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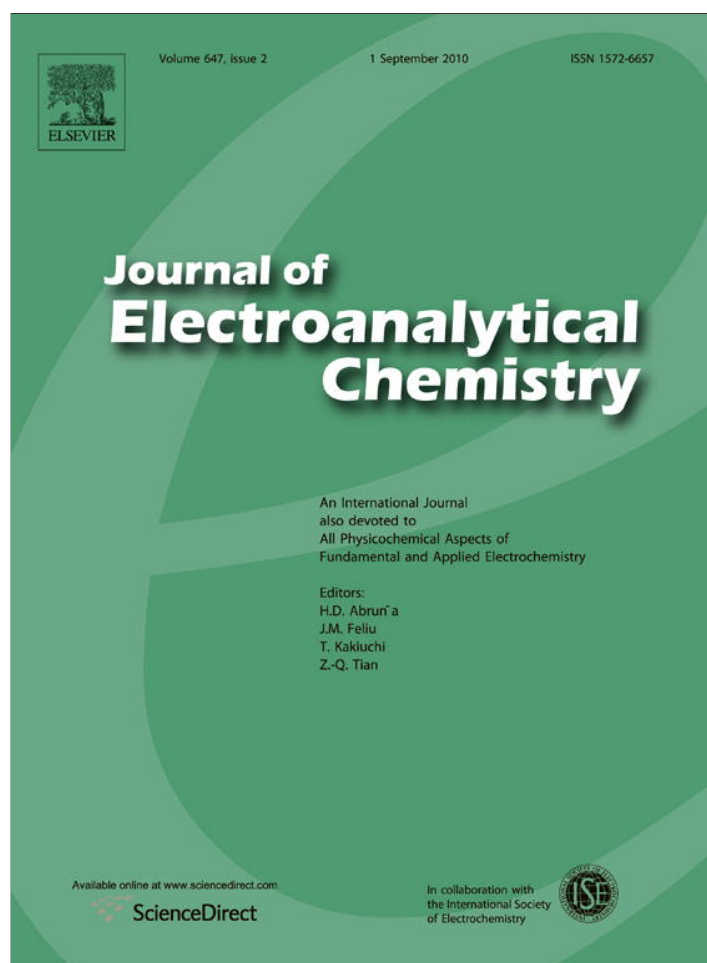


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Analytical solution of system of coupled non-linear reaction diffusion equations. Part I: Mediated electron transfer at conducting polymer ultramicroelectrodes

A. Meena, L. Rajendran *

Department of Mathematics, The Madura College (Autonomous), Madurai 625 011, Tamilnadu, India

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ABSTRACT

An analysis of reaction and diffusion within an electroactive polymer film deposited on an inlaid microdisc electrode is presented. The theoretical analysis of the steady-state amperometric response for a conducting polymer-modified ultramicroelectrodes is re-studied. The coupled processes of chemical reaction, substrate and mediator diffusion are examined. Simple analytical expressions for substrate and mediator concentrations for all values of reaction/diffusion parameters are presented. The variation of current in terms of m (which defines the ratio of the radius of the inlaid microdisc to the thickness of the polymer layer) is also discussed. The model is based on non-stationary system of coupled reaction/diffusion equations containing a non-linear term related to Michaelis–Menten kinetics of the enzymatic reactions. He's Homotopy perturbation method is used to give approximate analytical solutions of coupled non-linear reaction diffusion equations. A good agreement with available limiting case results is noticed.

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1. Introduction

Microelectrodes are powerful tools for understanding the mechanism and kinetics of fast reactions [1–3]. The electrochemical literature of recent years indicates an increasing interest in the development of ultramicroelectrodes for electrochemical measurements in view of their advantages such as lower interfacial capacitance, smaller time constant, reduced ohmic drop and enhanced current density. It may also be of advantage in special situation such as *in vivo* analysis, where only small perturbation to the system under study are sought, or in surface electrochemical studies where an extremely small area may allow for the study of the behavior of single catalytic centre or the formation and growth of single nuclei.

It is reasonable to state that much of the research effort in electrochemistry over the last 20 years has been focused on two major areas. The first topic of research area concerns the examination and development of chemically modified electrode materials for targeted applications in technological areas such as chemical sensing, electrocatalysis and energy storage/conversion [4–7]. The second area concerns the development of structures of very small size. Ultramicroelectrodes exhibit several advantageous properties compared with conventional electrodes. Ultramicroelectrodes are of small size. The latter property enables ultramicroelectrodes to be used as probes to monitor chemical events inside single biolog-

ical cells [8] or to monitor chemical events with very high spatial resolution, as evidenced by the increasing utilization of scanning tunneling microscopy and atomic force microscopy methodology in electrochemical investigations [9–11]. It is also established that the ratio of the faradic to the charging current is improved as the electrode size decreased.

Microelectrodes of many shapes have been described [12]. Microelectrodes of simple shapes are experimentally preferable because they are more easily fabricated and generally conformed to simpler voltammetric relationships. Those shapes with restricted size in all superficial dimensions are of special interest because many of these reach true steady-states under diffusion control in a semi infinite medium [13]. Nevertheless, there is interest in microelectrodes of more complicated shapes, only because the shapes of small experimental electrodes may not always be quite as simple as their fabricators intended. Moreover, and ironically, complex shapes may sometimes be more easily modeled than simpler ones [14]. However, many applications of microelectrodes of different shapes are impeded by lack of adequate theoretical description of their behavior.

The theoretical analysis of mediated electron transfer at electroactive polymer films, which have been deposited, on macro-sized electrode surfaces has been presented by Alberty and Hillman [15] and by Andrieux and co-workers' [16]. Recently Lyons and co-workers' have extended the analysis of mediated electroanalysis by considering substrate diffusion, Michaelis–Menten rate equation, and electromigration, sensing catalysis and charge percolation and chemical reaction [17–23]. Dong and Che [24] concentrated on

* Corresponding author. Tel.: +91 9442228951; fax: +91 0452 2675238.

E-mail address: raj_sms@rediffmail.com (L. Rajendran).

microelectrodes coated with redox polymer films and developed an analysis which was strictly analogous to that developed by Andrieux et al. [25] for macro-size chemically modified electrodes. Dong and Che [24] obtained the current equation of the electrocatalytic reaction at a microdisc electrode modified with redox species. The linear relationship between the plateau limiting current and the radius of the microdisc electrode is verified experimentally by Dong and Che [24]. Rebouillat et al. [26] have derived the expressions of concentration and current for mediated electron transfer for conducting the polymer ultramicroelectrode for six limiting cases only. Senthamarai and Rajendran derived the approximate analytical expressions for the substrate, mediator concentrations and current for the non-linear Michaelis–Menten kinetic scheme in a system of coupled non-linear reaction–diffusion processes at conducting polymer-modified ultramicroelectrodes [27] exhibits spillover using the variational iteration method.

However, to the best of author's knowledge, no general analytical results of substrate and mediator concentrations for the mediated electron transfer at conducting polymer ultramicroelectrodes for all values of reaction/diffusion parameters γ_s and γ_E have been published. The purpose of this communication is to derive approximate analytical expressions for the steady-state concentration and current for a polymer-modified ultramicroelectrode for all values of m , γ_s and γ_E using Homotopy perturbation method. These parameters are explained below Eq. (1b).

2. Formulation of the boundary value problem and analysis

In general, it was assumed the conducting polymer film adopts a hemispherical geometry when electrodeposited on an ultramicrodisc surface. Fig. 1 represents the schematic representation of the hemispherical geometry adopted by an electroactive polymer film which has been deposited on an inlaid ultramicrodisc electrode [24,26]. Here the polymer film is not only deposited on the surface but also spills over into the insulating sheath. Transport within the hemisphere is based on spherical diffusion as represented by Eqs. (1a) and (1b), and ξ is the dimensionless radial distance originating from the origin of the polymer hemisphere. Dong and Che [24] also assumed that the polymer film is thin. This model will take into account the fact that the polymer film may exhibit spillover. The reaction mechanism model is shown in Fig. 2. This is the general model for this processes taking place. In the presented analysis we have assumed that redox conduction through the layer is not assumed to be rapid. This may be a sensible approximation for

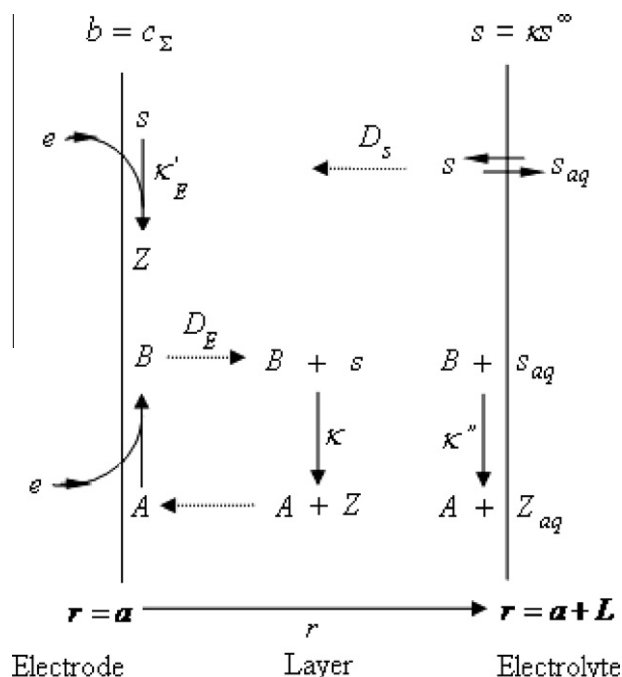


Fig. 2. Model and notation for a modified electrode.

electronically conducting polymer materials, but it may not be a good approximation for redox polymer materials such as poly (vinylferrocene). For the latter class of redox polymer materials the electron hopping diffusion coefficient D_E may be low and the redox conductivity of the layer may be rate limiting [28]. The assumption and physical description of the problem have been fully described in Rebouillat et al. [26] and so we only present a brief summary here for completeness. The normalized forms of the coupled reaction/diffusion equations for steady-state have the following forms:

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left\{ \xi^2 \frac{du}{d\xi} \right\} - \frac{\gamma_s uv}{1 + \alpha u} = 0 \quad (1a)$$

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left\{ \xi^2 \frac{dv}{d\xi} \right\} - \frac{\gamma_E uv}{1 + \alpha u} = 0 \quad (1b)$$

where u and v denote the normalized concentrations of oxidized substrate and mediator species within the film and we define:

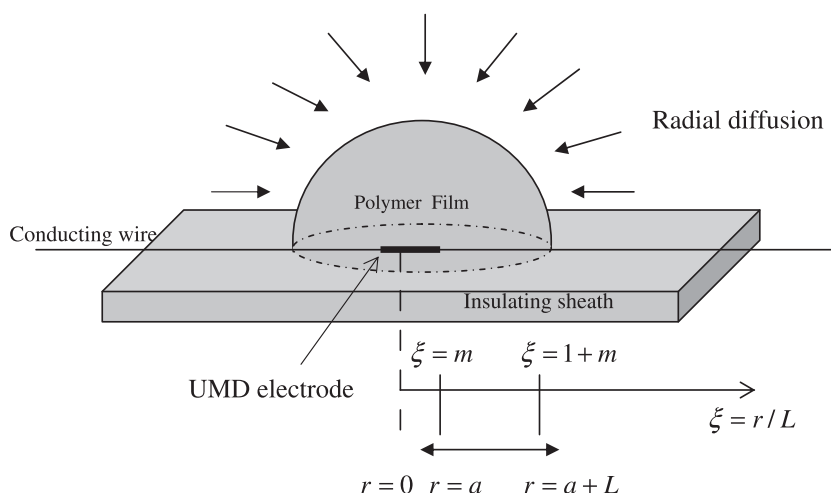


Fig. 1. Schematic representations of the geometry adopted by the polymer coated microelectrode.

$$u = \frac{s}{K_S^\infty}; \quad v = \frac{b}{C_S}; \quad \xi = \frac{r}{L}; \quad \gamma_E = \frac{kK_S^\infty a^2}{D_E K_M} = \frac{f_R}{f_E} = \frac{\lambda}{\rho \sigma^2};$$

$$\gamma_s = \frac{kC_S a^2}{D_S K_M} = \frac{f_R}{f_s} = \frac{\lambda}{\sigma^2} \quad (2)$$

where γ_s and γ_E are reaction/diffusion parameters, D_E and D_s denote the diffusion coefficient respectively. The saturation parameter α is given by $\alpha = K_S^\infty/K_M$ where K_M denotes the Michaelis constant. We have also used characteristic parameters σ , ρ and λ introduced many years ago by Andrieux et al. [25]. Eqs. (1a) and (1b) represent the system of coupled non-linear reaction/diffusion equations. These equations are not readily solved using standard analytical methods, because they have non-linear chemical reaction terms. Hence approximate solutions have to be obtained. The current is a function of only these three independent dimensionless parameters. The parameter σ can be taken as

$$\sigma = \frac{\kappa D_s \delta}{D_s' L} = \frac{f_s}{f_D} \quad (2a)$$

and compares the substrate diffusion in the film vs. substrate diffusion in the solution. The parameter ρ is given by

$$\rho = \frac{D_E C_S}{\kappa D_s S^\infty} = \frac{f_E}{f_s} \quad (2b)$$

and compares the electron diffusion vs. substrate diffusion in the film. Here the parameter

$$\lambda = \frac{\kappa^2 k C_S D_s \delta^2}{D_s^2} = \frac{f_R f_s}{f_D^2} \quad (2c)$$

which expresses the efficiency of the chemical reaction of the substrate with the active form of the catalyst in the film as related to the diffusion of the substrate in the solution. Also

$$\gamma_s = \frac{k C_S a^2}{D_s} = \frac{\lambda}{\sigma^2} \quad (2d)$$

represents the catalytic reaction vs. substrate diffusion in the film and

$$\gamma_E = \frac{k K_S^\infty a^2}{D_E} = \frac{\lambda}{\rho \sigma^2} \quad (2e)$$

represents the catalytic reaction vs. electron diffusion in the film. Now the boundary conditions are [26]

$$\xi = \frac{a}{L} = m; \quad v = 1; \quad \frac{du}{d\xi} = 0 \quad (3a)$$

$$\xi = \frac{a+L}{L} = 1+m; \quad \frac{dv}{d\xi} = 0; \quad 1-u = \sigma \left(\frac{du}{d\xi} \right) \quad (3b)$$

The normalized current is then given by

$$\psi = 1 - u_{\xi=1+m} = \sigma \left(\frac{du}{d\xi} \right)_{\xi=1+m} = -\rho \sigma \left(\frac{dv}{d\xi} \right)_{\xi=m} \quad (4)$$

The set of expressions presented in Eqs. (1a), (1b), (2), (2a)–(2c), (2e), (3a), (3b), (4) define the boundary value problem. The Homotopy perturbation method [29–35] is used to give approximate analytical solutions of coupled non-linear reaction/diffusion Eqs. (1a) and (1b). Using Homotopy perturbation method (see Appendix A) the approximate solutions of Eqs. (1a) and (1b) are

$$u(\xi) = 1 - \frac{1}{3(1+\alpha)} \gamma_s \sigma (1+m)$$

$$+ \frac{1}{3(1+\alpha)} \gamma_s m^3 \left[\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right]$$

$$+ \frac{1}{6(1+\alpha)} \gamma_s (\xi^2 - (1+m)^2) \quad (5a)$$

$$v(\xi) = 1 + \left| \frac{1}{3(1+\alpha)} \gamma_E (1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) \right|$$

$$+ \left| \frac{1}{6(1+\alpha)} \gamma_E (\xi^2 - m^2) \right| \quad (5b)$$

Using Eq. (4), we can obtain the current as

$$\psi = \frac{\sigma \gamma_s}{3(1+\alpha)} \left(\frac{(1+m)^3 - m^3}{(1+m)^2} \right) \quad (6a)$$

Eq. (6a) denotes the new dimensionless analytical approximation of current ψ for all values of parameters γ_s , α , m and σ . In the limiting cases, the above equation becomes

$$\psi = \frac{\sigma \gamma_s}{3(1+\alpha)} [1 + m + 3m^3 + 9m^4] \quad \text{when } m \rightarrow 0 \quad (6b)$$

$$= \frac{\sigma \gamma_s}{3(1+\alpha)} [3 - 3/m + 4/m^2 + 7/m^3 + 3/m^4] \quad \text{when } m \rightarrow \infty \quad (6c)$$

3. Discussion

Eqs. (5a) and (5b) represent the new approximate analytical expression for the substrate and mediator concentration profiles for all values of parameters γ_s , γ_E and α . It satisfies the boundary conditions Eqs. (3a) and (3b). In Fig. 3a–d, we present the series of the normalized concentration profiles for a substrate u as a function of reaction diffusion parameters γ_s , γ_E , radial/planar diffusion ratio m ($m = a/L$) and saturation parameter α . From these figures, it is inferred that, the value of u is approximately equal to 1 when $\gamma_s \leq 1$ for all values of α and ξ . When the value of $\alpha > 5$, the value of $u \approx 1$ for all values of γ_s (see Fig. 3c and d). The concentration differs significantly only when $\alpha \leq 5$ (see Fig. 3a and b). Mediator concentration $v(\xi)$ is plotted in Fig. 4a–d for various values of α and γ_E . When the value of γ_E increases, the value of v increases for all values of α . Also $v \approx 1$ when $\alpha > 10$ for all values of γ_E . The concentration of mediator v reaches the steady-state value when $\xi \geq 0.3$ for all values of α and γ_E . Fig. 5 represents the normalized current vs. γ_s for various values of α and for some fixed value of m and σ . The value of the current increases when γ_s increases and α decreases. Normalized amperometric response or catalytic efficiency ψ varies with the parameter $m = a/L$. From Fig. 6, it is confirmed that the value of the current depends on the radial/planar diffusion ratio m . Also the current reaches the steady-state value when $m \geq 5$. When $m \rightarrow 0$, the normalized current $\psi \approx \frac{\sigma \gamma_s}{3(1+\alpha)}$ and when $m \rightarrow \infty$, $\psi \approx \frac{\sigma \gamma_s}{(1+\alpha)}$.

4. Unsaturated (first order) catalytic kinetics

In this case, the substrate concentration in the film u is less than the Michaelis constant K_M . When $\alpha u \ll 1$, Eqs. (1a) and (1b) reduce to [26]

$$\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \gamma_s u v = 0 \quad (7a)$$

$$\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} - \gamma_E u v = 0 \quad (7b)$$

where γ_s and γ_E are defined in Eqs. (2d) and (2e). The set of expressions presented in Eqs. (7a) and (7b) define the boundary value problem. By using Homotopy perturbation method the approximate analytical solutions of coupled non-linear reaction/diffusion Eqs. (7a) and (7b) are

$$u(\xi) = 1 - \frac{1}{3} \gamma_s \sigma (1+m) + \frac{1}{3} \gamma_s m^3 \left[\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right]$$

$$+ \frac{1}{6} \gamma_s (\xi^2 - (1+m)^2) \quad (8a)$$

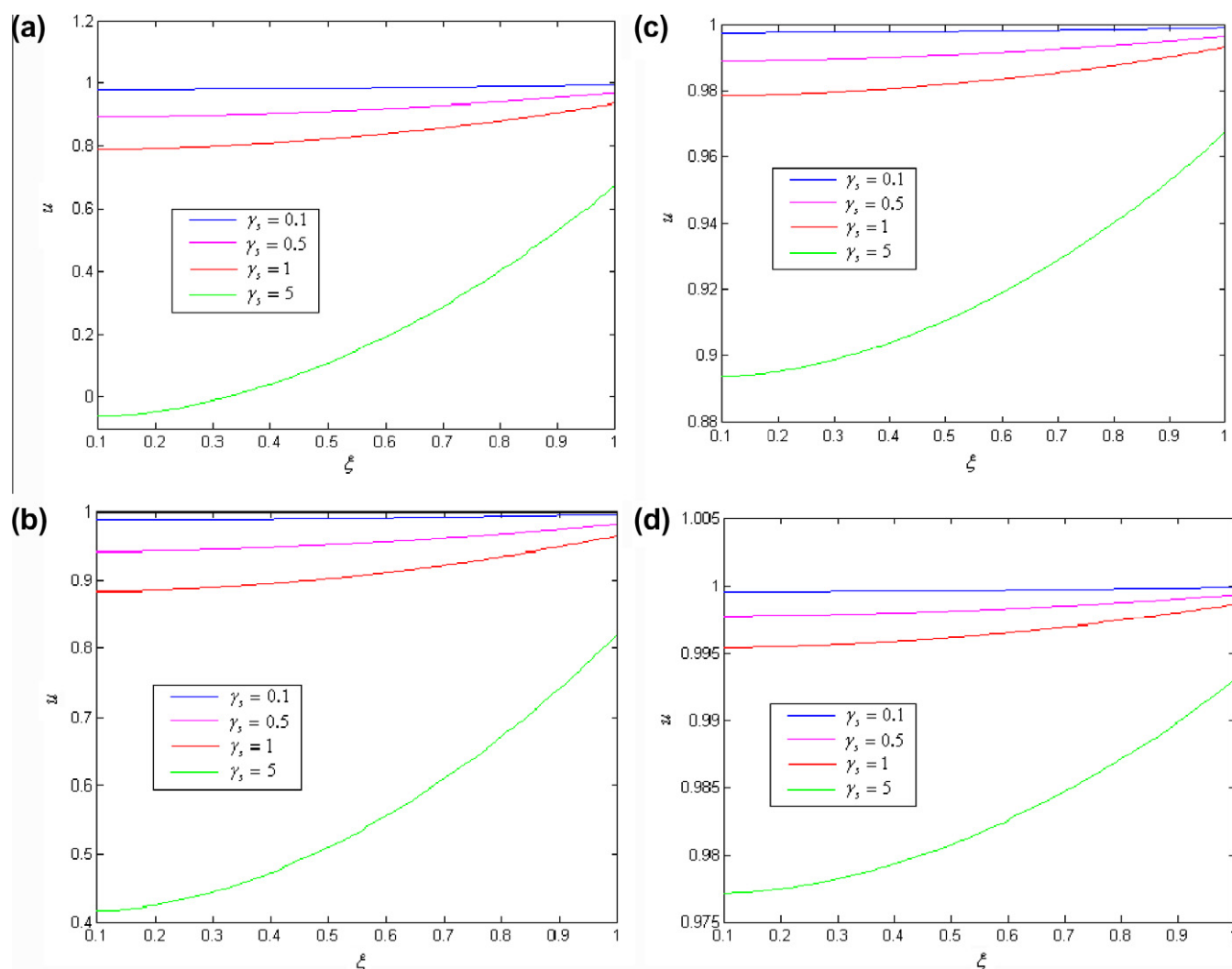


Fig. 3. Normalized substrate concentration u at a polymer microelectrode. The concentrations were computed using Eq. (5a) for various values of the reaction/diffusion parameter γ_s and for some fixed value of $m = 0.1$ and $\sigma = 0.1$ (a) $\alpha = 0.1$ (b) $\alpha = 1$ (c) $\alpha = 10$ (d) $\alpha = 50$.

