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ANALYTICAL EXPRESSIONS FOR SURFACE CONCENTRATION DISTRIBUTION IN A MODEL ELECTROCHEMICAL PROCESS WITH A PRECEDING CHEMICAL REACTION

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The goal of this study is unraveling the specific features of non-stationary surface concentration distribution of electroactive and inactive species in a model electrochemical process with a preceding homogeneous first-order chemical reaction (CE mechanism). For this purpose, the exact analytical expressions for the non-stationary concentration distributions of electroactive and inactive species in the thin layer attached to a planar electrode are analyzed. The both cases of equal and unequal diffusion coefficients of species taking part in the preceding chemical reaction are considered. In the former case, the exact analytical expressions for the concentration distributions of electroactive and inactive species on a planar electrode are obtained. The peculiarities of the limiting cases of zero and infinite frequency of an applied alternating current for the both cases of equal and unequal diffusion coefficients of species are discussed. It is shown that there is a phase shift between AC and the surface concentration of species that changes under the action of this current. At low frequencies, the phase angle tends to $\pi/2$, whereas at high frequencies it decreases to $\pi/4$. The phase angle is the function of the two important measures, namely, the ratio of the Nernst diffusion layer thickness to the oscillation diffusion layer thickness, and the ratio of the Nernst diffusion layer thickness to the reaction layer one. It is shown that the phase angle depends on the diffusion coefficient of species in different manner for low and high values of the rate constants of the chemical reaction. At low values of these parameters, the phase angle shifts slightly to the range of high frequencies with an increase of diffusion coefficient. At the high rate constants, the phase angle decreases with frequency more slowly, and its dependence on diffusion coefficient is observed only at middle frequencies. The surface concentration of electroactive and inactive species decreases with an increase of frequency, but for the inactive species this process is faster than that for the electroactive species. The influence of the inactive species on the surface concentration of electroactive species decreases at high frequencies and at low rate constants of the preceding chemical reaction. The results obtained shed the light on complex dynamics at an electrode/electrolyte interface under non-stationary conditions.

Keywords: CE mechanism, concentration distribution, preceding chemical reaction, diffusion coefficient, Nernst diffusion layer, reaction layer, oscillation diffusion layer, rate constant

INTRODUCTION

In many electrochemical processes, homogeneous reactions are coupled with electron transfer reactions [1–28]. 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. Recently, a rare type of CE mechanism in which the primary molecule is electroactive, and, in addition to participating in the electrode process through the CE mechanism, can also directly participate in the electrode process has been found experimentally for organic compounds [1]. Recent theoretical studies on the coupling of one

or more chemical reactions with the electrochemical reaction at the electrode surface can be found in Refs. [2–14, 25–28].

The first theoretical investigation on impedance of homogeneous first-order chemical reaction with a reversible charge transfer on a smooth mercury electrode was destructed in Ref. [15]. This is so-called Gerischer-type impedance. A semi-infinite diffusion with CEC type electrochemical reaction in a liquid electrolyte and equal diffusion coefficients was considered. A Gerischer-type impedance has been used to model a response of various electrochemical systems such as biosensors [12, 13], solid oxide fuel cells [16], oxide electrodes [18–20], mixed conducting solid electrolyte systems [20–22], electrocatalytic systems with hydrogen evolution

reaction [23], porous electrodes [24], rough and finite fractal electrodes [25, 26].

In Ref. [27], for the first time, an exact analytical expression for the Gerischer finite length impedance that arises from diffusion within a defined distance from the electrode was obtained for different diffusion coefficients of the species involved in the homogeneous first-order chemical reaction. Effect of difference between diffusion coefficients on impedance was shown. Concentration distribution of all species in diffusion layer for this CE mechanism was obtained.

In this theoretical study, we continue to analyze this mechanism in more detail. We answer the question how variation of the diffusion coefficients, and the rate constants of the preceding chemical reaction influences the concentration distributions of electroactive and electroinactive species on electrode surface under application of small amplitude alternating current (AC). The study considers a preceding homogeneous first-order chemical reaction with reversible heterogeneous electrochemical reaction at a planar electrode. The both cases of unequal and equal diffusion coefficients of the species involved in the preceding chemical reaction are considered. The analytical expressions for the surface concentration of species will be presented and discussed. Similar to Ref. [29], it will be shown that there is a phase shift between AC and the surface concentration of species that changes under the action of this current. The limiting cases of high and low frequency of AC will be considered, and the role of the kinetic (reaction) layer will be elucidated. Numerical simulations will be carried out with the parameters values within the range of most real-life values.

MODEL ELECTROCHEMICAL PROCESS WITH A PRECEDING HOMOGENEOUS FIRST-ORDER CHEMICAL REACTION

The scheme of the model process is as follows [27]:



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). The general case when the species B is not in excess and the diffusion coefficients of the species A and B are unequal is considered. The species B does not involve into the electrode process at a chosen potential value. The concentration field of C species does not affect the distribution of B and A species. The distribution of C species is affected only by the value of the current flowing through the interface.

