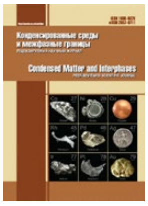

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Simulation of a non-stationary electrochemical process on rough electrodes under mixed kinetic-diffusion control

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Abstract

Objectives: In this work, the effect of electrode surface roughness on the rate of a transient electrochemical process under mixed transport-kinetic control is established. A mathematical model of the electrochemical process occurring on an electrode with a rough surface and characterized by a different ratio of the rate constant of the charge transfer stage and the coefficient of non-stationary bulk diffusion is constructed.

Experimental: Using the numerical method of finite element modeling, chronoamperograms of a transient electrochemical process were obtained under conditions of mixed transport and kinetic control on electrodes with different surface profiles defined by harmonic and fractal functions. The transient "roughness function - time" curves are calculated and the boundaries of the transition region are determined, within which it varies from the roughness factor to unity. It is found that the shape of the chronoamperogram depends in a complex way both on the geometric characteristics of the rough surface and on the ratio of the diffusion-kinetic parameters of the process. With relatively short durations, the gross process rate is equal to the charge transfer rate at a given potential and is proportional to the roughness factor. With relatively long durations, the chronoamperogram transforms into a current decay curve of the diffusion-controlled process, while the effect of roughness is nonlinear in this case and manifests itself only with relatively short process durations. Under these conditions, the thickness of the diffusion layer is much smaller than the size of the irregularities, and the rate of the process on the rough electrode is proportional to the true surface area and roughness factor.

Conclusions: The position of the transition region depends on the value of the rate constant of the charge transfer: in the case of a slow kinetic stage, the transition manifests itself over increasingly long periods and gradually widens, while depending on the geometric shape of the irregularity.

Keywords: Electrode process, Mixed kinetics, Roughness factor, Chronoamperogram, Finite element method, Roughness function, Harmonic profile, Fractal function

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1. Introduction

Morphological irregularity, or geometric heterogeneity of the electrode surface, is one of the most important factors affecting the kinetics of electrochemical processes. The shape, size, and distribution of irregularities along the electrode/solution interface are of both practical and fundamental importance. For example, in microelectronics, they strongly influence the efficiency and modes of implementation of TSV (through silicon vias) technology, when uniform electrodeposition of copper onto an electrode of complex macrogeometric configuration is required [1, 2]. In both theoretical and applied electrochemistry, the microgeometry of the surface, or the roughness of the electrode, plays an important role [3]. The roughness effect is most complexly manifested in the case of a tertiary current distribution, when concentration gradients form in an electrochemical system, and the mass transfer stage makes a significant contribution to the rate of a multi-stage heterogeneous electrode process. When studying the kinetics of such processes on solid electrodes, it is necessary to take into account that their roughness factor always differs from unity, since their surface is rough regardless of pretreatment. The roughness factor f_r is the ratio of the true area S, which is equal to the sum of the areas of all irregularities, to the geometric (visible) area S_g corresponding to the projection of the electrode boundary [4]:

$$f_r = S/S_g. \quad (1)$$

As a result, the extensive parameters of electrode reactions, corrosion processes, double electric layer, and adsorption are proportional to the area of the electrode/solution interface. At the same time, the influence of roughness on such parameters is often very significant. Thus, in double-layer phenomena, the roughness of the electrode leads to a large increase in the accumulated charge [5] and significantly reduces the interfacial resistance [6], which indicates that strongly roughened electrodes are promising for use in supercapacitor technology [7], where an increase in energy density is crucial. To reduce the effectiveness of the corrosion process, on the contrary, it is important to reduce the surface roughness of the electrode [8–11].

In order to correctly compare the extensive electrochemical parameters of various systems and processes with each other, they should generally be normalized to the area of the electrode/solution interface. However, the procedure for such normalization is not trivial, especially in the case of non-stationary electrochemical measurements, and it is far from always reduced to a simple division based on the area of the true surface of the electrode $S > S_g$, and normalization based on the area of the visible surface is generally applicable only in the case of liquid electrodes, since only they are perfectly smooth, so for them $S = S_g$. In [12–14], we theoretically substantiated and developed an algorithm for accounting for the effect of non-fractal, fractal, and statistically irregular roughness in the kinetics of diffusion-controlled processes. Within the framework of a number of theoretical models describing the electrode process, when the diffusion mass transfer stage is slow, and the charge transfer stage is very fast, it has been shown that the ratio of the thickness of the diffusion layer and the average size of the rough surface irregularities play a decisive role. It should be noted that most of the theoretical models available in the literature in non-stationary systems with rough electrodes have been developed specifically for reversible electrode processes, the limiting stage of which is diffusion mass transfer [15–17].

However, the kinetics of electrode processes are often not purely diffusive and/or the roughness effect is not limited to a geometric increase in the area of the electrochemically active surface. For example, the use of rough sensor electrodes allows for a higher sensitivity of electrochemical sensors not only due to an increase in area [18, 19], but also surface activity, which in the case of a rough surface is usually higher due to an increase in the number of active sites [20] or certain functional groups [21]. Such a dual effect of roughness plays a special role in the kinetics of electrocatalytic processes, since a correct estimation of the properties of an electrocatalyst requires a separation of the two effects: 1) an increase of its activity in a particular electrode reaction, and 2) an extensive rise in current due to an increase in the true surface area of the electrode. Otherwise, the estimation of electrocatalytic activity may lead to incorrect results, since the current density after normalization to the true surface area may be unchanged compared to a smooth electrode [22]. Therefore, it is urgent to identify a purely geometric roughness effect in the study of electrochemical processes occurring in the mixed transport-kinetic control, when the rates of the kinetic and diffusion stages are comparable.

The range of practically significant electrochemical processes occurring under mixed transport-kinetic control is quite wide, and for many of them a noticeable effect of roughness on the kinetics of the process has been revealed. For instance, a complex multi-stage process of cathodic reduction of CO_2 is morphologically sensitive, for which an enhancement in the efficiency of the electrochemical conversion of carbon dioxide into formic acid with an increase in the roughness of the electrode was found in [23, 24]. However, a procedure for the correct accounting of geometric roughness for such processes using non-stationary electrochemical methods (chronoampero-, chronopotentio-, and chronovoltamperometry) has not been developed. This is because the corresponding diffusion-kinetic problems have not been solved with different ratios of the charge transfer rate constant and the diffusion coefficient, which determine the contributions of kinetic and diffusion stages to the overall rate of the electrochemical process occurring on the surface of a rough electrode.