$$v(\xi) = 1 + \left| \frac{1}{3} \gamma_E (1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) \right| + \left| \frac{1}{6} \gamma_E (\xi^2 - m^2) \right| \quad (8b)$$

when $\alpha = 0$, Eqs. (5a) and (5b) is identically equal to Eqs. (8a) and (8b). To improve the accuracy of the result, we can also find the second iteration (Eqs. (9a) and (9b)),

$$u(\xi) = 1 - \frac{1}{3} \gamma_s \sigma (1+m) + \frac{1}{3} \gamma_s m^3 \left[\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right] + \frac{1}{6} \gamma_s (\xi^2 - (1+m)^2) + \gamma_s A \left[\frac{m^2}{\xi} + \xi - \frac{(1+m-\sigma)m^2 + (1+m)^2(1+m+\sigma)}{(1+m)^2} \right] \quad (9a)$$

$$v(\xi) = 1 + \left| \frac{1}{3} \gamma_E (1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) \right| + \left| \frac{1}{6} \gamma_E (\xi^2 - m^2) \right| + \gamma_E A \left[\frac{(1+m)^2}{\xi} - \frac{(1+m)^2}{m} - m + \xi \right] \quad (9b)$$

where

$$A = \frac{1}{6} (\gamma_E (1+m)^3 + \gamma_s m^3) = \frac{1}{6} (\lambda/\sigma^2) (1/\rho(1+m)^3 + m^3) \quad (10)$$

The normalized steady-state current response for all six limiting cases (ER, R, SR, etc) will be given by

$$\psi = \sigma \gamma_s \left[\frac{1}{3} \left((1+m) - \frac{m^3}{(1+m)^2} \right) + \frac{1}{6} (\gamma_E (1+m)^3 + \gamma_s m^3) \left(1 - \frac{m^2}{(1+m)^2} \right) \right] = \sigma (\lambda/\sigma^2) \left[\frac{1}{3} \left((1+m) - \frac{m^3}{(1+m)^2} \right) + \frac{1}{6} (\gamma_E (1+m)^3 + \gamma_s m^3) \left(1 - \frac{m^2}{(1+m)^2} \right) \right] \quad (11)$$

In the limiting cases, the above equation becomes

$$\psi = \frac{\sigma \gamma_s}{6} [(\gamma_E + 2) + m(3\gamma_E + 2) + 2\gamma_E m^2 + (\gamma_s + 6)m^3] \quad \text{when } m \rightarrow 0 \quad (12a)$$

$$\psi = \frac{\sigma \gamma_s}{6} [(\gamma_E + 6) + 3\gamma_E m + 3\gamma_E m^2 + (\gamma_E + \gamma_s)m^3 - 6/m + 8/m^2 + 14/m^3] \quad \text{when } m \rightarrow \infty \quad (12b)$$

Eqs. (9a) and (9b) represent the new approximate analytical expressions for the substrate and mediator concentration for all values of

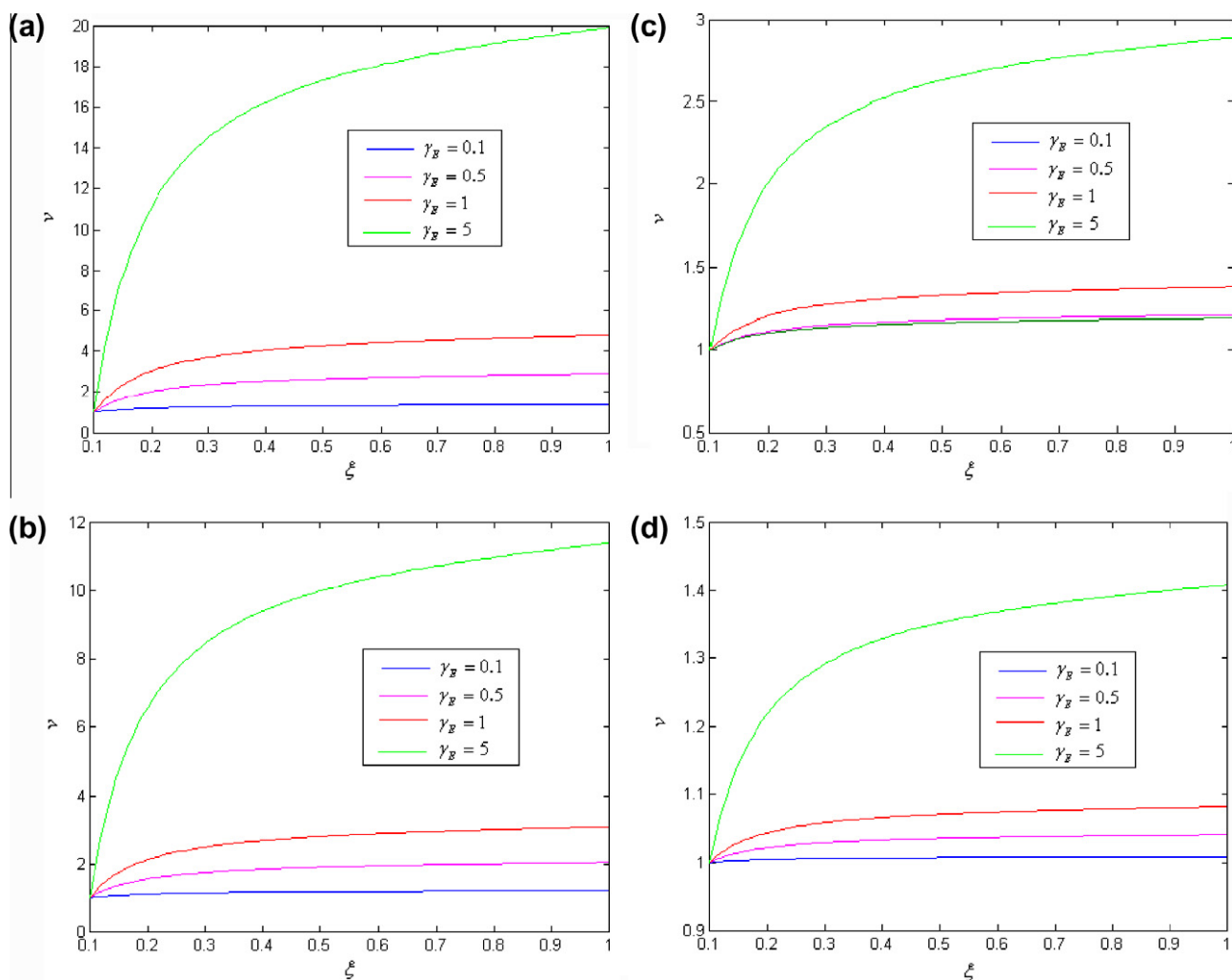


Fig. 4. Normalized mediator concentration ν at a polymer microelectrode. The concentrations were computed using Eq. (5b) for various values of the reaction/diffusion parameter γ_E and for some fixed value of $m = 0.1$ and $\sigma = 0.1$ (a) $\alpha = 0.1$ (b) $\alpha = 1$ (c) $\alpha = 10$ (d) $\alpha = 50$.

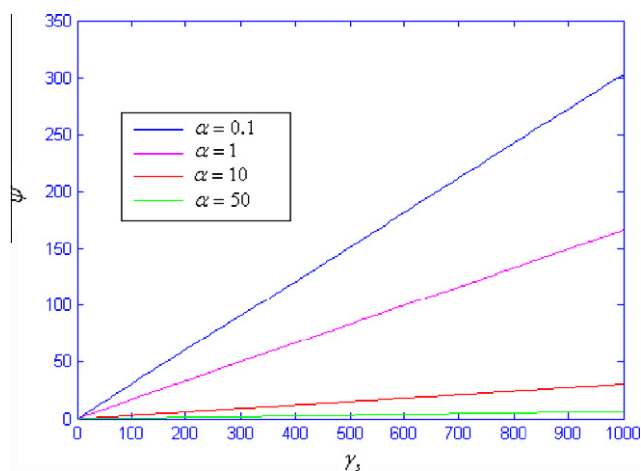


Fig. 5. Variation of normalized steady-state current response ψ with reaction/diffusion parameter γ_s and α and for some fixed values of $m = 0$ and $\sigma = 1$. The curves were computed using Eq. (6a).

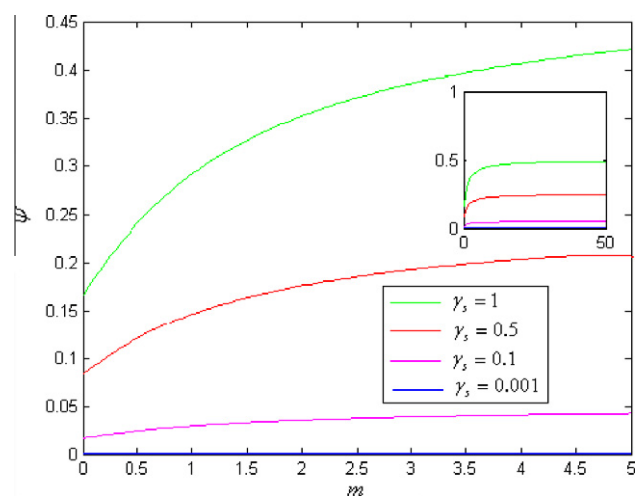


Fig. 6. Variation of normalized steady-state current response ψ with radial / diffusion ratio m for various values of γ_s and for some fixed values of $\sigma = 1$. The curves were computed using Eq. (6a).

γ_s , γ_E and m . It satisfies the boundary conditions Eqs. (3a) and (3b). Eq. (11) represents the new approximate analytical expression for the current for all values of parameters.

