

Modeling of electrocatalysis at chemically modified electrodes: a combination of second-order and Michaelis-type chemical kinetics

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Abstract The model presented accounts for the diffusion of a reactant and of charge carriers within the modifier layer placed at electrode surface, and redox interaction between reactant and an active center bearing charge carriers. The study extends our previous model by the use of a combination of two kinds of redox interaction—a simple chemical second-order reaction, and Michaelis-type redox reaction. Depending on relative increments from these two kinetic models, either linear, or hyperbolic dependencies of electric current on reactant concentration were obtained. The results obtained have been analyzed in terms of current-concentration interdependencies.

Keywords Modeling · Electro catalysis · Reaction-diffusion · Sensor · Modified electrode

1 Introduction

Electrocatalysis—acceleration of electrochemical processes by catalysts—is an important phenomenon, widely exploited for development of fuel cells, electro-synthesis systems, and sensors or biosensors. Among a variety of electrocatalytic systems, chemically modified electrodes play an important role. These electrodes contain a thin layer of either organic or inorganic substance which is able to act as an electrocatalyst in electrochemical conversion of solution species. Among

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many electrocatalytic systems of this kind known, our recent examples relate to electrocatalytic reduction of hydrogen peroxide at Prussian blue-modified electrode [1,2], electrooxidation of ascorbic acid at the same electrode [3], and electrooxidation of some organic species at electrode, modified with redox mediator poly(neutral red) [4], poly(toluidine blue) [5], polyaniline or its derivatives [6–8].

One of the most fundamental problems related to electrocatalysis at chemically modified electrodes relates to the location of reaction site. During electrocatalytic redox transformation of solution species, a balance of two partial processes establishes: the flow of species from the bulk of solution to the modifier-solution boundary along with the possible diffusion of species within the modifier layer appears to be compensated by charge carrier (electrons or holes) diffusion in the opposite direction, *viz.* from the background electrode through the modifier layer to the reaction zone. At a relatively fast diffusion of charge carriers within the modifier layer, the reaction site appears to be located at a modifier-solution boundary. Adversely, at a relatively slow diffusion of charge carriers, the reaction zone is located within this layer, and shifts within it towards the background electrode with decreasing mobility of charge carriers. Experimentally, both cases were observed with the use of *in situ* Raman spectroelectrochemistry. Electrooxidation of hydroquinone and ascorbic acid at electrode, modified with poly(toluidine blue), was found to occur at a modifier-solution interface (“metal-like electrocatalysis”) [5], whereas same or related processes proceeded within the modifier layer, as it was shown for electrodes, modified with polyaniline [7,8], or poly(neutral red) [4], or Prussian blue [1] (“redox electrocatalysis”).

Earlier, we studied the dependence of the location of reaction zone on various parameters [9]. As a result, the deviation from the linearity for the dependence of electric current on the concentration of solution species was shown. In our next study, we showed this nonlinearity to be dependent on the mobility of charge carriers [10]. At a fast diffusion of charge carriers, the reaction proceed at an outer interface, and the current-concentration dependence appears to be linear, whereas lowering of charge carrier mobility results both in the shift of reaction zone into the bulk of a modifier layer, and the deviation of the said dependence from linearity. On the other hand, a nonlinear, hyperbolic dependence of current on concentration is well known for biosensors–bioelectrocatalytic devices, based on enzyme-containing layer placed at an electrode surface [11]. For these devices, however, the nonlinearity is determined by the hyperbolic nature of Michaelis–Menten type enzyme kinetics, as distinct from simple electrocatalytic systems, where a simple bimolecular reaction of solution species with “active centers” of a modifier occurs [9,10]. The present study aims at the study of current-concentration dependencies for electrocatalytic systems, possessing a mixed Michaelis–Menten type (hyperbolic), and a simple bimolecular kinetics, describing the interaction of solution species with reaction sites of a modifier.

