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INFLUENCE OF THE NERNST DIFFUSION LAYER THICKNESS ON SURFACE CONCENTRATION IN A MODEL ELECTROCHEMICAL PROCESS WITH A PRECEDING CHEMICAL REACTION

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The influence of the Nernst diffusion layer thickness on the surface concentrations of electroactive and electroinactive species in a model electrochemical process with a preceding homogeneous first-order chemical reaction under application of a small amplitude alternating current has been investigated. A case of equal diffusion coefficients of species taking part in the preceding chemical reaction in a thin layer attached to a planar electrode is considered. It has been shown that, at low frequencies of an applied alternating current, the surface concentrations of electroactive and electroinactive species increase with increasing the Nernst diffusion layer thickness. At high frequencies, the surface concentrations of both species do not depend on this parameter. However, there is a range of frequencies where the surface concentrations of species can decrease with increasing the Nernst diffusion layer thickness. This range of frequencies can be influenced by a value of the Nernst diffusion layer thickness, the rate constants of chemical reaction, and the diffusion coefficient of species. There exists a phase shift between an alternating current and the surface concentrations of electroactive and electroinactive species that change under application of this current. It is a function of the Nernst diffusion layer thickness, the oscillation diffusion layer thickness, and the reaction layer thickness. In the case of electroactive species, the phase angle can take only a positive value. At low frequencies, it tends to $\pi/2$, whereas at high frequencies it decreases to $\pi/4$. For the case of electroinactive species, the phase angle can be positive, negative, and equal to zero depending on the value of the Nernst diffusion layer thickness, the rate constants of chemical reaction, and the diffusion coefficient of species. It approaches $-\pi/2$ at low frequencies, and at high frequencies it tends to $\pi/4$. The both phase angles can have the maxima and the minima. Their values are strongly dependent on the Nernst diffusion layer thickness, the diffusion coefficient of species, the rate constants of chemical reaction.

Keywords: *CE mechanism, surface concentration, phase angle, preceding chemical reaction, Nernst diffusion layer, reaction layer, oscillation diffusion layer, diffusion coefficient, rate constant*

INTRODUCTION

The role of diffusion layer in various electrochemical processes remains the subject of intensive studies [1–15]. The aim of this work is understanding the effect of the thickness of the Nernst diffusion layer on the non-stationary surface concentration distributions in a model electrochemical system with a preceding homogeneous first-order chemical reaction [16, 17]. Based on the analytical expressions and numerical simulations, we will show the peculiarities of the nonlinear response of the model electrochemical system with a preceding chemical reaction on this control parameter. The analysis of a phase shift between an alternating current and surface concentration that changes under application of this current will point out

the difference between the behavior of electroactive and electroinactive species.

MODEL ELECTROCHEMICAL PROCESS WITH A PRECEDING HOMOGENEOUS FIRST-ORDER CHEMICAL REACTION. NON-STATIONARY CONCENTRATION DISTRIBUTION IN NERNST DIFFUSION LAYER

The model electrochemical process with a preceding homogeneous first-order chemical reaction can be schematically presented as follows [16, 17]:

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

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

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). We consider the general case when the species B is not in excess and that 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.

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 are as follows:

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

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

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:

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

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 alternating current, the concentrations of each species can be presented in terms of equilibrium state and oscillating terms:

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

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

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), we get:

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

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

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

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

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

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

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:

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

The exact solutions to the differential equations (8, 9) for the concentration phasors of electroactive species A and inactive species B with unequal diffusion coefficients $D_A \neq D_B$ in the thin layer attached to a plane electrode were obtained in [17] and analyzed in [16] for the case of $x = 0$.

ANALYTICAL EXPRESSIONS FOR NON-STATIONARY SURFACE CONCENTRATIONS OF ELECTROACTIVE AND ELECTROINACTIVE SPECIES. PHASE ANGLES

In this paper, we present the analytical expressions for the non-steady-state surface concentration of the electroactive species A and electroinactive species B with equal diffusion coefficients, $D_A = D_B = D$, obtained in [16], in more explicit form as follows:

$$c_A^s = c_A^\infty + \Delta c_A^s = c_A^\infty + M\, r_A \sin(\omega t + \theta_A) \qquad (13)$$

$$c_B^s = c_B^\infty + \Delta c_B^s = c_B^\infty - M\, r_B \sin(\omega t - \theta_B). \qquad (14)$$