4.1. Case by case kinetic analysis

4.1.1. Electron percolation through the polymer layer more rapid than substrate transport

When $\rho \rightarrow \infty$ or $\gamma_E \rightarrow 0$, substrate diffusion in the polymer matrix is very slow compared with the electron diffusion through the film. Since substrate diffusion in the polymer matrix is slow, Eq. (5b) or (9b) reduces to $u \approx 1$. Now Eq. (7a) becomes

$$\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \gamma_s u = 0 \quad (13)$$

Using Variational iteration method, we can find the normalized substrate concentration u

$$u(\xi) = F[m \cosh(\sqrt{\gamma_s}(\xi - m)) + \sinh(\sqrt{\gamma_s}(\xi - m))/\sqrt{\gamma_s}] + a\xi^3 - 3am\xi^2 + (am(m+2) - F)\xi + F - am^2 \quad (14)$$

where

$$F = 1 + a + 2a\sigma, \quad a = \frac{1 + (m + \sigma)(\cosh(\sqrt{\gamma_s}) + 1) + (1 + \sqrt{\gamma_s}m\sigma) \sinh(\sqrt{\gamma_s})/\sqrt{\gamma_s}}{2\sigma^2 - \cosh(\sqrt{\gamma_s})(\sigma(1 + 2m + 2\sigma) + m) - (\sigma(\gamma_s m + 2\gamma_s \sigma m + 2) + 1) \sinh(\sqrt{\gamma_s})/\sqrt{\gamma_s}} \quad (15)$$

The normalized current is

$$\psi = \sigma(F \cosh(\sqrt{\gamma_s}) + Fm\sqrt{\gamma_s} \sinh(\sqrt{\gamma_s}) + (2am - 2a\sigma - 1)) \quad (16)$$

4.1.2. Substrate diffusion through the polymer layer more rapid than electron diffusion

When $\rho \rightarrow 0$ or ($\gamma_s \rightarrow 0$), substrate diffusion through the polymer layer more rapid than electron diffusion. Since substrate diffusion through the layer is fast, Eqs. (5a) or (9a) reduces to $u \approx 1$. Now Eq. (7b) becomes

$$\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} - \gamma_E v = 0 \quad (17)$$

By using reduction of order the concentration of mediator v can be expressed as follows:

$$v = \frac{m}{\xi(1 + H \exp(2\sqrt{\gamma_E}))} [\exp(\sqrt{\gamma_E}(\xi - m)) + H \exp(\sqrt{\gamma_E}(2 + m - \xi))] \quad (18)$$

where

$$H = \frac{\sqrt{\gamma_E} - (1 + m)^{-1}}{\sqrt{\gamma_E} + (1 + m)^{-1}} \quad (19)$$

The normalized current is given by

$$\psi = \frac{\rho\sigma\{(\sqrt{\gamma_E} + \frac{1}{m})H \exp[2\sqrt{\gamma_E}] - (\sqrt{\gamma_E} - \frac{1}{m})\}}{1 + H \exp[2\sqrt{\gamma_E}]} \quad (20)$$

Eqs. (18) and (20) represent the new analytical expression of concentration of mediator v and current for all values of γ_E .

5. Comparison with Rebouillat et al's [26] work

Rebouillat et al. [26] derived the analytical expressions of substrate and mediator concentrations for the limiting cases ($\rho \rightarrow \infty$ and $\rho \rightarrow 0$) only (e.g. R + S, R + E). We have derived the general ana-

lytical expressions for concentration of mediator and substrate for all cases. Rebouillat et al. [26] derived the expression of concentration for R + S case ($\rho \rightarrow \infty$) as follows:

$$u = \frac{A}{\xi} \exp\left[\sqrt{\frac{\lambda}{\sigma^2}}\xi\right] + \frac{B}{\xi} \exp\left[-\sqrt{\frac{\lambda}{\sigma^2}}\xi\right] \quad (21)$$

where

$$A = \frac{1 + m}{F_1 \exp\left[\sqrt{\frac{\lambda}{\sigma^2}}(1 + m)\right] + F_2 G \exp\left[2\sqrt{\frac{\lambda}{\sigma^2}}m\right] \exp\left[-\sqrt{\frac{\lambda}{\sigma^2}}(1 + m)\right]} \quad (22)$$

$$B = \frac{(1 + m)G \exp\left[2\sqrt{\frac{\lambda}{\sigma^2}}m\right]}{F_1 \exp\left[\sqrt{\frac{\lambda}{\sigma^2}}(1 + m)\right] + F_2 G \exp\left[2\sqrt{\frac{\lambda}{\sigma^2}}m\right] \exp\left[-\sqrt{\frac{\lambda}{\sigma^2}}(1 + m)\right]} \quad (23)$$

The normalized current is

$$\psi = \frac{1 + \left\{\frac{F_2 - 1}{F_1 - 1}\right\} G \exp\left(-2\sqrt{\lambda/\sigma^2}\right)}{\frac{F_1}{F_1 - 1} + \frac{F_2 G}{F_1 - 1} \exp\left(-2\sqrt{\lambda/\sigma^2}\right)} \quad (24)$$

where

$$F_1 = 1 + \sigma\left\{\sqrt{\lambda/\sigma^2} - 1/(1 + m)\right\}, \quad F_2 = 1 - \sigma\left\{\sqrt{\lambda/\sigma^2} + 1/(1 + m)\right\}, \quad \text{and } G = \frac{\sqrt{\lambda/\sigma^2} - 1/m}{\sqrt{\lambda/\sigma^2} + 1/m} \quad (25)$$

In the case of R + E ($\rho \rightarrow 0$) Rebouillat et al. [26] obtained the concentration and current equation as follows:

$$v = \frac{P}{\xi} \exp\left[\sqrt{\beta}\xi\right] + \frac{Q}{\xi} \exp\left[-\sqrt{\beta}\xi\right] \quad (26)$$

where

$$\beta = \frac{\lambda}{\rho\sigma^2}(1 - \psi) \quad (27)$$

$$P = \frac{m \exp[-\sqrt{\beta}m]}{1 + \mu(\beta, m) \exp[2\sqrt{\beta}]} \quad (28)$$

$$Q = \frac{m\mu(\beta, m) \exp[\sqrt{\beta}(2 + m)]}{1 + \mu(\beta, m) \exp[2\sqrt{\beta}]} \quad \text{and}$$

$$\mu(\beta, m) = \frac{\sqrt{\beta} - 1/(1 + m)}{\sqrt{\beta} + 1/(1 + m)} \quad (29)$$

From Eq. (26), the value of the mediator concentration can be obtained in terms of current only. The normalized current is given by

$$\psi = \frac{\rho\sigma\{(\sqrt{\beta} + 1/m)\mu \exp[2\sqrt{\beta}] - (\sqrt{\beta} - 1/m)\}}{1 + \mu \exp[2\sqrt{\beta}]} \quad (30)$$

Table 1 indicates the dimensionless concentration of substrate u for small values of α using Eq. (5a) together with the analytical results (Limiting cases) of Rebouillat et al. [26] using Eq. (21). The average relative error of substrate concentration u between Eq. (5a) and Rebouillat et al. [26] analytical result (Eq. (21)) are 0.0100% when $\gamma_s = 0.01$, 0.1762% when $\gamma_s = 0.5$ and -0.9147% when $\gamma_s = 1$ (refer Table 1). In Table 2, values of the dimensionless concentration u for large values of α using Eq. (5a) are reported. The

Table 1

Comparison of normalized substrate concentration u between Eqs. (21) and (5a) for various values of ξ and for some fixed values of $\alpha = 0.1, m = 0.1$ and $\sigma = 0.1$.

ξ	Concentration of u								
	u (when $\gamma_s = 0.01$)			u (when $\gamma_s = 0.5$)			u (when $\gamma_s = 1$)		
	Rebouillat et al. [26] Eq. (21)	This work Eq. (5a)	% of deviation between Eqs. (21) and (5a)	Rebouillat et al. [26] Eq. (21)	This work Eq. (5a)	% of deviation between Eqs. (21) and (5a)	Rebouillat et al. [26] Eq. (21)	This work Eq. (5a)	% of deviation between Eqs. (21) and (5a)
0.10	0.9977	0.9978	0.0100	0.8922	0.8938	0.1790	0.8001	0.7876	–1.5871
0.20	0.9977	0.9979	0.0200	0.8937	0.8953	0.1787	0.8028	0.7907	–1.5302
0.30	0.9978	0.9979	0.0100	0.8972	0.8988	0.1780	0.8090	0.7977	–1.4165
0.40	0.9979	0.9980	0.0100	0.9023	0.9040	0.1880	0.8182	0.8080	–1.2623
0.50	0.9980	0.9982	0.0200	0.9090	0.9107	0.1866	0.8303	0.8216	–1.0589
0.60	0.9982	0.9983	0.0100	0.9172	0.9190	0.1958	0.8453	0.8381	–0.8590
0.70	0.9984	0.9985	0.0100	0.9270	0.9288	0.1937	0.8632	0.8578	–0.6295
0.80	0.9987	0.9988	0.0100	0.9385	0.9402	0.1808	0.8842	0.8804	–0.4316
0.90	0.9990	0.9990	0.0000	0.9515	0.9530	0.1573	0.9085	0.9061	–0.2648
1.00	0.9993	0.9993	0.0000	0.9662	0.9674	0.1240	0.9360	0.9350	–0.1069
Average			0.0100			0.1762			–0.9147

Table 2

Normalized substrate concentration u using Eq. (5a) for various values of ξ and for some fixed values of $\alpha = 10, m = 0.1$ and $\sigma = 0.1$.

ξ	Concentration of u			
	u (when $\gamma_s = 0.01$) This work Eq. (5a)	u (when $\gamma_s = 0.5$) This work Eq. (5a)	u (when $\gamma_s = 1$) This work Eq. (5a)	u (when $\gamma_s = 5$) This work Eq. (5a)
0.10	0.9997	0.9894	0.9787	0.8938
0.20	0.9997	0.9895	0.9790	0.8953
0.30	0.9997	0.9899	0.9797	0.8988
0.40	0.9998	0.9904	0.9808	0.9040
0.50	0.9998	0.9911	0.9821	0.9107
0.60	0.9998	0.9919	0.9838	0.9190
0.70	0.9998	0.9929	0.9857	0.9288
0.80	0.9998	0.9940	0.9880	0.9402
0.90	0.9999	0.9953	0.9906	0.9530
1.00	0.9999	0.9967	0.9934	0.9674

Table 4

Normalized mediator concentration v using Eq. (5b) for various values of ξ and for some fixed values of $\alpha = 100, m = 0.1$ and $\sigma = 0.1$.

