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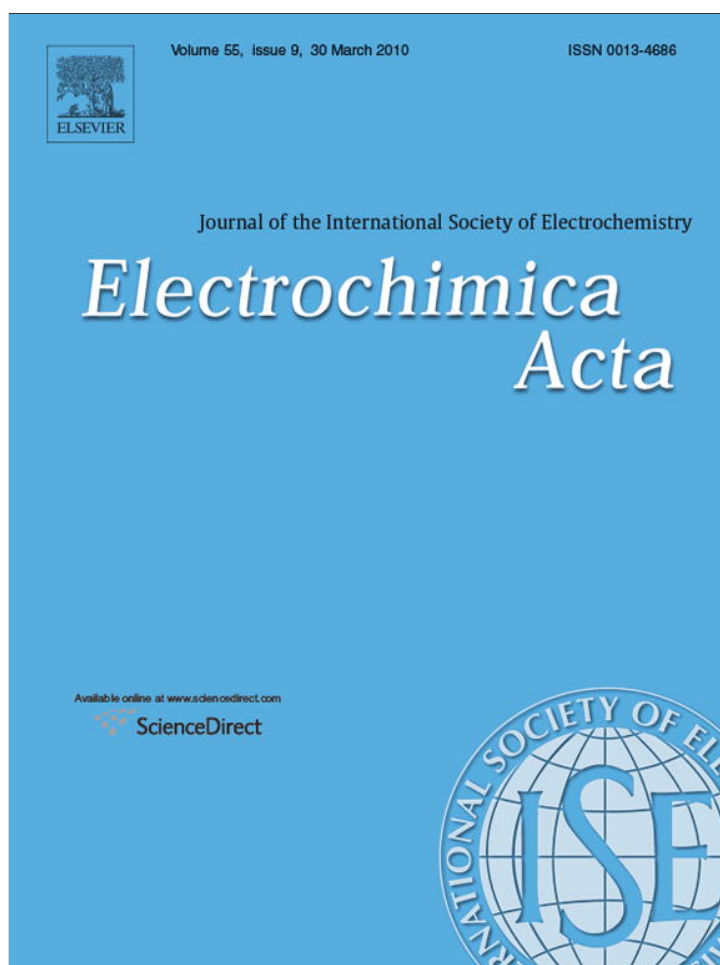


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# System of coupled non-linear reaction diffusion processes at conducting polymer-modified ultramicroelectrodes

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## ABSTRACT

The theoretical analysis of the steady-state amperometric response for conducting polymer-modified ultramicroelectrodes is discussed. The effect of substrate diffusion in the solution adjacent to the polymer film on both the concentration profile and current response is also examined. Simple analytical expressions for substrate and mediator concentrations and current responses for all values of reaction/diffusion parameters are presented. 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 variational iteration 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

Ultramicroelectrodes are powerful tools for understanding the mechanism, behavior of an electrochemical reaction and kinetics of fast reactions. Ultramicroelectrodes, having at least one dimension on the order of micrometers, offer a number of advantages in electrochemical measurement compared to traditional macroelectrodes of millimeter dimensions [1]. Ultramicroelectrodes are of small sizes. These advantages include enhanced current density, small cell time constants and reduced ohmic drop, etc. Ultramicroelectrode is also used in scanning tunneling microscopy, atomic force microscopy and scanning electrochemical microscopy for electrochemical investigations [2–4]. Ultramicroelectrodes exhibiting spherical or disc geometry display a time independent current response at reasonably short times which conveys both practical and theoretical advantages. Also ultramicroelectrodes have found numerous important applications in solar energy conversion and storage, molecular electronics, electrochromic display devices, corrosion protection, and electro-organic syntheses.

Polymer-modified electrodes have attracted considerable interest over the past two decades. Polymer-modified electrodes are particularly attractive for chemical sensing applications [5–8]. The operation of a polymer sensor operating under amperometric con-

ditions is simple in concept. Considerable progress has been made in recent years in the understanding of the dynamics of coupled ion, solvent and electronic transport in conducting electroactive organic thin film materials owing to the utilization of a combination of voltammetric, complex impedance, and probe beam deflection, spectroscopic and gravimetric measurements [9–12]. The properties of ultramicrodisc electrodes, which have been modified with thin electronically conducting polypyrrole films are discussed in this paper. We shall present an analysis of reaction and diffusion of a substrate within an electronically conducting polymer film deposited on a support surface of micrometers dimensions.

The theoretical analysis of mediated electron transfer at electroactive polymer films, which have been deposited, on macro-sized electrode surfaces has been presented by Alberly and Hillman [13] and by Andrieux et al. [14]. Recently Lyons et al. have extended the analysis of mediated electroanalysis by considering substrate diffusion, Michaelis–Menten rate equation, electromigration, sensing catalysis and charge percolation and chemical reaction [15–21]. Rebouillat et al. [22] derived the expression of concentration and current for six limiting cases only. However, to the best of author's knowledge, no general analytical results of substrate and mediator concentrations and current for all values of reaction/diffusion parameters  $\gamma_s$  and  $\gamma_E$  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  $\gamma_s$  and  $\gamma_E$  using variational iteration method.

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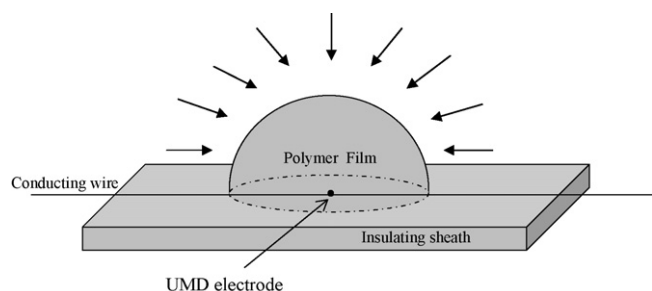


Fig. 1. Schematic representations of the geometry adopted by the polymer coated microelectrode.

## 2. Assumption and formulation of the boundary value problem

The system of coupled non-linear reaction/diffusion equations along with initial and boundary conditions are not readily solved using standard analytical methods, because they have non-linear chemical reaction terms. Hence approximate solutions have to be obtained. The assumption and physical description of the problem have been fully described in Rebouillat et al. [22] and so we only present a brief summary here for completeness. The possible rate-determining processes to be considered when analyzing the process of a polymer based mediator microstructure are: (i) substrate diffusion in the Nernst diffusion layer adjacent to the film–solution interface; (ii) substrate partitioning and diffusion within the polymer matrix characterized by a diffusion coefficient  $D_s$ ; (iii) electron percolation through the film characterized by a diffusion coefficient  $D_E$ ; and (iv) chemical reaction (usually bimolecular but can also be of Michaelis–Menten form in which a substrate–mediator complex is formed which subsequently decomposes to form products) between the immobilized mediator/catalyst species and substrate in a specific reaction zone within the film [22].

We can assume that substrate diffusion in the solution region next to the microelectrode will be rapid. We suggest that a conducting polymer film adopts a hemispherical geometry with minimal spillover, when it is electrodeposited on an ultramicrodisc surface. The microelectrode as described in this case is an electrodeposited polymer hemisphere coated on a disk electrode (cf. Fig. 1). Fig. 1 shows a hemispherical polymer sitting on a plane with a line within the insulating plane that represents a conducting wire that emerges at the origin of the hemisphere. Transport within the hemisphere is based on spherical diffusion as described by Eqs. (5a) and (5b) and  $x$  is the dimensionless radial distance emanating from the origin of the polymer hemisphere. Transport in the conducting polymer is spherical because the underlying electrode is a point source (disk electrode is infinitely small) at the origin of the hemisphere. We also treat that the diffusion of substrate within the thin film will be spherical and that the chemical reaction between substrate and mediator species will be bimolecular. We also consider that the deposited film as a homogeneous medium. We assume that the substrate partitions into the layer with a partition coefficient  $\kappa$  and that  $D_s$  and  $D_E$  represent the substrate and electron diffusion coefficient, respectively. The reaction mechanism model is shown in Fig. 2 [13]. This is the general model for this processes taking place. In this type of situation the coupled reaction diffusion equations for steady-state have the following forms [22].

$$D_E \frac{d^2 b}{dr^2} + \frac{2D_E}{r} \frac{db}{dr} - ksb = 0 \quad (1a)$$

$$D_s \frac{d^2 s}{dr^2} + \frac{2D_s}{r} \frac{ds}{dr} - ksb = 0 \quad (1b)$$

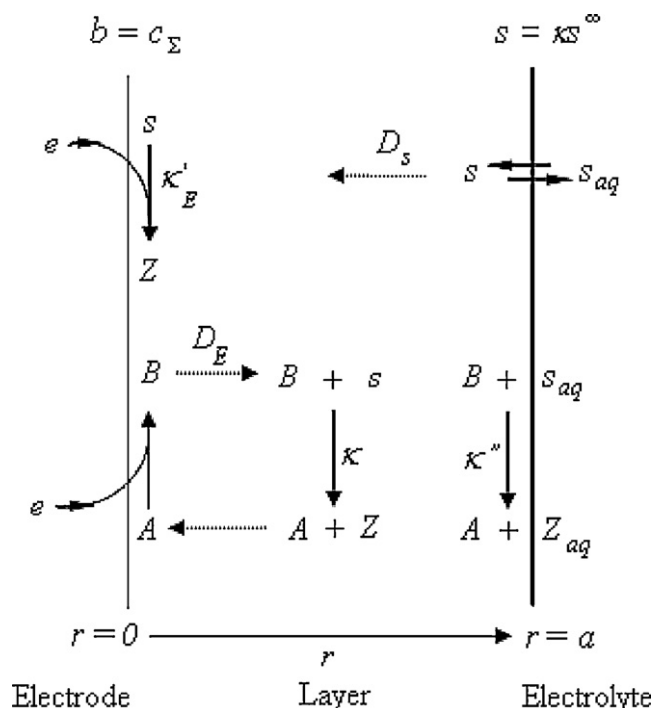


Fig. 2. Model and notation for a modified electrode.

