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Modeling of electrocatalysis at conducting polymer modified electrodes: nonlinear current-concentration profiles

Mantas Puida · Albertas Malinauskas · Feliksas Ivanauskas

Abstract A model of electrocatalytic processes taking place at electrodes modified with a layer of a conducting polymer presented earlier has been expanded to a wider variety of parameters related to electric conductivity of a modifier layer. Relatively low values of charge carrier diffusion coefficients within the modifier film have been used in calculations, thus modeling a semiconducting behaviour of conducting polymer film, typical for a wide range of these materials. As a result, nonlinear hyperbolic dependencies of current on concentration have been obtained and discussed for definite combinations of a linear term of chemical kinetics related to a simple second-order chemical redox reaction, and two diffusion processes, related to reactant and charge carriers. Concerning biosensor application of electrocatalysis, the performed analysis showed that nonlinear current-concentration profiles can be observed even in the absence of a hyperbolic Michaelis-Menten type kinetics.

M. Puida (✉) · F. Ivanauskas
Faculty of Mathematics and Informatics, Vilnius University, Naugarduko 24,
03225 Vilnius, Lithuania
e-mail: mantasp@gmail.com

A. Malinauskas
Institute of Chemistry, Center of Physical and Technology Sciences, Goštauto 9,
01108 Vilnius, Lithuania

1 Introduction

Electrocatalysis at electrodes, covered with conducting polymers and related materials, presents a remarkable phenomenon that finds diverse applications, especially in sensors and biosensors [1,2]. Earlier we presented a model of electrocatalytic processes taking place at conducting polymer modified electrodes [3]. The model presented accounts for three processes, *viz.* (i) diffusion of reactant from solution into a layer of conducting polymer, (ii) a chemical reaction (electron exchange) between reactant and catalytically active centers of a polymer layer, and (iii) diffusion of charge carriers (electrons or holes) from the background electrode through a polymer layer to reaction zone. It is essential that, within the frame of this model, the chemical redox interaction of reactant with active centers within the polymer film has been supposed to proceed as a simple second-order chemical reaction, *i.e.* as a linear term.

Next to this model, a number of similar sensor- or biosensor-related models have been developed and summarized in a monograph [4]. Amperometric biosensors contain biological recognition elements, usually an enzyme. Therefore, theoretical modeling of biosensors implies the use of a nonlinear term related to the Michaelis-Menten kinetic scheme for enzyme-catalyzed reactions. As a result, hyperbolic current-concentration relationships are obtained, from which the Michaelis constants (K_M) and maximum current can be obtained [5]. As usual, the Michaelis constant characterize an enzyme-catalyzed reaction, however, under certain conditions, especially under diffusional limitations for substrate, the "apparent" Michaelis constant can differ from that characteristic for the same catalytic process taking place in a solution. This well known phenomenon has been subjected to theoretical modeling, and it has been shown that, under certain conditions, the apparent Michaelis constant depend mainly on the topology of biosensor, and practically do not relate to enzyme kinetics [6]. Also, a substantial increase of the Michaelis constant has been shown at restricted diffusion of substrate through an outer membrane covering an enzyme layer [7]. This result appears to be of a great practical interest, since it enables to expand the linear dependence of biosensor response on analyte concentration towards the higher concentrations under the deep diffusion mode of biosensor operation, whereas the response time does not increase drastically [7].

On the other hand, experimentally observed nonlinear (hyperbolic) dependence of current on analyte concentration of any sensor is also often interpreted in terms of the Michaelis-Menten kinetics. Even in the absence of enzyme, the operation mode of the sensor is thus supposed to proceed *via* the formation of any intermediate complex between analyte and "active centers" at electrode [8–10]. The issue about the character of relationship between the current response and analyte concentration appears thus as a diagnostic criterion for the mechanism of interaction of analyte with active centers at electrode. The linear relationship could be provisionally related to a simple second-order redox interaction, whereas hyperbolic relationship observed probably means a more complex interaction with the formation of an intermediate complex. The present study aims at proving this intuitive assumption. More precisely, the problem is whether the direct second-order redox reaction between an analyte and active centers should always result in a linear relationship between the current response and

analyte concentration, or, alternatively, hyperbolic relationships can be obtained at a definite set of process parameters.