The purpose of the work is to establish the effect of electrode surface roughness on the rate of a non-stationary electrochemical process under mixed transport-kinetic control and potentiostatic polarization.

The objectives are as follows:

1. To obtain the theoretical chronoamperograms of an electrochemical process taking place in the mixed kinetics mode on a perfectly smooth flat surface of an electrode, as well as on surfaces with harmonic and fractal profiles with a given roughness factor and with a different ratio of the diffusion coefficient and the kinetic stage rate constant.
2. To calculate the roughness functions for the studied electrode surface profiles and various ratios of the diffusion coefficient and the rate constant of the kinetic stage.
3. By comparing the roughness functions obtained for different surface profiles, to identify the role of the shape of surface irregularities of a harmonic or fractal type, the surface roughness factor, as well as the ratio of contributions from the diffusion and charge transfer stages, in the potentiostatic current transient of the electrochemical process occurring under a mixed transport-kinetic control.

2. Formulation of the diffusion-kinetic problem and the method of computational experiment

The main task of the simulation was to find the spatiotemporal concentration profile of the electrochemically active diffusant *Ox*, a participant in the two-stage electrode process:

$$Ox^{v} \xrightarrow[D]{\text{diffusion}} Ox^{s} + ne^{-} \xrightarrow[k]{\text{charge transfer}} Red^{s}, \quad (2)$$

proceeding under a mixed transport-kinetic control on a rough (f_r = const) electrode/solution interface. The stages of non-stationary diffusion mass transfer and charge transfer are quantitatively characterized by certain values of the diffusion coefficient D (cm^2/s) and the charge transfer rate constant k (cm/s), respectively. Based on the ratio of these parameters, more precisely, based on the value of a dimensionless complex parameter k^2t/D in the case of a perfectly smooth flat electrode, one can judge the contribution of a particular stage to the kinetics of the process. The corresponding dependence of the process (2) rate on time, expressed in current units (chronoamperogram), for the potentiostatic conditions of electrode polarization, i.e. at constant overvoltage, η = const, is described by the following expression [25]:

$$i(t)_{\text{flat}} = nFkc^{\text{v}} \cdot \exp\left(k^2t/D\right) \cdot \operatorname{erfc}\left(kt^{1/2}/D^{1/2}\right). \quad (3)$$

Here F is the Faraday number (96485 C/mol), c^{v} is the bulk (initial) concentration of *Ox* in the electrolyte solution. In the limiting case, when the rate constant of the charge transfer stage (and the exchange current proportional to it) is very high, i.e. the parameter $k^2t/D \gg 1$, equilibrium is quickly established during the second stage of the electrode process (2), therefore, the rate is limited by diffusion mass transfer, and the chronoamperogram is described by the Cottrell equation [25]:

$$i(t)_{\mathrm{Cottrell}} = \frac{nFD^{1/2}c^{\mathrm{v}}}{(\pi t)^{1/2}}. \tag{3a}$$

On the contrary, if the kinetic stage is slowed down, which is performed using very small parameters $k^2t/D \ll 1$, then the rate of the electrode process does not change over time, but is determined by the overvoltage:

$$i(\eta) = nFk(\eta)c^{\mathrm{v}}. \tag{3b}$$

In this work, the chronoamperograms of the process (2) were calculated in a wide range of k^2t/D values for electrodes with a rough surface. The rough interphase boundary was represented as a two-dimensional surface corrugation of three different types: non-fractal, fractal, and statistically irregular. Non-fractal surface profiles (sinusoidal, sawtooth, trapezoidal, and a system of single projections) were modeled using various harmonic functions with a characteristic wavelength λ equal to the distance between adjacent irregularities [13]. Fractal surface profiles were modeled using a range-limited continuous modified one-dimensional Weierstrass function [3, 14, 26, 27]. A statistically irregular surface profile modeled using the Weierstrass–Mandelbrot random fractal function [14, 28, 29] most accurately reflected the real surface of a solid electrode. A feature of both fractal and statistically irregular surfaces is the dispersion of the characteristic wavelengths of irregularities in the range from minimum λ_{min} to maximum λ_{max}, inherent in the vast majority of solid surfaces. The method of mathematical modeling of the studied surface profiles is described in detail in [13, 14].

An electrolyte solution with a bulk concentration of diffusant c^{v} undergoing electrochemical transformation according to scheme (2) under potentiostatic cathodic polarization is considered as a model electrochemical system. The concentration of the diffusant in this case obeys the differential equation of Fick's second law:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{4}$$

with the initial condition

$$c\big|_{t=0} = c^{\mathrm{v}} \tag{5}$$

and the first boundary condition

$$c\big|_{z\to\infty} = c^{\mathrm{v}}. \tag{6}$$

It was assumed that the charge transfer stage is irreversible ($\vec{k} \gg \overleftarrow{k}$), i.e. *Red* oxidation has no effect on the overall rate of the process. In this case, the second boundary condition is valid, written in the following form:

$$D\frac{\partial c}{\partial \vec{n}}\bigg|_S = kc_S,$$

which is a condition for continuity of flux at the interface (*S*) and implies equality of the rate of charge transfer $\upsilon = kc_S$ and the density of the diffusion flux $j(t)\big|_S = D\frac{\partial c}{\partial \vec{n}}\Big|_S$ along the normal to the surface ($\vec{n}$). The diffusion flux density $j(t)\big|_S$ per unit geometric surface area of the electrode was calculated using the numerical finite element method [30] using the COMSOL Multiphysics software platform [31–34] for the following process parameters: bulk concentration of diffusant $c^{\mathrm{v}} = 1$ mol/m^3; number of electrons $n = 1$; temperature 298 K; diffusion coefficient: 10^{-6} cm^2/s; overvoltage: –0.1 V; the distance between adjacent irregularities (characteristic wavelength of the profile) of the rough electrode is $\lambda = 10^{-3}$ m. The value of the charge transfer rate constant varied in a wide range from 10^{-8} to 1 cm/s. The current density was calculated using the formula:

$$i(t)_{\mathrm{rough}} = nF\,j(t)\big|_S. \tag{8}$$

The effect of morphological heterogeneity of the electrode surface on the mixed kinetics of the electrochemical process (2) was analyzed using the roughness function:

$$\varphi = \frac{i(t)_{\mathrm{rough}}}{i(t)_{\mathrm{flat}}}. \tag{9}$$

Here $i(t)_{\mathrm{flat}}$ is the current density calculated by the formula (3), $i(t)_{\mathrm{rough}}$ – current density found in COMSOL Multiphysics by numerical simulation. Obviously, if $i(t)_{\mathrm{rough}} = i(t)_{\mathrm{flat}}$, then the roughness function is equal to the roughness factor f_{r}, which is determined by formula (1). The transient current density $i(t)_{\mathrm{rough}}$ was numerically calculated for different values of the dimensional-kinetic complex:

$$k_D = \frac{k}{D}\lambda, \tag{10}$$

the value of which can be used to judge the ratio of the contributions of the diffusion and kinetic stages to the rate of the overall process in the case of rough electrodes. The transient of the roughness function is represented in dimensionless coordinates $\varphi - Dt/\lambda^2$, which makes it possible to determine how many times at a given time the rate of the process (2) on a morphologically inhomogeneous electrode is higher due to the presence of irregularities on it compared to a perfectly smooth flat electrode. The use of the roughness function and the dimensionless parameters of the system (k_D, Dt/λ^2, k^2t/D) makes it possible to evaluate the role of roughness in the kinetics of electrochemical processes occurring under mixed transport-kinetic control, with a different ratio of the contributions of the stages of diffusion mass transfer and charge transfer to the overall rate of the process. The relative contribution of a particular stage is determined by the value of the dimensional-kinetic complex k_D, at the limiting values of which diffusion ($k_D \gg 1$) or kinetic ($k_D \ll 1$) control is realized. In this work, the simulation was carried out in a wide range of k_D values from 10^{-3} to 10^5.

During the preliminary stage of simulation, using the example of a perfectly smooth flat electrode, the adequacy of the numerical simulation results was verified by comparing it with the known exact solution described by the mathematical function (3) obtained in [25] by the analytical method of Laplace transformation. Fig. 1 presents logarithmic dimensionless Y,τ-chronoamperograms ($Y = \frac{i}{nFkc^{v}}$, $\tau = Dt/\lambda^2$) for an electrochemical process proceeding under mixed transport-kinetic control on a perfectly smooth flat electrode, obtained by equation (3) (solid lines), as well as calculated by the finite element method in the COMSOL Multiphysics program (markers). As expected, the calculated chronoamperograms have two linear sections in bilogarithmic coordinates. The first (horizontal) section corresponds to the slowed down stage of charge transfer, and formula (3b). The second section has a slope of $d\lg Y/d\lg\tau = -1/2$, which corresponds to the slowed down diffusion stage and the Cottrell equation (3a). The calculation showed that the results obtained by two methods, analytically and numerically, completely coincide, which makes it possible to use this approach for more complex systems with a rough electrode/solution interface.

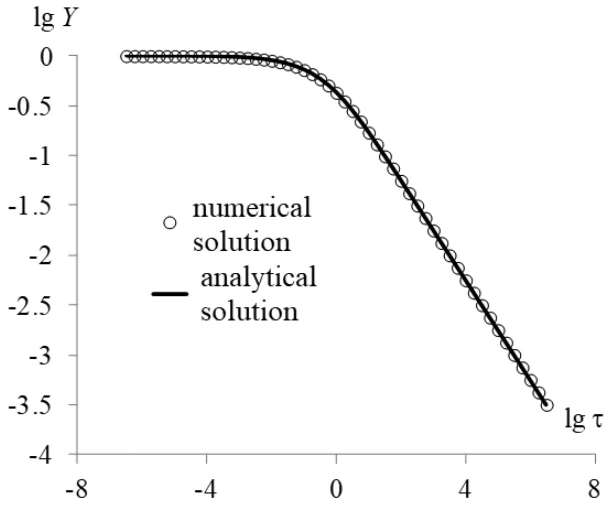


Fig. 1. Chronoamperograms of a non-stationary electrochemical process (1) on a flat electrode obtained by numerical and analytical methods for the mixed transport-kinetic control mode

3. Results and discussion

Harmonic roughness. Typical chronograms of the roughness function for electrodes, the surface of which is modeled by harmonic functions, are shown in Fig. 2. It turned out that for relatively large values of the dimensional-kinetic complex $k_D \geqslant 1$, the curve coincides with a similar dependence obtained earlier for processes controlled by the stage of non-stationary diffusion mass transfer [13]. This situation occurs with high values of the rate constant of the charge transfer stage and/or low values of the diffusion coefficient. The shape of the chronogram is quite indicative: for dimensionless time values $Dt/\lambda^2 < 10^{-3}$, the roughness function φ is equal to the roughness factor f_r (formula (1)). This means that the current density on a rough electrode is f_r times higher than on a flat electrode, i.e. $i(t)_{\text{rough}} = i(t)_{\text{flat}} \cdot f_r$, therefore, in this case, additional normalization of the experimental current density value by the roughness factor is necessary to correctly estimate the process speed. If $Dt/\lambda^2 > 1$, then the roughness function is equal to one, therefore

$i(t)_{\text{rough}} = i(t)_{\text{flat}}$, and roughness accounting is not required.

In another limiting case, when the value of the dimensional-kinetic complex k_D is very small (curve *1* in Fig. 2), during the entire period of transient measurements, the roughness function is equal to the roughness factor. As expected, if the kinetics of the process is purely electrochemical ($k_D << 1$), the current density should always be normalized by the roughness factor.