NON-STEADY-STATE CONCENTRATION DISTRIBUTIONS OF SPECIES WITH UNEQUAL DIFFUSION COEFFICIENTS IN NERNST DIFFUSION LAYER

The reaction-diffusion equations for the concentrations of the species A and B in the Nernst stagnant diffusion layer under non-stationary conditions for the case of a planar electrode can be written as:

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - k_1 c_B + k_2 c_A, \quad (3)$$

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

Here we neglected ionic migration, which is suppressed by a supporting electrolyte. Beyond the boundary of the Nernst diffusion layer, in the bulk electrolyte, the following condition is met:

$$c_B^\infty k_1 = c_A^\infty k_2 \quad (5)$$

where 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 , D_A and D_B are the diffusion coefficients of species A and B, x is a distance from electrode surface, t is time.

Under application of small amplitude AC, the concentrations of each species can be presented in terms of equilibrium state and oscillating terms:

$$c_A(x, t) = c_A^\infty + \text{Re}[\tilde{c}_A \exp(i\omega t)], \quad (6)$$

$$c_B(x, t) = c_B^\infty + \text{Re}[\tilde{c}_B \exp(i\omega t)] \quad (7)$$

where $i = \sqrt{-1}$, ω is the angular frequency, \tilde{c}_A and \tilde{c}_B are concentration phasors.

Substituting equations (6, 7) into the system of equations (3) and (4) yields:

$$\frac{d^2 \tilde{c}_B}{dx^2} - \frac{k_1 + i\omega}{D_B} \tilde{c}_B + \frac{k_2}{D_B} \tilde{c}_A = 0 \quad (8)$$

$$\frac{d^2 \tilde{c}_A}{dx^2} + \frac{k_1}{D_A} \tilde{c}_B - \frac{k_2 + i\omega}{D_A} \tilde{c}_A = 0. \quad (9)$$

Boundary conditions for the differential equations (8, 9) in the bulk electrolyte are as follows:

$$\tilde{c}_A(x=d, t) = 0; \quad \tilde{c}_B(x=d, t) = 0. \quad (10)$$

Boundary condition at the electrode surface for the reacting species is written as:

$$D_A \frac{\partial \tilde{c}_A}{\partial x} \Big|_{x=0} = -\frac{\tilde{i}}{nF} \quad (11)$$

where \tilde{i} is the current oscillation amplitude, F is the Faraday constant, d is the thickness of the Nernst diffusion layer. The species B does not participate in the electrode process:

$$\Psi = \frac{1}{2} \left(\frac{k_1}{D_B} + \frac{k_2}{D_A} + i\omega \left(\frac{1}{D_B} + \frac{1}{D_A} \right) \right), \quad (16)$$

$$W = \frac{1}{2} \sqrt{\left(\frac{k_1}{D_B} + \frac{k_2}{D_A} \right)^2 + 2i\omega \left(\frac{k_1}{D_B} - \frac{k_2}{D_A} \right) \left(\frac{1}{D_B} - \frac{1}{D_A} \right) - \omega^2 \left(\frac{1}{D_B} - \frac{1}{D_A} \right)^2}, \quad (17)$$

$$\alpha_1 = (\Psi_1 + W) \frac{D_A}{k_1}, \quad (18)$$

$$\alpha_2 = (\Psi_1 - W) \frac{D_A}{k_1}, \quad (19)$$

$$\Psi_1 = \frac{1}{2} \left(\frac{k_1}{D_B} - \frac{k_2}{D_A} + i\omega \left(\frac{1}{D_B} - \frac{1}{D_A} \right) \right). \quad (20)$$

To calculate the analytical expressions for non-steady state concentration distributions of electroactive $c_A(x, t)$ and inactive $c_B(x, t)$ species in the Nernst diffusion layer, it is necessary to substitute (13) and (14) into (6) and (7) and extract the real parts. We can solve this problem exactly for the case of $x = 0$.

$$D_B \frac{d\tilde{c}_B}{dx} \Big|_{x=0} = 0 \quad (12)$$

After some mathematic calculations, we can obtain the exact solutions to the differential equations (8, 9) for the concentration distribution of species A and B in the thin layer attached to a plane electrode in the following form:

$$\tilde{c}_A = \frac{\tilde{i}}{nFD_A(\alpha_1 - \alpha_2)} \left(\frac{\alpha_2 \operatorname{sh}(r_1(x-d))}{r_1 \operatorname{ch}(r_1 d)} - \frac{\alpha_1 \operatorname{sh}(r_2(x-d))}{r_2 \operatorname{ch}(r_2 d)} \right), \quad (13)$$

$$\tilde{c}_B = \frac{\tilde{i}}{nFD_A(\alpha_1 - \alpha_2)} \left(\frac{\operatorname{sh}(r_1(x-d))}{r_1 \operatorname{ch}(r_1 d)} - \frac{\operatorname{sh}(r_2(x-d))}{r_2 \operatorname{ch}(r_2 d)} \right). \quad (14)$$