Here the common factor M is written as:

$$M = \frac{\tilde{i}}{nF} \frac{d}{D} \frac{k_2}{(k_1 + k_2)} . \qquad (15)$$

The phase angles of non-steady-state surface concentration for electroactive and inactive species θ_A, and θ_B are determined as:

$$\theta_A = \arcsin\left(\frac{p_A}{r_A}\right), \qquad (16)$$

$$\theta_B = \arcsin\left(\frac{p_B}{r_B}\right), \qquad (17)$$

where the introduced functions are as follows:

$$r_A = \sqrt{p_A^2 + q_A^2}, \ r_B = \sqrt{p_B^2 + q_B^2}, \qquad (18)$$

$$p_A = \frac{k_1}{k_2} \frac{\mathrm{sh}\, y_1 + \sin y_1}{y_1(\mathrm{ch}\, y_1 + \cos y_1)} + \frac{2(c\,\mathrm{sh}(cy_2) + a\sin(ay_2))}{y_2(\mathrm{ch}(cy_2) + \cos(ay_2))} \qquad (19)$$

$$q_A = \frac{k_1}{k_2} \frac{\mathrm{sh}\, y_1 - \sin y_1}{y_1(\mathrm{ch}\, y_1 + \cos y_1)} + \frac{2(a\,\mathrm{sh}(cy_2) - c\sin(ay_2))}{y_2(\cos(ay_2) + \mathrm{ch}(cy_2))}, \qquad (20)$$

$$p_B = -\frac{\mathrm{sh}\, y_1 + \sin y_1}{y_1(\mathrm{ch}\, y_1 + \cos y_1)} + \frac{2(c\,\mathrm{sh}(cy_2) + a\sin(ay_2))}{y_2(\mathrm{ch}(cy_2) + \cos(ay_2))}, \qquad (21)$$

$$q_B = -\frac{\mathrm{sh}\, y_1 - \sin y_1}{y_1(\mathrm{ch}\, y_1 + \cos y_1)} + \frac{2(a\,\mathrm{sh}(cy_2) - c\sin(ay_2))}{y_2(\mathrm{ch}(cy_2) + \cos(ay_2))}, \qquad (22)$$

$$y_1 = d\sqrt{\frac{2\omega}{D}}, \ y_2 = \frac{2d}{\sqrt{D}}\left(\omega^2 + (k_1 + k_2)^2\right)^{1/4}, \qquad (23)$$

$$a = \sin\left(\frac{1}{2}\mathrm{arctg}\frac{\omega}{k_1 + k_2}\right), \ c = \cos\left(\frac{1}{2}\mathrm{arctg}\frac{\omega}{k_1 + k_2}\right). \qquad (24)$$

The expressions (13) and (14) indicate that there is a phase shift between the applied AC and the surface concentration of species that changes under the action of this current. The phase shifts for electroactive species θ_A, and inactive species θ_B differ from each other. In both cases the phase angle is a function of the two important measures, namely, the ratio of the Nernst diffusion layer thickness d to the oscillation diffusion layer thickness $d_f = \sqrt{D/\omega}$ [18], and the ratio of the Nernst diffusion layer thickness d to the reaction layer thickness $\delta_k = \sqrt{D/(k_1 + k_2)}$ [19].

LIMITING CASES OF ZERO AND INFINITE FREQUENCY

Zero frequency. According to the expressions (18–24), the introduced above functions at $\omega = 0$ are as follows:

$$q_{A,B} = 0, \ p_A = \frac{k_1}{k_2} + \frac{\mathrm{th}(y_2/2)}{y_2/2},$$

$$p_B = -1 + \frac{\mathrm{th}(y_2/2)}{y_2/2}, \ y_1 = 0, \ y_2 = 2d\sqrt{\frac{k_1 + k_2}{D}},$$

$$a = 0, \ c = 1 \qquad (25)$$

Thus, the phase angle for electroactive species reaches $\theta_A \to \pi/2$, whereas for inactive species it tends to $\theta_B \to -\pi/2$. The expressions (13, 14) for the stationary surface concentrations of electroactive and inactive species are written as:

$$\Delta c_A^s\big|_{\omega=0} = M\left(\frac{k_1}{k_2} + \frac{\mathrm{th}(d/\delta_k)}{d/\delta_k}\right) \qquad (26)$$

$$\Delta c_B^s\big|_{\omega=0} = M\left(\frac{\mathrm{th}(d/\delta_k)}{d/\delta_k} - 1\right). \qquad (27)$$

Infinite frequency. When $\omega \to \infty$, the functions defined by the expressions (18–24) take the following forms:

$$q_{A,B} = p_{A,B} = 0, \qquad y_1 = d\sqrt{\frac{2\omega}{D}}, \qquad y_2 = y_1\sqrt{2},$$

$$a = c = 1/\sqrt{2} \ . \qquad (28)$$

The phase shifts θ_A, and θ_B tend to $\pi/4$, and the non-stationary surface concentrations of electroactive and inactive species tend to zero:

$$\Delta c_A^s\big|_{\omega\to\infty} = 0 \qquad (29)$$

$$\Delta c_B^s\big|_{\omega\to\infty} = 0 . \qquad (30)$$

RESULTS AND DISCUSSION

Electroactive species. Fig. 1 *a–d* presents the frequency dependence of the phase angle θ_A between an applied alternating current and the surface concentration of electroactive species defined by Eq. (16) with a variation of the Nernst diffusion layer thickness d. This dependence is analyzed at various values of the diffusion coefficient of species D and the rate constants of