The position and shape of the chronograms of the roughness function with intermediate values of the dimensional-kinetic complex k_D, i.e. for the mixed-kinetic control, depends on the ratio of the charge transfer rate constant and the diffusion coefficient, therefore, on the contribution of one stage or another to the rate of the electrochemical process. As the rate constant k increases, i.e. as the kinetic stage accelerates, a transition region appears on the chronogram of the roughness function, the position and duration of which depends on the dimensional-kinetic complex k_D: as it decreases, the transition region appears, firstly, with increasing durations, and secondly, it gradually widens. This effect is also confirmed by analyzing similar dependences of the roughness function on time found for different harmonic roughness factors (Fig. 3). It can be seen that the higher the f_r, the greater the value of the roughness function with short durations. In turn, with a decrease in k_D, the area of constancy of the roughness function is noticeably widened.

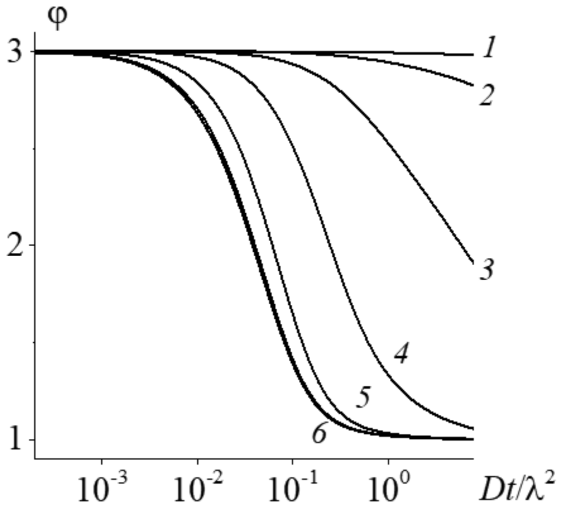


Fig. 2. Chronograms of the roughness function for an unsteady electrochemical process operating in mixed transport-kinetic control mode on an electrode with a sinusoidal surface ($f_r = 3$) for different values of the dimensional-kinetic complex $k_D = 10^{-5}$ (*1*), 10^{-4} (*2*), 10^{-3} (*3*), 10^{-2} (4), 10^{-1} (*5*), ⩾1 (*6*)

Since the roughness function is the ratio of currents on a rough and flat electrode, the described effects are reflected in the form of chronoamperograms, which are shown in Fig. 4 for different values of the dimensional-kinetic complex k_D in comparison with similar curves for a perfectly smooth flat electrode.

It can be seen that if $k_D >> 1$ (diffusion kinetics, Fig. 4a), then the chronoamperogram over the entire time range is a current decay curve, partially (with short and long durations) straightening in double logarithmic coordinates with a slope $d\lg i/d\lg t = -1/2$, which corresponds to the Cottrell equation (3a). At the same time, in the region with short durations, the currents on

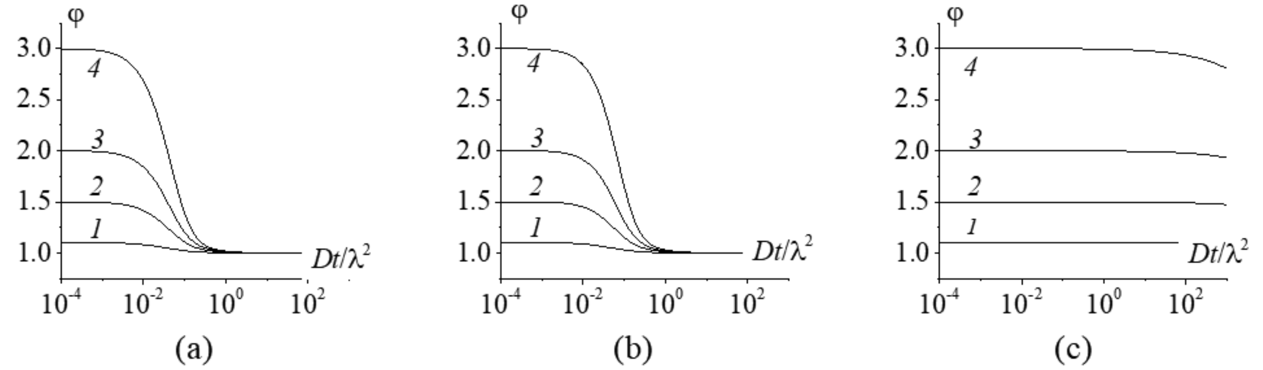
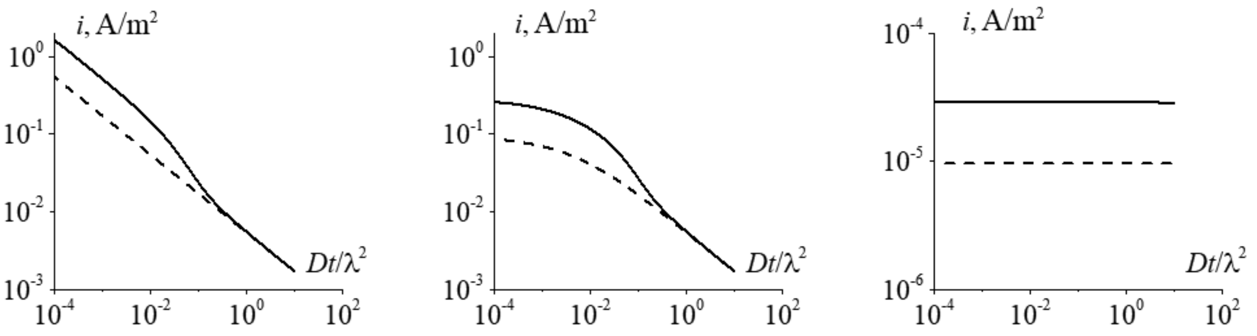


Fig. 3. Transients of the roughness function calculated for a sinusoidal surface profile for different values of the roughness factor $f_r = 1.1$ (*1*), 1.5 (*2*), 2.0 (*3*), 3.0. (*4*) and the dimensional kinetic complex $k_D = 10^5$ (a), 10 (b), 10^{-3} (c)



(a) (b) (c)

Fig. 4. Chronoamperograms of a non-stationary electrochemical process occurring in mixed transport-kinetic control mode on an electrode with a sinusoidal surface (f_r = 3) for different values of the dimensional-kinetic complex $k_D = 10^5$ (a), 10 (b), 10^{-3} (c). Dotted lines are chronoamperograms for an ideal smooth flat electrode

the rough electrode are f_r times higher than on the flat one, and with long durations, the curves for both electrodes, on the contrary, coincide.