Here r_1 and r_2 are the roots of the characteristic equation of the reaction-diffusion system of the differential equations (8, 9) with boundary conditions (10–12) as follows:

$$r_1 = \sqrt{\Psi + W}, \quad r_2 = \sqrt{\Psi - W}. \quad (15)$$

The introduced functions Ψ , W , α_1 , α_2 , Ψ_1 are written as:

ANALYTICAL EXPRESSIONS FOR SURFACE CONCENTRATIONS OF SPECIES WITH EQUAL DIFFUSION COEFFICIENTS

At the electrode surface, $x = 0$, the concentration phasors \tilde{c}_A and \tilde{c}_B take the following forms:

$$\tilde{c}_A|_{x=0} = \tilde{c}_A^s = -\frac{\tilde{i}}{nFD_A(\alpha_1 - \alpha_2)} \left(\frac{\alpha_2 \operatorname{th}(r_1 d)}{r_1} - \frac{\alpha_1 \operatorname{th}(r_2 d)}{r_2} \right), \quad (23)$$

$$\tilde{c}_B|_{x=0} = \tilde{c}_B^s = -\frac{\tilde{i}}{nFD_A(\alpha_1 - \alpha_2)} \left(\frac{\operatorname{th}(r_1 d)}{r_1} - \frac{\operatorname{th}(r_2 d)}{r_2} \right). \quad (24)$$

Surface concentrations of species A, and B with equal diffusion coefficients, $D_A = D_B = D$, can be obtained after substitution (23), and (24) into (6), and (7), as follows:

$$c_A^s = c_A^\infty + \Delta c_A^s = c_A^\infty + \frac{\tilde{i}d}{nFD \left(1 + \frac{k_1}{k_2}\right)} \operatorname{Re} \left[e^{i\omega t} \left(\frac{k_1 \operatorname{th} \sqrt{i\omega d^2 / D}}{k_2 \sqrt{i\omega d^2 / D}} + \frac{\operatorname{th} \sqrt{(i\omega + k_1 + k_2) d^2 / D}}{\sqrt{(i\omega + k_1 + k_2) d^2 / D}} \right) \right], \quad (25)$$

$$c_B^s = c_B^\infty + \Delta c_B^s = c_B^\infty + \frac{\tilde{i}d}{nFD \left(1 + \frac{k_1}{k_2}\right)} \operatorname{Re} \left[e^{i\omega t} \left(-\frac{\operatorname{th} \sqrt{i\omega d^2 / D}}{\sqrt{i\omega d^2 / D}} + \frac{\operatorname{th} \sqrt{(i\omega + k_1 + k_2) d^2 / D}}{\sqrt{(i\omega + k_1 + k_2) d^2 / D}} \right) \right]. \quad (26)$$

To obtain the oscillating terms Δc_A^s , and Δc_B^s , the same procedure is applied as in Ref. [29]:

$$\Delta c_A^s = \Phi_1 + \Phi_2, \quad (27)$$

$$\Delta c_B^s = -\frac{k_2}{k_1} \Phi_1 + \Phi_2. \quad (28)$$

Here we introduce the following functions:

$$\begin{aligned} \Phi_1 &= \frac{\tilde{i}}{nF} \frac{d}{D} \frac{k_1}{(k_1 + k_2)} l_1 \sin(\omega t + \theta_1), \\ \Phi_2 &= \frac{\tilde{i}}{nF} \frac{d}{D} \frac{k_2}{(k_1 + k_2)} l_2 \sin(\omega t + \theta_2), \end{aligned} \quad (29)$$

$$\begin{aligned} y_1 &= d \sqrt{\frac{2\omega}{D}}, \quad l_1 = \frac{\sqrt{2} [\sin^2 y_1 + \operatorname{sh}^2 y_1]^{1/2}}{y_1 (\cos y_1 + \operatorname{ch} y_1)}, \\ \theta_1 &= \arcsin \frac{\sin y_1 + \operatorname{sh} y_1}{\sqrt{2} [\sin^2 y_1 + \operatorname{sh}^2 y_1]^{1/2}}, \end{aligned} \quad (30)$$

$$\begin{aligned} y_2 &= \frac{2d}{\sqrt{D}} \left(\omega^2 + (k_1 + k_2)^2 \right)^{1/4} = 2d \sqrt{\frac{\omega}{D}} \left(1 + \left(\frac{k_1 + k_2}{\omega} \right)^2 \right)^{1/4}, \\ \theta_2 &= \arcsin \frac{a \sin(ay_2) + c \operatorname{sh}(cy_2)}{[\sin^2(ay_2) + \operatorname{sh}^2(cy_2)]^{1/2}}, \end{aligned} \quad (31)$$

$$l_2 = \frac{2[\sin^2(ay_2) + \operatorname{sh}^2(cy_2)]^{1/2}}{y_2 (\cos(ay_2) + \operatorname{ch}(cy_2))},$$

$$a = \sin \left(\frac{1}{2} \operatorname{arctg} \frac{\omega}{k_1 + k_2} \right),$$

$$c = \cos \left(\frac{1}{2} \operatorname{arctg} \frac{\omega}{k_1 + k_2} \right). \quad (32)$$