ξ	Concentration of v			
	v (when $\gamma_E = 0.01$) This work Eq. (5b)	v (when $\gamma_E = 1$) This work Eq. (5b)	v (when $\gamma_E = 5$) This work Eq. (5b)	v (when $\gamma_E = 10$) This work Eq. (5b)
0.10	1.0000	1.0000	1.0000	1.0000
0.20	0.9997	0.9780	0.8904	0.7808
0.30	0.9997	0.9708	0.8542	0.7084
0.40	0.9996	0.9673	0.8365	0.6730
0.50	0.9996	0.9652	0.8263	0.6525
0.60	0.9996	0.9639	0.8198	0.6397
0.70	0.9996	0.9631	0.8157	0.6314
0.80	0.9996	0.9626	0.8130	0.6260
0.90	0.9996	0.9622	0.8113	0.6227
1.00	0.9996	0.9620	0.8105	0.6209

values of the concentration v for different values of γ_E are given in Table 3. Our analytical expression for mediator concentration v is not able to compare with Eq. (26) because the analytical expression of v (Eq. (26)) is in terms of current ψ . Table 4 shows the dimensionless concentration of mediator v for large values of α . From Fig. 7a–c, it is inferred that the concentration u increases when γ_E decreases and γ_s increases. Fig. 8 represents the mediator concentration v for various values of γ_s and γ_E . The dimensionless current ψ using Eq. (11) is given in Figs. 9 and 10. It is compared with Eq. (24). There is a significant difference in current values when the

values of $m \geq 5$. Fig. 11 shows the dimensionless steady-state current ψ using Eq. (11) vs. m for various values of γ_s and for some fixed values of $\sigma = 0.1$ and $\gamma_E = 0.1$. Table 5 indicates that the comparison of normalized current ψ of this work and Rebouillat et al. [26] work. From this table, we can see that the average relative error of current ψ between Eq. (16)) (first iteration) and Rebouillat et al. [26] analytical result Eq. (24) are 0.0102% when $\gamma_s = 0.1$, 0.0800% when $\gamma_s = 1$ and 0.0257% when $\gamma_s = 10$ (see Table 5). As seen in Fig. 12, the normalized concentration of mediator v decreases when γ_E increases and reaches the steady-state value when $\xi \geq 0.4$. Fig. 13 represents the normalized steady-state current using Eq. (20) for various values of parameters.

Table 3

Normalized mediator concentration v using Eq. (5b) for various values of ξ and for some fixed values of $\alpha = 0.1, m = 0.1$ and $\sigma = 0.1$.

ξ	Concentration of v		
	v (when $\gamma_E = 0.01$) This work Eq. (5b)	v (when $\gamma_E = 0.1$) This work Eq. (5b)	v (when $\gamma_E = 1$) This work Eq. (5b)
0.10	1.0000	1.0000	0.9999
0.20	0.9798	0.7988	1.0121
0.30	0.9732	0.7323	1.6767
0.40	0.9699	0.6998	2.0022
0.50	0.9681	0.6809	2.1903
0.60	0.9669	0.6692	2.3080
0.70	0.9662	0.6616	2.3844
0.80	0.9656	0.6566	2.4337
0.90	0.9654	0.6536	2.4640
1.00	0.9652	0.6520	2.4800

6. Saturated (zero order) catalytic kinetics

In this case, the substrate concentration u is greater than Michaelis constant K_M . When $\alpha u \gg 1$, Eqs. (1a) and (1b) reduce to

$$\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \frac{\gamma_s}{\alpha} v = 0 \quad (31a)$$

$$\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} - \frac{\gamma_E}{\alpha} v = 0 \quad (31b)$$

By solving Eqs. (31a) and (31b) using the reduction of order method, we can obtain the concentration of substrate u and v , which is as follows:

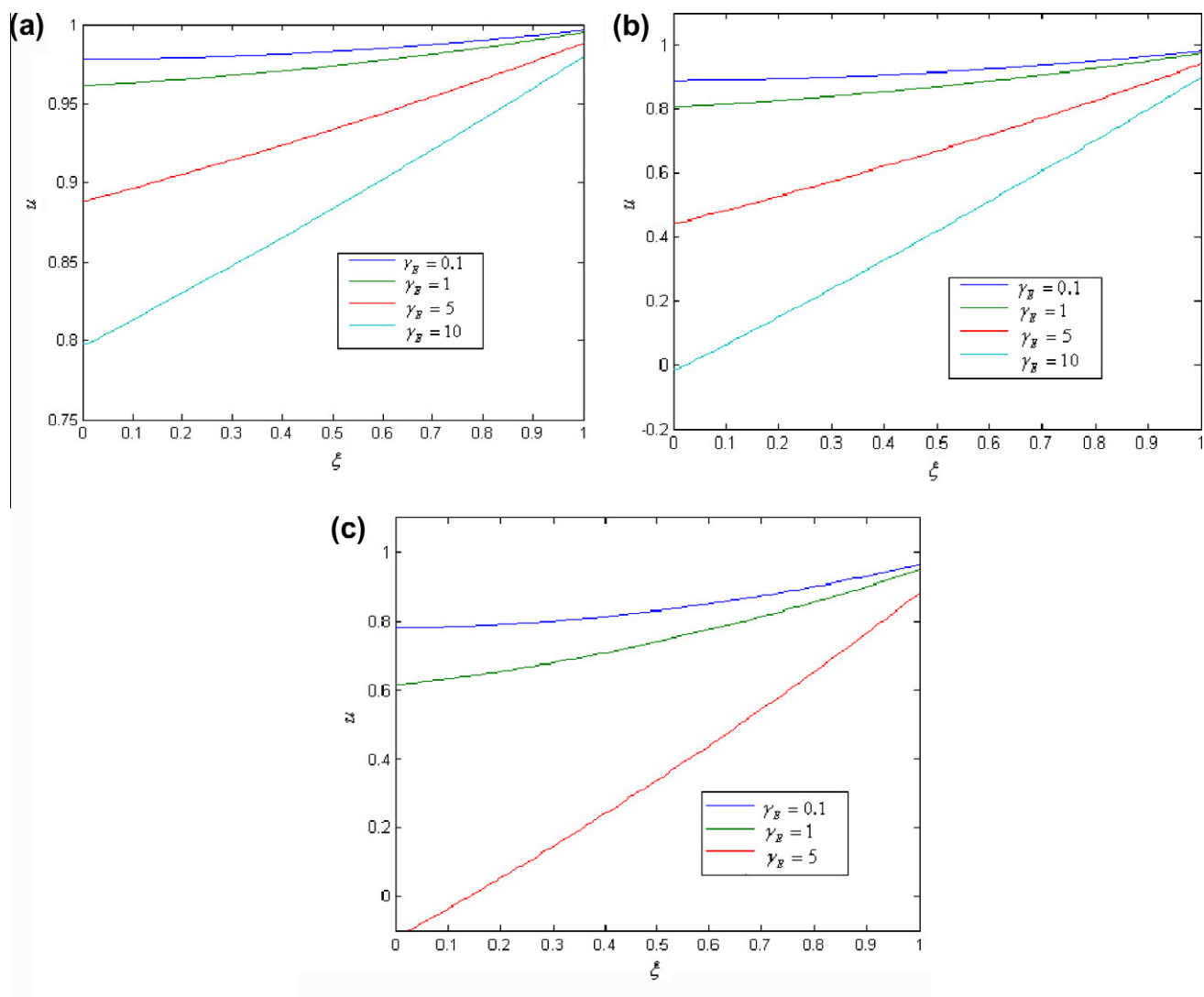


Fig. 7. Normalized substrate concentration u at a polymer microelectrode. The concentrations were computed using Eq. (9a) for various values of the reaction/diffusion parameter γ_E and for some fixed value of $m = 0.001$ and $\sigma = 0.1$ (a) $\gamma_s = 0.1$ (b) $\gamma_s = 0.5$ (c) $\gamma_s = 1$.

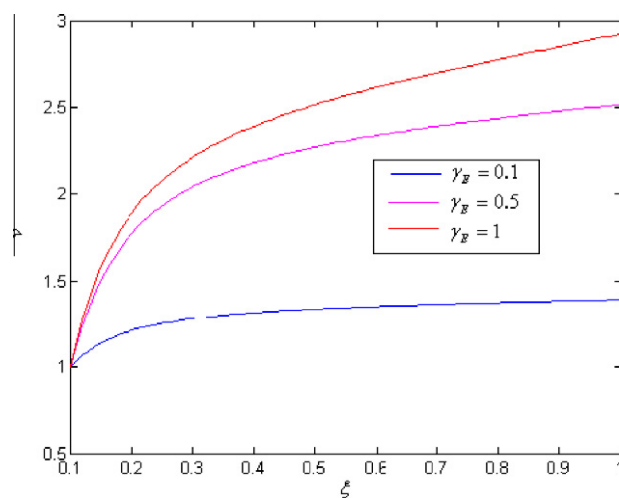


Fig. 8. Normalized mediator concentration v at a polymer microelectrode. The concentrations were computed using Eq. (9b) for various values of the reaction/diffusion parameter γ_E and the values of $\gamma_s = 0.1, 1, 5, 10$, $m = 0.1$ and $\sigma = 0.1$.

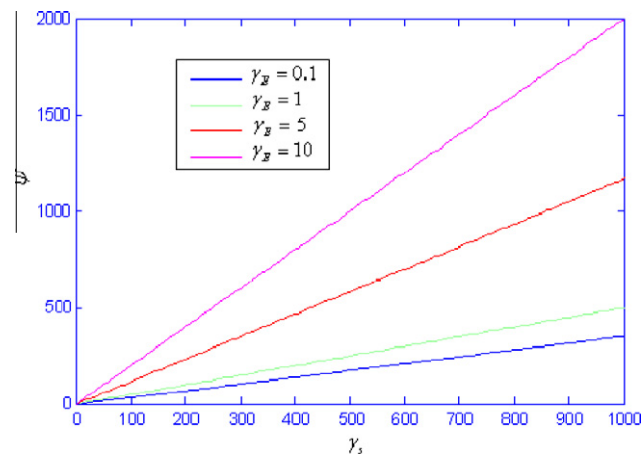


Fig. 9. Variation of normalized steady-state current response ψ for various values of γ_s and γ_E . The curves were computed using Eq. (11) for the values of $m = 0$ and $\sigma = 1$.

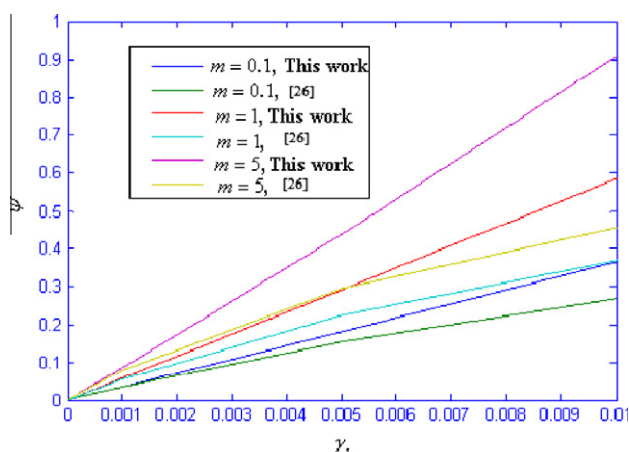


Fig. 10. Comparison of variation of the normalized current response ψ for the case $R + S$ with reaction parameter γ_s . The curves were computed using Eqs. (11) and (24).