2 The model and approximations

A simple model, closely similar to that described earlier [3], 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. Three values for d have been taken into consideration, viz. 10^{-6}, 10^{-5}, and 10^{-4}m (i.e., 1, 10, and 100 μm). 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:

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2}, \tag{1}$$

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). The electrochemical charge transfer process is described by a single equation:

$$R + n = P, \tag{2}$$
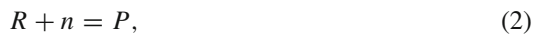
where R and P are reactant and reaction product, respectively, and n is a charge carrier, i.e. an electron for cathodic reduction, or a hole for anodic oxidation processes.

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

$$\frac{dP}{dt} = -\frac{dR}{dt} = kRn, \tag{3}$$

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

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

$$\frac{\partial R}{\partial t} = D \frac{\partial^2 R}{\partial x^2} - kRn, \tag{4}$$

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + kRn, \tag{5}$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} - kRn, \tag{6}$$

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

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 ($t = 0$)

$$R(0, x) = \begin{cases} R_0, & x = d, \\ 0, & x \in [0, d[, \end{cases} \tag{7}$$
$$P(0, x) = 0, \quad n(0, x) = n_0, \quad x \in [0, d].$$

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

$$\frac{\partial R(t, 0)}{\partial x} = 0, \quad R(t, d) = R_0,$$
$$\frac{\partial P(t, 0)}{\partial x} = 0, \quad P(t, d) = 0, \tag{8}$$
$$n(t, 0) = n_0, \quad \frac{\partial n(t, d)}{\partial x} = 0.$$

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

$$I(t) = n_e F D_n \frac{\partial n(0, t)}{\partial x}, \tag{9}$$

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

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

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

The problem (4)–(8) 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 $D = 10^{-9}$ m^2/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} m^2/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, compared to our previous study [3]. In a physical sense, the electrode matter (conducting polymer) is considered here as a semiconductor.

As in the previous work [3], the only value for $n_0 = 4 \times 10^3$ mol/m^3 (4 mol/l) has been taken. The redox reaction rate constant (k) has been varied within the limits of three orders of magnitude between 10^{-2} m^3/mol·s (or $10^1 l$/mol·s) and 10^1 m^3/mol·s (or $10^4 l$/mol · s), whereas the reactant concentration R has been varied within the limits of 1 to 10 mol/m^3 (1 to 10 mM) at intervals of 1 mol/m^3

3 Results and discussion

The results of digital simulation, obtained for three thicknesses of a catalytic layer at electrode surface, are presented in Figs. 1–3. From these, some important conclusions could be drawn.
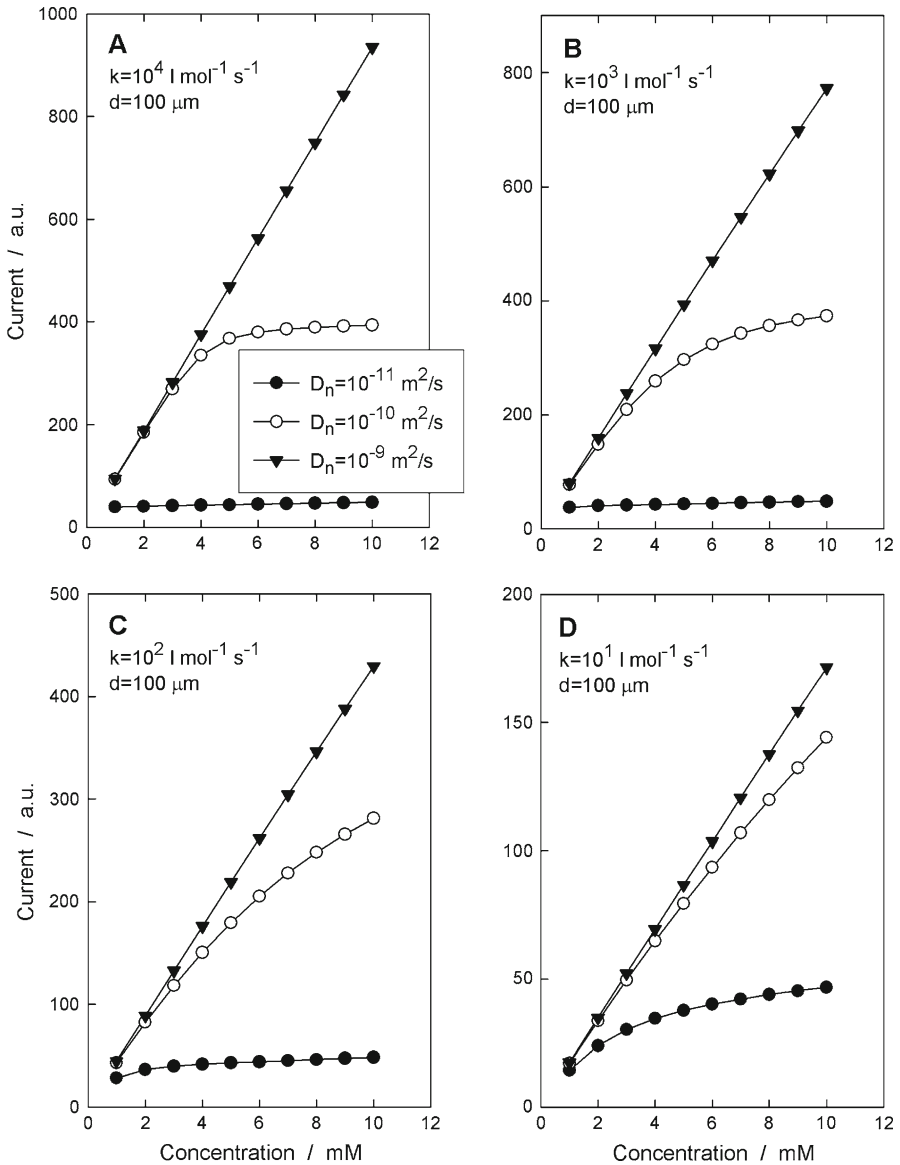