2 The model and approximations

A simple model, closely similar to that described earlier [9,10], was used. A flat surface of electrode is assumed to be covered with a uniform layer of a conducting

polymer of a definite thickness d . For the seek of simplicity, as distinct from [9, 10], the only value for d of 10^{-6} m (or 1 μ m) has been taken into account. The electrode is immersed into a solution containing reactant. No concentration gradient is assumed to be either for reactant or for reaction product outside of a polymer layer in the course of electrocatalytic process.

The diffusion of reactant into a polymer layer is described by the Fick's law:

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2}, \quad (1)$$

where R means the concentration of reactant, t —time, x is a space coordinate, and D is the diffusion coefficient for reactant.

By applying a suitable electrode potential, electrochemical conversion of a reactant into product proceeds. This conversion means either anodic oxidation (i.e., withdrawing of electrons from reactant), or cathodic reduction (i.e., addition of electrons to reactant). As distinct from our previous studies [9, 10], it is supposed here that the charge transfer process follows two mechanisms. One of them relates to a simple redox reaction with active centres (charge carriers) in polymer film according to relation:



where R and P are reactant and reaction product, respectively, and n is a charge carrier, i.e. an electron for cathodic reduction, or a hole for anodic oxidation processes.

The rate of this reaction is described by a simple equation of chemical kinetics:

$$\frac{dP}{dt} = -\frac{dR}{dt} = kRn, \quad (3)$$

where k is a second-order rate constant of chemical reaction, and R and n are mean concentrations of reactant and charge carrier, respectively.

The second mechanism for the conversion of R to P proceeds following Michaelis–Menten type mechanism, which involve the formation of a virtual complex of R with active centres carrying electric charges, and the next following split of this complex leading to reaction product P :



where R and P have same meaning as in (2), and $[R * n]$ presents the transient complex.

For this mechanism, it is supposed that the complex formation (4) proceeds in both (forward and backward) directions, characterized by two rate constants k_{-1} and k_1 for forward and backward reactions, respectively, whereas complex split (5) is a one-directional process characterized by the catalytic first-order rate constant k_{cat} . In accordance with this Michaelis–Menten type mechanism, the rate expression appears to be as follows:

$$\frac{dP}{dt} = \frac{k_{cat} Rn}{K_M + R}, \quad (6)$$

where K_M presents Michaelis constant—a combination of all three rate constants in the processes (4) and (5):

$$K_M = \frac{k_{-1} + k_{cat}}{k_1} \quad (7)$$

A combination of both possible mechanisms is modelled here by the dimensionless coefficient α , varying between 0 and 1. For $\alpha = 1$, the reaction follows a simple chemical reaction (2) without any increment from Michaelis–Menten-like mechanism. In contrary, the reaction follows Michaelis–Menten type mechanism (4, 5) without any increment from a simple chemical reaction for $\alpha = 0$. In calculations, α values ranging from 0 to 1 at increments of 0.1 have been used.

By combining the diffusion equation (1) with simple kinetic equation (3) and Michaelis–Menten kinetic equation (6), the rate equations for R , P and n could be expressed as follows:

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2} - \alpha k Rn - (1 - \alpha) \frac{k_{cat} Rn}{K_M + R}, \quad (8)$$

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + \alpha k Rn + (1 - \alpha) \frac{k_{cat} Rn}{K_M + R}, \quad (9)$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} - \alpha k Rn - (1 - \alpha) \frac{k_{cat} Rn}{K_M + R}, \quad (10)$$

$x \in]0, d[, t > 0.$

Let $x = 0$ represent the electrode/polymer film boundary while $x = d$ is the thickness of a polymer layer. The electrocatalytic processes start when the reactant appears over the surface of a polymer layer. This is used in the initial conditions ($t = 0$)

$$\begin{aligned} R(0, x) &= \begin{cases} R_0, & x = d, \\ 0, & x \in [0, d[, \end{cases} \\ P(0, x) &= 0, \quad n(0, x) = n_0, \quad x \in [0, d]. \end{aligned} \quad (11)$$

Consequently, the boundary conditions are ($t > 0$)

$$\begin{aligned} \frac{\partial R(t, 0)}{\partial x} &= 0, \quad R(t, d) = R_0, \\ \frac{\partial P(t, 0)}{\partial x} &= 0, \quad P(t, d) = 0, \\ n(t, 0) &= n_0, \quad \frac{\partial n(t, d)}{\partial x} = 0. \end{aligned} \quad (12)$$

