layer, the derivation of the expressions for the stationary concentration profiles of electroactive and electroinactive species in this layer, as well as the expressions for the stationary concentration of the species at a planar electrode surface. The third section demonstrates the results of numerical simulations [15] that are discussed and followed by the conclusions and the references.

THEORY

Main equations for a model electrochemical process with CE mechanism. We consider the following electrode process with a preceding homogeneous first-order chemical reaction. An electrochemical process in which a chemical step occurs first and is followed by an electron transfer we refer to it as following a CE mechanism. Here C denotes chemical reaction and E dealing with electrochemical one [13]:

$$\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{A} \tag{1}$$

$$\mathrm{A} + ne \underset{k_{s2}}{\overset{k_{s1}}{\rightleftarrows}} \mathrm{C} \tag{2}$$

where k_1 and k_2 are the rate constants for the chemical reaction, k_{s1} and k_{s2} are the electrochemical rate constants in the forward (reduction) and reverse (oxidation) directions, n is the number of electrons participating in an elementary act of reaction (2). In our case, the species B is not in excess and its diffusion coefficient can be unequal to the diffusion coefficient of species A, $D_B \neq D_A$. The distribution of the species C does not affect the distribution of the species B and A. It is affected only by the value of the current flowing through the interface.

Neglecting ionic migration, which is suppressed by a supporting electrolyte, the following differential equations describing the variations of the concentrations of the participating species A and B with distance to planar electrode surface x and time t can be written:

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - k_1 c_B + k_2 c_A \tag{3}$$

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} + k_1 c_B - k_2 c_A\,. \tag{4}$$

The species B do not involve into the electrode process at a chosen potential value. It is electroinactive, so a gradient of concentration of the species at electrode surface is equal to zero:

$$D_B \frac{dc_B}{dx}\Big|_{x=0} = 0\,. \tag{5}$$

The diffusive flux of electroactive species A at electrode surface under application of constant current is given as:

$$D_A \frac{dc_A}{dx}\Big|_{x=0} = -\frac{i}{nF}\,, \tag{6}$$

where i is an applied current density, F is the Faraday constant.

Here we will investigate the concentration profiles of species A and B in a thin stagnant layer attached to the electrode surface, namely in the Nernst diffusion layer with the thickness d. Beyond the boundary of the Nernst diffusion layer, in the bulk electrolyte, the following condition is met:

$$c_B^{\infty} k_1 = c_A^{\infty} k_2 . \tag{7}$$

Here c_B^{∞}, c_A^{∞} are the equilibrium concentrations of species B and A coinciding with the bulk concentrations of species c_B^0, c_A^0:

$$c_B(d) = c_B^{\infty} \tag{8}$$

$$c_A(d) = c_A^{\infty} . \tag{9}$$

Stationary concentration profiles of species A and B in Nernst diffusion layer. Under steady-state conditions $\partial c_B / \partial t = 0$ and $\partial c_A / \partial t = 0$, we have the following system of differential equations for determination of the stationary concentration of electroactive and electroinactive species:

$$D_B \frac{\partial^2 c_B}{\partial x^2} - k_1 c_B + k_2 c_A = 0 , \tag{10}$$

$$D_A \frac{\partial^2 c_A}{\partial x^2} + k_1 c_B - k_2 c_A = 0 . \tag{11}$$

The solutions for the system of differential equations (10), and (11) can be found in the following form [14]:

$$c_A^{st}(x) = \frac{k_1}{k_2} p_0 + \frac{k_1}{k_2} p_3 x - \frac{D_B}{D_A} p_1 \mathrm{ch}(rx) - \frac{D_B}{D_A} p_2 \mathrm{sh}(rx) \tag{12}$$

$$c_B^{st}(x) = p_1 \mathrm{ch}(rx) + p_2 \mathrm{sh}(rx) + p_3 x + p_0 . \tag{13}$$