Fig. 1 Dependence of current on concentration, as obtained for different k and D_n (as indicated) at $d = 100\,\mu m$
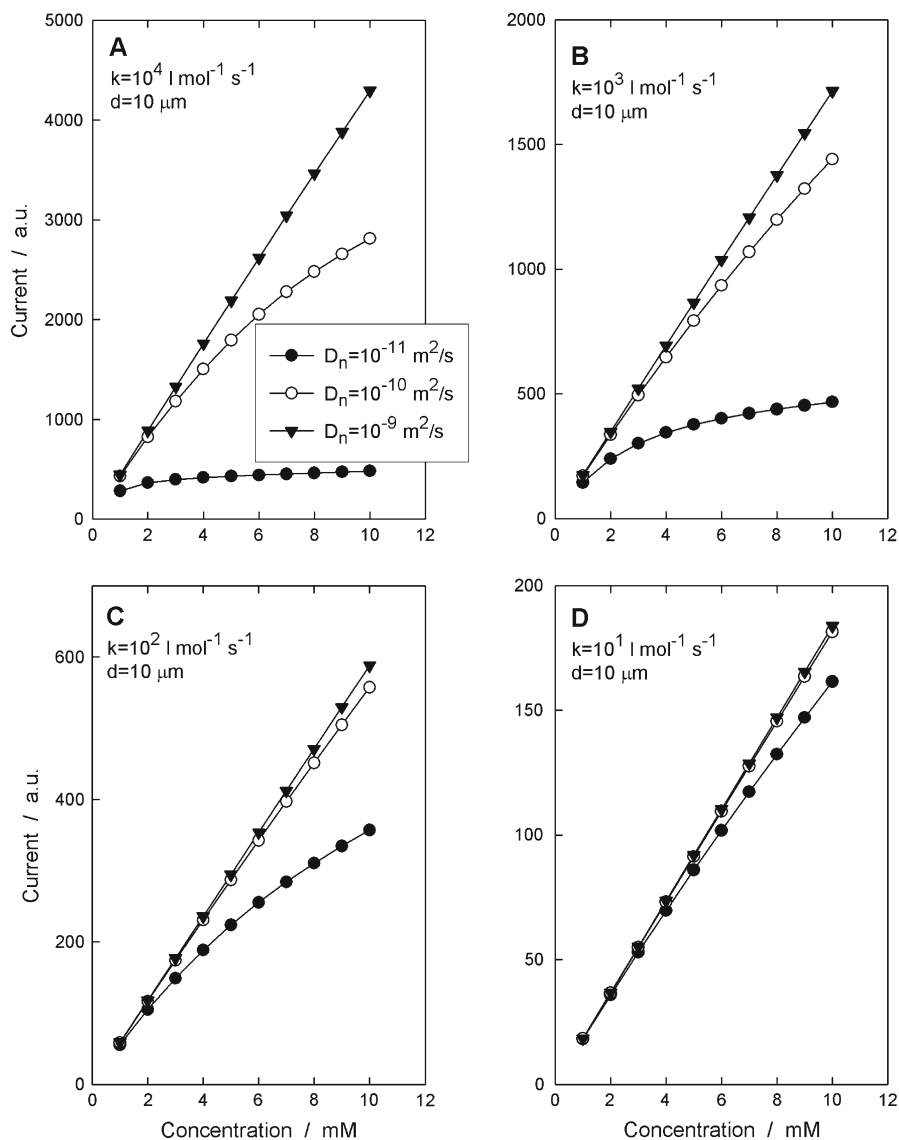
Fig. 2 Dependence of current on concentration, as obtained for different k and D_n (as indicated) at $d = 10\,\mu m$