The density $I(t)$ of the current at time t can be obtained explicitly

$$I(t) = n_e F D_n \frac{\partial n(0, t)}{\partial x}, \quad (13)$$

where $n_e = 1$ and represents the number of electrons involved in a charge transfer, F is Faraday constant, $F \approx 9,65 \times 10^4 \text{ l/mol}$. We assume, that the system (8)–(12) approaches a steady-state as $t \rightarrow \infty$

$$I_\infty = \lim_{t \rightarrow \infty} I(t).$$

I_∞ is assumed to be the steady-state current.

The problem (8)–(12) was solved numerically using the finite difference technique [11].

For simplicity, the diffusion coefficients for R and P have been chosen to be equal, and a typical value of $D = 10^{-9} \text{ m}^2/\text{s}$ has been taken for calculations. Three values for the diffusion coefficient of charge carriers D_n of 10^{-9} , 10^{-10} , and $10^{-11} \text{ m}^2/\text{s}$, have been used. The upper limit of D_n chosen coincides with D for reactant or product species, whereas the lower limit of D_n has been chosen as being up to two orders of magnitude lower. This means that, in a physical sense, the electrode matter (conducting polymer) is considered here as a semiconductor.

Like as in our previous work [10], the only value for $n_0 = 4 \times 10^3 \text{ mol/m}^3$ (4 mol/l) has been taken. The redox reaction rate constant (k) has been varied within the limits of two orders of magnitude between $10^{-2} \text{ m}^3 \text{ mol} \cdot \text{s}$ (or $10^1 \text{ l/mol} \cdot \text{s}$) and $10 \text{ m}^3 \text{ mol} \cdot \text{s}$ (or $10^3 \text{ l/mol} \cdot \text{s}$), whereas the reactant concentration R has been varied within the limits of $1\text{--}10 \text{ mol/m}^3$ ($1\text{--}10 \text{ mM}$) at intervals of 1 mol/m^3 . Additionally, three values for catalytic constant k_{cat} of 1, 10, and 100 s^{-1} , and, for simplicity, the only value for K_M of 5 mol/m^3 (0.005 mol/l) were taken for calculations. The numerical values are summarized in Table 1.

3 Results and discussion

Figure 1 presents typical current-concentration profiles, obtained for a selected value of $k = 10^3 \text{ l/mol} \cdot \text{s}$, and varying k_{cat} . At the lowest value of k_{cat} (0.1 s^{-1}), almost no current response is observed for “pure” Michaelis–Menten type reaction (for $\alpha = 0$). An increase of α , as it could be expected, results in a progressive increase of the slope for the corresponding profiles, which retain their linear character (Fig. 1a). An increase of k_{cat} by one order of magnitude (up to 1 s^{-1}) causes an increase of the slope for current-concentration profile at $\alpha = 0$, whereas the increment from Michaelis-like mechanism diminishes with increasing α and appears to be negligible for α approaching 1 (Fig. 1b). It is seen from Fig. 1b, that the current-concentration dependence bears a hyperbolic character for $\alpha = 0$, and turns gradually into a linear dependence at increasing α up to $\alpha = 1$. A progressive increase of k_{cat} leads to further increase of the slope for profiles, and a phenomenon of “compensation” could be observed at a definite ratio of k_{cat} and k , as shown in Fig. 1c. Here, for $k_{cat} = 10 \text{ s}^{-1}$, close related