Here the coefficients p_1, p_2, p_3, p_0 are determined by the boundary conditions (5–9) and the parameter r is as follows:

$$p_1 = -\frac{i}{nFD_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} \frac{\mathrm{th}(rd)}{r} , \tag{14}$$

$$p_2 = \frac{i}{nFr \cdot D_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} , \tag{15}$$

$$p_3 = -\frac{i}{nFD_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} , \tag{16}$$

$$p_0 = c_B^{\infty} + \frac{i \cdot d}{nFD_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} , \tag{17}$$

$$r = \sqrt{\frac{k_1}{D_B} + \frac{k_2}{D_A}} . \tag{18}$$

The functions $c_A^{st}(x)$, and $c_B^{st}(x)$ determine the stationary concentration profiles of species A and B in the Nernst diffusion layer.

Stationary concentration of species A and B at a planar electrode surface. At $x = 0$, the expressions (12) and (13) are simplified to the following forms:

$$c_{stA}^{s} = -\frac{D_B}{D_A} p_1 + \frac{k_1}{k_2} p_0 \tag{19}$$

$$c_{stB}^{s} = p_1 + p_0 . \tag{20}$$

Taking into account the expressions (14) and (17) for the coefficients p_1 and p_0, and the boundary conditions (5–9), we get the expressions for the stationary surface concentrations of electroactive and electroinactive species as follows:

$$c_{stA}^{s} = c_A^{\infty} + \frac{i \cdot d}{nFD_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} \left(\frac{k_1}{k_2} + \frac{D_B}{D_A} \frac{\mathrm{th}(rd)}{rd} \right) , \tag{21}$$

$$c_{stB}^{s} = c_B^{\infty} + \frac{i \cdot d}{nFD_A\left(\dfrac{k_1}{k_2} + \dfrac{D_B}{D_A}\right)} \left(1 - \frac{\mathrm{th}(rd)}{rd} \right) . \tag{22}$$

If the diffusion coefficients of species are equal, $D_A = D_B = D$, then the expressions (21), and (22) can be rewritten as:

$$c_{stA}^{s} = c_{A}^{\infty} + \frac{i \cdot d}{nFD\left(\frac{k_1}{k_2}+1\right)}\left(\frac{k_1}{k_2}+\frac{\mathrm{th}(rd)}{rd}\right), \qquad (23)$$

$$c_{stB}^{s} = c_{B}^{\infty} + \frac{i \cdot d}{nFD\left(\frac{k_1}{k_2}+1\right)}\left(1-\frac{\mathrm{th}(rd)}{rd}\right). \qquad (24)$$

It is worth mentioning that the parameter r is reciprocal to the kinetic (reaction) layer δ_k [1], $r = 1/\delta_k$. The kinetic layer δ_k is a distance from an electrode surface at which the following condition satisfies: $k_1 c_B \approx k_2 c_A$. Near the electrode surface, the equilibrium will be disturbed, since on the surface itself species A disappear as a result of the electrode reaction. Outside the kinetic layer δ_k, the bulk chemical reaction proceeds in an equilibrium manner. Only in the solution layer with the thickness δ_k does the kinetic (non-equilibrium) chemical process occur. The parameter δ_k decreases when the rate constants of chemical reaction increase, and increases if the diffusion coefficients of species increase.