where  $b$  denotes the concentration of oxidized mediator and  $s$  denotes the concentration of substrate species within the film.  $k$  is the bimolecular rate constant for the mediator–substrate reaction. Let  $r$  denotes the radial variable. The boundary conditions may be presented as follows:

$$r = 0 \quad b = c_\Sigma; \quad \frac{ds}{dr} = 0 \quad (2a)$$

$$r = a \quad \frac{db}{dr} = 0; \quad s = ks^\infty \quad (2b)$$

where  $c_\Sigma = s + b$  denotes the total concentration of reduced and oxidized mediator species,  $a$  is the radius of the electrode and  $s^\infty$  represents the bulk concentration of the substrate species in solution. The net current  $I$  is given by

$$I = \frac{i}{nFA} = -D_E \left( \frac{db}{dr} \right)_{r=0} = D_s \left( \frac{ds}{dr} \right)_{r=a} \quad (3)$$

where  $A$  denotes area of the hemispherical electrode,  $F$  denotes the Faraday constant and  $n$  denotes the charge number of the electrode reaction. We make the non-linear PDE outlined in Eqs. (1a) and (1b) dimensionless by introducing the following parameters:

$$u = \frac{s}{ks^\infty}; \quad v = \frac{b}{c_\Sigma}; \quad x = \frac{r}{a}; \quad \gamma_E = \frac{kks^\infty a^2}{D_E} = \frac{f_R}{f_E} = \frac{\lambda}{\rho\sigma^2}; \quad \gamma_s = \frac{kc_\Sigma a^2}{D_s} = \frac{f_R}{f_s} = \frac{\lambda}{\sigma^2} \quad (4)$$

where  $f_i$  denotes the relevant flux factor ( $R$ ,  $S$  and  $E$  denoting rate-determining bimolecular chemical reaction, substrate transport in the polymer matrix and charge percolation, respectively [26]). A pair of reaction/diffusion parameters  $\gamma_E$  and  $\gamma_s$  are introduced which serve to quantify the ratio of the rates of chemical reaction (defined via the bimolecular rate constant  $k$ ) to that of charge percolation (defined by the diffusion coefficient for the diffusion-like propagation of electrons in the film  $D_E$ ) or the ratio of chemical reaction to the rate of substrate diffusion in the layer (defined by substrate diffusion coefficient  $D_s$ ). We have also used characteristic parameters  $\sigma$ ,  $\rho$  and  $\lambda$  introduced many years ago by Andrieux et

**Table 1**

Numerical values of  $l$  and  $m$  for various values of  $\gamma_E$  and  $\gamma_S$  calculated using Eqs. (9a) and (9c).

| Parameter | $\gamma_E = 0.1$ |                |                |                 | $\gamma_E = 1$   |                |                |                 | $\gamma_E = 5$   |                |                |                 | $\gamma_E = 10$  |                |                |                 |
|-----------|------------------|----------------|----------------|-----------------|------------------|----------------|----------------|-----------------|------------------|----------------|----------------|-----------------|------------------|----------------|----------------|-----------------|
|           | $\gamma_S = 0.1$ | $\gamma_S = 1$ | $\gamma_S = 5$ | $\gamma_S = 10$ | $\gamma_S = 0.1$ | $\gamma_S = 1$ | $\gamma_S = 5$ | $\gamma_S = 10$ | $\gamma_S = 0.1$ | $\gamma_S = 1$ | $\gamma_S = 5$ | $\gamma_S = 10$ | $\gamma_S = 0.1$ | $\gamma_S = 1$ | $\gamma_S = 5$ | $\gamma_S = 10$ |
| $l$       | 0.9841           | 0.8519         | 0.4292         | 0.1129          | 0.9880           | 0.8868         | 0.7185         | 0.2614          | 0.9933           | 0.9351         | 0.7185         | 0.5170          | 0.9949           | 0.9507         | 0.7809         | 0.6154          |
| $m$       | 0.0476           | 0.0476         | 0.0476         | 0.0476          | 0.3333           | 0.3333         | 0.3333         | 0.3333          | 0.7143           | 0.7143         | 0.7143         | 0.7143          | 0.8333           | 0.8333         | 0.8333         | 0.8333          |

al. [27]. The current is a function of only these three independent dimensionless parameters. The parameter  $\sigma$  can be taken as

$$\sigma = \frac{\kappa D_s \delta}{D_s L} = \frac{f_s}{f_D} \quad (4a)$$

and compares the substrate diffusion in the film versus substrate diffusion in the solution. The parameter  $\rho$  is given by

$$\rho = \frac{D_E c_\Sigma}{\kappa D_s s^\infty} = \frac{f_E}{f_s} \quad (4b)$$

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

$$\lambda = \frac{\kappa^2 \kappa c_\Sigma D_s \delta^2}{D_s^2} = \frac{f_R f_s}{f_D^2} \quad (4c)$$

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

$$\gamma_s = \frac{\kappa c_\Sigma a^2}{D_s} = \frac{\lambda}{\sigma^2} \quad (4d)$$

represents the catalytic reaction versus substrate diffusion in the film and

$$\gamma_E = \frac{\kappa c_\Sigma^\infty a^2}{D_E} = \frac{\lambda}{\rho \sigma^2} \quad (4e)$$

represents the catalytic reaction versus electron diffusion in the film. The normalized forms of the coupled reaction/diffusion Eqs. (1a) and (1b) are

$$\frac{d^2 u}{dx^2} + \frac{2}{x} \frac{du}{dx} - \gamma_s uv = 0 \quad (5a)$$

$$\frac{d^2 v}{dx^2} + \frac{2}{x} \frac{dv}{dx} - \gamma_E uv = 0 \quad (5b)$$

where  $\gamma_s$  and  $\gamma_E$  are defined in Eqs. (4d) and (4e). Now the boundary conditions are

$$x = 0; \quad v = 1; \quad \frac{du}{dx} = 0 \quad (6a)$$

$$x = 1; \quad \frac{dv}{dx} = 0; \quad u = 1 \quad (6b)$$

The normalized current is then given by

$$\psi = \frac{ia}{nFAD_E c_\Sigma} = -\left(\frac{dv}{dx}\right)_{x=0} \quad (7a)$$

or

$$\psi = \frac{ia}{nFAD_s \kappa s^\infty} = \left(\frac{du}{dx}\right)_{x=1} \quad (7b)$$

The set of expressions presented in Eqs. (5a)–(7b) define the boundary value problem. The variational iteration method [24] is used to give approximate analytical solutions of coupled non-linear reaction/diffusion Eqs. (5a) and (5b). Using variational iteration method (see Appendix A) the approximate solutions of Eqs. (5a) and (5b) are

$$u(x) = l + \frac{x^2}{4}(2l - 2 + l\gamma_s) - \frac{x^3}{3}lm\gamma_s + \frac{x^4}{8}(1 - l + lm)\gamma_s + \frac{x^5}{5}(l - 1)\gamma_s m + \frac{x^6}{12}m\gamma_s(1 - l) \quad (8a)$$

**Table 2**

Numerical values of  $l$  and  $m$  for limiting case values of  $\gamma_E$  and  $\gamma_S$  calculated using Eqs. (9a) and (9c).

| Kinetic cases  | Limiting cases   | $l$  | $m$ |
|----------------|--|------|-----|
| ER             | $\gamma_E \rightarrow \infty, \gamma_S \rightarrow 0$      | 1    | 1   |
| R              | $\gamma_E \rightarrow 0, \gamma_S \rightarrow 0$           | 1    | 0   |
| SR             | $\gamma_E \rightarrow 0, \gamma_S \rightarrow \infty$      | 1    | 0   |
| E, S and S + E | $\gamma_E \rightarrow \infty, \gamma_S \rightarrow \infty$ | 0.25 | 1   |

$$v(x) = 1 + \frac{x^2}{4}(l\gamma_E - 2m) - \frac{x^3}{3}lm\gamma_E + \frac{x^4}{8}(1 - l + lm)\gamma_E + \frac{x^5}{5}(l - 1)\gamma_E m + \frac{x^6}{12}m\gamma_E(1 - l) \quad (8b)$$

where

$$l = \frac{(360 - \gamma_S \gamma_E - 30\gamma_S + 180\gamma_E)}{(360 + 4\gamma_S \gamma_E + 30\gamma_S + 180\gamma_E)} \quad (9a)$$

$$= \frac{[360 - \{(\lambda/\sigma^2)^2/\rho\} - 30(\lambda/\sigma^2) + \{180(\lambda/\sigma^2)/\rho\}]}{[360 + \{4(\lambda/\sigma^2)^2/\rho\} + 30(\lambda/\sigma^2) + \{180(\lambda/\sigma^2)/\rho\}]} \quad (9b)$$

and

$$m = \frac{\gamma_E}{\gamma_E + 2} = \frac{(\lambda/\sigma^2 \rho)}{(\lambda/\sigma^2 \rho) + 2} \quad (9c)$$

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

$$\psi = \left(\frac{du}{dx}\right)_{x=1} = |l - 1| + \frac{1}{2}(1 - m)\gamma_s \quad (10a)$$

$$= \frac{5\{(\lambda/\sigma^2)^2/\rho\} + 60(\lambda/\sigma^2)}{[360 + 4\{(\lambda/\sigma^2)^2/\rho\} + 30(\lambda/\sigma^2) + \{180(\lambda/\sigma^2)/\rho\}]} + \frac{(\lambda/\sigma^2)}{\{(\lambda/\sigma^2 \rho) + 2\}} \quad (10b)$$

In the limiting cases, the above equation becomes

$$\psi = \frac{2(\lambda/\sigma^2)}{3} - \frac{(1 + (23/\rho))(\lambda/\sigma^2)^2}{72} \quad \text{when } (\lambda/\sigma^2) \rightarrow 0 \quad (10c)$$

$$= \frac{5}{4} + \rho - \frac{(16\rho^2 - 45\rho + 450)}{8(\lambda/\sigma^2)} \quad \text{when } (\lambda/\sigma^2) \rightarrow \infty \quad (10d)$$

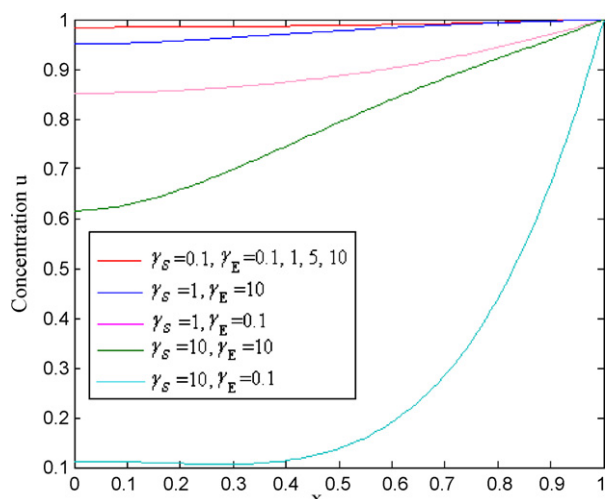
When  $\gamma_s = \gamma_E$  and the parameter  $\rho = 1$ , the current  $\psi$  becomes

$$\psi = \frac{2(\lambda/\sigma^2)}{3} - \frac{(\lambda/\sigma^2)^2}{3} \quad \text{when } (\lambda/\sigma^2) \rightarrow 0 \quad (10e)$$

$$= \frac{9}{4} - \frac{421}{8(\lambda/\sigma^2)} \quad \text{when } (\lambda/\sigma^2) \rightarrow \infty \quad (10f)$$