If $k_D \ll 1$ (electrochemical kinetics, Fig. 4b), then in almost the entire time interval the process proceeds under kinetic control, so the current density takes a constant value corresponding to a given overvoltage. In this case, the ratio of currents on the rough and flat electrodes is equal to the roughness factor during the entire period of transient measurements.

In the intermediate range of values of the dimensional-kinetic complex k_D, the chronoamperogram takes on the most complex and non-trivial form. With short durations, chronoamperograms on both rough and flat electrodes are nonlinear in double logarithmic coordinates, since the mixed transport-kinetic control is implemented. The region of *i* relative constancy, when the contribution of the charge transfer stage to the kinetics is large enough, is replaced by a decrease in current caused by an increase in concentration polarization. The ratio of currents on rough and flat electrodes in a given time interval is equal to the roughness factor. Over time, the bilogarithmic curves of the rough and flat electrodes gradually converge, as the contribution of the kinetic stage decreases. With long durations, both chronoamperograms coincide and are linearized in accordance with the Cottrell equation (3a): the control completely passes to the stage of diffusive mass transfer.

Thus, when studying the kinetics of processes characterized by comparable rates of diffusion and kinetic stages on solid rough electrodes, it is necessary to take into account the complex, non-linear and non-stationary effect of electrode roughness on the current density recorded during the experiment. As a result, the normalization procedure for the roughness factor is not always reduced to a simple division by the roughness factor, and under certain conditions is not necessary at all. Correct consideration of the roughness effect in such cases requires a preliminary estimation of the k_D value, which means necessity of the exchange current, diffusion coefficient, and estimated average size of the irregularities.

The potentiostatic response of the rough electrode on the surface of which the process (2) is taking place can be interpreted using data on the concentration distribution near the rough electrode/solution interface. Figures 5 and 6 show the concentration profiles of the electroactive diffusant *Ox*, calculated for the value of the dimensional-kinetic complex k_D = 10 in the time range from 30 to 10^4 s, i.e. over a wide range of values of the complex diffusion-kinetic parameter k^2t/D from 0.3 to 10^2. It can be seen that only with short durations the diffusion front completely repeats the surface profile, and over time, the sensitivity to irregularities is leveled, and the diffusion front is smoothed out. As a result, only when $k^2t/D < 1$, the density of the diffusion flux, and hence the current density, should be normalized to the roughness factor. Obviously, such a situation can occur over a fairly wide time range, but only if the charge transfer rate constant is so small that the electrode process (2) is almost completely controlled by the electrochemical stage, as is observed in Fig. 4c.

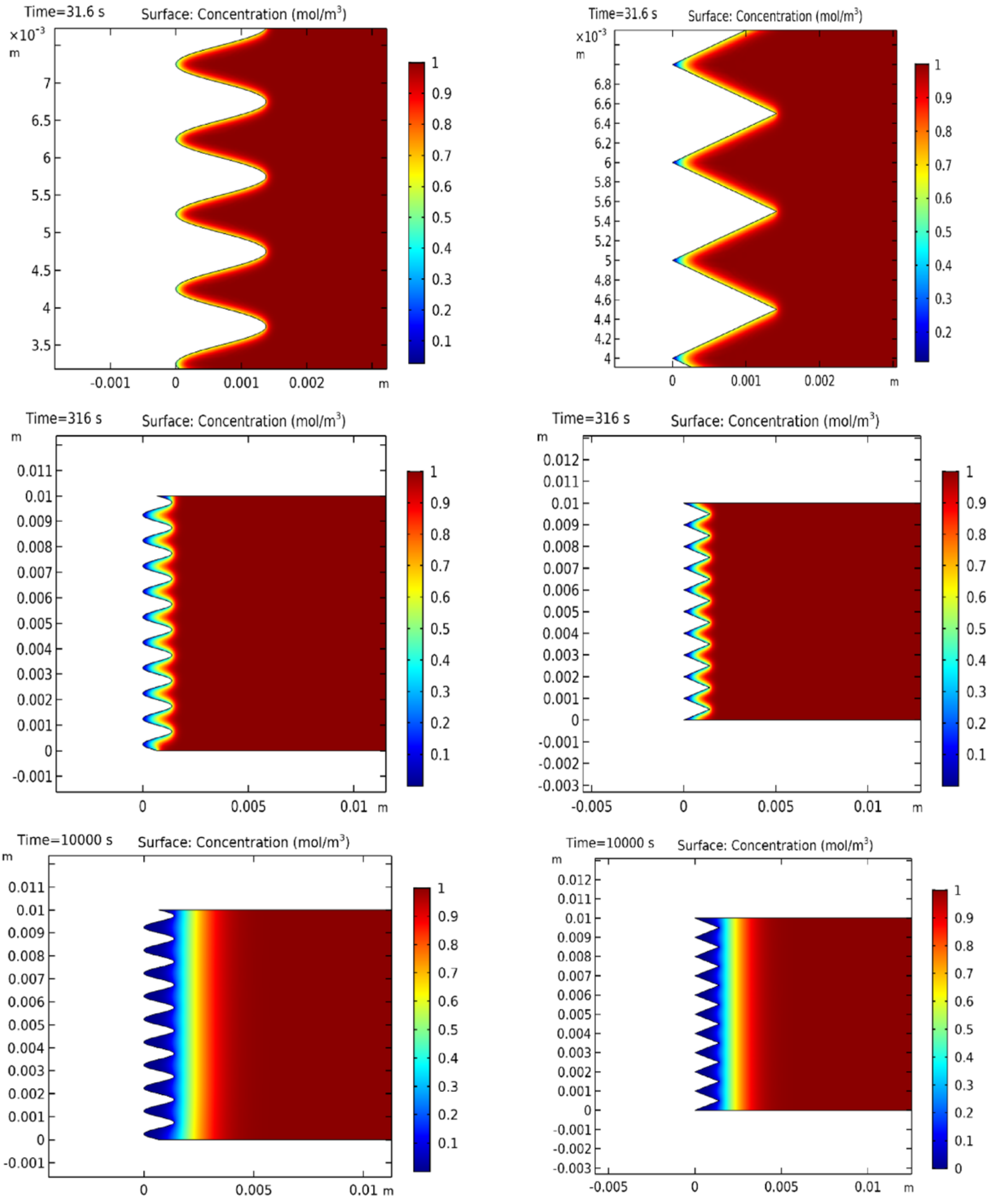


Fig. 5. The concentration field of a diffusant near a sinusoidal and sawtooth surface ($f_r = 3$) during a non-stationary potentiostatic process in mixed transport-kinetic control mode with different durations. The dimensional-kinetic complex $k_D = 10$