APPROXIMATIONS FOR SURFACE CONCENTRATIONS OF SPECIES WITH UNEQUAL DIFFUSION COEFFICIENTS

High-frequency range. Analytical expressions for surface concentrations of electroactive and inactive species with unequal diffusion coefficients, $D_A \neq D_B$ are difficult to derive in general case. We can do this for the limiting cases of infinite and zero frequencies. Let's consider the case of high frequencies of an applied alternating current, when $\omega \rightarrow \infty$. In this case, the functions Ψ , W , α_1 , α_2 , Ψ_1 , r_1 , and r_2 defined by (15–20) are written as:

$$\begin{aligned} \Psi &= \frac{i\omega}{2} \left(\frac{1}{D_B} + \frac{1}{D_A} \right), \quad W = \frac{i\omega}{2} \left(\frac{1}{D_B} - \frac{1}{D_A} \right), \\ \Psi_1 &= \frac{i\omega}{2} \left(\frac{1}{D_B} - \frac{1}{D_A} \right), \end{aligned} \quad (33)$$

$$\alpha_1 = \frac{i\omega D_A}{k_1} \left(\frac{1}{D_B} - \frac{1}{D_A} \right), \quad \alpha_2 = 0, \quad r_1 = \sqrt{i\omega/D_B},$$

$$r_2 = \sqrt{i\omega/D_A}. \quad (34)$$

Therefore, in the case of $\omega \rightarrow \infty$, the expressions for the surface concentrations of electroactive and electroinactive species are as follows:

$$c_A^s |_{\omega \rightarrow \infty} = c_A^\infty + \frac{\tilde{i}}{nF\sqrt{D_A\omega}} \cos\left(\omega t - \frac{\pi}{4}\right), \quad (35)$$

$$c_B^s |_{\omega \rightarrow \infty} = c_B^\infty. \quad (36)$$

Zero frequency. Let's consider the case of $\omega \rightarrow 0$, and $D_A \neq D_B$. The functions Ψ , W , α_1 , α_2 , Ψ_1 , r_1 , and r_2 from (15–20) take the following forms:

$$\Psi = \frac{1}{2} \left(\frac{k_1}{D_B} + \frac{k_2}{D_A} \right), \quad W = \frac{1}{2} \left(\frac{k_1}{D_B} + \frac{k_2}{D_A} \right),$$

$$\Psi_1 = \frac{1}{2} \left(\frac{k_1}{D_B} - \frac{k_2}{D_A} \right), \quad \alpha_1 = \frac{D_A}{D_B}, \quad \alpha_2 = -\frac{k_2}{k_1}, \quad (37)$$

$$r_1 = \sqrt{\frac{k_1}{D_B} + \frac{k_2}{D_A}} = 1/\delta_k, \quad r_2 = 0. \quad (38)$$

Here δ_k is the kinetic (reaction) layer thickness [30, 31]. It 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, the bulk chemical reaction proceeds in an equilibrium manner. Only in the solution layer with the thickness δ_k the kinetic (non-equilibrium) chemical process does occur. The parameter δ_k decreases when the rate constants of chemical reaction increase, and increases if the diffusion coefficients of species increase.

Thus, from the expressions (6), (7), (23), (24), (37), and (38), we can obtain the expressions for the stationary surface concentrations of electroactive and inactive species with unequal diffusion coefficients, $D_A \neq D_B$, in the model CE reaction mechanism as follows:

$$c_A^s |_{\omega=0} = c_A^\infty + \frac{\tilde{i} d \delta_k^2}{nFD_A} \left(\frac{k_1}{D_B} + \frac{k_2}{D_A} \frac{\text{th}(d/\delta_k)}{d/\delta_k} \right), \quad (39)$$

$$c_B^s |_{\omega=0} = c_B^\infty - \frac{\tilde{i} d \delta_k^2 k_2}{nFD_A D_B} \left(1 - \frac{\text{th}(d/\delta_k)}{d/\delta_k} \right). \quad (40)$$