### 3. Discussion

Eqs. (8a) and (8b) represent the new approximate analytical expressions for the substrate and mediator concentration profiles for all values of  $\gamma_s$  and  $\gamma_E$ . The numerical values of  $l$  and  $m$  for various values of  $\gamma_s$  and  $\gamma_E$  are given in Tables 1 and 2. In Fig. 3, we



**Fig. 3.** Normalized substrate concentration  $u$  at a polymer microelectrode. The concentrations were computed using Eq. (8a) for various values of the reaction/diffusion parameters  $\gamma_E$  and  $\gamma_s$ .

present the series of normalized concentration profile for a substrate  $u$  as a function of the reaction/diffusion parameters  $\gamma_s$  and  $\gamma_E$ . From this figure, it is inferred that, the value of  $u \approx 1$  for all values of  $\gamma_E$  and  $\gamma_s \leq 1$ . Also the value of  $u$  is small when  $\gamma_E$  and  $\gamma_s \geq 10$  and  $x \leq 0.5$ . Fig. 4 represents concentration  $v$  for all values of  $\gamma_E$  and  $\gamma_s$ . From Fig. 4(a) and (b), it is inferred that the mediator concentration  $v \approx 1$  when both  $\gamma_E$  and  $\gamma_s \leq 1$ . From Fig. 4(a)–(d), the concentration  $v(x)$  increases when  $\gamma_E$  increases or  $\gamma_s$  decreases. The kinetic case diagram for the concentration of  $u$  and  $v$  for the six limiting kinetic situations is given in Fig. 5. The diagram consist of a plot of  $\log \gamma_s$  versus  $\log \gamma_E$ , where  $\log \gamma_E$  serves as an abscissa and  $\log \gamma_s$  serves as the ordinate. The case diagram (Fig. 5) is a schematic representation of the substrate and mediator concentration profiles for each of the limiting situation. From this case diagram and Table 2, the following results are obtained. When  $\gamma_E$  and  $\gamma_s$  are small (for the case R),  $u = v = 1$ . When  $\gamma_E$  is small (for the cases SR and R),  $v = 1$  for all values of  $\gamma_s$ . When  $\gamma_s$  is small (for the case R and ER),  $u = 1$  for all values of  $\gamma_E$  (Table 3).

Fig. 6(a) represents the normalized current response for various values of  $\gamma_E$  and  $\gamma_s$ . Fig. 6(b) shows the dimensionless steady-state current  $\psi$  for various values of the parameter  $\lambda/\sigma^2$  (for all kinetic cases) for some fixed values of  $\rho$  (i.e.)  $\rho = 0.1, 1$  and  $10$ . From this figure, it is inferred that the current reaches the steady-state value for all values of  $\rho$  when  $\lambda/\sigma^2 \geq 100$ . Fig. 6(c) shows the dimensionless steady-state current  $\psi$  for small values of the parameter  $\lambda/\sigma^2$  (for the cases R, S+E, R+E) for  $\rho = 0.1, 1$  and  $10$ . From this figure,

**Table 3**

Numerical values of  $l$  and  $m$  for various values of  $\alpha$ ,  $\gamma_E$  and  $\gamma_s$  calculated using Eqs. (31a) and (31b).

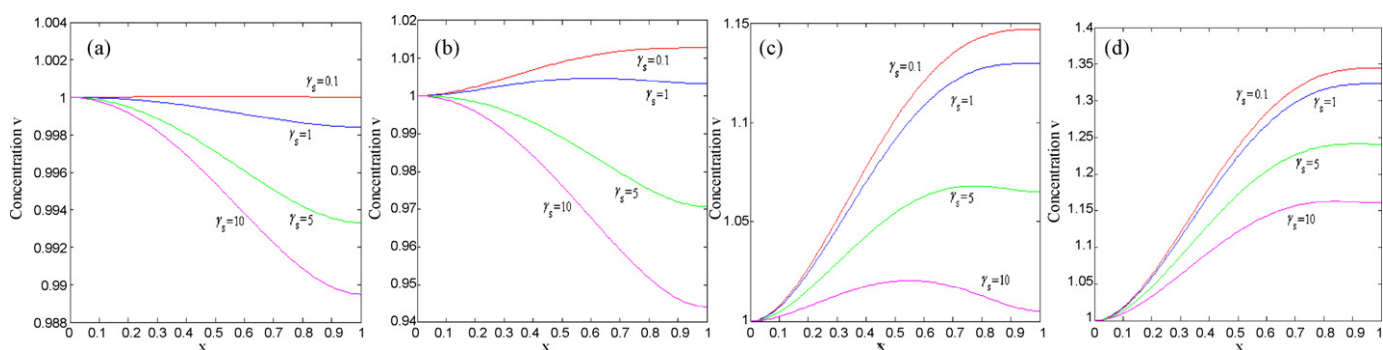
| $\alpha$ | $\gamma_s$ | $\gamma_E$ | $l$     | $m$    |
|----------|------------|------------|---------|--------|
| 0.1      | 0.1        | 0.1        | 0.9711  | 0.0435 |
| 0.1      | 0.1        | 1.0        | 0.9764  | 0.3125 |
| 0.1      | 0.1        | 10.0       | 0.9864  | 0.8197 |
| 0.1      | 1.0        | 0.1        | 0.7519  | 0.0435 |
| 0.1      | 1.0        | 1.0        | 0.7928  | 0.3125 |
| 0.1      | 1.0        | 10.0       | 0.8757  | 0.8197 |
| 0.1      | 10.0       | 0.1        | −0.0056 | 0.0435 |
| 0.1      | 10.0       | 1.0        | 0.0884  | 0.3125 |
| 0.1      | 10.0       | 10.0       | 0.3390  | 0.8197 |
| 1        | 0.1        | 0.1        | 0.9837  | 0.0244 |
| 1        | 0.1        | 1.0        | 0.9856  | 0.2000 |
| 1        | 0.1        | 10.0       | 0.9913  | 0.7143 |
| 1        | 1.0        | 0.1        | 0.8470  | 0.0244 |
| 1        | 1.0        | 1.0        | 0.8644  | 0.2000 |
| 1        | 1.0        | 10.0       | 0.9166  | 0.7143 |
| 1        | 10.0       | 0.1        | 0.1269  | 0.0244 |
| 1        | 10.0       | 1.0        | 0.1916  | 0.2000 |
| 1        | 10.0       | 10.0       | 0.4302  | 0.7143 |
| 10       | 0.1        | 0.1        | 0.9970  | 0.0045 |
| 10       | 0.1        | 1.0        | 0.9971  | 0.0435 |
| 10       | 0.1        | 10.0       | 0.9976  | 0.3125 |
| 10       | 1.0        | 0.1        | 0.9700  | 0.0045 |
| 10       | 1.0        | 1.0        | 0.9708  | 0.0435 |
| 10       | 1.0        | 10.0       | 0.9762  | 0.3125 |
| 10       | 10.0       | 0.1        | 0.7186  | 0.0045 |
| 10       | 10.0       | 1.0        | 0.7256  | 0.0435 |
| 10       | 10.0       | 10.0       | 0.7747  | 0.3125 |

when  $\rho \geq 1$ ,  $\psi = (2/3)(\lambda/\sigma^2)$ . Here the current is linearly proportional to the parameter  $\lambda/\sigma^2$ . Fig. 6(d) shows the dimensionless steady-state current  $\psi$  for large values of the parameter  $\lambda/\sigma^2$  (for the cases ER, S, R+S, SR+E and SR) for  $\rho = 0.1, 1$  and  $10$ . From this figure it is inferred that the current reaches the steady-state when  $\lambda/\sigma^2 \geq 100$ .

From Fig. 6(b) it is inferred that the current reaches the constant value when  $\lambda/\sigma^2 \geq 20$  and  $\rho \leq 1$ . Also it reaches the constant value when  $\lambda/\sigma^2 > 100$  and  $\rho > 1$ . From Fig. 6(c) the current is linear for all values of  $\rho$  when  $\lambda/\sigma^2$  is small. From Fig. 6(d) and Eq. (10d), it is inferred that the approximate expression of current  $\psi = (5/4) + \rho$  when  $\lambda/\sigma^2$  is large. We also include in the case diagram a schematic representation of the current for each of the kinetically limiting situations (cf. Fig. 7).

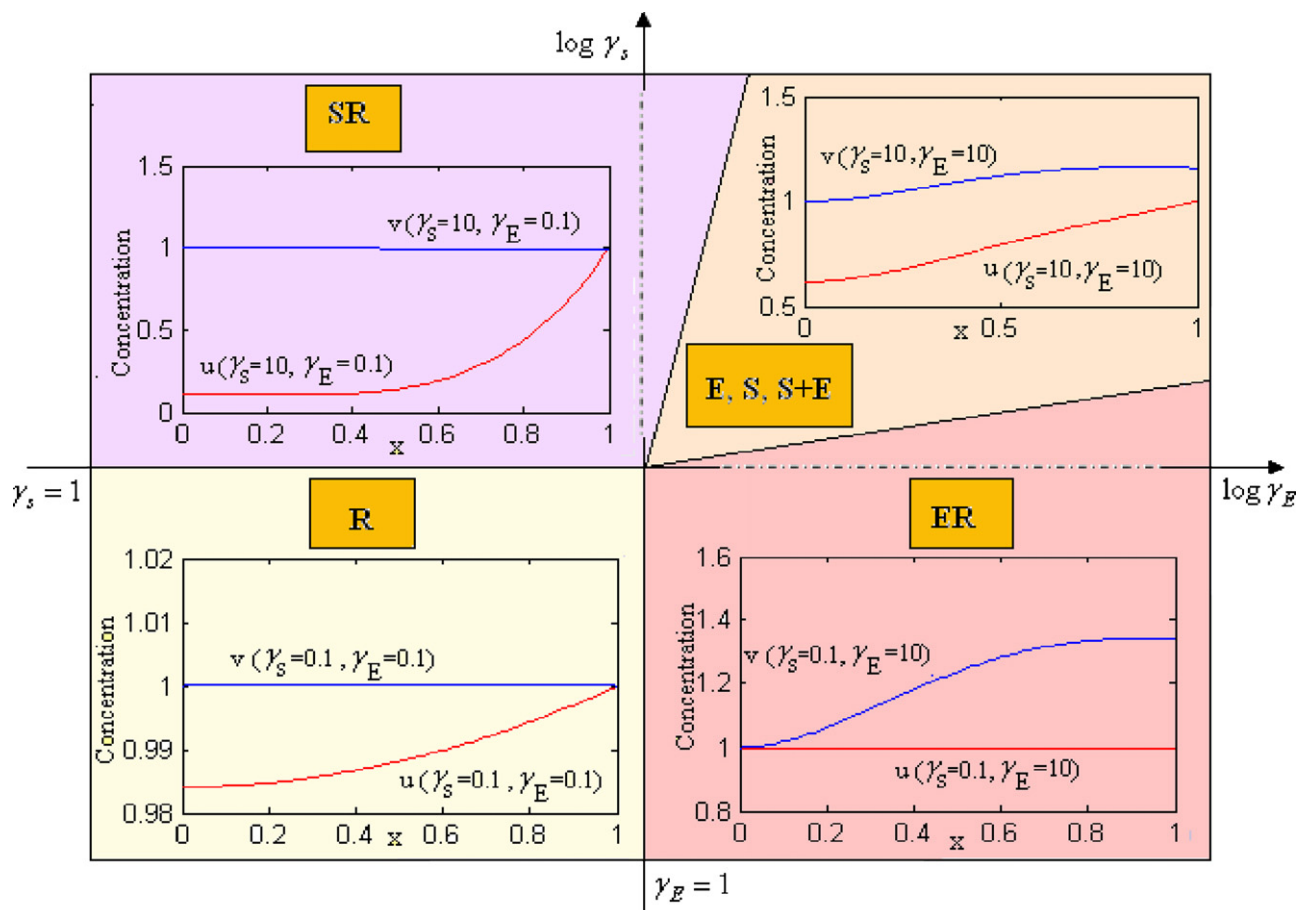
#### 4. Comparison with Rebouillat et al.'s [22] work