For the thickest modifier layer of $100\,\mu m$, a nearly linear relationship of current on concentration is observed only at the fastest diffusion of charge carriers taken into account, for D_n of $10^{-9}\,m^2/s$ (Fig. 1). At lower values of D_n, substantial deviations from linearity are observed. Noteworthy, a linear relationship is obtained for $D_n = D$, *viz.* when the diffusion of charge carriers proceeds as fast as the diffusion of a reactant within the electrocatalyst layer, whereas deviations from linearity correspond to slower charge carriers diffusion as compared to that of a reactant. It is also seen from
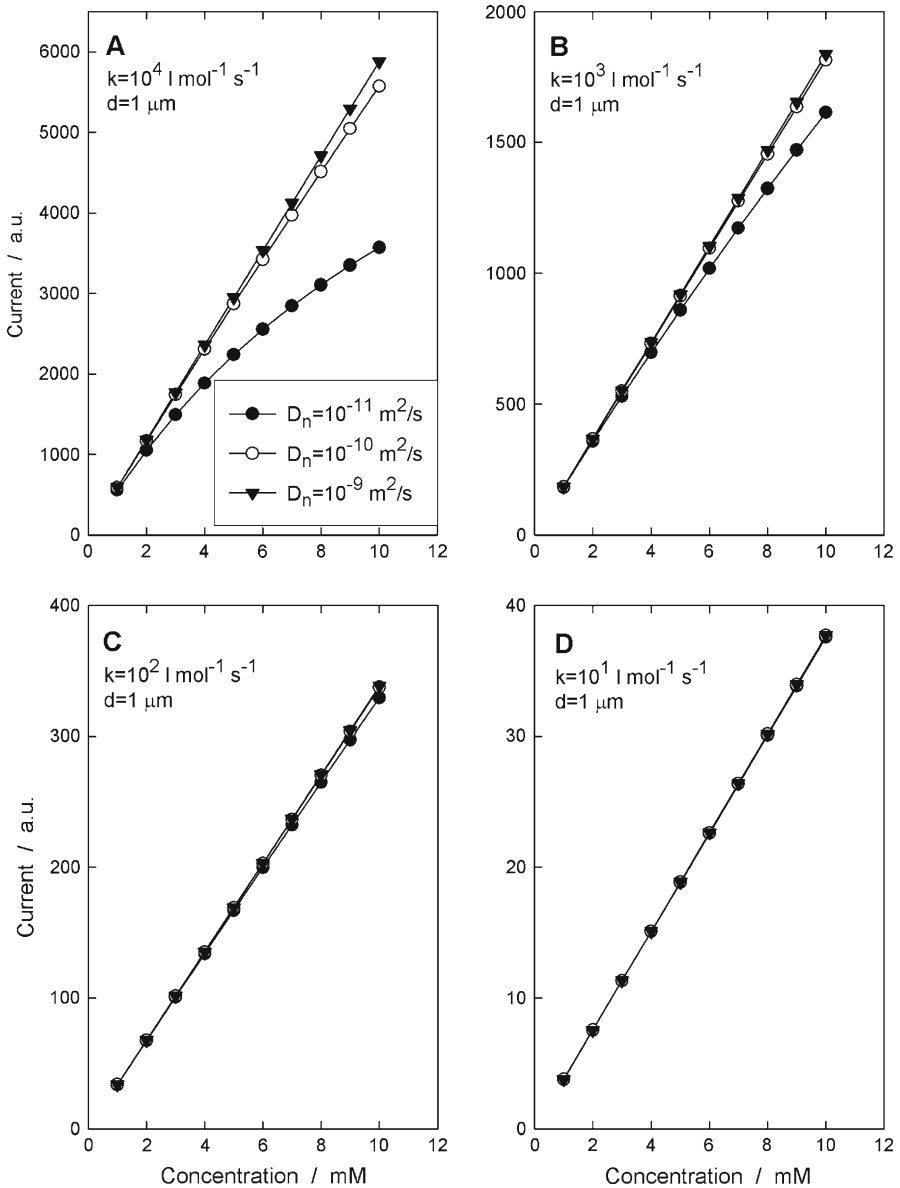
Fig. 3 Dependence of current on concentration, as obtained for different k and D_n (as indicated) at $d = 1\,\mu$m