Table 1 Numerical values for parameters, taken into consideration

Parameter	Dimension	Numerical values
d (thickness of polymer layer)	(m)	10^{-6}
	(μm)	1
D (diffusion coefficient for reactant and product)	(m^2/s)	10^{-9}
D_n (diffusion coefficient for charge carriers)	(m^2/s)	10^{-11} , 10^{-10} , 10^{-9}
k (second-order reaction rate constant)	($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	10^{-2} , 10^{-1} , 10^0
	($1 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	10, 10^2 , 10^3
R (concentration of reactant in solution)	(mol/m^3)	1 to 10
	(mol/l)	10^{-3} to 10^{-2}
n (concentration of charge carriers)	(mol/m^3)	$4 \cdot 10^3$
	(mol/l)	4
k_{cat} (catalytic rate constant)	(s^{-1})	1, 10, 10^2
K_M (Michaelis constant)	(mol/m^3)	5
	(mol/l)	0.005

slopes are observed for α varying between 0 and 1, i.e. independent on a relative increment of either chemical, or Michaelis-like reaction. The only difference in this case is that the dependence obtained possesses either a linear, or a hyperbolic character for chemical ($\alpha = 1$) or Michaelis-like ($\alpha = 0$) reaction mechanisms, respectively. As it could be expected, further increase of k_{cat} causes an increase of a relative increment from Michaelis-like reaction, exceeding that from a simple chemical interaction. For k_{cat} exceeding 10 s^{-1} , a decrease of current response is observed for α increasing from 0 to 1, as opposed to $k_{\text{cat}} < 10 \text{ s}^{-1}$ (Fig. 1d). Again, a hyperbolic dependence of current on concentration is obtained for $\alpha = 0$, i.e. without any increment from a simple second order chemical reaction.

Significant changes occur by changing k . Figure 2 (a, b) displays the dependencies, obtained for $k = 10^2 \text{ l/mol} \cdot \text{s}$. In Fig. 2a, again, a “compensation”, i.e. close related slopes for varying α , is evident. Similarly like for a combination of $k = 10^3 \text{ l/mol} \cdot \text{s}$ and $k_{\text{cat}} = 10 \text{ s}^{-1}$ as depicted in Fig. 1c, same effect is achieved here for a combination of $k = 10^2 \text{ l/mol} \cdot \text{s}$ and $k_{\text{cat}} = 1 \text{ s}^{-1}$, where both rate constants are lower by an order of magnitude. It is also seen from Fig. 2a that a hyperbolic dependence, characteristic for Michaelis-like kinetics (at $\alpha = 0$) develops gradually into a linear dependence, characteristic for a simple second-order chemical reaction with an increase of α up to 1. For the said combination of $k = 10^2 \text{ l/mol} \cdot \text{s}$ and $k_{\text{cat}} = 1 \text{ s}^{-1}$ (Fig. 2a), the slopes of current-concentration dependencies are approximately 5- or 6-fold lower than for a combination of $k = 10^3 \text{ l/mol} \cdot \text{s}$ and $k_{\text{cat}} = 10 \text{ s}^{-1}$ (Fig. 1c). An interesting observation for this couple of rate constants should be noted. An intersection point, where current response do not depend on α , appears for concentration values between 5 and 6 mM (Fig. 2a), whereas it appears to be located between 8 and 9 mM for a combination of $k = 10^3 \text{ l/mol} \cdot \text{s}$ and $k_{\text{cat}} = 10 \text{ s}^{-1}$ (Fig. 1c), although the ratio of k/k_{cat} appears to be the same in both these cases.