Rebouillat et al. [22] derived the expressions of substrate and mediator concentrations for the limiting cases only (e.g. R+S, R+E).



**Fig. 4.** Normalized mediator concentration  $v$  at a polymer microelectrode. The concentrations were computed using Eq. (8b) for various values of the reaction/diffusion parameters  $\gamma_E$  and  $\gamma_s$ . (a)  $\gamma_E = 0.1$ ; (b)  $\gamma_E = 1$ ; (c)  $\gamma_E = 5$ ; (d)  $\gamma_E = 10$ .





**Fig. 5.** The kinetic case diagram for the six major limiting kinetic situations. The diagram consist of a plot of  $\log \gamma_s$  versus  $\log \gamma_E$ , where  $\log \gamma_E$  serves as an abscissa and  $\log \gamma_s$  serves as the ordinate. Included in the case diagram is a schematic representation of the mediator and substrate concentration profiles for each of the limiting situations.

We have derived the general analytical expressions for concentration of mediator and substrate for all cases.

#### 4.1. Electron percolation through polymer layer more rapid than substrate transport

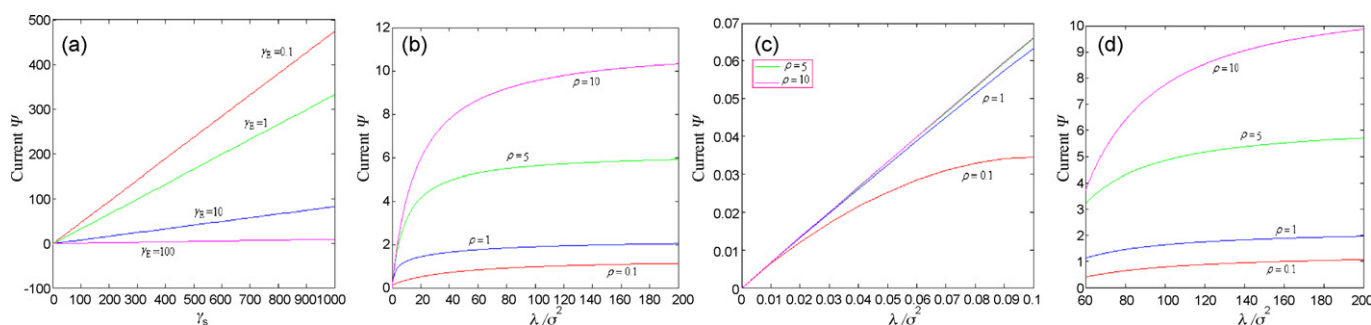
When  $\gamma_E/\gamma_s \ll 1$  or  $\kappa D_s s^\infty \ll D_E c_\Sigma$  or  $\rho \rightarrow \infty$ , the electrons percolate across the layer more readily than substrate. Since charge percolation of electrons along the polymer chains is assumed to be rapid and provided that chemical reaction between mediator and substrate species is too fast, then very little mediator

species will be consumed across the polymer layer and Rebouillat et al. [22] assumed that  $\nu = 1$  and so Eq. (5a) reduced to

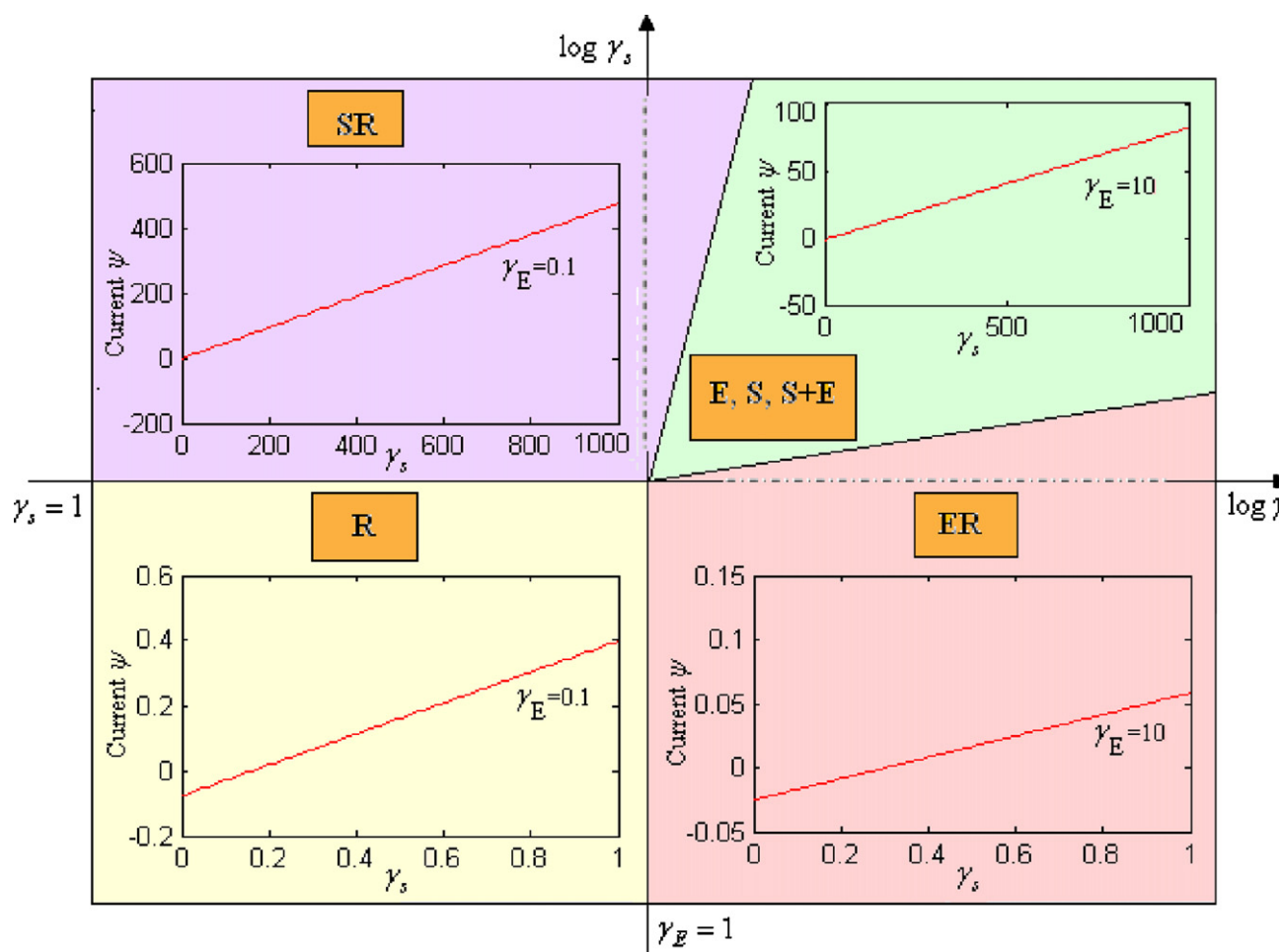
$$\frac{d^2 u}{dx^2} + \frac{2}{x} \frac{du}{dx} - \gamma_s u = 0 \quad (11)$$

This differential equation represents the  $R+S$  case. From the above Eq. (11) Rebouillat et al. [22] obtained the following expressions for the substrate concentration and normalized steady-state current.

$$u(x) = \frac{\sinh(\sqrt{\gamma_s} x)}{x \sinh(\sqrt{\gamma_s})} \quad (12)$$



**Fig. 6.** (a) Variation of normalized steady-state current response  $\psi$  for various values of  $\gamma_s$  and  $\gamma_E$ . The curves were computed using Eq. (10a). (b–d) Variation of normalized steady-state current  $\psi$  for all values of  $\lambda/\sigma^2$  by using Eq. (10b). (c) Current  $\psi$  versus  $\lambda/\sigma^2$  when  $(\lambda/\sigma^2) \rightarrow 0$  computed using Eq. (10c). (d) Current  $\psi$  versus  $\lambda/\sigma^2$  when  $(\lambda/\sigma^2) \rightarrow \infty$  computed using Eq. (10d).