chemical reaction k_1, and k_2. As one can see, an increase in the value of the Nernst diffusion layer thickness d leads to a shift of the curves of the frequency dependence of the phase angle θ_A in a range of low frequencies ω. A significant effect of the parameter d on the phase angle θ_A can be seen in Fig. 1 *a*, where a value of the diffusion coefficient of species D is high and the rate constants of chemical reaction k_1, and k_2 are

small. The curves of the phase angle θ_A for different values of the parameter d are separate from each other in a wide range of frequencies ω. The two curves corresponding to the smaller values of the parameter d have both a maximum and a minimum (curves 1, 2 in Fig. 1 *a*). At these extreme points, the phase angle θ_A is close to 45°. The extreme points are situated in the range of middle and high frequencies ω (Table 1). At
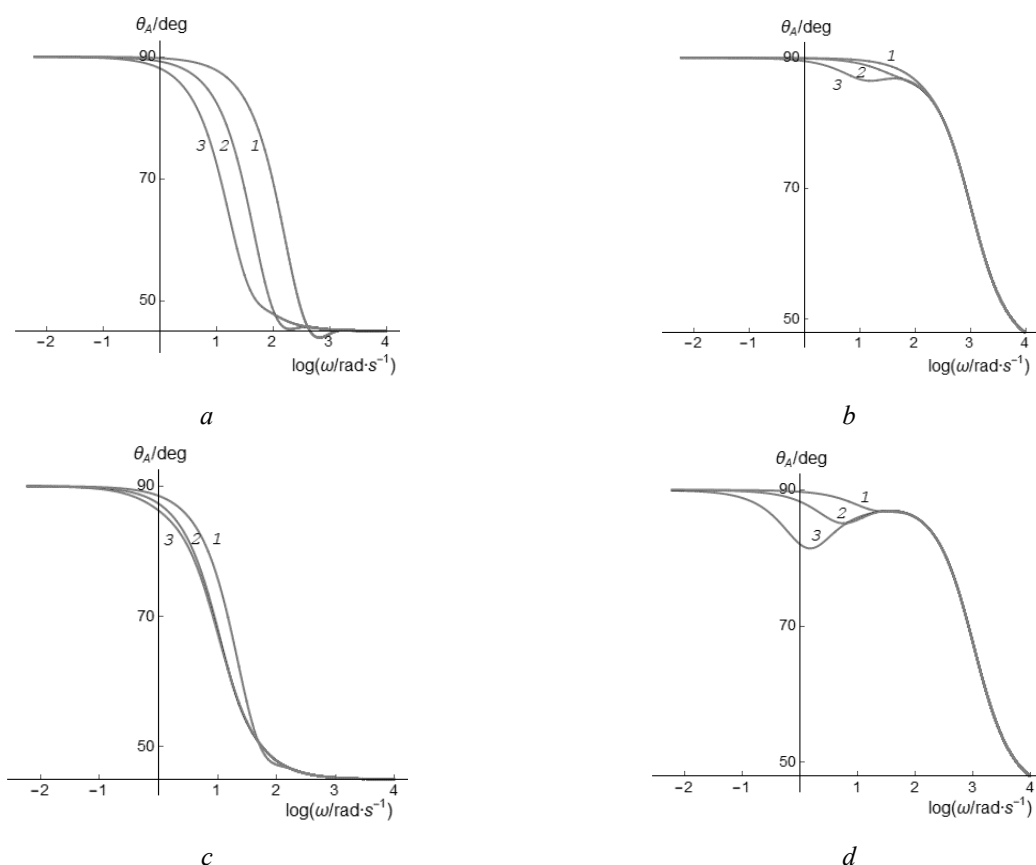
Fig. 1. Frequency dependence of phase angle θ_A for electroactive species at different values of the Nernst diffusion layer thickness d, cm, as follows: (*1*) $5 \cdot 10^{-4}$, (*2*) 10^{-3}, (*3*) $2 \cdot 10^{-3}$, and the following values of diffusion coefficient, and chemical reaction rate constants: (*a*) $D = 2 \cdot 10^{-5}$ cm²/s, $k_1 = 0.1$ s⁻¹ and $k_2 = 10$ s⁻¹; (*b*) $D = 2 \cdot 10^{-5}$ cm²/s, $k_1 = 10$ s⁻¹ and $k_2 = 1000$ s⁻¹; (*c*) $D = 2 \cdot 10^{-6}$ cm²/s, $k_1 = 0.1$ s⁻¹ and $k_2 = 10$ s⁻¹; (*d*) $D = 2 \cdot 10^{-6}$ cm²/s, $k_1 = 10$ s⁻¹ and $k_2 = 1000$ s⁻¹. Here and below, $i = 10^{-2}$ mA/cm², $T = 300$ K, $n = 1$

Table 1. The extreme points of the phase angle θ_A at various values of the Nernst diffusion layer thickness d, the diffusion coefficient of species D, and the rate constants of chemical reaction k_1, and k_2 as in Fig. 1 *a–d*