Fig. 1a–d that the slope of a linear dependence (for high D_n) diminishes with decreasing chemical reaction rate constant k. However, no linear correlation between the slope and reaction rate constant is observed: a decrease of k by an order of magnitude from 10^4 to $10^3 l/$mol $\cdot$ s causes a 1.07-fold decrease of slope, whereas further decrease of k to 10^2 and $10^1 l/$mol $\cdot$ s results in 2.22- and 2.28-fold decrease of the slope,

correspondingly. For $D_n < 10^{-9}\,\mathrm{m^2/s}$, the dependence of current on concentration bears a hyperbolic character, that is subjected to changes with variations of k. At the same time, a drastic decrease of current is observed at the lowest values of D_n taken into account ($10^{-11}\,\mathrm{m^2/s}$).

For moderate thick layers of a modifier ($10\,\mu\mathrm{m}$), again, a linear dependence of current on concentration is observed at the fastest diffusion of charge carriers (Fig. 2). However, the slope of the current-concentration dependence appears to be stronger affected by the rate constant of a chemical reaction, as compared to thicker modifier layers. The consecutive decrease of k from 10^4 to $10^1\,l/\mathrm{mol}\cdot\mathrm{s}$ at the steps of one order of magnitude results in 2.5-, 2.9- and 3.2-fold decrease of the slope, as it could be deduced from the data presented in Fig. 2a–d). This means that the influence of the rate constant of chemical interaction appears to be stronger for thinner layers of electrocatalyst. As in the previous case, again, deviations from linearity in current-concentration relationships are observed at slower diffusion of charge carriers. These deviations, however, appear to be less expressed as compared to thicker layers. Within the concentration range studied, only negligible deviations from linearity, not exceeding a few percent, are observed for k of 10^1 or even $10^2\,l/\mathrm{mol}\cdot\mathrm{s}$ at a relatively slow diffusion of charge carriers ($D_n = 10^{-10}\,\mathrm{m^2/s}$) (Fig. 2c, d). Even for the lowest value of $D_n = 10^{-11}\,\mathrm{m^2/s}$, the above-mentioned relationship tends to linearity in case of the slowest chemical interaction.

Similar tendencies should be noted for the thinnest films of electrocatalyst taken into account ($10\,\mu\mathrm{m}$) (Fig. 3). Here, the decrease of k from 10^4 to $10^1\,l/\mathrm{mol}\cdot\mathrm{s}$ at the steps of one order of magnitude results in 3.2-, 5.4- and 8.9-fold decrease of the slope in current-concentration relationships. Also, the deviations from linearity appear in this case less expressed as for thicker layers, especially for slower chemical redox interaction. Negligible or even no deviations from linearity have been obtained at k of 10^1 and $10^2\,l/\mathrm{mol}\cdot\mathrm{s}$ for all values of D_n varying from 10^{-9} to $10^{-11}\,\mathrm{m^2/s}$. In the latter case, nearly coinciding dependencies of current on concentration are observed, indicating no dependence of current on concentration with varying k and D_n (Fig. 3c, d). Generally, the following generalizations, that seem to be of practical interest, could be made:

1. Linear relationships of current and concentration are obtained for the fast diffusion of charge carriers within the modifier film, whereas slow diffusion causes deviations from linearity.
2. The deviation from linearity appears to be stronger for thicker films of a modifier.
3. The decrease of a layer thickness results in an increase of current, provided the rate constant of a chemical interaction is sufficiently high.