**Fig. 7.** The kinetic case diagram of current for the six limiting kinetic situations. The diagram consists of a plot of  $\log \gamma_s$  versus  $\log \gamma_E$ , where  $\log \gamma_E$  serves as an abscissa and  $\log \gamma_s$  serves as the ordinate. Included in the case diagram is a schematic representation of the current profiles for each of the limiting situations.

$$\psi = \left( \frac{du}{dx} \right)_{x=1} = \sqrt{\gamma_s} (\coth \sqrt{\gamma_s} - 1) \quad (13)$$

The above equations represent the normalized concentration of substrate and current as a function of reaction/diffusion parameter  $\gamma_s$ . But we have presented the concentration of substrate and mediator and current as a function of reaction/diffusion parameters  $\gamma_s$  and  $\gamma_E$  (Eqs. (8a), (8b) and (9a)). Using variational iteration method, we obtained the substrate concentration  $u(x)$  in the first iteration (Eq. (14a)),

$$u(x) \approx u_1(x) = H - Hx + (1 - H)x^2 - (1 - H)x^3 + \frac{H \sinh(\sqrt{\gamma_s}x)}{\sqrt{\gamma_s}} \quad (14a)$$

To improve the accuracy of the result, we can also find the second iteration (Eq. (14b)),

$$u(x) \approx u_2(x) = H - 2Hx + x^2 - 2(1 - H)x^3 + (1 - H)x^4 + \frac{H(2 - x) \sinh(\sqrt{\gamma_s}x)}{\sqrt{\gamma_s}} \quad (14b)$$

where

$$H = \frac{\sqrt{\gamma_s}}{\sinh(\sqrt{\gamma_s})} \quad (15)$$

From our Eq. (8b), when  $\gamma_E \rightarrow 0$  we obtained the mediator concentration  $v$  as follows

$$v(x) = 1 \quad (16)$$

In this case, the normalized current (Eq. (7b)) using Eq. (14a) or (14b) can be approximated as:

$$\psi = \left( \frac{du}{dx} \right)_{x=1} = \frac{H[\sqrt{\gamma_s} \cosh(\sqrt{\gamma_s}) - \sinh(\sqrt{\gamma_s})]}{\sqrt{\gamma_s}} \quad (17a)$$

$$= \sqrt{\gamma_s} \coth(\sqrt{\gamma_s}) - 1 \quad (17b)$$

The equation of the normalized current (Eq. (17b)) derived by us is identically equal to Rebouillat et al.'s [22] result (Eq. (13)). Comparison of our normalized substrate concentration  $u$  and current with Rebouillat et al.'s [22] work at a polymer microelectrode is illustrated in Fig. 8(a) and (b). This will be discussed further in Section 5.

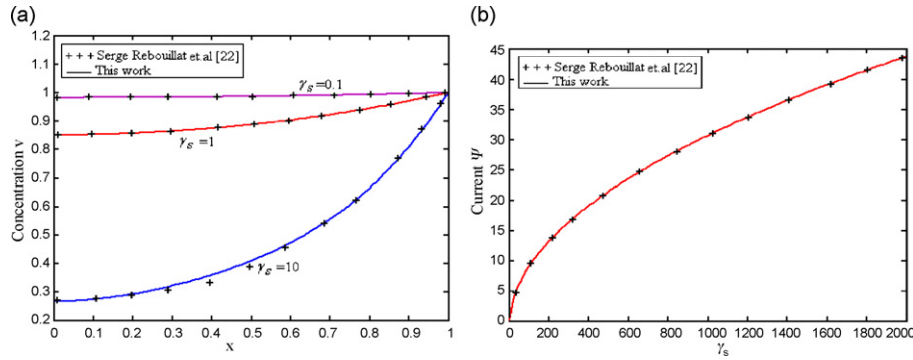
#### 4.2. Substrate diffusion through the polymer layer more rapid than electron diffusion

When  $\gamma_E/\gamma_s \gg 1$  or  $\kappa D_s s^\infty \gg D_{EC} \Sigma$  or  $\rho \rightarrow 0$ , substrate diffusion through the polymer layer more rapid than electron diffusion. Since substrate diffusion through the layer is fast, Rebouillat et al. [22] assumed that little substrate is consumed on passage across the layer and they assumed that  $u = 1$  and so Eq. (5b) reduced to

$$\frac{d^2 v}{dx^2} + \frac{2}{x} \frac{dv}{dx} - \gamma_E v = 0 \quad (18)$$

This differential equation represents R+E case. By solving the above Eq. (18), Rebouillat et al. [22] obtained the expression for the





**Fig. 8.** (a) Comparison of normalized substrate concentration  $u$  with Rebouillat et al.'s [22] works at a polymer microelectrode. The concentrations were computed using Eq. (12) (Rebouillat et al. [22]) and Eqs. (14a) and (14b) (this work) for various values of the reaction/diffusion parameter  $\gamma_s$ . (b) Normalized steady-state current response  $\psi$  for various values of  $\gamma_E$ . The curves were computed using Eqs. (13), (17a) and (17b).

mediator concentration for this case as follows.

$$v(x) = \frac{\exp(-\sqrt{\gamma_E})}{\sqrt{\gamma_E} F(\gamma_E) x} \{ f(\gamma_E) \exp[-\sqrt{\gamma_E}(1-x)] - \exp[\sqrt{\gamma_E}(1-x)] \} \quad (19)$$

where

$$F(\gamma_E) = 1 + f(\gamma_E) \exp(-2\sqrt{\gamma_E}) \quad (20)$$

and

$$f(\gamma_E) = \frac{(1 + \sqrt{\gamma_E})}{(1 - \sqrt{\gamma_E})} \quad (21)$$

In this case, the normalized current [22] can be approximated as:

$$\psi = -\left(\frac{dv}{dx}\right)_{x=0} = \sqrt{\gamma_E} G(\gamma_E) \quad (22)$$

where

$$G(\gamma_E) = \frac{[1 - f(\sqrt{\gamma_E}) \exp(-2\sqrt{\gamma_E})]}{[1 + f(\sqrt{\gamma_E}) \exp(-2\sqrt{\gamma_E})]} \quad (23)$$

The above equations represent the normalized concentration and current as a function of reaction/diffusion parameter  $\gamma_E$ . But we have derived the concentration of mediator and current as a function of reaction/diffusion parameters  $\gamma_s$  and  $\gamma_E$ . When  $\gamma_s \rightarrow 0$ , our analytical expressions reduce to

$$u(x) = 1 \quad (24)$$

$$v(x) = 1 + \frac{x^2}{4}(l\gamma_E - 2m) - \frac{x^3}{3}lm\gamma_E + \frac{x^4}{8}(1 - l + lm)\gamma_E + \frac{x^5}{5}(l - 1)\gamma_E m + \frac{x^6}{12}m\gamma_E(1 - l) \quad (25)$$

where

$$l = \frac{360 - \rho\gamma_E^2 - 30\rho\gamma_E + 180\gamma_E}{360 + 4\rho\gamma_E^2 + 30\rho\gamma_E + 180\gamma_E} \text{ and } m = \frac{\gamma_E}{\gamma_E + 2} \quad (26)$$

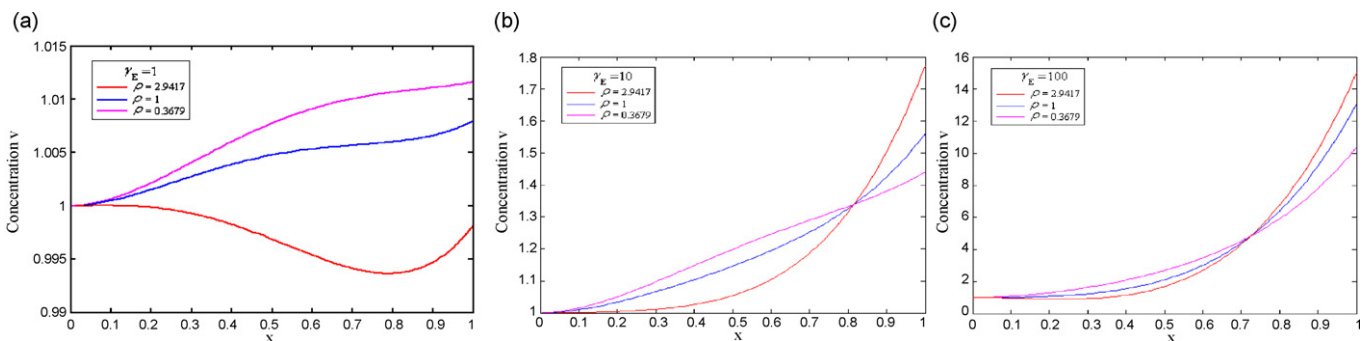
In this case the normalized current (Eq. (10a)) can be approximated as:

$$\psi = -\left(\frac{dv}{dx}\right)_{x=0} = |1 - l| + \frac{\rho\gamma_E}{2}(1 - m) \quad (27)$$

## 5. Comparison of results

Fig. 8(a) represents the comparison of normalized substrate concentration  $u$  of this work and Rebouillat et al.'s [22] work. It is inferred that the small values of  $\gamma_s$ , both works give the same result. When  $\gamma_s$  increases, there is a little difference between the two works. The average relative error of substrate concentration  $u$  between Eq. (14a) (first iteration) and Rebouillat et al.'s [22] analytical result (Eq. (12)) are 0% when  $\gamma_s = 0.1$ , 0.0396% when  $\gamma_s = 1$  and 3.1770% when  $\gamma_s = 10$  (refer Table 4A and Fig. 8(a)) whereas the average relative error of substrate concentration  $u$  between Eq. (14b) (second iteration) and Rebouillat et al.'s [22] analytical result (Eq. (12)) are 0% when  $\gamma_s = 0.1$ , 0.0195% when  $\gamma_s = 1$  and 1.6798% when  $\gamma_s = 10$  (refer Table 4B and Fig. 8(b)). The maximum error happens when  $\gamma_s = 10$ . Fig. 8(b) represents the comparison of normalized steady-state current  $\psi$  (for various values of  $\gamma_E$ ) of this work and Rebouillat et al.'s [22] work. From this figure, we observed that the value of current is equal in Rebouillat et al.'s [22] work and our Eq. (17b).

Fig. 9(a)–(c) represent the normalized mediator concentration  $v$  at a polymer microelectrode. The concentration was computed for various values of  $\gamma_E$  (1, 10 and 100). From Fig. 9(a), it is inferred that the concentration  $v$  increases when  $\rho$  decreases. When  $\gamma_E \geq 10$  and  $x \leq 0.8$ , the concentration  $v$  increases when  $\rho$  decreases. The



**Fig. 9.** Normalized mediator concentration  $v$  at a polymer microelectrode. The concentrations were computed using Eq. (25) when  $\rho = 0.3679$ , 1 and 2.9417. For the reaction diffusion parameter (a)  $\gamma_E = 1$ , (b)  $\gamma_E = 10$ , (c)  $\gamma_E = 100$ .

**Table 4A**  
Comparison of normalized substrate concentration  $u$  between Eqs. (12) and (14a) for various values of  $x$  and for some fixed values of  $\gamma_s$  [=0.1, 1, 10].