	$d = 5 \cdot 10^{-4}$ cm				$d = 10^{-3}$ cm				$d = 2 \cdot 10^{-3}$ cm			
	$\frac{\omega_{min}}{rad/s}$	$\frac{\theta_{A\,min}}{deg}$	$\frac{\omega_{max}}{rad/s}$	$\frac{\theta_{A\,max}}{deg}$	$\frac{\omega_{min}}{rad/s}$	$\frac{\theta_{A\,min}}{deg}$	$\frac{\omega_{max}}{rad/s}$	$\frac{\theta_{A\,max}}{deg}$	$\frac{\omega_{min}}{rad/s}$	$\frac{\theta_{A\,min}}{deg}$	$\frac{\omega_{max}}{rad/s}$	$\frac{\theta_{A\,max}}{deg}$
a	654.11	43.95	1863.62	45.21	198.73	45.33	387.86	45.71				
b									15.69	86.48	42.32	86.84
c												
d					5.74	85.10	36.24	86.96	1.49	81.42	35.87	86.95

the highest chosen value of the parameter d, the function θ_A does not have any extreme point, i.e. its derivative with respect to ω is not equal to zero at any frequency (curve 3 in Fig. 1 *a*). However, when the rate constants k_1, and k_2 become high, the extreme points appear namely at this highest value of the parameter d (curve 3 in Fig. 1 *b*). At the extreme points, the phase angle θ_A approaches 86°. They belong to a range of low and middle frequencies ω. A slight dependence of the phase angle θ_A on the Nernst diffusion layer thickness d is observed when the values of the parameters D, k_1, and k_2 become small (Fig. 1 *c*). In this case, there are no extreme points. They can appear at high values of the rate constants of chemical reaction k_1, and k_2 (Fig. 1 *d*). A minimum and a maximum on a curve of the phase angle θ_A occur only at the two higher values of the parameter d (curves 2, 3 in Fig. 1 *d*). The two maxima on these two curves coincide with each other in a range of middle frequencies. At these extreme points, the phase angle θ_A is approximately 86°. The most pronounced minimum of the phase angle θ_A corresponds to the case of the highest chosen value of the parameter d. Its value is around 81°. It is located in a range of small frequencies ω. For the smallest chosen value of the parameter d (curve 1 in Fig. 1 *d*), there is neither a maximum nor a minimum on the curve of frequency dependence of the phase angle θ_A. There is only an inflection point, where the concavity of the curve changes. As one can see, at high values of the rate constants k_1, and k_2, and frequencies ω that are higher than those corresponding to the extreme points, a value of the parameters d, and D does not affect the frequency dependence of the phase angle θ_A (Fig. 1 *b*, *d*). All the curves are merged into one.

Thus, all the cases demonstrated in Fig. 1 prove the strong influence of the parameters d, D, k_1, and k_2 on the frequency dependence of the phase angle θ_A. If the parameters k_1, and k_2 are high, a noticeable dependence of the phase angle θ_A on the parameter d can be observed only at low and middle frequencies. The phase angle θ_A can have the extreme points at high values of the parameter d. At these extreme points, a value of the phase angle θ_A is around 90°. Contrary, at low values of the rate constants k_1, and k_2, a distinct dependence of the phase angle θ_A on the Nernst diffusion layer thickness d can exist at middle and high frequencies, but only at high

values of the diffusion coefficient of species D. The extreme points of the phase angle θ_A appear only at small values of the parameter d. At these extreme points, the phase angle θ_A is close to 45°. At zero frequency, the phase angle θ_A reaches 90°, whereas at infinite frequency, it decreases to 45°. The same critical values of the phase angle between an applied alternating current and surface concentration of reacting species were calculated in Ref. [18], where a redox process at a flat interface under polarization by AC was considered. The phase angle was a function of the Nernst diffusion layer thickness d and the oscillating length $d_f = \sqrt{D/\omega}$. However, in Ref. [18], the curve of the frequency dependence of the phase angle had only a minimum that was independent on either the Nernst diffusion layer thickness d or the diffusion coefficient of species D. As was shown in Ref. [18], a reason for the phase angle between an applied alternating current and the surface concentration of reacting species that changes under the action of this current was diffusion of species in a near-electrode layer under application of a harmonic perturbation. In our case, the phase angle θ_A is a function of the Nernst diffusion layer thickness d, the oscillation diffusion layer thickness $d_f = \sqrt{D/\omega}$, and the reaction layer thickness $\delta_k = \sqrt{D/(k_1 + k_2)}$. These scales regulate the system behavior. At low frequencies, the system is kinetically controlled, and at high frequencies, the system is controlled by diffusion [20]. It is also important to note that the phase angle θ_A can take only a positive value at any value of the parameters d, D, k_1, and k_2. Thus, the non-stationary surface concentration of electroactive species c_A^s can only lag behind an applied alternating current i, as in Ref. [18].