For the cases where a linear dependence of current on the concentration is observed, a normalized current (respectively to concentration) presents a measure of the system's sensitivity to the concentration of chemical species in the solution, which is important for the potential use of electrocatalytic system as amperometric sensor. Therefore, the dependencies of calculated normalized current on selected variables should be analyzed. Fig. 4a presents the dependence of normalized current on the thickness of a modifier layer. For thin modifier films, the normalized current greatly depends on the chemical reaction rate constant, whereas the thickening of a modifier layer leads
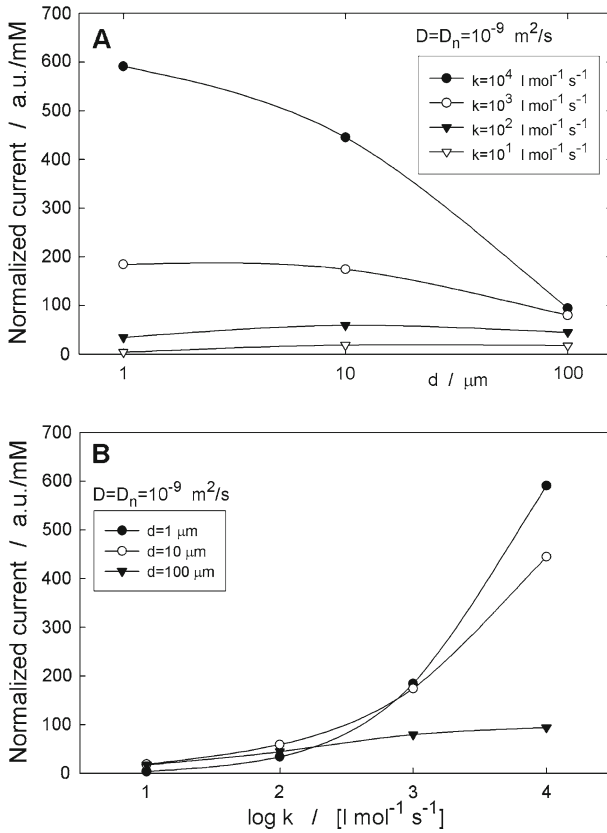
Fig. 4 Dependence of normalized current on d and k, as obtained from linear parts of current-concentration profiles at a fast diffusion of charge carriers ($D_n = 10^{-9} \, \text{m}^2/\text{s}$)

to diminished dependence of current on k. For example, the ratio of current, obtained for $k = 10^4 \, l/\text{mol} \cdot \text{s}$, to current for $k = 10^1 \, l/\text{mol} \cdot \text{s}$, diminishes from 157 to 5.4 by the thickening of a modifier layer from 1 to $100 \, \mu\text{m}$. It is also seen from Fig. 4 that the current diminishes with increasing layer thickness in the case of a fast chemical interaction, whereas slow chemical kinetics results in a complex dependence possessing a maximum. For example, a 4.9-fold growth of normalized current is observed by thickening the layer from 1 to $10 \, \mu\text{m}$, whereas further thickening to $100 \, \mu\text{m}$ results in a slight decrease of current by *ca.* 6%. Fig. 4b shows the dependence of normalized current on the rate constant of chemical interaction. From this, a great influence of k on the current for thin modifier layers, and a much lower influence for thick layers should be noted.