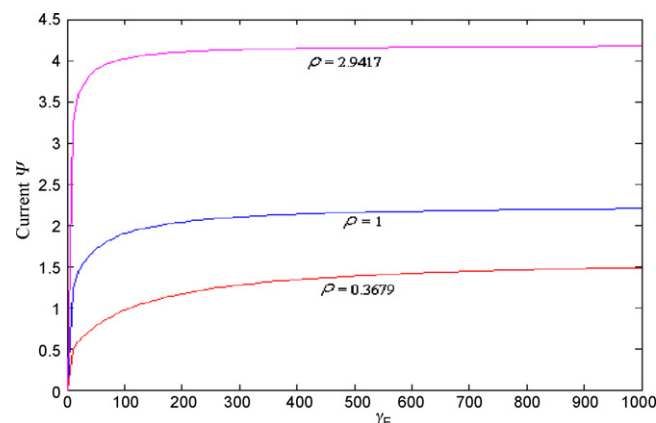
| $x$     | Concentration $u$                  |                        |  |                                    |                        |   |
|---------|------------------------------------|------------------------|--|------------------------------------|------------------------|---|
|         | $u$ (when $\gamma_s = 0.1$ )       |                        |  | $u$ (when $\gamma_s = 1$ )         |                        |   |
|         | Rebouillat et al.<br>[22] Eq. (12) | This work Eq.<br>(14a) | % of deviation<br>between Eqs. (12)<br>and (14a) | Rebouillat et al.<br>[22] Eq. (12) | This work<br>Eq. (14a) | % of deviation between<br>Eqs. (12) and (14a) |
| 0.01    | 0.9835                             | 0.9835                 | 0.0000   | 0.8509                             | 0.8509                 | 0.0000  |
| 0.10    | 0.9837                             | 0.9837                 | 0.0000   | 0.8523                             | 0.8524                 | 0.0117  |
| 0.20    | 0.9842                             | 0.9842                 | 0.0000   | 0.8566                             | 0.8568                 | 0.0233  |
| 0.30    | 0.9850                             | 0.9850                 | 0.0000   | 0.8637                             | 0.8642                 | 0.0579  |
| 0.40    | 0.9862                             | 0.9862                 | 0.0000   | 0.8738                             | 0.8744                 | 0.0686  |
| 0.50    | 0.9876                             | 0.9876                 | 0.0000   | 0.8868                             | 0.8875                 | 0.0789  |
| 0.60    | 0.9894                             | 0.9894                 | 0.0000   | 0.9029                             | 0.9036                 | 0.0775  |
| 0.70    | 0.9916                             | 0.9916                 | 0.0000   | 0.9221                             | 0.9227                 | 0.0650  |
| 0.80    | 0.9941                             | 0.9941                 | 0.0000   | 0.9446                             | 0.9450                 | 0.0423  |
| 0.90    | 0.9969                             | 0.9969                 | 0.0000   | 0.9705                             | 0.9706                 | 0.0103  |
| 1.00    | 1.0000                             | 1.0000                 | 0.0000   | 1.0000                             | 1.0000                 | 0.0000  |
| Average |                                    |                        | 0.0000   |                                    |                        | 0.0396  |

**Table 4B**  
Comparison of normalized substrate concentration  $u$  between Eqs. (12) and (14b) for various values of  $x$  and for some fixed values of  $\gamma_s$  [=0.1, 1, 10].

| $x$     | Concentration $u$                  |                        |  |                                    |                        |   |
|---------|------------------------------------|------------------------|--|------------------------------------|------------------------|---|
|         | $u$ (when $\gamma_s = 0.1$ )       |                        |  | $u$ (when $\gamma_s = 1$ )         |                        |   |
|         | Rebouillat et al.<br>[22] Eq. (12) | This work Eq.<br>(14b) | % of deviation<br>between Eqs. (12)<br>and (14b) | Rebouillat et al.<br>[22] Eq. (12) | This work<br>Eq. (14b) | % of deviation between<br>Eqs. (12) and (14b) |
| 0.01    | 0.9835                             | 0.9835                 | 0.0000   | 0.8509                             | 0.8509                 | 0.0000  |
| 0.10    | 0.9837                             | 0.9837                 | 0.0000   | 0.8523                             | 0.8524                 | 0.0117  |
| 0.20    | 0.9842                             | 0.9842                 | 0.0000   | 0.8566                             | 0.8568                 | 0.0233  |
| 0.30    | 0.9850                             | 0.9850                 | 0.0000   | 0.8637                             | 0.8640                 | 0.0347  |
| 0.40    | 0.9862                             | 0.9862                 | 0.0000   | 0.8738                             | 0.8741                 | 0.0343  |
| 0.50    | 0.9876                             | 0.9876                 | 0.0000   | 0.8868                             | 0.8872                 | 0.0451  |
| 0.60    | 0.9894                             | 0.9894                 | 0.0000   | 0.9029                             | 0.9032                 | 0.0332  |
| 0.70    | 0.9916                             | 0.9916                 | 0.0000   | 0.9221                             | 0.9223                 | 0.0217  |
| 0.80    | 0.9941                             | 0.9941                 | 0.0000   | 0.9446                             | 0.9447                 | 0.0106  |
| 0.90    | 0.9969                             | 0.9969                 | 0.0000   | 0.9705                             | 0.9705                 | 0.0000  |
| 1.00    | 1.0000                             | 1.0000                 | 0.0000   | 1.0000                             | 1.0000                 | 0.0000  |
| Average |                                    |                        | 0.0000   |                                    |                        | 0.0195  |

**Table 5**  
Normalized mediator concentration  $\nu$  by using Eqs. (19) and (25) for various values of  $x$  and some fixed values of  $\gamma_E$  [=1.01, 1.5, 10, 100].

| $x$  | Concentration $\nu$                |                                |                                    |                                |
|------|------------------------------------|--------------------------------|------------------------------------|--------------------------------|
|      | $\nu$ (when $\gamma_E = 1.01$ )    | $\nu$ (when $\gamma_E = 1.5$ ) | $\nu$ (when $\gamma_E = 10$ )      | $\nu$ (when $\gamma_E = 100$ ) |
|      | Rebouillat et al. [22]<br>Eq. (19) | This work<br>Eq. (25)          | Rebouillat et al. [22]<br>Eq. (19) | This work<br>Eq. (25)          |
| 0.01 | 104.2734                           | 1.0000                         | –1040.9530                         | 1.0000                         |
| 0.10 | 11.3807                            | 1.0007                         | –103.9674                          | 1.0014                         |
| 0.20 | 6.2748                             | 1.0026                         | –52.6544                           | 1.0048                         |
| 0.30 | 4.6151                             | 1.0049                         | –36.0772                           | 1.0093                         |
| 0.40 | 3.8203                             | 1.0074                         | –28.1950                           | 1.0141                         |
| 0.50 | 3.3743                             | 1.0097                         | –23.8045                           | 1.0184                         |
| 0.60 | 3.1053                             | 1.0116                         | –21.1754                           | 1.0220                         |
| 0.70 | 2.9402                             | 1.0129                         | –19.5700                           | 1.0245                         |
| 0.80 | 2.8423                             | 1.0137                         | –18.6232                           | 1.0261                         |
| 0.90 | 2.7917                             | 1.0141                         | –18.1354                           | 1.0267                         |
| 1.00 | 2.7766                             | 1.0141                         | –17.9903                           | 1.0268                         |
|      | Rebouillat et al. [22]<br>Eq. (19) | This work<br>Eq. (25)          | Rebouillat et al. [22]<br>Eq. (19) | This work<br>Eq. (25)          |
| 0.01 | 104.2734                           | 1.0000                         | –1040.9530                         | 1.0000                         |
| 0.10 | 11.3807                            | 1.0007                         | –103.9674                          | 1.0014                         |
| 0.20 | 6.2748                             | 1.0026                         | –52.6544                           | 1.0048                         |
| 0.30 | 4.6151                             | 1.0049                         | –36.0772                           | 1.0093                         |
| 0.40 | 3.8203                             | 1.0074                         | –28.1950                           | 1.0141                         |
| 0.50 | 3.3743                             | 1.0097                         | –23.8045                           | 1.0184                         |
| 0.60 | 3.1053                             | 1.0116                         | –21.1754                           | 1.0220                         |
| 0.70 | 2.9402                             | 1.0129                         | –19.5700                           | 1.0245                         |
| 0.80 | 2.8423                             | 1.0137                         | –18.6232                           | 1.0261                         |
| 0.90 | 2.7917                             | 1.0141                         | –18.1354                           | 1.0267                         |
| 1.00 | 2.7766                             | 1.0141                         | –17.9903                           | 1.0268                         |



**Fig. 10.** Variation of the normalized current response  $\psi$  expected for the  $R + E$  situation with reaction diffusion parameter  $\gamma_E$ . The curves were computed using Eq. (27) when  $\gamma_E$  varies from 0 to 1000 and  $\rho = 0.3679, 1$  and  $2.9417$ .

concentration  $\nu$  and the value of  $\rho$  increase when  $x \geq 0.8$ . The concentration of mediator  $\nu$  (Eq. (19)) derived by Rebouillat et al. [22] does not satisfy the boundary condition (Eq. (6a)) for all values of  $\gamma_E$  (cf. Table 5) and also their concentration  $\nu$  is negative when  $\gamma_E \geq 1.5$  and reaches zero when  $\gamma_E = 100$  and  $x = 1$ . Fig. 10 represents the normalized steady-state current response  $\psi$  (Eq. (27)) expected for  $R + E$  situation with various values of reaction/diffusion parameter  $\gamma_E$ . From this figure, it is inferred that the current increases and also the current reaches the constant value when  $\gamma_E \geq 100$ .