RESULTS AND DISCUSSION

Electroactive species. Figures 1, 2, and 3 show the stationary concentration profiles of species A defined by Eq. (12) and normalized to a value of the bulk concentration c_A^0 for three sets of the chemical reaction rate constants k_1 and k_2, at different values of the diffusion coefficient of electroactive species D_A, and fixed value of the diffusion coefficient of electroinactive species D_B. In order to satisfy the condition defined by Eq. (7), and for the case of $k_1/k_2 << 1$, the bulk concentrations of species A and B were fixed at the values of $c_A^0 = 8 \cdot 10^{-6}\,\mathrm{mol\,cm^{-3}}$, and $c_B^0 = 8 \cdot 10^{-4}\,\mathrm{mol\,cm^{-3}}$. As can be seen from Figs. 1, 2, and 3, the dimensionless function $c_A^{st}(x)/c_A^0$ decreases with distance to a planar electrode surface, $0 < x < d$. Beyond the boundary of the Nernst diffusion layer, $x \ge d$, the stationary concentration of electroactive species $c_A^{st}(x)$ reaches a value of the bulk concentration c_A^0, *i.e.* $c_A^{st}(x)/c_A^0 = 1$. The points of intersection of the curves $c_A^{st}(x)/c_A^0$ with the axis of ordinate correspond to the normalized values of the stationary surface concentration of electroactive species c_{stA}^{s}/c_A^0 defined by Eq. (21).

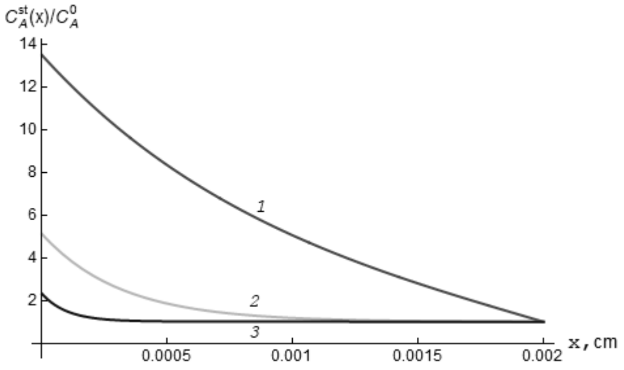

Fig. 1. Dimensionless concentration profiles of species A in the Nernst diffusion layer for different sets of the chemical reaction rate constants (*1*) $k_1 = 0.01$ s^{-1} and $k_2 = 1$ s^{-1}; (*2*) $k_1 = 0.1$ s^{-1} and $k_2 = 10$ s^{-1}; (*3*) $k_1 = 1$ s^{-1} and $k_2 = 100$ s^{-1}; and at fixed values of the diffusion coefficients of species: $D_A = 10^{-6}$ cm^2/s, $D_B = 2 \cdot 10^{-5}$ cm^2/s. Here and below, $d = 2 \cdot 10^{-3}$ cm, $i = 10^{-2}$ mA/cm^2, $T = 300$ K, $n = 1$

An increase in the chemical reaction rate constants k_1 and k_2 results in a decrease of the function $c_A^{st}(x)/c_A^0$. The significant effect of the parameters k_1, and k_2 on this function can be observed for low values of the parameter D_A (Fig. 1). In this case, the curves of the function $c_A^{st}(x)/c_A^0$ are well separated from each other and descend most sharply with distance x. As the parameter D_A increases, the curves of the function $c_A^{st}(x)/c_A^0$ for different values of the parameters k_1, and k_2 approach each other and decline slowly with distance x (Figs. 2, 3). This indicates a reduction in the influence of the parameters k_1, and k_2 on the system. The calculations show that the impact of the parameter D_B on the function $c_A^{st}(x)/c_A^0$ can be observed only at high values of the parameters k_1, and k_2. As in the case of the parameter D_A, the function $c_A^{st}(x)/c_A^0$ decreases with an increase in the parameter D_B. This statement is also true for the case of the stationary surface concentration of electroactive species c_{stA}^s.