In the case of equal diffusion coefficients, $D_A = D_B = D$, the expressions (39), and (40) take the following forms:

$$c_A^s |_{\omega=0} = c_A^\infty + \frac{\tilde{i} d}{nFD(k_1/k_2 + 1)} \left(\frac{k_1}{k_2} + \frac{\text{th}(d/\delta_k)}{d/\delta_k} \right), \quad (41)$$

$$c_B^s |_{\omega=0} = c_B^\infty + \frac{\tilde{i} d}{nFD(k_1/k_2 + 1)} \left(\frac{\text{th}(d/\delta_k)}{d/\delta_k} - 1 \right). \quad (42)$$

Here the kinetic layer thickness equals to $\delta_k = \sqrt{D/(k_1 + k_2)}$. The same expressions as (41), and (42) we can also derive from the expressions (25–32). As at $\omega = 0$, the functions defined by (30–32) are as follows:

$$y_1 = 0, \quad y_2 = 2d\sqrt{(k_1 + k_2)/D}, \quad l_1 = 1, \quad l_2 = 0,$$

$$\theta_1 = \theta_2 = \frac{\pi}{2}, \quad a = 0, \quad c = 1. \quad (43)$$

RESULTS AND DISCUSSION

Fig. 1 *a, b* presents the phase angle θ between the surface concentration of electroactive species and an applied alternating current as a function of logarithm of frequency ω at two values of the diffusion coefficient $D_A = D_B = D$, and different sets of the rate constants of the chemical reaction k_1 and k_2 . As one can see, at low frequencies, the phase angle tends to $\pi/2$, whereas at high frequencies it decreases to $\pi/4$. The phase angle depends on the diffusion coefficient of species in different manner for low and high values of the rate constants of the chemical reaction. At low values of k_1 , and k_2 , the phase angle shifts slightly to the range of high frequencies with an increase of D (Fig. 1 *a*). The similar result was obtained in Ref. [29], where a redox process at a flat interface under polarization by AC was considered. When diffusion coefficient of reduced species was greater than that of oxidized species, a shift of the curve of phase angle for the reduced form took place in the range of high frequencies. The phase shift was also a function of the ratio of the

Nernst diffusion layer thickness d to the oscillation diffusion layer thickness, $d_f = \sqrt{D/\omega}$, as in the expressions (29–32). In Ref. [29], it was mentioned that a reason for the phase angle between current and concentration that changes under the action of this current is due to diffusion of particles in a near-electrode layer under application of a harmonic perturbation, and such a behavior of the phase

angle was determined by boundary conditions. In our case, in addition to the influence of diffusion on the phase angle, we have also the influence of the chemical reaction. As can be noticed from Fig. 1 *b*, at high values of the parameters k_1 , and k_2 , the phase angle θ decreases with frequency more slowly, and its dependence on D reveals only at middle frequencies.

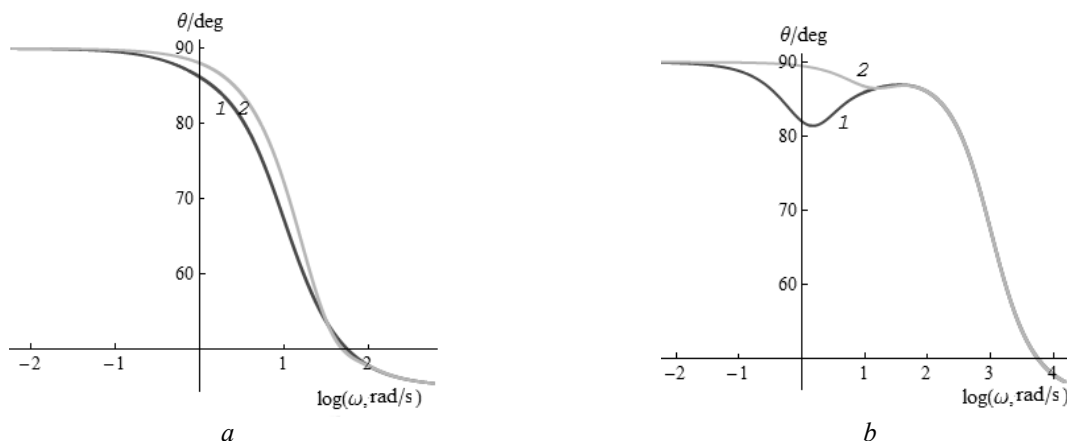


Fig. 1. The phase angle between the surface concentration and the applied alternating current, θ/deg , for electroactive species as a function of logarithm of frequency, $\log(\omega/\text{rad}\cdot\text{s}^{-1})$, for different values of the diffusion coefficient, D , cm^2/s , as follows: (1) $2\cdot 10^{-6}$; (2) $2\cdot 10^{-5}$, and the following sets of the chemical reaction rate constants: (a) $k_1 = 0.1\text{ s}^{-1}$ and $k_2 = 10\text{ s}^{-1}$; (b) $k_1 = 10\text{ s}^{-1}$ and $k_2 = 1000\text{ s}^{-1}$. Here and below, $d = 2\cdot 10^{-3}\text{ cm}$, $i = 10^{-2}\text{ mA}/\text{cm}^2$, $T = 300\text{ K}$, $n = 1$