## 6. Elaboration of the model for more complex kinetic situations

In this section we have solved the system of coupled non-linear partial differential equations using variational iteration method. This is some extension to the theoretical model outlined in this paper. To author's knowledge, no analytical and numerical solution for this equation have been reported [22,23]. In the presented analysis we have assumed that redox conduction through the layer is rapid. This may be a sensible approximation for 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. In this type of situation the reaction diffusion equations assume the following forms [22,23]:

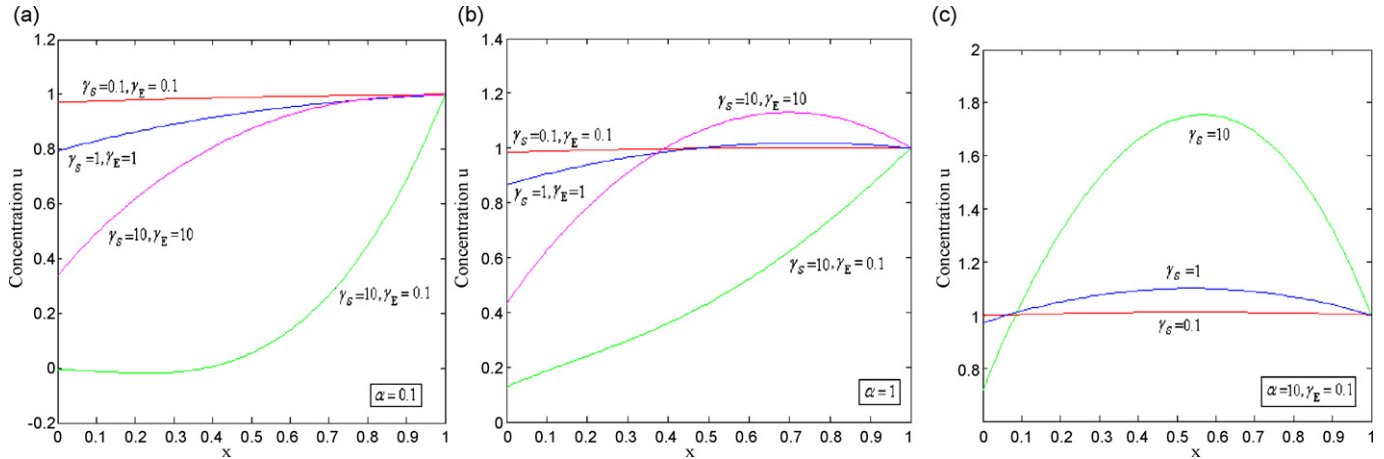
$$x \frac{d^2 u}{dx^2} + 2 \frac{du}{dx} - \frac{\gamma_s uv}{1 + \alpha u} = 0 \quad (28a)$$

$$x \frac{d^2 v}{dx^2} + 2 \frac{dv}{dx} - \frac{\gamma_E uv}{1 + \alpha u} = 0 \quad (28b)$$

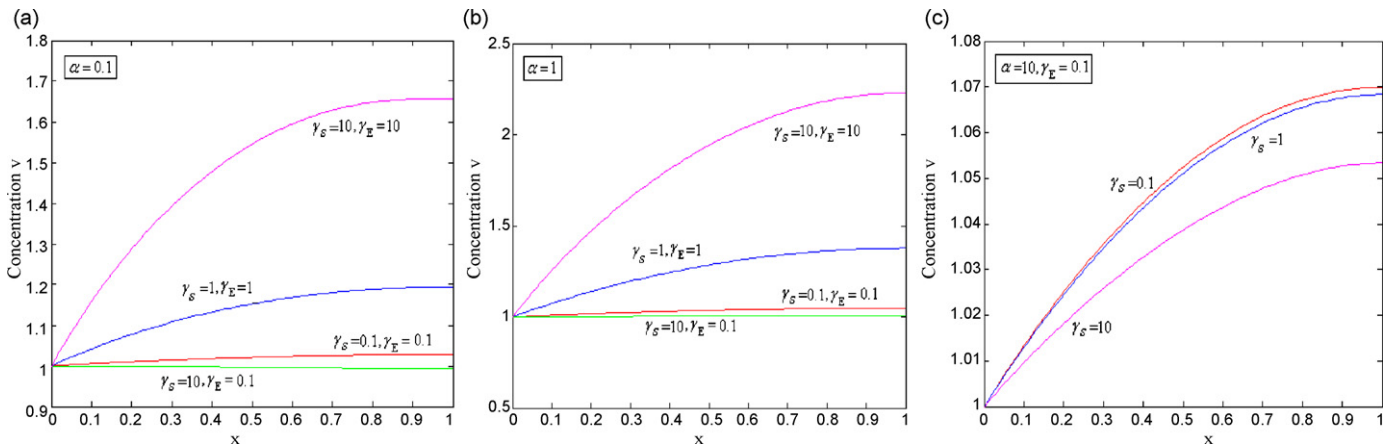
where  $u$  and  $v$  denote the dimensionless concentrations of substrate and mediator,  $\gamma_E$  and  $\gamma_s$  are reaction/diffusion parameters (cf. Eq. (4)) and  $\alpha$  denotes a saturation parameter. The latter expressions must be solved subject to the boundary conditions presented in Eqs. (6a) and (6b). Since the equations are non-linear because of the Michaelis–Menten kinetic term and are coupled, it will be problematic to obtain a fully rigorous solution [22]. However we have derived the approximate analytical solution of this problem using the variational iteration method. The boundary conditions are

$$x = 0; \quad v = 1; \quad \frac{du}{dx} = 0 \quad (29a)$$

$$x = 1; \quad \frac{dv}{dx} = 0; \quad u = 1 \quad (29b)$$



**Fig. 11.** Normalized substrate concentration  $u$  at a polymer microelectrode. The concentrations were computed using Eq. (30a) for various values of the reaction/diffusion parameters  $\gamma_E$ ,  $\gamma_s$  and  $\alpha$ .



**Fig. 12.** Normalized substrate concentration  $v$  at a polymer microelectrode. The concentrations were computed using Eq. (30b) for various values of the reaction/diffusion parameters  $\gamma_E$ ,  $\gamma_s$  and  $\alpha$ .

By using the same procedure (variational iteration method) as in the previous problem, we obtain the analytical expressions of  $u(x)$  and  $v(x)$  as follows,

$$u(x) = l + \frac{1}{2}l\gamma_s x - \frac{x^2}{2}(1 + 2l + 3\alpha l - 3l - 3\alpha l^2 + \gamma_s l m) + \frac{\gamma_s x^3}{6} \times (1 + l m - l) - \frac{x^4}{4}(3\alpha - 6\alpha l + 3\alpha l^2 - \gamma_s l m + \gamma_s m) + \frac{x^5}{10}\gamma_s(m - l m) \quad (30a)$$

$$G = -45\alpha\gamma_E - 90\alpha^2 - 90\alpha = -45\alpha(\lambda/\rho\sigma^2) - 90\alpha^2 - 90\alpha,$$

$$B = -9\gamma_E\gamma_s - 180 - 40\gamma_s - 180\alpha - 40\alpha\gamma_s - 90\gamma_E = -9(\lambda/\sigma^2)^2(1/\rho) - 180 - 40(\lambda/\sigma^2) - 180\alpha - 40\alpha(\lambda/\sigma^2) - 90(\lambda/\rho\sigma^2)$$

$$C = -\gamma_E\gamma_s + 180 - 20\gamma_s + 270\alpha - 20\gamma_s\alpha + 90\alpha^2 + 45\alpha\gamma_E + 90\gamma_E = (45\alpha + 90 - (\lambda/\sigma^2)(\lambda/\rho\sigma^2) - 20(\lambda/\sigma^2)(1 + \alpha) + 90\alpha^2 + 270\alpha + 180) \quad (32)$$

$$v(x) = 1 + \frac{x}{2}(l\gamma_E + 4\alpha l m) - \frac{x^2}{2}(m + 3\alpha l m + \gamma_E l m) + \frac{x^3}{6}(4m\alpha - 4l m\alpha + \gamma_E + l m\gamma_E - l\gamma_E) - \frac{x^4}{4}(3\alpha m - 3\alpha l m - \gamma_E l m + m\gamma_E) + \frac{x^5}{10}\gamma_E m(1 - l) \quad (30b)$$

The unknown parameters  $l$  and  $m$  to be determined using above results with the boundary conditions (Eqs. (29a) and (29b)).

$$l = \frac{-B - \sqrt{B^2 - 4GC}}{2G} \quad (31a)$$

and

$$m = \frac{\gamma_E}{\gamma_E + 2(\alpha + 1)} = \frac{(\lambda/\rho\sigma^2)}{(\lambda/\rho\sigma^2) + 2(\alpha + 1)} \quad (31b)$$

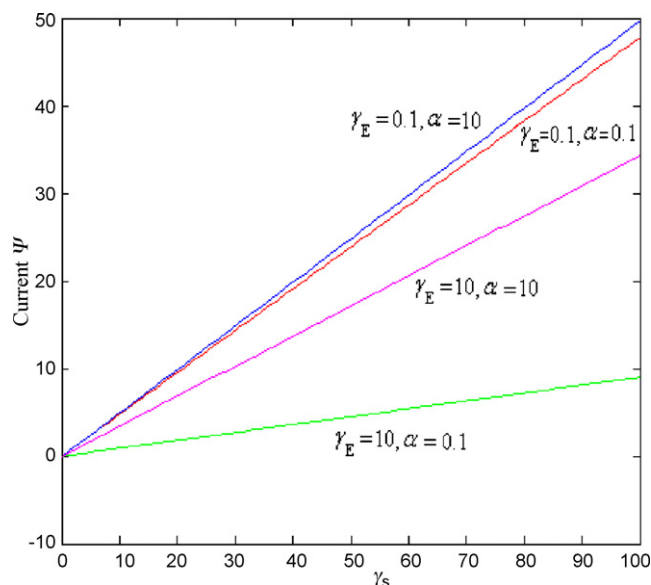
where

The normalized current is

$$\psi = \left(\frac{du}{dx}\right)_{x=1} = (3\alpha + 1)(l - 1) + \frac{\gamma_s}{2}(1 - m) \quad (33a)$$

$$= (3\alpha + 1)(l - 1) + \frac{(\lambda/\sigma^2)}{2}(1 - m) \quad (33b)$$

Eqs. (30a) and (30b) represent the most general new approximate analytical expressions for the substrate and mediator concentration



**Fig. 13.** Variation of normalized steady-state current response  $\psi$  expected for the situations (1)  $\gamma_E = 0.1, \alpha = 10$ , (2)  $\gamma_E = 0.1, \alpha = 0.1$ , (3)  $\gamma_E = 10, \alpha = 10$  and (4)  $\gamma_E = 10, \alpha = 0.1$  with reaction/diffusion parameter  $\gamma_s$ . The curves were computed using Eq. (33a).

profiles for all values of  $\gamma_s$ ,  $\gamma_E$  and  $\alpha$ . Eqs. (33a) and (33b) represent the normalized steady-state current response  $\psi$ .