Fig. 2 *a–d* shows how a change in the Nernst diffusion layer thickness d affects the non-stationary surface concentration of electroactive species, i.e. an absolute value of the oscillating term Δc_A^s defined by Eq. (13). If the frequency ω approaches zero, the function $\left| \Delta c_A^s \right|$ takes its stationary value from Eq. (26). In this range of low frequencies ω, an increase in a value of the parameter d results in an increase in the function $\left| \Delta c_A^s \right|$.
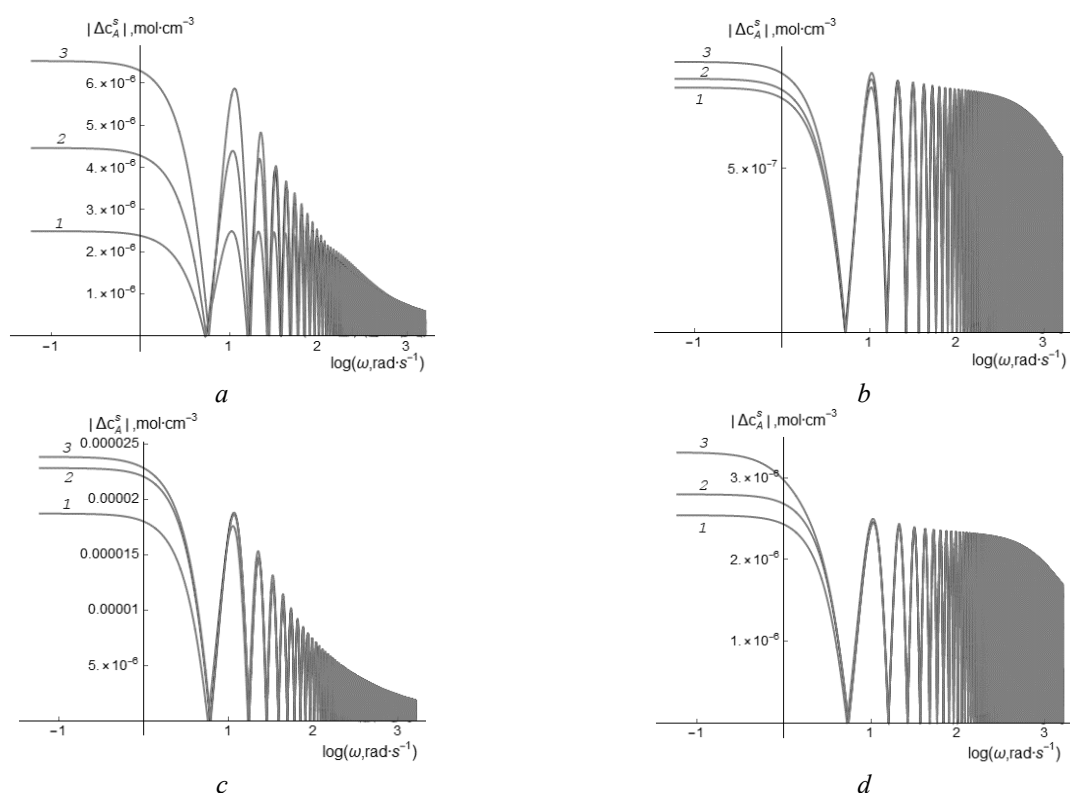
Fig. 2. An absolute value of deviation of surface concentration from equilibrium one under application of a small amplitude AC with frequency ω for electroactive species, $\left|\Delta c_A^s\right|$, mol×cm^{-3} as a function of logarithm of frequency, $\log(\omega, \text{rad·s}^{-1})$, at the Nernst diffusion layer thickness d, cm as follows (*1*) $5 \cdot 10^{-4}$, (*2*) 10^{-3}, (*3*) $2 \cdot 10^{-3}$, and the same fixed values of the parameters as in Fig. 1, and $t = 0.3$ s

At high frequencies ω, similar to the behavior of the phase angle θ_A, the function $\left|\Delta c_A^s\right|$ does not depend on a value of the parameter d. If the rate constants of chemical reaction k_1, and k_2 are high, this range of the frequencies become wider (Fig. 2 *b, d*). In a range of middle frequencies ω, the dependence of the function $\left|\Delta c_A^s\right|$ on the parameter d can change. As can be seen in Fig. 2 *a*, the function $\left|\Delta c_A^s\right|$ can decrease with increasing the parameter d. A decrease in the function $\left|\Delta c_A^s\right|$ is as faster as higher the parameter d. At low values of the parameters D, k_1, and k_2, the range of frequencies where the function $\left|\Delta c_A^s\right|$ descends as the parameter d ascends narrows and shifts to lower frequencies (Fig. 2 *c*). At high values of the rate constants of chemical reaction k_1, and k_2, this range of the frequencies becomes almost negligible (Fig. 2 *b, d*).

Electroinactive species. An influence of the Nernst diffusion layer thickness d on the frequency dependence of the phase shift θ_B defined by Eq. (17) can be seen in Fig. 3 *a–d*. The fixed values of the parameters D, k_1, and k_2 were the same as in Fig. 1 *a–d*. As can be noted, this dependence for electroinactive species differ from that for electroactive species. In contrast to the function θ_A that can take only a positive value at any value of the control parameters, the function θ_B can change a sign, i.e. turns to zero at some critical frequencies (Table 2). Thus, the non-stationary surface concentration of electroinactive species c_B^s can lag behind an applied alternating current i, be ahead or in phase with it.