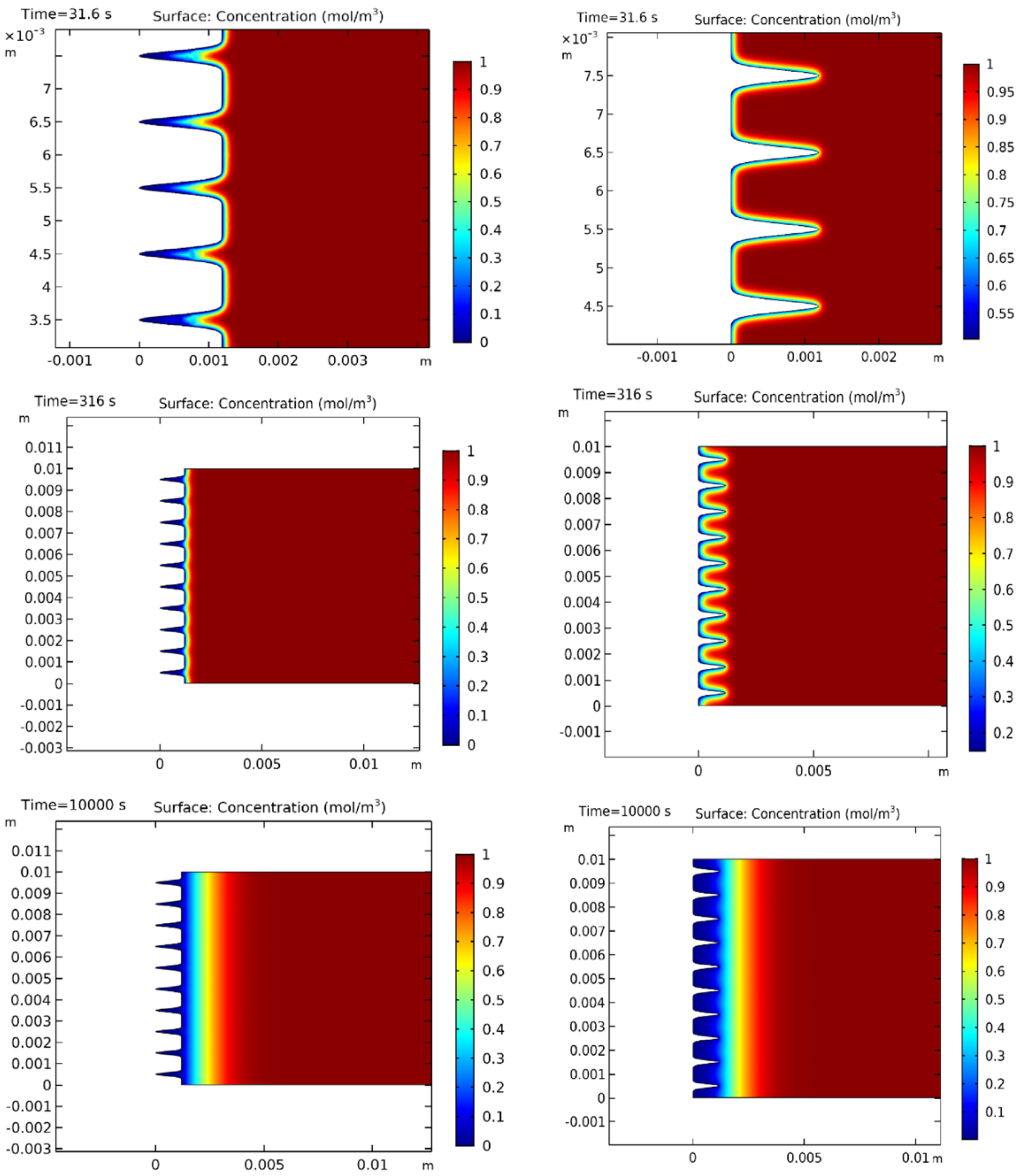


Fig. 6. The concentration field of a diffusant near single protrusions and a trapezoidal surface ($f_r = 3$) during a non-stationary potentiostatic process in mixed transport-kinetic control mode with different durations. The dimensional-kinetic complex $k_D = 10$

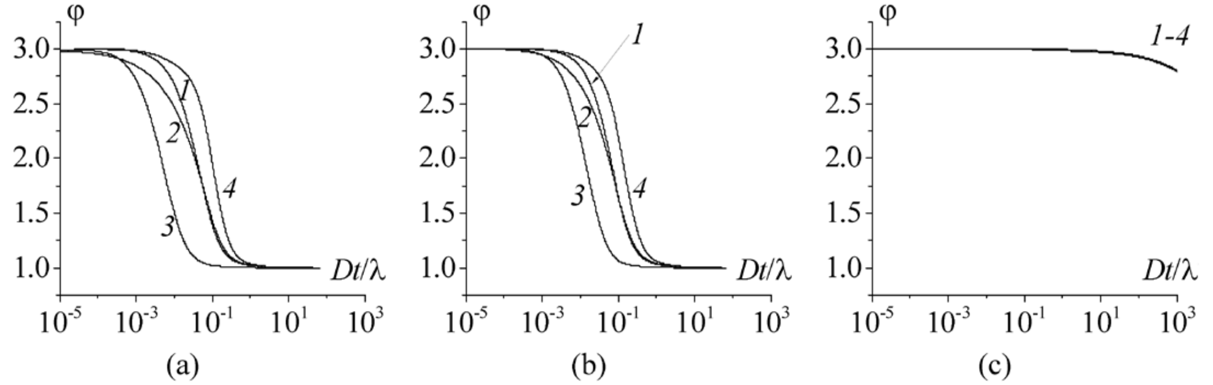
Comparative analysis has shown that the difference in transients of roughness functions of different harmonic types is quite noticeable (Fig. 7), although it decreases with decreasing size-kinetic complex k_D. At $k_D \ll 1$, the chronograms coincide, which indicates that under conditions of purely electrochemical control, the determining role is played not by the shape of the micro irregularities, but by the macrogeometric parameter, i.e. by the roughness factor. Considering that the real surface profile of a solid electrode usually consists of a set of harmonics of various sizes and shapes, the roughness effect was modeled using fractal and statistically irregular functions. The fact is that their use makes it possible to describe the morphology of the electrode/solution interface as realistically as possible [14], since the profiles constructed according to these mathematical functions are a combination of various irregularities, the average lateral size of which lies in a given range from λ_{min} to λ_{max}.