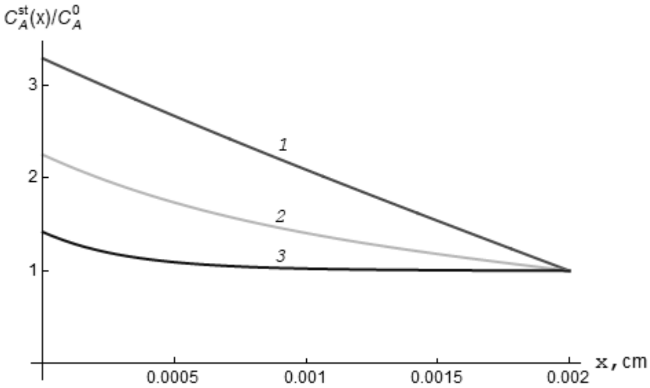

Fig. 2. Dimensionless concentration profiles of species A in the Nernst diffusion layer for different sets of the chemical reaction rate constants as in Fig. 1 and at fixed values of the diffusion coefficients of species: $D_A = 10^{-5}$ cm^2/s, $D_B = 2\ 10^{-5}$ cm^2/s

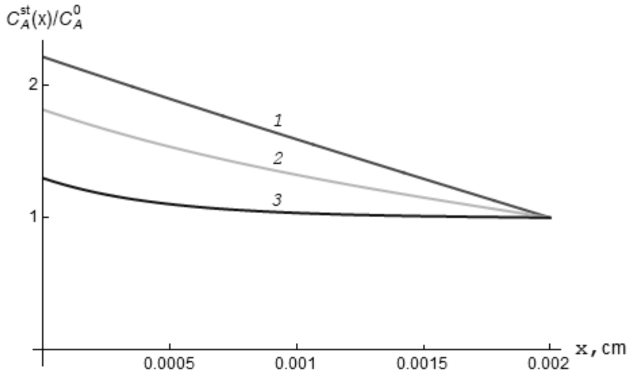

Fig. 3. Dimensionless concentration profiles of species A in the Nernst diffusion layer for different sets of the chemical reaction rate constants as in Fig. 1 and at fixed values of the diffusion coefficients of species: $D_A = 2\ 10^{-5}$ cm^2/s, $D_B = 2\ 10^{-5}$ cm^2/s

Figures 4 and 5 present the dimensionless stationary surface concentration of electroactive species, c_{stA}^s/c_A^0, as a function of the both diffusion coefficients D_A and D_B, at low and high values of the chemical reaction rate constants k_1, and k_2, respectively. At low values of the parameters k_1, and k_2, the function c_{stA}^s/c_A^0 is practically independent on the parameter D_B and reaches high values if the parameter D_A is small, as in the case of the function $c_A^{st}(x)/c_A^0$ (Fig. 4). At high values of the parameters k_1, and k_2, the function c_{stA}^s/c_A^0 is dependent on both the parameters D_A, and D_B. It decreases with their increase (Fig. 5).

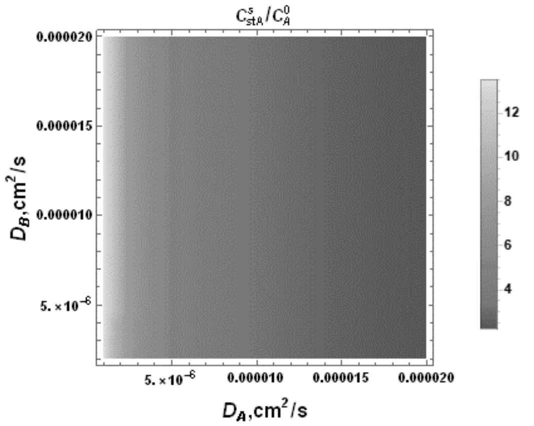

Fig. 4. Density plots of dimensionless stationary surface concentration of species A, c^s_{stA} / c^0_A, as a function of the diffusion coefficients D_A and D_B, at fixed values of the chemical reaction rate constants: $k_1 = 0.01$ s^{-1} and $k_2 = 1$ s^{-1}