The critical frequencies at which the function θ_B equals zero increase with increasing the parameters k_1, and k_2. They become almost independent on a value of the parameters d and D at high values of the rate constants of chemical reaction k_1, and k_2.

Table 2. The critical values of frequency at which the phase angle θ_B turns to zero at various values of the Nernst diffusion layer thickness d, the diffusion coefficient of species D, and the rate constants of chemical reaction k_1, and k_2 as in Fig. 1 *a–d*

	$d = 5 \cdot 10^{-4}$ **cm**	$d = 10^{-3}$ **cm**	$d = 2 \cdot 10^{-3}$ **cm**
	$\omega, \mathrm{rad \cdot s}^{-1}$	$\omega, \mathrm{rad \cdot s}^{-1}$	$\omega, \mathrm{rad \cdot s}^{-1}$
a	208.67	56.08	17.56
b	641.39	655.97	654.28
c	25.36	9.53	6.17
d	654.27	654.28	654.28
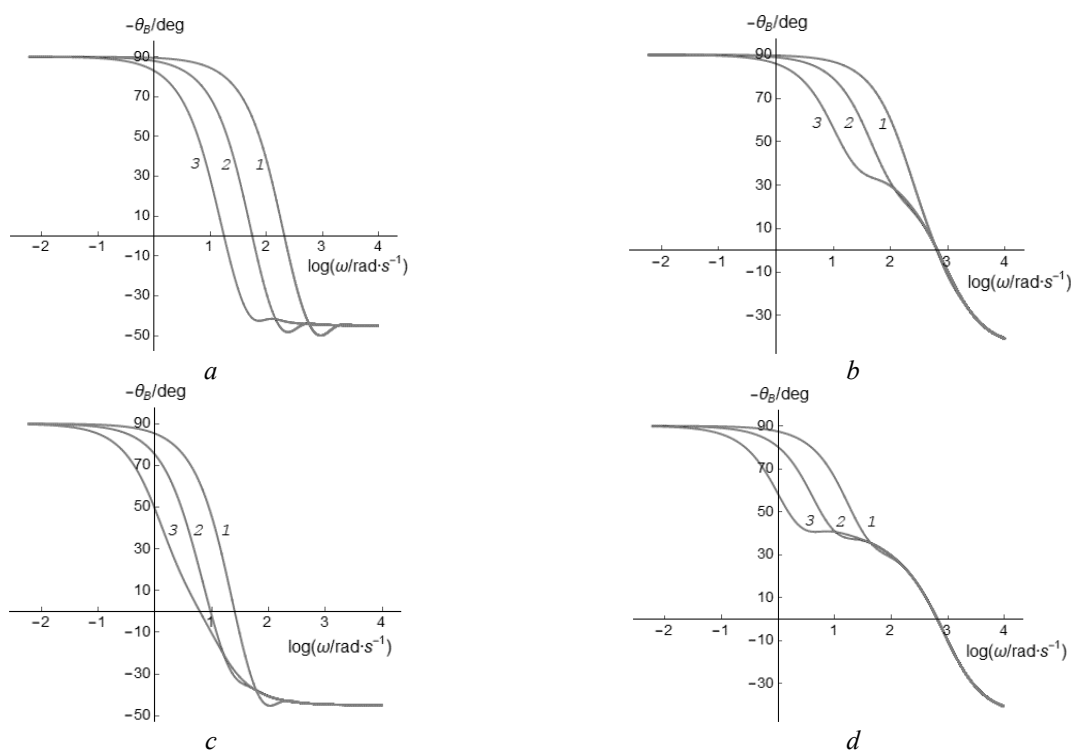
Fig. 3. Frequency dependence of phase angle θ_B for electroinactive species at different values of the Nernst diffusion layer thickness d, cm, as follows: (*1*) $5 \cdot 10^{-4}$, (*2*) 10^{-3}, (*3*) $2 \cdot 10^{-3}$, and the same fixed values of the parameters as in Fig. 1

Table 3. The extreme points of the phase angle θ_B at various values of the Nernst diffusion layer thickness d, the diffusion coefficient of species D, and the rate constants of chemical reaction k_1, and k_2 as in Fig. 1 *a–d*

	$d = 5 \cdot 10^{-4}$ **cm**				$d = 10^{-3}$ **cm**				$d = 2 \cdot 10^{-3}$ **cm**			
	ω_{min} rad/s	$\theta_{B\,min}$ deg	ω_{max} rad/s	$\theta_{B\,max}$ deg	ω_{min} rad/s	$\theta_{B\,min}$ deg	ω_{max} rad/s	$\theta_{B\,max}$ deg	ω_{min} rad/s	$\theta_{B\,min}$ deg	ω_{max} rad/s	$\theta_{B\,max}$ deg
a	925.91	49.93	2430.17	44.43	242.23	48.25	584.08	43.90	73.68	42.58	124.34	41.58
b												
c	106.32	45.22	216.49	42.79								
d									4.58	-40.67	7.48	-40.91

In contrast to this, at low values of the parameters k_1, and k_2, the critical frequencies become sensitive to a value of the parameters d and D. A decrease in the parameter D leads to a decrease in these frequencies, whereas a decrease in the parameter d results in their increase. Similar to the phase angle θ_A, the phase angle θ_B has the extreme points that are influenced by a value of the Nernst diffusion layer thickness d, the diffusion coefficient of species D and the rate constants of chemical reaction k_1, and k_2 (Table 3). As the frequency ω tends to zero, the phase angle θ_B reaches $-\pi/2$, whereas at infinite frequency, the phase angle θ_B tends to $\pi/4$ as the phase angle θ_A does.