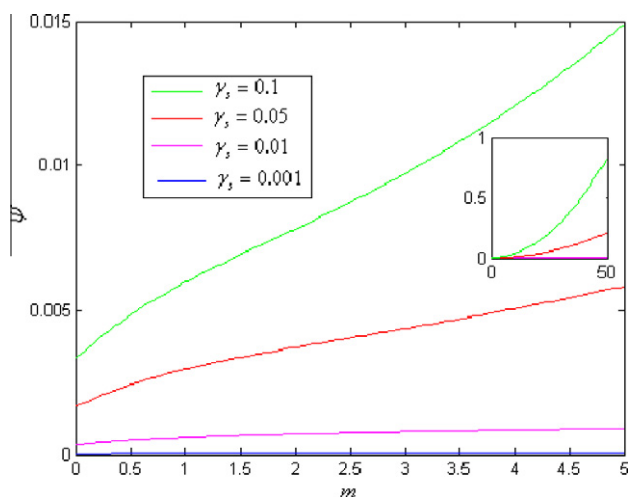


Fig. 11. Variation of normalized steady-state current response ψ with radial/diffusion ratio m for various values of γ_s . The curves were computed using Eq. (11) for some fixed values of $\gamma_E = 0.1$ and $\sigma = 0.1$.

$$u(\xi) = \frac{\gamma_s m}{\gamma_E (1 + \theta \exp(2\beta))} \left[\frac{\exp(\beta(\xi - m)) + \theta \exp(\beta(2 + m - \xi))}{\xi} + \frac{\exp(\beta) \{ \sigma \beta (1 - \theta) + (1 + \theta)(1 - \sigma/(1 + m)) \}}{1 + m} \right] + N + 1 \quad (32a)$$

$$v(\xi) = \frac{m [\exp(\beta(\xi - m)) + \theta \exp(\beta(2 + m - \xi))]}{\xi (1 + \theta \exp(2\beta))} \quad (32b)$$

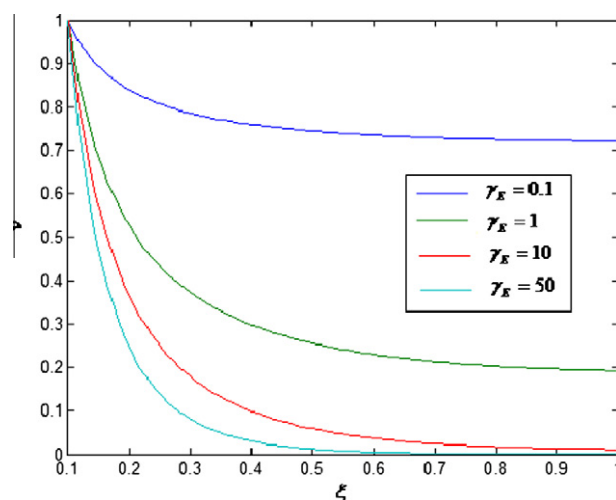


Fig. 12. Normalized mediator concentration ν for the case $R + E$. The concentrations were computed using Eq. (18) for various values of γ_E and for some fixed value of $m = 0.1$.

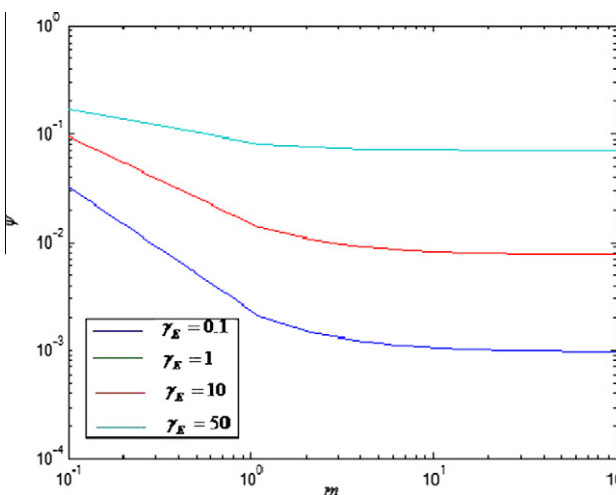


Fig. 13. Variation of normalized steady-state current response ψ with radial/diffusion ratio m for various values of reaction/diffusion parameter. The curves were computed using Eq. (20).

where

$$\theta = \frac{\beta - (1 + m)^{-1}}{\beta + (1 + m)^{-1}} \quad (33)$$

Table 5
Comparison of normalized steady-state current for some value of $\sigma = 1000$.

m	Current ψ			ψ (when $\gamma_s = 1$)			ψ (when $\gamma_s = 10$)		
	ψ (when $\gamma_s = 0.1$)								
	Rebouillat et al. [26] Eq. (24)	This work Eq. (16)	% of deviation between Eqs. (24) and (16)	Rebouillat et al. [26] Eq. (24)	This work Eq. (16)	% of deviation between Eqs. (24) and (16)	Rebouillat et al. [26] Eq. (24)	This work Eq. (16)	% of deviation between Eqs. (24) and (16)
0.1	0.9732	0.9737	0.0513	0.9970	0.9970	0.0000	0.9995	0.9995	0.0000
10	0.9888	0.9888	0.0000	0.9986	0.9988	0.0200	0.9997	1.0000	0.0300
20	0.9892	0.9892	0.0000	0.9986	0.9992	0.0600	0.9997	1.0000	0.0300
30	0.9894	0.9894	0.0000	0.9987	0.9996	0.0900	0.9997	1.0000	0.0300
40	0.9895	0.9895	0.0000	0.9987	1.0000	0.1300	0.9997	1.0000	0.0300
50	0.9896	0.9896	0.0000	0.9987	1.0000	0.1300	0.9997	1.0000	0.0300
100	0.9897	0.9899	0.0202	0.9987	1.0000	0.1300	0.9997	1.0000	0.0300
Average			0.0102			0.0800			0.0257

Table 6
Analytical expressions of concentration of substrate, mediator and current for all values of parameters.

Conditions	Concentrations u , v and current	Figures
For all values of α	$u(\xi) = 1 - \frac{1}{3(1+\alpha)}\gamma_s\sigma(1+m) + \frac{1}{3(1+\alpha)}\gamma_s m^3 \left[\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right] + \frac{1}{6(1+\alpha)}\gamma_s(\xi^2 - (1+m)^2)$	Eq. (5a) Fig. 3a–d
	$v(\xi) = 1 + \frac{1}{3(1+\alpha)}\gamma_E(1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) + \frac{1}{6(1+\alpha)}\gamma_E(\xi^2 - m^2)$	Eq. (5b) Fig. 4a–d
	$\psi = \frac{\sigma\gamma_s}{3(1+\alpha)} \left(\frac{(1+m)^3 - m^3}{(1+m)^2} \right)$	Eq. (6) Figs. 5 and 6
$\alpha u < 1$	$u(\xi) = 1 - \frac{1}{3}\gamma_s\sigma(1+m) + \frac{1}{3}\gamma_s m^3 \left[\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right] + \frac{1}{6}\gamma_s(\xi^2 - (1+m)^2) + \gamma_s A \left[\frac{m^2}{\xi} + \xi - \frac{(1+m-\sigma)m^2 + (1+m)^2(1+m+\sigma)}{(1+m)^2} \right]$	Eq. (9a) Fig. 7a–c
	$v(\xi) = 1 + \frac{1}{3}\gamma_E(1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) + \frac{1}{6}\gamma_E(\xi^2 - m^2) + \gamma_E A \left[\frac{(1+m)^2}{\xi} - \frac{(1+m)^2}{m} - m + \xi \right]$	Eq. (9b) Fig. 8
	$\psi = \sigma\gamma_s \left[\frac{1}{3} \left((1+m) - \frac{m^3}{(1+m)^2} \right) + \frac{1}{6} \left(\gamma_E(1+m)^3 + \gamma_s m^3 \right) \left(1 - \frac{m^2}{(1+m)^2} \right) \right]$	Eq. (11) Figs. 9–11
$\alpha u > 1$	$u(\xi) = \frac{\gamma_s m}{\gamma_E(1+\theta \exp(2\beta))} \left[\frac{\exp(\beta(\xi-m)) + \theta \exp(\beta(2+m-\xi))}{\xi} + \frac{\exp(\beta)(\sigma\beta(1-\theta) + (1+\theta)(1-\sigma/(1+m)))}{1+m} \right] + N + 1$	Eq. (32a) Fig. 14a–d
	$v(\xi) = \frac{m[\exp(\beta(\xi-m)) + \theta \exp(\beta(2+m-\xi))]}{\xi(1+\theta \exp(2\beta))}$	Eq. (32b) Fig. 15a–d
	$\psi = \frac{\sigma\gamma_s m}{\gamma_E(1+m)^2(1+\theta \exp(2\beta))} (\beta\{\exp(\beta)(\theta-1)(1+m) + m - \exp(2\beta)\theta(1+m)\} - 1 + \exp(\beta)(1+\theta))$	Eq. (35a) Figs. 16 and 17

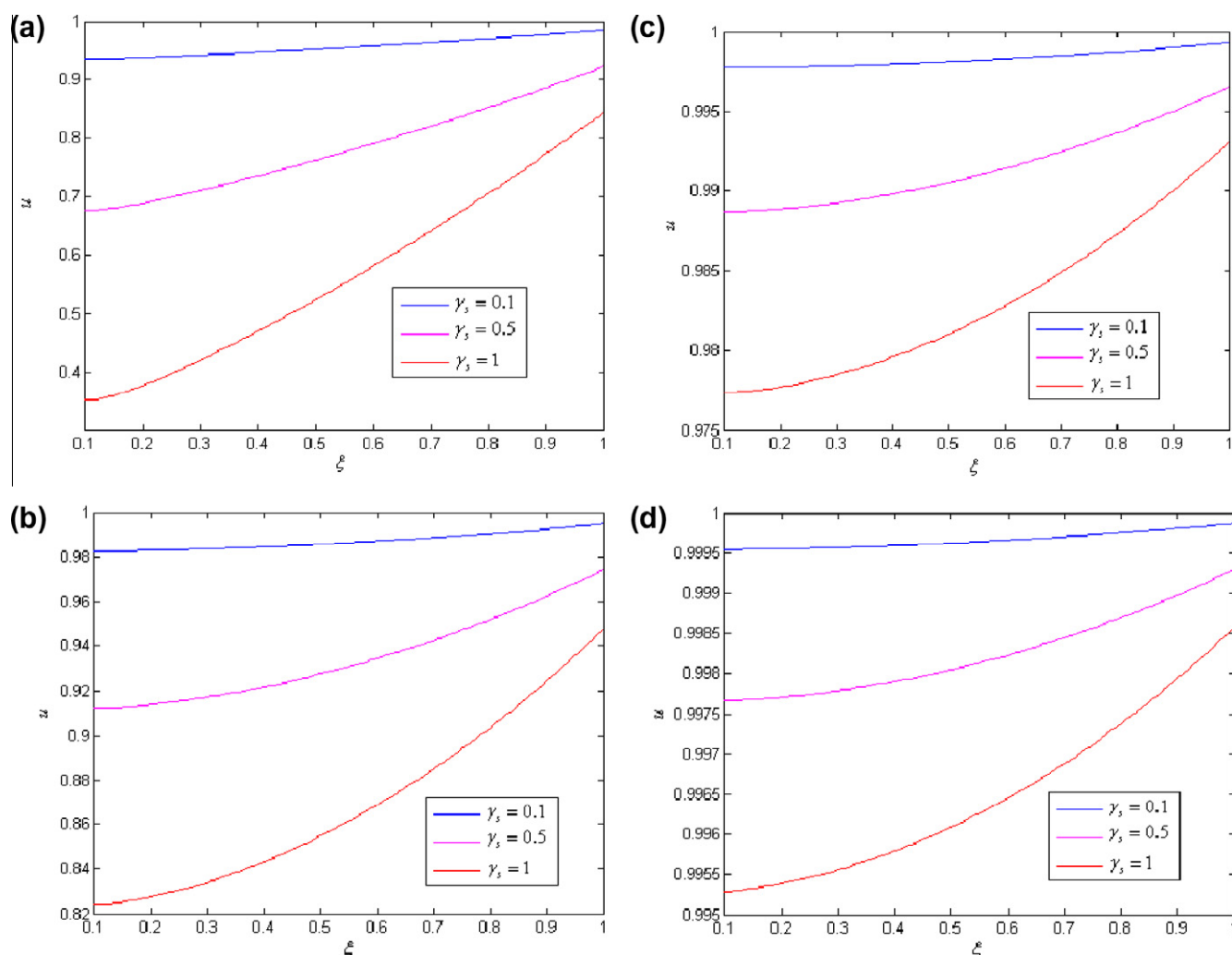


Fig. 14. Normalized substrate concentration u at a polymer microelectrode. The concentrations were computed using Eq. (32a) for various values of the reaction/diffusion parameter γ_s for some fixed value of $m = 0.1$ and $\sigma = 0.1$ (a) $\alpha = 0.1$ (b) $\alpha = 1$ (c) $\alpha = 10$ (d) $\alpha = 50$.