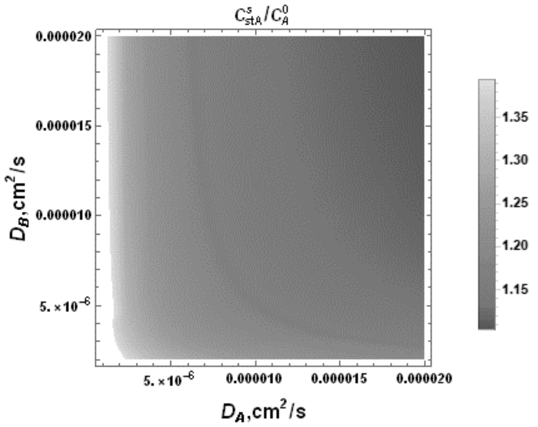

Fig. 5. Density plots of dimensionless stationary surface concentration of species A, c^s_{stA} / c^0_A, as a function of diffusion coefficients D_A and D_B, at fixed values of the chemical reaction rate constants: $k_1 = 10$ s^{-1} and $k_2 = 1000$ s^{-1}

Electroinactive species. Figures 6, 7, and 8 illustrate the dimensionless concentration profiles of species B in the Nernst diffusion layer for different values of the chemical reaction rate constants k_1, and k_2, and the diffusion coefficients of species D_A and D_B. Contrary to the function $c^{st}_A(x) / c^0_A$, an increase in the parameters k_1, and k_2 leads to a slight increase of the function $c^{st}_B(x) / c^0_B$. The calculations demonstrate a strong influence of the parameter D_B on the function $c^{st}_B(x) / c^0_B$. As can be seen from Fig. 6, at a high value of this parameter, the curves of the function $c^{st}_B(x) / c^0_B$ for different sets of the parameters k_1, and k_2 merge into one curve corresponding to $c^{st}_B(x) / c^0_B \approx 1$. The curve is almost parallel to the abscissa axis. This means that the stationary concentration of electroinactive species B does not change with the distance to a planar electrode surface x and is independent on the chemical reaction rate constants k_1, and k_2.

At low values of the parameter D_B, the curves of the function $c^{st}_B(x) / c^0_B$ can be separated from each other (Fig. 7). A high value of the parameter D_A can magnify this effect (Fig. 8). In these cases, there is a mere dependence of the function $c^{st}_B(x) / c^0_B$ on the distance x. Similar to the function $c^{st}_A(x) / c^0_A$, the function $c^{st}_B(x) / c^0_B$ can decrease with x, but very slightly. Figs. 9 and 10 represent the dependence of the dimensionless stationary surface concentration of electroinactive species, c^s_{stB} / c^0_B, on the diffusion coefficients of species D_A and D_B, at low and high values of the chemical reaction rate constants k_1, and k_2, respectively.

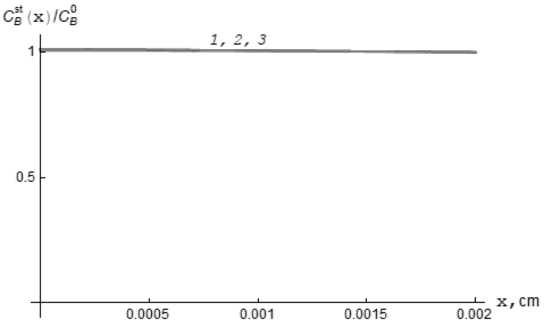

Fig. 6. Dimensionless concentration profiles of species B in the Nernst diffusion layer for different sets of the chemical reaction rate constants as in Fig. 1 and at fixed values of the diffusion coefficients of species: $D_A = 10^{-6}$ cm²/s, $D_B = 2\ 10^{-5}$ cm²/s