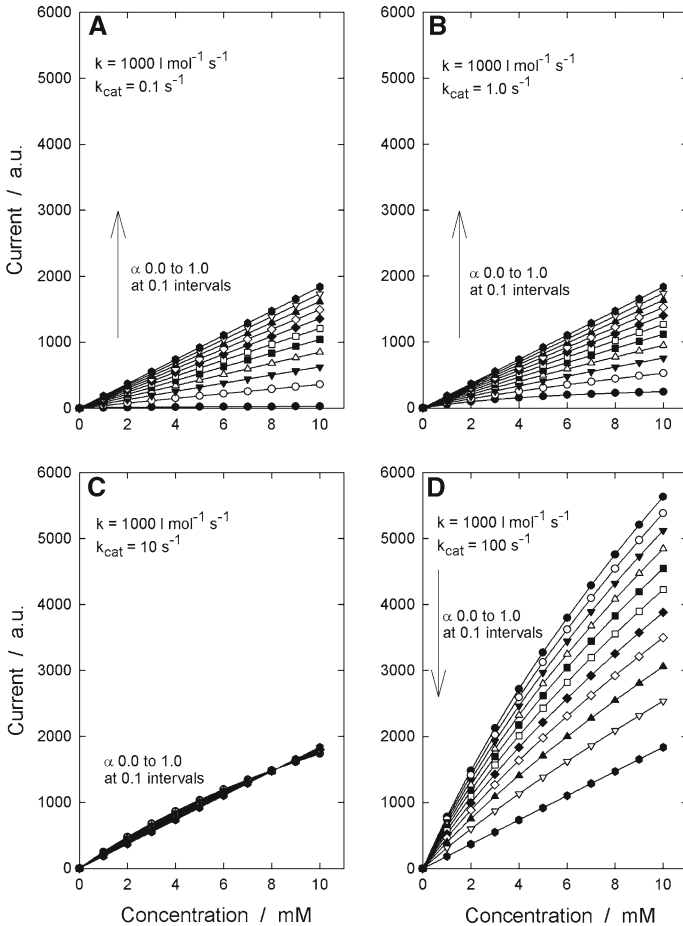


Fig. 1 Dependence of current on concentration, as obtained for different k_{cat} and α (as indicated) at $k = 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $D_n = 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$

An increase in k_{cat} leads to a drastic increase of current response (Fig. 2b). It is well seen from Figs. 1 and 2, that the slope of graphs obtained and thus the sensitivity of response to concentration increases at increasing α for the ratio of $k/k_{cat} > 100 \text{ l/mol}$, or decreases for $k/k_{cat} < 100 \text{ l/mol}$. This decrease appears well expressed for the lowest values of $k/k_{cat} = 1$ or even 0.1 as depicted in Fig. 2b, d, respectively. Also, the evolution of hyperbolic to linear character for these dependencies with increasing α is well seen for all combinations of k and k_{cat} .

It is of interest to analyze the results obtained within the frame of Michaelis–Menten kinetics. In all calculations, K_M value of 5 mM has been used. However, it is well known in the field of biosensors that K_M (or, more exactly, the apparent Michaelis constant $K_{M(app)}$) is subjected to changes depending on various factors, mainly on diffusion conditions within a modifier layer on the electrode surface [11]. Also, for α approaching 1, the only way for conversion of reactant to product is the direct