Form the expressions (35), and (36), we can conclude that the influence of the electroinactive species B on the surface concentration of species A decreases at high frequencies. The system behavior is determined mainly by the characteristics of the electroactive species, as in Ref. [27]. Fig. 2 *a* verifies this statement. Here, the contour plots of the surface concentration of species A as a function of the diffusion coefficients D_A , and D_B at the chosen high values of ω , k_1 , k_2 , and a fixed value of t are shown. As one can see, the function $\Delta c_A^s = \text{Re}[\tilde{c}_A^s \exp(i\omega t)]$, where \tilde{c}_A^s is defined by the expression (23), decreases with the growth of D_A , and is almost independent on D_B . Fig. 2 *b* presents the contour plots of the function $\Delta c_B^s = \text{Re}[\tilde{c}_B^s \exp(i\omega t)]$, with \tilde{c}_B^s defined by the expression (24), dependent on the parameters D_A and D_B at the same fixed values of frequency, preceding chemical reaction, and time. In contrast to the function Δc_A^s , the function Δc_B^s is dependent on the both

parameters D_A and D_B . It decreases when these parameters increase.

As can be seen from the expressions (39–42), the stationary surface concentration of electroactive and inactive species is a function of the ratio of the Nernst diffusion layer thickness d to the kinetic layer thickness $\delta_k = 1/\sqrt{k_1/D_B + k_2/D_A}$. To our knowledge, references [30, 31] were the first theoretical works that introduced the notion of the kinetic layer thickness for equal and unequal diffusion coefficients of reacting species. It is worth also mentioning that the expressions (39–42) coincide with the expressions for the stationary surface concentrations of electroactive and inactive species in the model electrocatalytic process with a preceding chemical reaction, in Ref. [28]. However, in our case, instead of the rate of adsorption-desorption of electroactive species at the electrode surface, we have the factor $-\tilde{i}/nF$ defined by the boundary conditions (11) for the electroactive species.

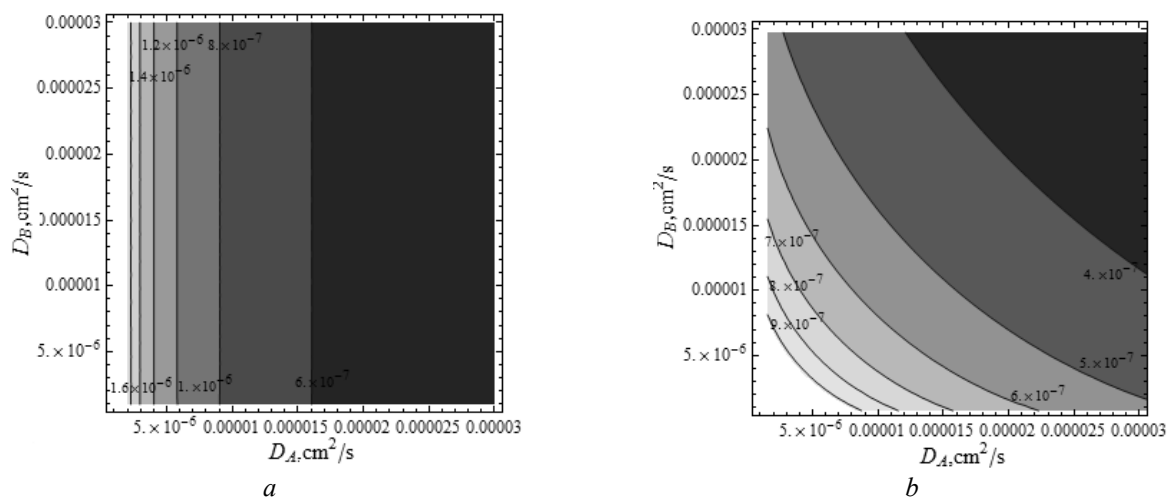


Fig. 2. Six contour lines of the functions Δc_A^s (a), and Δc_B^s (b) with a variation of the diffusion coefficients D_A , and D_B at the fixed values of the following parameters: $\omega = 600$ rad/s, $k_1 = 10$ s $^{-1}$, $k_2 = 1000$ s $^{-1}$, $t = 0.3$ s. Along a contour the function has the same value. The darker the area, the lower the value of the function