Perhaps the most important issue of the present study relates to an analysis of the relationships obtained within the frame of the Michaelis-Menten enzyme kinetics scheme. According to this scheme, the rate of enzyme catalyzed reaction (v) could be expressed as
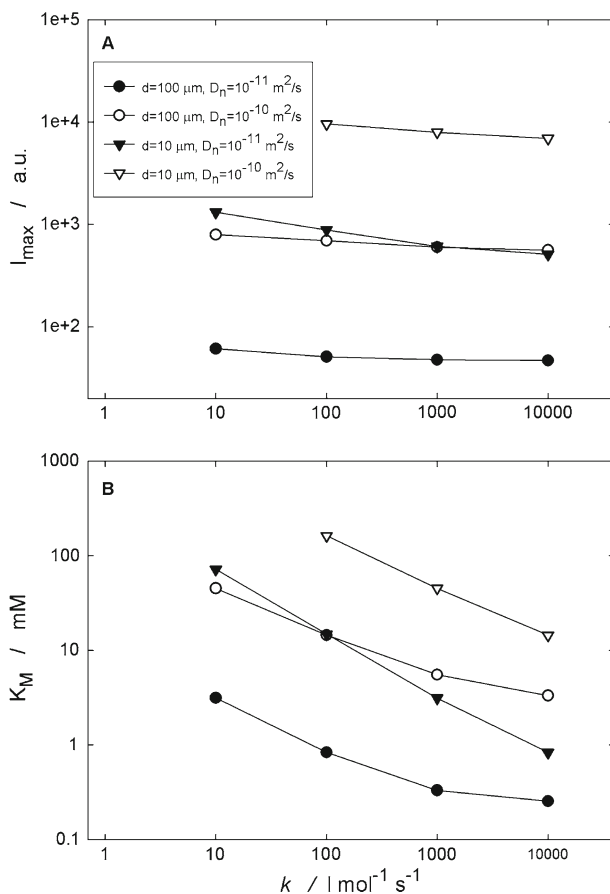
Fig. 5 Dependence of I_{max} and K_M on k, as obtained for different values of d and D_n (as indicated).

$$v = \frac{v_{max}[S]}{K_M + [S]},$$

where $[S]$ represents substrate concentration, v_{max} – maximum rate, attained at indefinitely high $[S]$, and K_M – the Michaelis constant (that means substrate concentration, for which a half of a maximum rate is attained).

Taking into account well known assumptions [4], this relationship could be applied for bioelectrocatalytic systems like amperometric biosensors, whereas reaction rate could be substituted by electric current:

$$I = \frac{I_{max}[S]}{K_M + [S]},$$

where I and I_{max} represent current and its maximum value, respectively.

It is seen from Figs. 1–3 that some current-concentration dependencies bear hyperbolic character, similar to that could be predicted by the given Michaelis-Menten

equation. The hyperbolic character is well expressed, particularly, for thicker modifier layers, and slower diffusion of charge carriers. Therefore, the results obtained have been transformed according to the Michaelis-Menten equation, and presented in Fig. 5. It is seen from Fig. 5a that I_{max} values calculated depend mainly on the layer thickness and charge carrier diffusion rate within the layer, whereas the dependence of I_{max} on chemical reaction rate appears weakly expressed. The physical meaning for this is that the chemical interaction rate has little influence in the case if the process appears to be limited by the diffusion of charge carriers. It is also seen that, at a given thickness of modifier layer, I_{max} increases roughly by an order of magnitude by analogous increase in charge carrier diffusion coefficient. Also, I_{max} increases for more than one order of magnitude by the 10-fold lowering of layer thickness.

As it is shown in Fig. 5b, the calculated values of K_M vary greatly on varying of k, d, and D_n. In all cases, K_M tends to diminish by increasing k. An increase of k for 3 orders of magnitude, *viz.* from 10^1 to $10^4 \, l/\text{mol} \cdot \text{s}$, results in a decrease of K_M by one order (for $D_n = 10^{-11} \, \text{m}^2/\text{s}$) or even by two orders of magnitude (for $D_n = 10^{-10} \, \text{m}^2/\text{s}$). Thickening of an electrocatalyst layer by an order of magnitude also leads to a decrease of K_M by an order or even more. In general, a variation of K_M within a very broad range of 2 or 3 orders of magnitude has been obtained by varying of system parameters within the values indicated.

4 Conclusions

The results obtained demonstrate that hyperbolic dependencies of current on the concentration of chemical species in a solution can be observed even in the absence of a nonlinear kinetic term related to chemical interaction like that characteristic of enzyme catalyzed reactions. Opposite to the Michaelis-Menten type kinetics, the hyperbolic relationships have been obtained here as a consequence of a combination of a linear kinetic term related to a simple second-order chemical redox reaction, and two diffusion processes, related to a reactant and charge carriers within the layer of electrocatalyst. As far as sensors and biosensors are concerned, the results achieved show that deviations of current-concentration relationships from linearity, or even more a hyperbolic I-c dependence, often observed experimentally, does not always indicate a nonlinear chemical kinetics like that of the Michaelis-Menten type to proceed. Instead, the results presented here show that the nonlinearity can be caused by a combination of system variables like the thickness of electrocatalyst layer and diffusion coefficients for reactant and charge carriers, even in the case of a linear dependence of chemical reaction rate on the concentration.

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