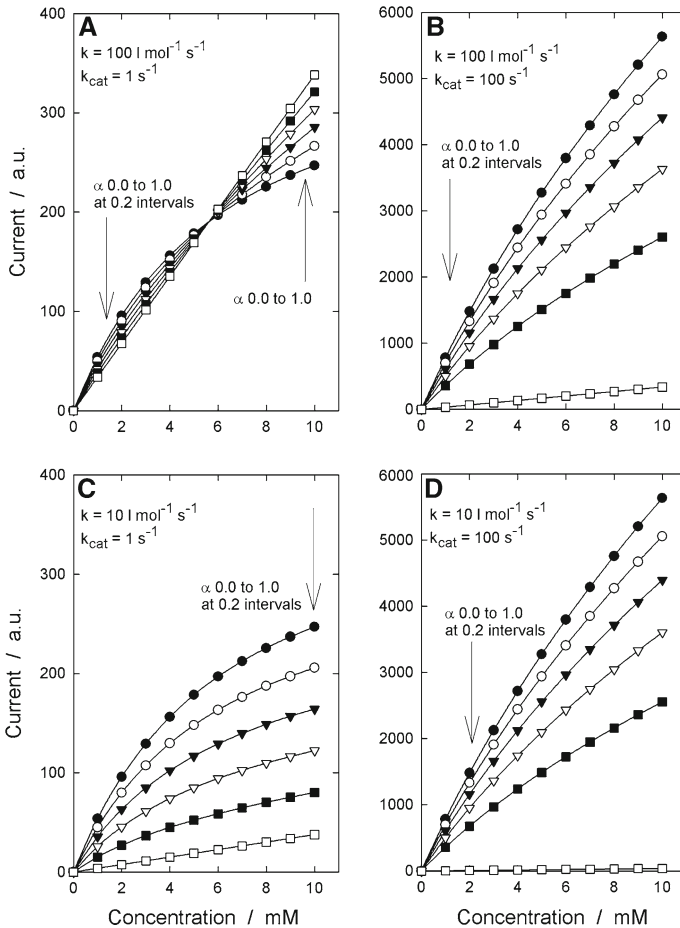


Fig. 2 Dependence of current on concentration, as obtained for different α (as indicated), $k = 10^2 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (a, b) or $10^1 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (c, d), and $k_{\text{cat}} = 1 \text{ s}^{-1}$ (a, c) or 100 s^{-1} (b, d) at $D_n = 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$

chemical interaction according to Eq. (2). In this case, K_M should be indefinitely high, provided that diffusion of reactant within the modifier layer proceeds fast as compared to chemical reaction. However, even for this “pure” chemical interaction, a hyperbolic Michaelis–Menten like dependencies can be observed, caused by the relatively slow diffusion of reactant, as it was shown in our previous study [10].

Figure 3a, b, discloses the dependence of an apparent K_M on kinetic characteristics. For $\alpha = 0$ (i.e., Michaelis–Menten like mechanism), K_M depends greatly on k_{cat} . For the lowest value of k_{cat} of 1 s^{-1} , $K_M = 6.5 \text{ mM}$, and does not differ greatly from that taken into calculations. For greater values of k_{cat} (10 and 100 s^{-1}), K_M increases up to 20.2, and 24.6 mM, correspondingly (Fig. 3a). It could be concluded that an increase of the rate of catalytic transformation of reactant according to Eqs. (3, 4) leads to increase of an apparent K_M . Indeed, an increase of k_{cat} under a constant diffusion coefficient for reactant D means a progressive decrease of a relative diffusion rate as

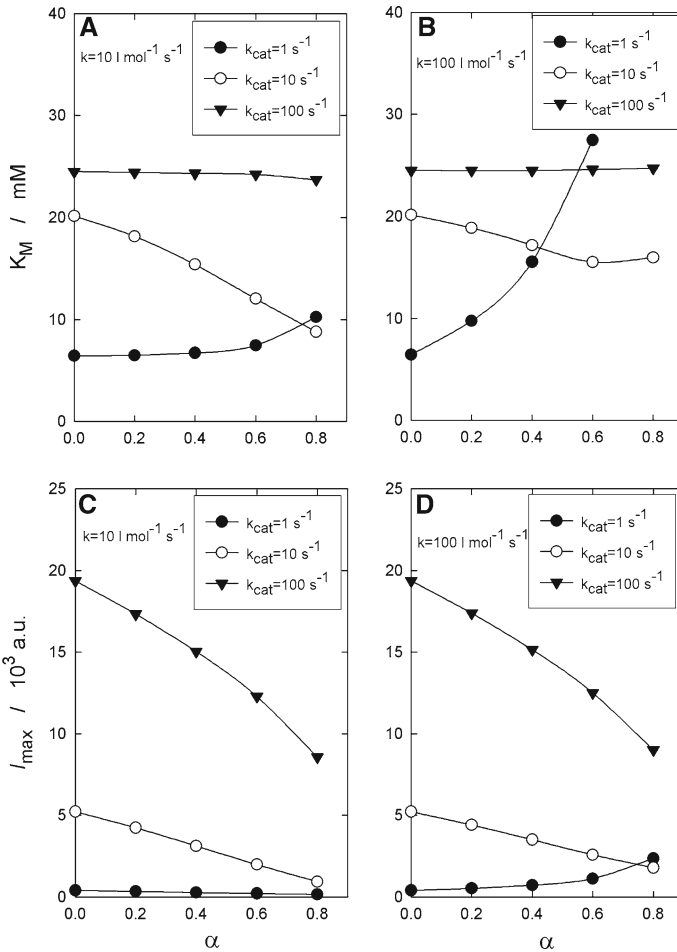


Fig. 3 Dependence of K_M (a, b) and I_{max} (c, d) on α , as obtained for different k_{cat} (as indicated), $k = 10^1 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (a, c) or $10^2 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (b, d) at $D_n = 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$