Fractal and statistically irregular roughness. Figure 8 shows the chronograms of the roughness function for a non-stationary electrochemical process proceeding under mixed transport and kinetic control on model surfaces defined by the fractal Weierstrass function and the statistically rough Weierstrass-Maldenbrot function. As in the case of the process on harmonic-type surfaces, for relatively small values of k_D, a horizontal section is formed on the current decay curves, within which the function $\varphi = f_{\text{r}}$. The duration of this section increases with a decrease in k_D, i.e. with a decrease in the rate constant of the charge transfer stage and/or an increase in the diffusion coefficient.

A distinctive feature of the chronograms of roughness functions for fractal and statistically irregular surfaces is a significant broadening of the transition region compared to roughened electrodes with a harmonic-type surface. This effect is probably due to the presence of irregularities of various sizes on the surface. Indeed, the average distance between adjacent irregularities in the case of both fractal and statistically irregular surfaces lies in the range $\lambda_{\text{min}} < \lambda < \lambda_{\text{max}}$ [14], while harmonic profiles are characterized by the absence of a distribution of irregularities in their size (λ = const).

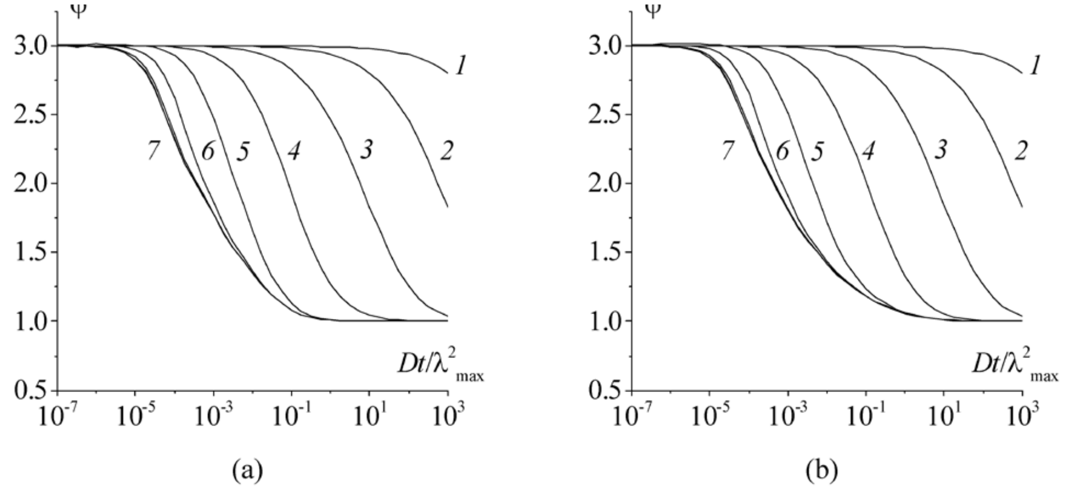
This effect can be explained by analyzing the concentration profiles of an electrochemically active diffusant near the fractal and statistically irregular electrode surface, calculated for k_D = 10 in the time range t from 0.5 to $5 \cdot 10^4$ s, i.e. over a wide range of values of the diffusion-kinetic parameter k^2t/D (Fig. 9). It can be seen that with short durations, the diffusion front completely repeats the profile of the surface with a minimum wavelength (λ_{min}). However, over time, the sensitivity to such irregularities decreases, and therefore the diffusion front gradually smooths out, taking the form of a longer-wavelength harmonic, until at some point it coincides in shape with the profile with the maximum wavelength (λ_{max}), after which it quickly becomes flat.

The described changes in the shape of the diffusion front lead to a gradual decrease in its area, and consequently, the flow and the roughness function over time. In contrast to the φ obtained for surfaces defined by harmonic



(a) (b) (c)

Fig. 7. Transients of the roughness function calculated for different harmonic surface profiles: sinusoidal (*1*), sawtooth (*2*), trapezoidal (*3*), a system of single protrusions (*4*) with a roughness factor f_{r} = 3 for the values of the dimensional kinetic complex $k_D = 10^5$ (a), 10 (b), 10^{-3} (c)



(a) (b)

Fig. 8. Transients of the roughness function (f_r = 3.0) calculated for fractal (a) and statistically irregular (b) surfaces for different values of the dimensional-kinetic complex $k_D = 10^{-3}$ (*1*), 10^{-2} (*2*), 10^{-1} (*3*), 1 (*4*), 10^1 (*5*), 10^2 (*6*), $\geqslant 10^3$ (*7*)

functions, the transition region in the case of Weierstrass and Weierstrass-Mandelbrot profiles is characterized by significant broadening not only at low k_D corresponding to the purely electrochemical kinetics of the process (2), but also at values of the dimensional kinetic complex valid for diffusion control. In addition, a decrease in the rate constant of the charge transfer stage leads to a significant shift of the transition region to the region of a larger *t*.

Thus, the roughness effect in the kinetics of electrochemical processes, which are characterized by mixed transport-kinetic control, turns out to be much more complex than in cases of purely diffusion or electrochemical kinetics. The characteristic criterion for the correct estimation of the roughness effect on the kinetics of such processes is, first of all, the dimensional-kinetic complex $k_D = \frac{k}{D}\lambda$. The simplest way is to take into account the roughness effect when $k_D \ll 1$, i.e. the charge transfer stage is limiting. In this case, the current density must necessarily be normalized to the roughness factor of the electrode surface. In the case where the electrochemical stage and the diffusion mass transfer stage proceed at comparable rates $(k_D \geq 1)$, or diffusion is slowed down compared to charge transfer, roughness accounting is reduced to dividing the current density by the roughness factor only for very short durations, otherwise an estimation of the roughness function at a given time is required.