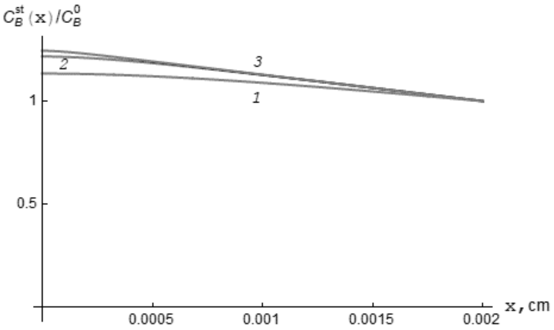

Fig. 7. Dimensionless concentration profiles of species B in the Nernst diffusion layer for different sets of the chemical reaction rate constants as in Fig. 1 and at fixed values of the diffusion coefficients of species: $D_A = 10^{-6}$ cm²/s, $D_B = 10^{-6}$ cm²/s

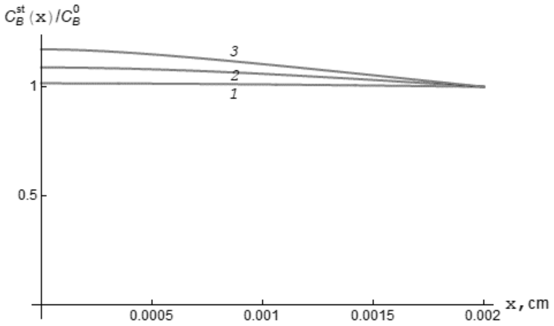

Fig. 8. Dimensionless concentration profiles of species B in the Nernst diffusion layer for different sets of the chemical reaction rate constants as in Fig. 1 and at fixed values of the diffusion coefficients of species: $D_A = 2\ 10^{-5}$ cm²/s, $D_B = 10^{-6}$ cm²/s

As can be seen from Figs. 9 and 10, the function c^s_{stB} / c^0_B slightly increases with increasing the parameters k_1, and k_2, but its value is close to 1, as in the case of the function $c^{st}_B(x) / c^0_B$. At low values of the parameters k_1, and k_2, there is the strong influence of the both diffusion coefficients of species D_A and D_B on the function c^s_{stB} / c^0_B (Fig. 9). It decreases with increasing these parameters.

At high values of the parameters k_1, and k_2, the dependence of the function c^s_{stB} / c^0_B on the parameter D_A becomes weak (Fig. 10). It is worth mentioning the influence of the Nernst diffusion layer thickness *d* on the system. The numerical simulations show that the parameter *d* affects the stationary concentrations of electroactive and electroinactive species A and B in the same manner. The functions $c_A^{st}(x)/c_A^0$ and $c_B^{st}(x)/c_B^0$ as well as c_{stA}^s/c_A^0 and c_{stB}^s/c_B^0 decrease with decreasing the parameter *d*. This effect is especially significant at low values of the chemical reaction rate constants k_1, and k_2.

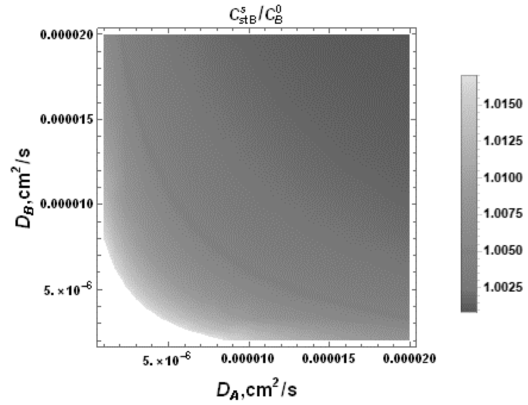

Fig. 9. Density plots of dimensionless stationary surface concentration of species B, c_{stB}^s/c_B^0, as a function of diffusion coefficients D_A and D_B, at fixed values of the chemical reaction rate constants: $k_1 = 0.01$ s^{-1} and $k_2 = 1$ s^{-1}