compared to the rate of chemical transformation of reactant. It is seen from Fig. 3, that an increase of α causes different changes of K_M , greatly influenced by the value of k_{cat} . For $k = 10 \text{ l/mol} \cdot \text{s}$ (Fig. 3a), and the lowest k_{cat} of 1 s^{-1} , a slight increase of K_M from 6.5 to 10.4 mM is observed for $\alpha = 0.8$, whereas a sharp decrease of K_M from 20.2 to 8.9 mM proceeds by changing of α from 0.0 to 0.8 for k_{cat} of 10 s^{-1} , and negligible changes of K_M from 24.6 to 23.7 mM occur by changing α from 0.0 to 0.8 for the biggest k_{cat} taken into calculation of 100 s^{-1} . These tendencies possess complicated character, and could not be predicted without calculations. Noteworthy changes in the dependence of K_M on α occur by increasing k , viz. by increasing of a relative rate of a direct chemical interaction relative to Michaelis-type one. As an example, Fig. 3b depicts the corresponding dependencies for $k = 100 \text{ l/mol} \cdot \text{s}$. Here, the tendency for an increase of K_M for lowest k_{cat} with increasing α appears much

stronger as for lower value of k . Also, the decrease of K_M for the intermediate k_{cat} of 10 s^{-1} appears not as steep as for lower k . For the greatest k_{cat} of 100 s^{-1} , almost no changes of K_M occur with increasing α . In all cases (except for a combination of lowest k_{cat} and highest k), however, K_M values do not approach indefinite high values at α approaching 1, as it could be expected for “pure” chemical interaction according to Eq. (2), and for very fast diffusion of reactant. This means that, even at a relatively high increment from “pure” chemical interaction (and low increment from Michaelis-like kinetics, accordingly), the dependence of current on concentration bears hyperbolic (non-linear) character.

An important characteristic for these hyperbolic dependencies is the maximum current (I_{max}), viz. the current response to an indefinitely high reactant concentration. Some examples of these tendencies are presented in Fig. 3c, d. As it could be expected, for $\alpha = 0$, I_{max} depends greatly on k_{cat} . For k_{cat} values of 1, 10, and 100 s^{-1} , I_{max} values of roughly 0.5, 5.3, and 19.4 a.u. were obtained for $k = 10 \text{ l/mol} \cdot \text{s}$. In this case, an increase of α from 0 up to 0.8 causes the decrease of the corresponding values of I_{max} to a different degree, up to 60, 20, and 45 %, respectively. In case of increasing increment from “pure” chemical kinetics relative to Michaelis-like kinetic increment, the decrease of I_{max} with growing α proceeds to a lesser degree (cf. d and c in Fig. 3). For the lowest value of k_{cat} , an increase of I_{max} with growing α is observed. Clearly, all these tendencies hardly could be predicted without the present modeling. In a physical sense, the presence of I_{max} , and its dependencies on various parameters chosen show the limits for the efficiency of electrocatalysis under the specified conditions.

4 Conclusions

The results obtained show that two increments from chemical kinetics, one related to a simple second-order reaction, and another to hyperbolic Michaelis-like reaction scheme, could be simply combined into one electrocatalytic process. Depending on relative increments from these two kinetic models, either linear, or hyperbolic dependencies of electric current on reactant concentration can be obtained. It has been shown that the value for an apparent Michaelis constant K_M exceeds in all cases the corresponding value taken into calculation. Even in absence of an increment from a simple second-order reaction, a higher value of K_M is obtained because of a relative slow diffusion of charge carriers taken into account. Because of restricted diffusion of charge carriers, an increase of catalytic constant in Michaelis-like kinetics results in a significant increase of K_M . The dependencies of K_M and of maximum current obtained at indefinitely high reactant concentration, on a relative increment from Michaelis-like, as well as second-order chemical kinetics are mainly controlled by the ratio of the corresponding rate constants. The results obtained could be applied for electrocatalytic processes, where to types of interaction of reactant with reaction centers is possible.

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