## 7. Discussion

Eqs. (30a) and (30b) represent the new approximate analytical expressions for the substrate and mediator concentration profiles for all values of  $\gamma_s$ ,  $\gamma_E$  and  $\alpha$ . The relation between the concentration of substrate and mediator is  $v = 1 + (u - 1)/\rho$  (see Appendix B). When  $\gamma_s = \gamma_E$ ,  $v = u + 1 - 1$ . Fig. 11(a)–(c) show concentration profiles of the substrate in the enzyme membrane ( $x \in (0, 1)$ ). From these figures, it is noted that the variation in the substrate concentration  $u$  is very small when  $\alpha \leq 1$ ,  $\gamma_s$  and  $\gamma_E \leq 1$ . For all values of  $\alpha$  and  $\gamma_s$  and  $\gamma_E \leq 1$ , the substrate concentration  $u \approx 1$ . When  $\alpha \geq 10$ , the value of substrate concentration does not depend upon  $\gamma_s$  and  $\gamma_E$  (reaction/diffusion parameters). When  $\gamma_s \geq 10$  and  $\alpha \leq 1$ , the variation of concentration is not significant. The concentration reaches the maximum value when  $0.5 < x < 0.6$  for  $\alpha \geq 10$  and decreases slowly to the value 1. Fig. 12(a)–(c) show concentration profiles of the mediator in the enzyme membrane ( $x \in (0, 1)$ ). From these graphs, it should be noted that the mediator concentration  $v = 1$  when  $\gamma_E \leq 0.1$  or  $\gamma_s \leq 0.1$  for all values of  $\alpha$ . The concentration of mediator  $v$  increases when  $\gamma_E$  increases for all values of  $\alpha$  and  $\gamma_s$ . From these figures, it is also inferred that the value of the mediator concentration  $v$  decreases when  $\gamma_s$  increases and  $\alpha = \gamma_E$ . Fig. 13 shows the dynamics of normalized steady-state current  $\psi$  of different values of  $\alpha$ ,  $\gamma_s$  and  $\gamma_E$ . For small values of  $\gamma_E$  ( $\gamma_E \leq 0.1$ ) and for any value of  $\alpha$ , the current is significant. The current grows notably faster at higher values of  $\gamma_s$  for the above case. But in the case of  $\gamma_E \geq 10$  and  $\alpha = 0.1$ , the current does not increase.

## 8. Conclusions

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 (Eqs. (8a) and (30a)) and mediator (Eqs. (8b) and (30b)) concentrations and current (Eqs. (10a), (10b), (33a) and (33b)) are given in terms of  $\alpha$ ,

$\gamma_s$  and  $\gamma_E$ . The transport and kinetics are quantified in terms of fundamental reaction/diffusion polymer parameters  $\gamma_E$  and  $\gamma_s$  and saturation parameter  $\alpha$ ,  $\lambda/\sigma^2$  and  $\rho$ .

The analytical expression for the substrate concentration and mediated concentration profiles within the polymer film are derived using variational iteration method. We have also presented an analytical expression for the steady-state current. The variational iteration method is an extremely simple method and it is also a promising method to solve other non-linear equations. The extension of procedure to other cases of spillover models and steady-state of this problem, etc. apart from the study of amperometric biosensor [25] seems possible.

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## Appendix A.

In this appendix, we derived the general solution of non-linear reaction diffusion Eqs. (5a) and (5b) using He's variational iteration method [24]. To illustrate the basic concepts of variational iteration method (VIM), we consider the following non-linear partial differential equation [24]

$$L[u(x)] + N[u(x)] = g(x) \quad (A1)$$

where  $L$  is a linear operator,  $N$  is a non-linear operator, and  $g(x)$  is a given continuous function. According to the variational iteration method, we can construct a correct functional as follows [24]

$$u_{n+1}(x) = u_n(x) + \int_0^x \lambda [L[u_n(\tau)] + N[\tilde{u}_n(\tau)] - g(\tau)] d\tau \quad (A2)$$

where  $\lambda$  is a general Lagrange multiplier which can be identified optimally via variational theory,  $u_n$  is the  $n$ th approximate solution, and  $\tilde{u}_n$  denotes a restricted variation, i.e.  $\delta \tilde{u}_n = 0$ . In this method, a trial function (an initial solution) is chosen with some unknown parameters, which is identified after a few iterations according to the given boundary conditions. Using above variational iteration method we can write the correction functional of Eqs. (5a) and (5b) as follows

$$u_{n+1}(x) = u_n(x) + \int_0^x \lambda_1 [\tilde{\xi} u_n''(\xi) + 2u_n'(\xi) - \gamma_s \xi u_n(\xi) v_n(\xi)] d\xi \quad (A3)$$

$$v_{n+1}(x) = v_n(x) + \int_0^x \lambda_2 [\tilde{\xi} v_n''(\xi) + 2v_n'(\xi) - \gamma_E \xi u_n(\xi) v_n(\xi)] d\xi \quad (A4)$$

Taking variation with respect to the independent variable  $u_n$  and  $v_n$ , we get

$$\delta u_{n+1}(x) = \delta u_n(x) + \delta \int_0^x \lambda_1 [\tilde{\xi} u_n''(\xi) + 2u_n'(\xi) - \gamma_s \xi u_n(\xi) v_n(\xi)] d\xi \quad (A5)$$



$$\delta v_{n+1}(x) = \delta v_n(x) + \delta \int_0^x \lambda_2 [\xi v_n''(\xi) + 2v_n'(\xi) - \gamma_E \xi u_n(\xi) v_n(\xi)] d\xi \quad (\text{A6})$$

where  $\lambda_1$  and  $\lambda_2$  are general Lagrangian multipliers,  $u_0$  and  $v_0$  are initial approximations or trial functions with unknowns,  $\xi v_n''(\xi)$ ,  $\xi v_n'(\xi)$  and  $\xi u_n(\xi) v_n(\xi)$  are considered as restricted variations, i.e.  $\delta \tilde{u}_n = 0$ ,  $\delta \tilde{v}_n = 0$  and  $\delta \tilde{u}_n \tilde{v}_n = 0$ . Making the above correction functional (A5) and (A6) stationary, noticing that  $\delta u_n(0) = 0$ ,  $\delta v_n(0) = 0$  and  $\delta u_n(0) v_n(0) = 0$ .

$$\delta u_n : 1 + 2\lambda_1(\xi) \Big|_{\xi=x} = 0, \quad \delta v_n : 1 + 2\lambda_2(\xi) \Big|_{\xi=x} = 0 \quad (\text{A7})$$

$$\delta u_n : -2\lambda_1'(\xi) \Big|_{\xi=x} = 0, \quad \delta v_n : -2\lambda_2'(\xi) \Big|_{\xi=x} = 0 \quad (\text{A8})$$

The above equations are called Lagrange–Euler equations. The Lagrange multipliers, can be identified as

$$\lambda_1(\xi) = \lambda_2(\xi) = -\frac{1}{2} \quad (\text{A9})$$

Substituting the Lagrangian multipliers and  $n=0$  in the iteration formula (Eqs. (A3) and (A4)) we obtain,

$$u_1(x) = u_0(x) - \frac{1}{2} \int_0^x [\xi u_0''(\xi) + 2u_0'(\xi) - \gamma_s \xi u_0(\xi) v_0(\xi)] d\xi \quad (\text{A10})$$

$$v_1(x) = v_0(x) - \frac{1}{2} \int_0^x [\xi v_0''(\xi) + 2v_0'(\xi) - \gamma_E \xi u_0(\xi) v_0(\xi)] d\xi \quad (\text{A11})$$

Assuming that its initial approximate solution which satisfies the boundary conditions (6a) and (6b) have the form

$$\begin{aligned} u_0(x) &= l + |1 - l|x^2 \\ v_0(x) &= 1 + mx(x - 2) \end{aligned} \quad (\text{A12})$$

where  $l$  and  $m$  are unknown constants to be further determined. By the iteration formulas (A10) and (A11) we have,

$$\begin{aligned} u_1(x) &= l + \frac{x^2}{4}(2l - 2 + l\gamma_s) - \frac{x^3}{3}lm\gamma_s + \frac{x^4}{8}(1 - l + lm)\gamma_s \\ &\quad + \frac{x^5}{5}(l - 1)\gamma_s m + \frac{x^6}{12}m\gamma_s(1 - l) \end{aligned} \quad (\text{A13})$$

$$\begin{aligned} v_1(x) &= 1 + \frac{x^2}{4}(l\gamma_E - 2m) - \frac{x^3}{3}lm\gamma_E + \frac{x^4}{8}(1 - l + lm)\gamma_E \\ &\quad + \frac{x^5}{5}(l - 1)\gamma_E m + \frac{x^6}{12}m\gamma_E(1 - l) \end{aligned} \quad (\text{A14})$$

In the above Eqs. (A13) and (A14), the last four terms are equal. Considering the boundary conditions (6a) and (6b) we can identify the unknown constants  $l$  and  $m$  are given in Eqs. (9a) and (9c). The numerical values of  $l$  and  $m$  for various values  $\gamma_s$  and  $\gamma_E$  are given in Tables 1 and 2. The remaining components of  $u_n(x)$  and  $v_n(x)$  be completely determined such that each term is determined by the previous term using Eqs. (A10) and (A11). Since  $u_1$  and  $v_1$  are convergent series, we are taking  $u_1(x) = u(x)$  and  $v_1(x) = v(x)$ .

## Appendix B.

In this appendix, we have derived the relationship between  $u(x)$  and  $v(x)$  for the two cases. We can obtain the following results from Eqs. (5a) and (5b).

$$\frac{1}{\gamma_s} \frac{d}{dx} \left( x^2 \frac{du}{dx} \right) = \frac{1}{\gamma_E} \frac{d}{dx} \left( x^2 \frac{dv}{dx} \right) \quad (\text{B1})$$

$$\frac{d}{dx} \left( x^2 \frac{du}{dx} \right) = \frac{\gamma_s}{\gamma_E} \frac{d}{dx} \left( x^2 \frac{dv}{dx} \right) \quad (\text{B2})$$

$$\frac{d}{dx} \left( x^2 \frac{du}{dx} \right) = \rho \frac{d}{dx} \left( x^2 \frac{dv}{dx} \right) \quad (\text{B3})$$

where the parameter

$$\rho = \frac{\gamma_s}{\gamma_E} \quad (\text{B4})$$

Integrating Eq. (B3) gives

$$\frac{du}{dx} = \rho \left( \frac{dv}{dx} \right) + \frac{l}{x^2} \quad (\text{B5})$$

Again integrating we get

$$u = \rho v - \frac{c_1}{x} + c_2 \quad (\text{B6})$$

$$ux = \rho vx - c_1 + xc_2 \quad (\text{B7})$$

When  $x=0$ , we obtain

$$c_1 = 0 \quad (\text{B8})$$

Therefore Eq. (B7) becomes

$$u = \rho v + c_2 \quad (\text{B9})$$

To find the constant  $m$ , substitute  $x=0$  in Eqs. (8a) and (8b) and using (B9) we get

$$c_2 = l - \rho \quad (\text{B10})$$

Now (B6) implies

$$v = 1 + \frac{u - l}{\rho} \quad (\text{B11})$$

where  $l$  is given in Eqs. (9a) and (9b). This is the relation between the concentrations of substrate and mediator.

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