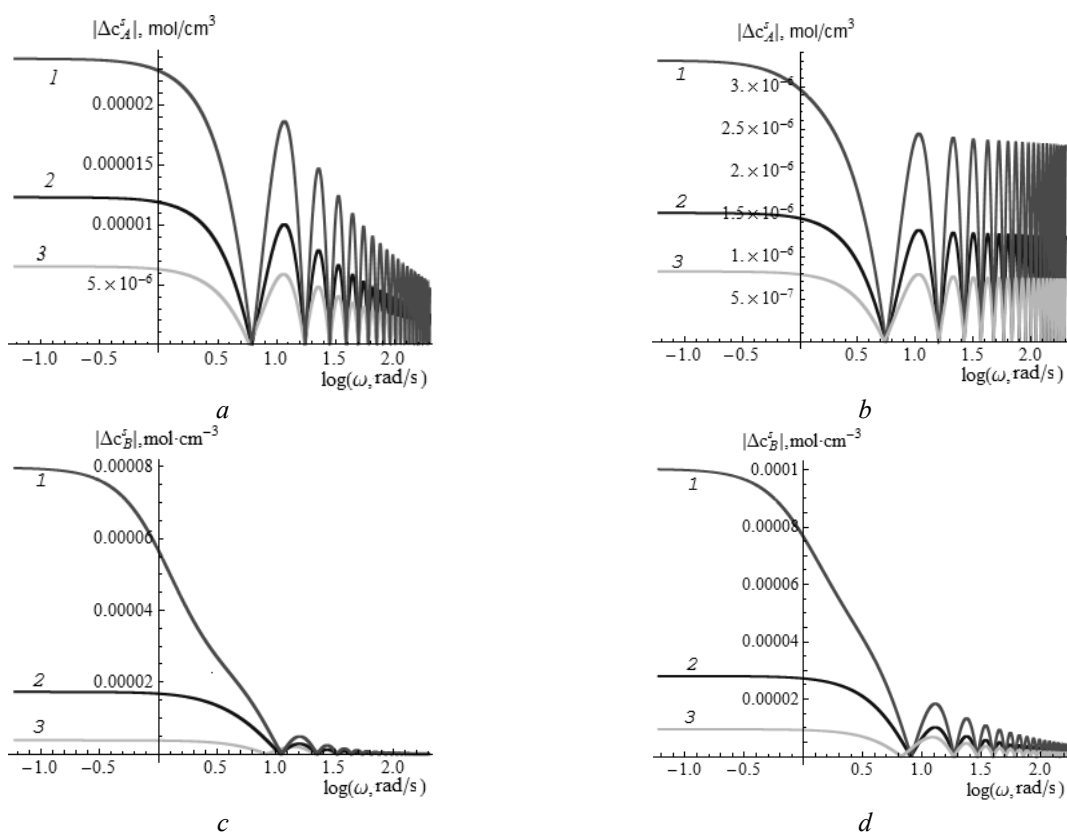


Fig. 3. The absolute value of deviation of surface concentration from equilibrium one under application of a small amplitude AC with frequency ω for electroactive (a, b) species, $|\Delta c_A^s|, \text{mol} \times \text{cm}^{-3}$, and inactive (c, d) species, $|\Delta c_B^s|, \text{mol} \times \text{cm}^{-3}$, as a function of logarithm of frequency, $\log(\omega / \text{rad} \cdot \text{s}^{-1})$, at the following values of the diffusion coefficient, $D, \text{cm}^2/\text{s}$: (1) $2 \cdot 10^{-6}$; (2) $7 \cdot 10^{-6}$; (3) $2 \cdot 10^{-5}$, and the following sets of the chemical reaction rate constants: (a, c) $k_1 = 0.1$ s $^{-1}$ and $k_2 = 10$ s $^{-1}$; (b, d) $k_1 = 10$ s $^{-1}$ and $k_2 = 1000$ s $^{-1}$

Let's consider in more detail the influence of the rate constants of chemical reaction on a value of oscillating terms Δc_A^s , and Δc_B^s . As one can see from the expressions (25–28) for the case of equal diffusion coefficients, the function Δc_A^s includes the factor k_1/k_2 , and the function Δc_B^s has a reciprocal value of the ratio of these parameters. As $c_B^\infty k_1 = c_A^\infty k_2$, and the chosen values of the equilibrium concentrations of species A, and B are as follows: $c_A^\infty = 8 \cdot 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$, and $c_B^\infty = 8 \cdot 10^{-4} \text{ mol} \cdot \text{cm}^{-3}$, so we have the following inequality, $k_1/k_2 \ll 1$. Hence, the surface concentration of electroactive species will decrease with increasing the rate constants of chemical reaction, whereas the surface concentration of inactive species will increase with these parameters. Fig. 3 *a–d* confirms this conclusion. Here we consider an absolute value of the surface concentration deviation from equilibrium concentration.