Fig. 4 *a–d* shows the non-stationary surface concentration of electroinactive species defined by Eq. (14) at the chosen values of the Nernst diffusion layer thickness d. As frequency ω tends to zero, the function $\left|\Delta c_B^s\right|$ reaches its stationary value defined by Eq. (27). It increases with increasing the parameter d. Similar to the

behavior of the function $\left|\Delta c_A^s\right|$, there is a range of frequencies where the function $\left|\Delta c_B^s\right|$ can decrease with increasing the parameter d. This range depends on a value of the parameters k_1, k_2, and D. At high values of the parameters k_1, and k_2, the function $\left|\Delta c_B^s\right|$ performs similar to the function $\left|\Delta c_A^s\right|$ at low values of the parameters k_1, and k_2, because an increase in these parameters leads to an increase in the function $\left|\Delta c_B^s\right|$, and to a decrease in the function $\left|\Delta c_A^s\right|$. It should be noted that the function $\left|\Delta c_B^s\right|$ declines with ω much faster than the function $\left|\Delta c_A^s\right|$ does, especially for low values of the parameters k_1, k_2, and D. Thus, in this case, the effect of the parameter d on the function $\left|\Delta c_B^s\right|$ is weak.
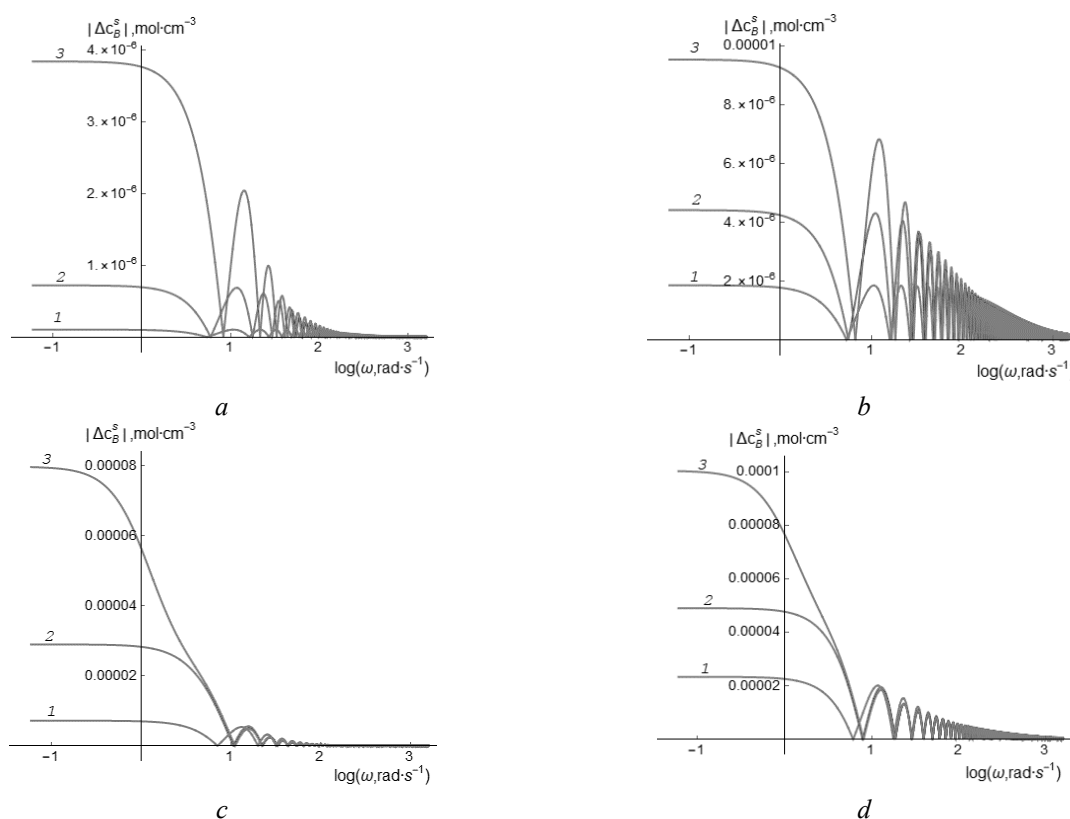
Fig. 4. An absolute value of surface concentration deviation from equilibrium one under application of a small amplitude AC with frequency ω for electroinactive species, $\left|\Delta c_B^s\right|$, mol×cm^{-3} as a function of logarithm of frequency, $\log(\omega,$ rad·s$^{-1})$, at the Nernst diffusion layer thickness d, cm as follows: (*1*) $5 \cdot 10^{-4}$, (*2*) 10^{-3}, (*3*) $2 \cdot 10^{-3}$, and the same fixed values of the parameters as in Fig. 1, and $t = 0.3$ s