and

$$N = \frac{\gamma_s m}{\gamma_E} \left[\frac{(1 - \theta) \beta \exp(2\beta) m}{(1 + \theta \exp(2\beta))} - 1 \right] \left[\frac{1}{\xi} - \frac{1}{(1 + m)} + \frac{\sigma}{(1 + m)^2} \right] \quad (34)$$

The normalized current is given by

$$\psi = \frac{\sigma \gamma_s m}{\gamma_E (1 + m)^2 (1 + \theta \exp(2\beta))} \{ \beta \{ \exp(\beta) (\theta - 1) (1 + m) + m - \exp(2\beta) \theta (1 + m) \} - 1 + \exp(\beta) (1 + \theta) \} \quad (35a)$$

In the limiting cases, the current in the above equation becomes

$$\psi = \frac{-\sigma \gamma_s}{2 \gamma_E} [(\beta - 1) + (1 + 1/\beta) \exp(-2\beta)] \quad \text{when } m \rightarrow 0 \quad (35b)$$

$$= \frac{\sigma \gamma_s}{\gamma_E (1 + \exp(2\beta))} \left[\frac{\beta}{m} (1 - 2/m) \right] \quad \text{when } m \rightarrow \infty \quad (35c)$$

where $\beta = \sqrt{\gamma_E/\alpha}$. The expression of concentration of substrate, mediator and current for all the cases are summarized in Table 6.

7. Discussion for saturated (zero order) catalytic kinetics

Fig. 14a–d represents the normalized substrate concentration u at a polymer microelectrode. The concentration was computed for various values of γ_s (0.1, 0.5 and 1). From Fig. 14a, it is inferred that

the concentration u increases when ξ increases. When $\alpha \geq 5$ the concentration u is approximately equal to 1 (see Fig. 14c and d). From Fig. 15a–d, it is seen that the value of the mediator concentration decreases when ξ increases. Mediator concentration v

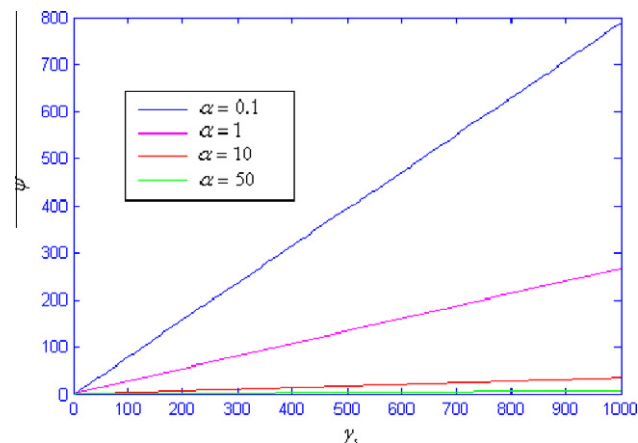


Fig. 16. Variation of normalized steady-state current response ψ with reaction/diffusion parameter γ_s and α for some fixed values of $m = 0.1$, $\gamma_E = 0.1$ and $\sigma = 1$. The curves were computed using Eq. (35a).

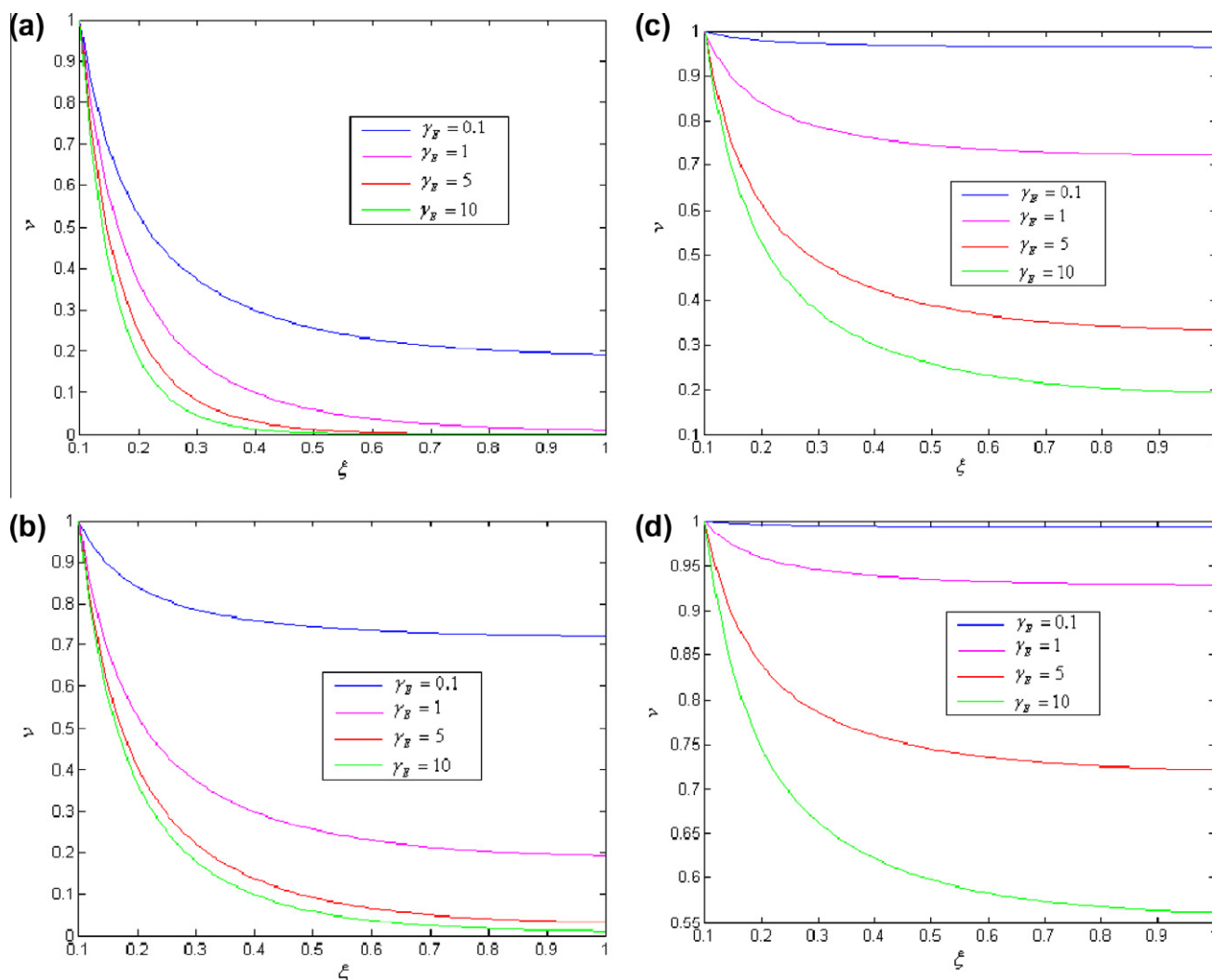


Fig. 15. Normalized mediator concentration v at a polymer microelectrode. The concentrations were computed using Eq. (32b) for various values of the reaction/diffusion parameter γ_E and for some fixed value of $m = 0.1$ and $\sigma = 0.1$ (a) $\alpha = 0.1$ (b) $\alpha = 1$ (c) $\alpha = 10$ (d) $\alpha = 50$.

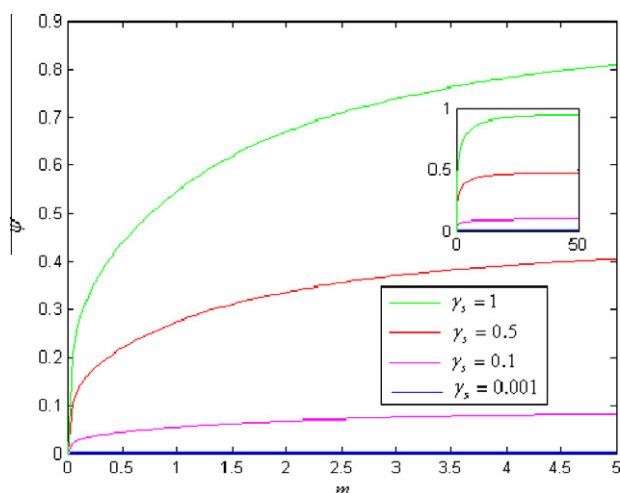


Fig. 17. Variation of normalized steady-state current response ψ with radial/diffusion ratio m for various values of reaction/diffusion parameter γ_s and for some fixed values of $\alpha = 1$, $\sigma = 1$ and $\gamma_E = 0.1$. The curves were computed using Eq. (35a).

reaches the steady-state value when $\xi \geq 0.5$. Fig. 16 represents the normalized steady-state current response ψ (Eq. (35a)) with various values of saturation parameter α . From this figure, it is inferred that the current increases when γ_s increases. Fig. 17 shows the normalized steady-state current vs. m with various values of reaction/diffusion parameter γ_s . From this figure, we can see that the current increases when γ_s increases and reaches the steady-state value when $m \geq 2$.

8. Conclusions

A non-linear time independent equation has been formulated and solved analytically using Homotopy perturbation method. The primary result of this work is the first approximate calculations of substrate, mediator concentrations and current for non-linear Michaelis–Menten kinetic scheme. A simple closed form of analytical expressions of steady-state substrate and mediator concentrations and current are given in terms of m , γ_s and γ_E . The analytical expression for the substrate concentration and mediated concentration profiles within the polymer film are derived using Homotopy perturbation method. We have also presented an analytical expression for the steady-state current. Homotopy perturbation method is an extremely simple method and it is also a promising method to solve other non-linear equations. The extension of this procedure to other direct reaction of substrate at underlying microdisc electrode surface seems possible.