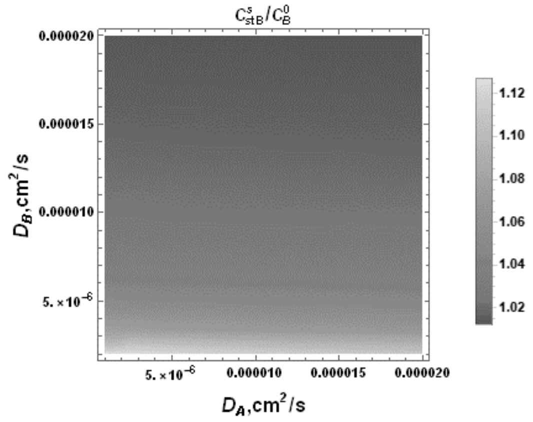

Fig. 10. Density plots for dimensionless stationary surface concentration of species B, c_{stB}^s/c_B^0, as a function of diffusion coefficients D_A and D_B, at fixed values of the chemical reaction rate constants: $k_1 = 10$ s^{-1} and $k_2 = 1000$ s^{-1}

CONCLUSIONS

Thus, it has been shown how the stationary concentration distribution of electroactive species A and electroinactive species B can change with a variation of the diffusion coefficients of both species and the chemical reaction rate constants in a model electrochemical process with a preceding chemical reaction under constant current. As was found, the impact of the species B on the stationary concentration distribution of the species A increases at high rate constants of the preceding chemical reaction. The stationary surface concentration of the species A strongly differs from the bulk concentration value at low diffusion coefficients of the species A. This theoretical analysis can be useful to predict the possible behaviors of various electrochemical systems with CE mechanism such as biosensors, solid oxide fuel cells, oxide electrodes, mixed conducting solid electrolyte systems, electrocatalytic systems with hydrogen evolution reaction, porous electrodes, *etc*.

Вплив кінетичних параметрів і коефіцієнтів дифузії на стаціонарну концентрацію електроактивних та електронеактивних частинок у модельному електрохімічному процесі з попередньою хімічною реакцією

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Метою даної роботи є встановлення впливу кінетичних параметрів та коефіцієнтів дифузії на стаціонарний розподіл концентрації електроактивних та електронеактивниих частинок у модельному електрохімічному процесі з попередньою хімічною реакцією при постійному струмі. Ми розглядаємо попередню гомогенну хімічну реакцію першого порядку з обротною гетерогенною електрохімічною реакцією на поверхні плаского електрода. Для встановлення особливостей стаціонарного розподілу концентрації електроактивних та електронеактивниих частинок у тонкому нерухомому шарі біля поверхні плаского електрода були проаналізовані точні розв'язки системи диференційних рівнянь, що описують зміну концентрацій реагуючих частинок із відстанню до поверхні плаского електрода. Розглядалися випадки однакових та різних коефіцієнтів дифузії частинок, які беруть участь у попередній хімічній реакції. Показано, що коефіцієнти дифузії обох реагуючих частинок можуть впливати на їхні концентраційні профілі у тонкому нерухомому шарі біля поверхні електрода. Показано, що стаціонарна концентрація електроактивних та електронеактивниих частинок зменшується зі зростанням коефіцієнтів дифузії. Вплив констант швидкості попередньої хімічної реакції на стаціонарну концентрацію є різним для електроактивних та електронеактивниих частинок. Зростання констант швидкості попередньої хімічної реакції веде до зменшення стаціонарної концентрації електроактивних частинок, тоді як стаціонарна концентрація електронеактивних частинок дещо збільшується. Це також стосується і випадку зі стаціонарною поверхневою концентрацією електроактивних та електронеактивниих частинок. Товщина тонкого нерухомого шару біля поверхні плаского електрода, де відбувається зміна концентрації електроактивних частинок, також впливає на концентраційні розподіли. Вплив цього параметра особливо визначальний при низьких значеннях констант швидкості хімічної реакції.

***Ключові слова**: CE механізм, концентраційний профіль, поверхнева концентрація, попередня хімічна реакція, дифузійний шар Нернста, реакційний шар, коефіцієнт дифузії, константа швидкості хімічної реакції, стаціонарні умови*

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