It is worth mentioning that both functions $\left|\Delta c_A^s\right|$, and $\left|\Delta c_B^s\right|$ can only decrease as the parameter D increases at all chosen values of the parameters d, k_1, and k_2 [16]. Contrary to the parameter d, which influence on both functions $\left|\Delta c_A^s\right|$, and $\left|\Delta c_B^s\right|$ is strongly dependent on the other system parameters. The analytical and numerical results [21] obtained in this paper can help us to understand deeply the non-linear dynamics at an electrode/electrolyte interface under non-stationary conditions.

CONCLUSIONS

In summary, there is an influence of the Nernst diffusion layer thickness d on the surface concentration of electroactive and electroinactive species in the model electrochemical process with a preceding homogeneous first-order chemical reaction under application of a small amplitude alternating current. At low frequencies, the surface concentration of both species can only increase with increasing the parameter d. At high frequencies, the surface concentration of both species is independent on the Nernst diffusion layer thickness. However, there is a range of frequencies where the surface concentration of both species can decrease with increasing the parameter d. This decrease is as faster as higher the Nernst diffusion layer thickness is. This range of frequencies can be influenced not only by a value of the Nernst diffusion layer thickness, but also by a value of the rate constants of chemical reaction k_1, and k_2, and by the diffusion coefficient of species D. There exists a phase shift between an alternating current and the surface concentration that changes under application of this current. It is a function of the Nernst diffusion layer thickness, the oscillation diffusion layer thickness, and the reaction layer thickness. In the case of electroactive species, the phase angle can take only a positive value at any value of the parameters d, D, k_1, and k_2. Thus, the surface concentration of electroactive species can only lag behind an applied alternating current. The phase angle for electroactive species tends to $\pi/2$ at low frequencies, whereas at high frequencies it decreases to $\pi/4$. For the case of electroinactive species, the phase angle can be negative, positive, and equal to zero depending on a value of the parameters d, D, k_1, and k_2. Therefore, the surface concentration of electroinactive species can lag behind an applied alternating current, be ahead of it or in phase with it. The phase angle for electroinactive species approaches to $-\pi/2$ at low frequencies, and at high frequencies it tends to $\pi/4$. The both phase angles can have the extreme points that are strongly dependent on the parameters d, D, k_1, and k_2.

Вплив товщини дифузійного шару Нернста на поверхневу концентрацію в модельному електрохімічному процесі з попередньою хімічною реакцією

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У цій роботі досліджується вплив товщини дифузійного шару Нернста на поверхневу концентрацію електроактивних та електронеактивних частинок у модельному електрохімічному процесі з попередньою гомогенною хімічною реакцією першого порядку при накладанні змінного струму малої амплітуди. Розглядається випадок однакових коефіцієнтів дифузії частинок, які беруть участь у попередній хімічній реакції у тонкому шарі біля поверхні плаского електрода. Показано, що на низьких частотах прикладеного змінного струму, поверхнева концентрація електроактивних та електронеактивних частинок може лише зростати при зростанні товщини дифузійного шару Нернста. На високих частотах поверхнева концентрація обох частинок не залежить від цього параметра. Однак, існує область частот, де поверхнева концентрація як електроактивних так і електронеактивних частинок може зменшуватися зі зростанням товщини дифузійного шару Нернста. Ця область частот залежить від товщини дифузійного шару Нернста, констант швидкості хімічної реакції та коефіцієнта дифузії частинок. Між змінним струмом і

поверхневою концентрацією електроактивних та електронеактивних частинок існує зсув фаз. Він є функцією товщини дифузійного шару Нернста, товщини осцилюючого дифузійного шару та товщини реакційного шару. У випадку електроактивних частинок фазовий кут може приймати лише позитивне значення. На низьких частотах він прямує до π/2, тоді як на високих частотах він зменшується до π/4. У випадку електронеактивних частинок фазовий кут може бути позитивним, негативним та дорівнювати нулю в залежності від товщини дифузійного шару Нернста, констант швидкості хімічної реакції та коефіцієнта дифузії частинок. Він прямує до –π/2 на низьких частотах, а на високих частотах він приймає значення π/4. Обидва фазові кути можуть мати максимуми та мінімуми. Їхня величина сильно залежить від товщини дифузійного шару Нернста, коефіцієнта дифузії частинок, констант швидкості хімічної реакції.

Ключові слова: СЕ механізм, поверхнева концентрація, фазовий кут, попередня хімічна реакція, дифузійний шар Нернста, реакційний шар, осцилюючий дифузійний шар, коефіцієнт дифузії, константа швидкості

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