As one can see from Fig. 3 *a–d*, the both functions $|\Delta c_A^s|$, and $|\Delta c_B^s|$ decrease when the parameter D increases. The function $|\Delta c_B^s|$ increases with an increase of the parameters k_1 and k_2 , in contrast to the function $|\Delta c_A^s|$ that decreases. It should be noted that the function $|\Delta c_B^s|$ decreases with an increase of ω much faster than the function $|\Delta c_A^s|$ does especially for low values of the parameters k_1 , k_2 , and D_A , as can be shown also by the numerical simulations based on the expressions (6), (7), (23), (24) for the case of $D_A \neq D_B$. It is important to note that in the case of simultaneous occurrence of diffusion and homogeneous first-order chemical reaction, there are two phenomenological length scales: a diffusion layer thickness $L_D = (D/\omega)^{1/2}$ and a reaction layer thickness $L_R = (D/k)^{1/2}$ [15]. The diffusion layer thickness is a measure of size of the diffusion limited layer near electrode. The effective thickness of the reaction layer is determined by the distance traveled by an electrochemically active species during its mean life time. The mean life time is reciprocal to the rate of the reaction leading to the loss of the species. At low frequencies, if $L_D/L_R > 1$, the system is kinetically controlled. At high frequencies, if $L_D/L_R < 1$, the system is controlled

by diffusion. These limits determine the behavior of the system.

CONCLUSIONS

Thus, the obtained analytical results and numerical simulations reveal the following features of the model electrochemical process with a preceding homogeneous first-order chemical reaction under application of small amplitude AC:

- There is a phase shift between AC and the surface concentration of species that changes under the action of this current. At low frequencies, the phase angle tends to $\pi/2$, whereas at high frequencies it decreases to $\pi/4$.

- The phase angle is a function of the two important measures, namely, the ratio of the Nernst diffusion layer thickness to the oscillation diffusion layer thickness, and the ratio of the Nernst diffusion layer thickness to the reaction layer thickness. Hence, the phase angle depends on the diffusion coefficient of species in different manner for low and high values of the rate constants of the chemical reaction. At low values of these parameters, the phase angle shifts slightly to the range of high frequencies with an increase of diffusion coefficient. At high the rate constants, the phase angle decreases with frequency more slowly, and its dependence on diffusion coefficient is observed only at middle frequencies.

- The surface concentration of electroactive and inactive species decreases with an increase of frequency, but for inactive species this process is faster than for electroactive species. The influence of the inactive species on the surface concentration of electroactive species decreases at high frequencies.

- The influence of the inactive species on the system behavior increases at high values of the preceding chemical reaction rate constants because the surface concentration of inactive species increases with an increase of these parameters, in contrast to the surface concentration of electroactive species that decreases with an increase of the preceding chemical reaction rate constants.

The surface concentration of electroactive and inactive species decreases with an increase of diffusion coefficient of species.

Аналітичні вирази для поверхневого розподілу концентрації в модельному електрохімічному процесі з попередньою хімічною реакцією

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Метою даної роботи є встановлення характерних особливостей нестационарного поверхневого розподілу концентрації електроактивних та неактивних частинок у модельному електрохімічному процесі з попередньою гомогенною хімічною реакцією першого порядку (СЕ mechanism). Для її виконання проводиться аналіз точних аналітичних виразів для нестационарного розподілу концентрації електроактивних та неактивних частинок у тонкому шарі біля поверхні плоского електрода. Розглядаються обидва випадки однакових та різних коефіцієнтів дифузії частинок, які беруть участь у попередній хімічній реакції. Отримано точні аналітичні вирази для розподілу концентрації електроактивних та неактивних частинок на поверхні плоского електрода. Обговорюються особливості граничних випадків, коли частота прикладеного змінного струму прямує до нуля та нескінченності. Показано, що існує зсув фаз між змінним струмом та поверхневою концентрацією частинок, яка змінюється під дією цього струму. На низьких частотах цей фазовий кут прямує до $\pi/2$, тоді як на високих частотах він зменшується до $\pi/4$. Фазовий кут є функцією двох важливих величин, а саме: відношення товщини дифузійного шару Нернста до осцилюючого дифузійного шару та відношення товщини дифузійного шару Нернста до товщини реакційного шару. Показано, що залежність фазового кута від коефіцієнтів дифузії частинок є різною для малих та високих значень констант швидкості хімічної реакції. При малих значеннях цих параметрів фазовий кут трохи збільшується у бік більших частот зі збільшенням коефіцієнта дифузії частинки. При великих константах швидкості фазовий кут зменшується з частотою повільніше і його залежність від коефіцієнта дифузії частинки спостерігається тільки на середніх частотах. Поверхнева концентрація електроактивних та неактивних частинок зменшується зі збільшенням частоти, але для неактивних частинок цей процес відбувається швидше, ніж для електроактивних частинок. Вплив неактивних частинок на поверхневу концентрацію електроактивних частинок зменшується на високих частотах та низьких константах швидкості хімічної реакції. Отримані результати допоможуть у розумінні складної динаміки на межі поділу фаз електрод/електроліт за нестационарних умов.

Ключові слова: СЕ механізм, розподіл концентрації, попередня хімічна реакція, коефіцієнт дифузії, дифузійний шар Нернста, реакційний шар, осцилюючий дифузійний шар, константа швидкості

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