4. Conclusions

1. The concentration profiles of an electroactive diffusant have been calculated by numerical finite element modeling. The chronoamperograms of an electrochemical process occurring under mixed transport and kinetic control on rough surfaces described by various harmonic and fractal functions with a given roughness factor with different ratios of the rate constant of the kinetic stage of the electrochemical process have been obtained.

2. The shape of the chronoamperogram of an electrochemical process in a mixed diffusion-kinetic regime depends both on the characteristics of the rough surface (roughness factor, average size of irregularities) and on the ratio of the rate constant of the charge transfer stage and the diffusion coefficient. With short durations, the overall process rate is equal to the charge transfer rate at a given potential. With long durations, the chronoamperogram coincides with the curve of the diffusion-controlled process, which is explained by the transition from the kinetic to the diffusion mode of the electrochemical process.

3. The effect of roughness is manifested only at relatively short process durations, and if the thickness of the diffusion layer is much smaller than the size of the irregularities, then the ratio

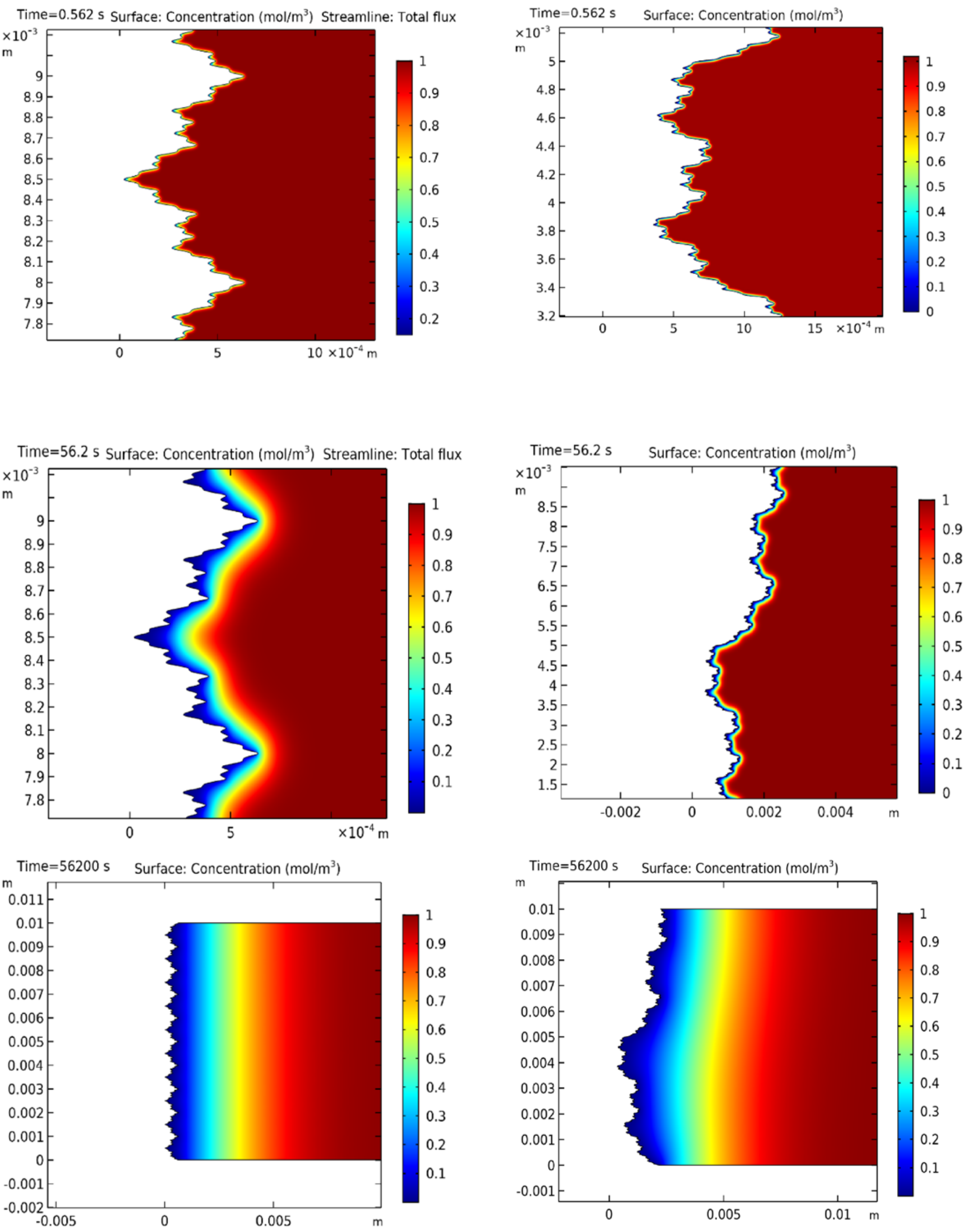


Fig. 9. The concentration field of a diffusant near a fractal and statistically rough surface (f_r = 3) during a non-stationary potentiostatic process in the mixed transport-kinetic control mode for different durations. The dimensional-kinetic complex k_D = 10

of process rates on rough and perfectly smooth electrodes is equal to the roughness factor. With long durations, the diffusion front is smoothed out so that there is no need to take roughness into account when calculating the process rate. In the intermediate time interval, the effect of roughness on the process rate is nonlinear. When the rate constant decreases, i.e. as the kinetic stage decelerates, the transition region manifests itself over increasingly long periods of time and gradually widens, while it is almost independent of the shape of the irregularity. As a result, under these conditions, taking into account the roughness effect is mandatory and amounts to normalizing the current density by the roughness factor.

Contribution of the authors

Vdovenkov F. A. – conducting a computational experiment. Kolosov A. N. – conducting a computational experiment, writing a text. Kuzmenko G. A. – conducting a computational experiment. Kozaderov O. A. – scientific guidance, research concept, methodology development, text editing, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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