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Appendix A. Solution of Eqs. (1a) and (1b) using Homotopy perturbation method

In this appendix, we indicate how Eqs. (5a) and (5b) in this paper are derived. To find the solution of Eqs. (1a) and (1b) we first construct a Homotopy as follows

$$(1-p) \left[\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} \right] + p \left[\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \frac{\gamma_s u v}{1 + \alpha u} \right] = 0 \quad (\text{A1})$$

$$(1-p) \left[\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} \right] + p \left[\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} - \frac{\gamma_E u v}{1 + \alpha u} \right] = 0 \quad (\text{A2})$$

and the initial approximations are as follows:

$$\begin{aligned} \xi = \frac{a}{L} = m; \quad v_0 = 1; \quad \frac{du_0}{d\xi} = 0 \\ \xi = \frac{a+L}{L} = 1+m; \quad \frac{dv_0}{d\xi} = 0; \quad 1-u_0 = \sigma \left(\frac{du_0}{d\xi} \right) \\ \xi = \frac{a}{L} = m; \quad v_i = 0; \quad \frac{du_i}{d\xi} = 0 \\ \xi = \frac{a+L}{L} = 1+m; \quad \frac{dv_i}{d\xi} = 0; \quad 1-u_i = \sigma \left(\frac{du_i}{d\xi} \right) \quad \forall i = 1, 2, \dots \end{aligned} \quad (\text{A3})$$

and

$$\begin{cases} u = u_0 + p u_1 + p^2 u_2 + p^3 u_3 + \dots \\ v = v_0 + p v_1 + p^2 v_2 + p^3 v_3 + \dots \end{cases} \quad (\text{A4})$$

Substituting Eq. (A4) into Eqs. (A1) and (A2) and arranging the coefficients of powers p

$$p^0: \frac{d^2 u_0}{d\xi^2} + \frac{2}{\xi} \frac{du_0}{d\xi} = 0 \quad (\text{A5})$$

$$p^1: \frac{d^2 u_1}{d\xi^2} + \frac{2}{\xi} \frac{du_1}{d\xi} - \frac{\gamma_s u_0 v_0}{1 + \alpha u_0} = 0 \quad (\text{A6})$$

and

$$p^0: \frac{d^2 v_0}{d\xi^2} + \frac{2}{\xi} \frac{dv_0}{d\xi} = 0 \quad (\text{A7})$$

$$p^1: \frac{d^2 v_1}{d\xi^2} + \frac{2}{\xi} \frac{dv_1}{d\xi} - \frac{\gamma_E u_0 v_0}{1 + \alpha u_0} = 0 \quad (\text{A8})$$

Solving Eqs. (A5)–(A8) using reduction of order, and using the initial conditions (A3), we can find the following results

$$u_0(\xi) = 1 \quad (\text{A9})$$

$$\begin{aligned} u_1(\xi) = & -\frac{1}{3(1+\alpha)} \gamma_s \sigma (1+m) \\ & + \frac{1}{3(1+\alpha)} \gamma_s m^3 \left(\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right) \\ & + \frac{1}{6(1+\alpha)} \gamma_s (\xi^2 - (1+m)^2) \end{aligned} \quad (\text{A10})$$

and

$$v_0(\xi) = 1 \quad (\text{A11})$$

$$v_1(\xi) = \frac{1}{3(1+\alpha)} \gamma_E (1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) + \frac{1}{6(1+\alpha)} \gamma_E (\xi^2 - m^2) \quad (\text{A12})$$

According to the HPM, we can conclude that

$$u(\xi) = \lim_{p \rightarrow 1} u(\xi) = u_0 + u_1 \quad (\text{A13})$$

$$v(\xi) = \lim_{p \rightarrow 1} v(\xi) = v_0 + v_1 \quad (\text{A14})$$

After putting Eqs. (A9) and (A10) into Eqs. (A13), (A11) and (A12) into Eq. (A14) the final results can be described in Eqs. (5a) and (5b) in the text. The remaining components of $u_n(x)$ and $v_n(x)$ be completely determined such that each term is determined by the previous term.

Appendix B. Solution of Eqs. (7a) and (7b) using Homotopy perturbation method

In this appendix, we indicate how Eqs. (8a) and (8b) in this paper are derived. To find the solution of Eqs. (7a) and (7b) we first construct a Homotopy as follows:

$$(1-p) \left[\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} \right] + p \left[\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \gamma_s u v \right] = 0 \quad (\text{B1})$$

$$(1-p) \left[\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} \right] + p \left[\frac{d^2 v}{d\xi^2} + \frac{2}{\xi} \frac{dv}{d\xi} - \gamma_E u v \right] = 0 \quad (\text{B2})$$

and the initial approximations are as follows:

$$\begin{aligned} \xi = \frac{a}{L} = m; \quad v_0 = 1; \quad \frac{du_0}{d\xi} &= 0 \\ \xi = \frac{a+L}{L} = 1+m; \quad \frac{dv_0}{d\xi} &= 0; \quad 1-u_0 = \sigma \left(\frac{du_0}{d\xi} \right) \\ \xi = \frac{a}{L} = m; \quad v_i = 0; \quad \frac{du_i}{d\xi} &= 0 \\ \xi = \frac{a+L}{L} = 1+m; \quad \frac{dv_i}{d\xi} &= 0; \quad -u_i = \sigma \left(\frac{du_i}{d\xi} \right) \quad \forall i = 1, 2, \dots \end{aligned} \quad (\text{B3})$$

and

$$\begin{cases} u = u_0 + p u_1 + p^2 u_2 + p^3 u_3 + \dots \\ v = v_0 + p v_1 + p^2 v_2 + p^3 v_3 + \dots \end{cases} \quad (\text{B4})$$

Substituting Eq. (B4) into Eqs. (B1) and (B2) and arranging the coefficients of powers p , we can obtain the following differential equations

$$p^0: \frac{d^2 u_0}{d\xi^2} + \frac{2}{\xi} \frac{du_0}{d\xi} = 0 \quad (\text{B5})$$

$$p^1: \frac{d^2 u_1}{d\xi^2} + \frac{2}{\xi} \frac{du_1}{d\xi} - \gamma_s u_0 v_0 = 0 \quad (\text{B6})$$

$$p^2: \frac{d^2 u_1}{d\xi^2} + \frac{2}{\xi} \frac{du_1}{d\xi} - \gamma_s (u_0 v_1 + u_1 v_0) = 0 \quad (\text{B7})$$

and

$$p^0: \frac{d^2 v_0}{d\xi^2} + \frac{2}{\xi} \frac{dv_0}{d\xi} = 0 \quad (\text{B8})$$

$$p^1: \frac{d^2 v_1}{d\xi^2} + \frac{2}{\xi} \frac{dv_1}{d\xi} - \gamma_E u_0 v_0 = 0 \quad (\text{B9})$$

$$p^2: \frac{d^2 u_1}{d\xi^2} + \frac{2}{\xi} \frac{du_1}{d\xi} - \gamma_E (u_0 v_1 + u_1 v_0) = 0 \quad (\text{B10})$$

Solving Eqs. (B5)–(B10) using reduction of order (see Appendix C) for solving Eq. (B6), and using the initial conditions (B3), we can find the following results:

$$u_0(\xi) = 1 \quad (\text{B11})$$

$$\begin{aligned} u_1(\xi) = & -\frac{1}{3} \gamma_s \sigma (1+m) + \frac{1}{3} \gamma_s m^3 \left(\frac{1}{\xi} - \frac{1}{1+m} + \frac{\sigma}{(1+m)^2} \right) \\ & + \frac{1}{6} \gamma_s (\xi^2 - (1+m)^2) \end{aligned} \quad (\text{B12})$$

$$u_2(\xi) = \gamma_s A \left(\frac{m^2}{\xi} + \xi - \frac{(1+m-\sigma)m^2 + (1+m)^2(1+m+\sigma)}{(1+c)^2} \right) \quad (\text{B13})$$

and

$$v_0(\xi) = 1 \quad (\text{B14})$$

$$v_1(\xi) = \frac{1}{3} \gamma_E (1+m)^3 \left(\frac{1}{\xi} - \frac{1}{m} \right) + \frac{1}{6} \gamma_E (\xi^2 - m^2) \quad (\text{B15})$$

$$v_2(\xi) = \gamma_E A \left(\frac{(1+m)^2}{\xi} - \frac{(1+m)^2}{m} - m + \xi \right) \quad (\text{B16})$$

According to the HPM, we can conclude that

$$u(\xi) = \lim_{p \rightarrow 1} u(\xi) = u_0 + u_1 \quad (\text{B17})$$

$$v(\chi) = \lim_{p \rightarrow 1} v(\chi) = v_0 + v_1 \quad (\text{B18})$$

After putting Eqs. (B11) and (B13) into Eqs. (B17), (B14) and (B16) into Eq. (B18) the final results can be described in Eqs. (8a) and (8b) in the text. The remaining components of $u_n(x)$ and $v_n(x)$ be completely determined such that each term is determined by the previous term.

Appendix C

In this appendix, we derive the solution of Eq. (B6) using reduction of order. To illustrate the basic concepts of reduction of order, we consider the equation

$$\frac{d^2 c}{d\xi^2} + P \frac{dc}{d\xi} + Qc = R \quad (\text{C1})$$

where P, Q, R are function of r . Eq. (B6) can be simplified to

$$\frac{d^2 u}{d\xi^2} + \frac{2}{\xi} \frac{du}{d\xi} - \gamma_s = 0 \quad (\text{C2})$$

Using reduction of order, we have

$$P = \frac{2}{\xi}; \quad Q = 0; \quad \text{and} \quad R = \gamma_s \quad (\text{C3})$$

Let

$$u = c v \quad (\text{C4})$$

Substitute (C4) in (C1), if u is so chosen that

$$2 \frac{dc}{d\xi} + Pc = 0 \quad (\text{C5})$$

Substituting the value of P the above equation becomes

$$c = \frac{1}{\xi} \quad (\text{C6})$$

The given Eq. (C3) reduces to

$$v'' + Q_1 v = R_1 \quad (\text{C7})$$

where

$$Q_1 = Q - \frac{P^2}{4} - \frac{P'}{2} = 0, \quad R_1 = \frac{R}{c} = \gamma_s \xi \quad (\text{C8})$$

Substituting (C8) in (C7), we obtain

$$v'' - \gamma_s \xi = 0 \quad (\text{C9})$$

Integrating Eq. (C9) twice, we obtain

$$v = \frac{1}{6} \gamma_s \xi^3 + A\xi + B \quad (\text{C10})$$

Substituting (C5) and (C10) in (C11), we have

$$u = \frac{1}{\xi} \left(\frac{1}{6} \gamma_s \xi^3 + A\xi + B \right) \quad (\text{C11})$$

Using the boundary conditions (B3), we can obtain the value of the constant A and B . Substituting the value of the constant A and B in Eq. (C11) we obtain Eq. (B12). Similarly we can solve the other differential Eqs. (B5), (B7), (B8), (B9) and (B10) using reduction of order method.

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