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# Solutions of the Coupled Reaction and Diffusion Equations within Polymer-Modified Ultramicroelectrodes

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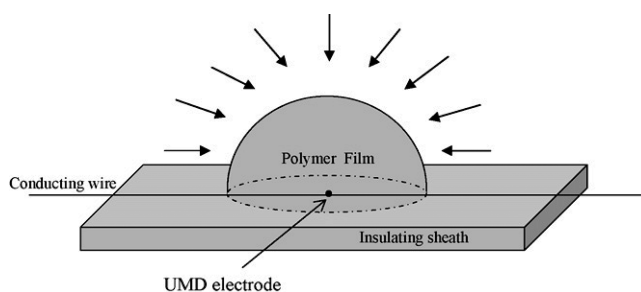
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In this work, we have theoretically analyzed the non-steady-state current response witnessed at conducting polymer-modified ultramicroelectrodes when the electrode is operating under batch amperometric conditions. Furthermore, the effect of substrate diffusion in the solution adjacent to the polymer film on both the concentration profiles and current response was examined. Analytical expressions pertaining to substrate concentration, mediator concentration, and current response pertaining to all values of diffusion parameters are presented. In addition, we have employed “reduction of order method” to evaluate the approximate analytical solutions of reaction diffusion equations.

## Introduction

Ultramicroelectrodes (UMEs) are defined as the electrodes with one of their critical dimension  $<20\ \mu\text{m}$ . Upon comparison, UMEs offer several advantages over the conventional sized electrodes. The advantages of the UME include smaller double-layer capacitance, smaller current, and in vivo measurements.<sup>1</sup> The small currents observed at UME open up the possibility of analysis in resistive media such as solvents without any electrolytes and super critical fluids.<sup>1,2</sup> Furthermore, the smaller double-layer capacitance of the UME enables them to monitor various complex chemical events in single cells and neuronal region that occur on the submicrosecond time scale.<sup>3</sup> Moreover, UMEs have enhanced fluxes that in turn can enhance the signal-to-noise ratio during trace metal ion analysis.<sup>4</sup> UME can also be employed in scanning electron microscopy (SEM) by combining UME with a micropositioner capable of moving in three dimensions to achieve a spatially resolved view of chemical events much like the physical characterization provided by other scanning probe microscopies.<sup>5</sup> Furthermore, UMEs have made great progress in understanding the in vitro neurotransmitter release, 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, probe beam deflection, spectroscopic, and gravimetric measurements.<sup>6–12</sup> Moreover, modification of UME with polymers enables specific and selective biosensing.

The theoretical analysis of mediated electron transfer at electroactive polymer film deposited on the conventional sized electrode surfaces was proposed by Alberly et al.<sup>13</sup> and Andrieux et al.<sup>14</sup> Recently, Lyons et al.<sup>15,16</sup> have reported the analysis of mediated substrate diffusion, Michaelis–Menten rate equation, electromigration, sensing catalysis, charge percolation, and chemical reaction.<sup>15–20</sup> Rebouillat et al.<sup>21</sup> have calculated the concentration and current for the limiting cases. However, to the best of our knowledge, to date, no general analytical results corresponding



**Figure 1.** Schematic representations of the geometry adopted by the polymer-coated microelectrode and the expected diffusion profile adopted by the analytes.

to the non-steady-state substrate, mediator concentrations, and current for all values of diffusion parameters  $\gamma_S$  and  $\gamma_E$  have been reported. The purpose of this article is to derive an analytical expression for non-steady-state concentration and current at a polymer-modified ultramicroelectrode based on “reduction of order method”.

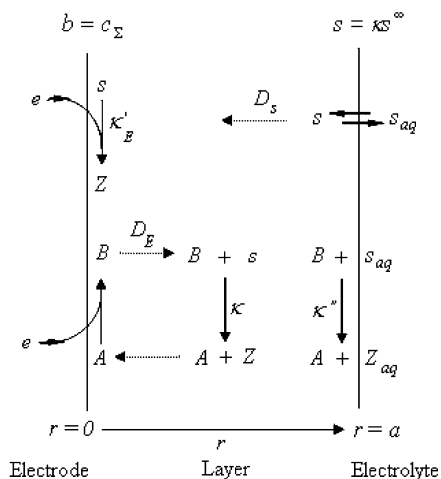
## Mathematical Formulation of the Boundary Value Problem

In general, it was assumed that the conducting polymer film adopts a hemispherical geometry when electrodeposited on an ultramicrodisc surface. Following this, the microelectrodes are considered to be an electrodeposited polymeric hemisphere coated on a disk electrode. Figure 1 represents a hemispherical polymer on top of a plane with a line within the insulating plane representing a conducting wire that emerges at the origin of the hemisphere. Transport within the hemisphere is based on spherical diffusion as represented by eqs 6 and 7, and  $r$  is the dimensionless radial distance originating from the origin of the polymer hemisphere. Furthermore, the underlying electrode serves as a point source at the origin of the hemisphere resulting in spherical diffusion within the conducting polymer. The diffusion of substrate within the thin film is considered to be a spherical and the chemical reaction between substrate and mediator species as bimolecular. Next, the substrate partitions

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**Figure 2.** Schematic model and a basic notation of a modified electrode.

into the layer are represented by a partition coefficient,  $\kappa$ , and the substrate and electron diffusion coefficient are represented by  $D_S$  and  $D_E$ , respectively. A brief reaction mechanistic model<sup>13</sup> is shown in Figure 2. Under these conditions, the coupled reaction diffusion equations for non-steady-state assume the form reported elsewhere.<sup>21</sup>

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

$$D_S \frac{d^2 s}{dr^2} + \frac{2D_S ds}{r dr} - ksb = \frac{ds}{dt} \quad (2)$$

where  $b$  and  $s$  represent the concentrations of oxidized mediator and substrate species and  $k$  is the bimolecular rate constant for the mediator–substrate reaction. The initial and boundary conditions are

$$t = 0; b = c_\Sigma; s = 0 \quad (3a)$$

$$r = 0; b = c_\Sigma; \frac{ds}{dr} = 0 \quad (3b)$$

$$r = a; \frac{db}{dr} = 0; s = \kappa s^\infty \quad (3c)$$

where,  $c_\Sigma = a + b$  corresponds to the total concentration of the reduced and oxidized mediator species,  $a$  is the radius of the electrode, and  $s^\infty$  denotes the bulk concentration of the substrate. The current (flux)  $j$  is given by the following expression

$$j = \frac{i}{nFA} = -D_E \left( \frac{db}{dr} \right)_{r=0} = D_S \left( \frac{ds}{dr} \right)_{r=a} \quad (4)$$

where  $A$  denotes the area of the hemispherical electrode,  $F$  denotes the Faraday constant, and  $n$  denotes the charge number of the electrode reaction. Here we can assume that  $D_E = D_S = D$ . Equations 1 and 2 are transformed to nondimensional form using the following nondimensional variables

$$u = \frac{s}{\kappa s^\infty}; v = \frac{b}{c_\Sigma}; \rho = \frac{r}{a}; \gamma_E = \frac{k\kappa s^\infty a^2}{D_E}; \gamma_S = \frac{k c_\Sigma a^2}{D_S}; \tau = \frac{Dt}{a^2} \quad (5)$$

The coupled diffusion equations in nondimensional form are

$$\frac{d^2 u}{d\rho^2} + \frac{2}{\rho} \frac{du}{d\rho} - \gamma_S uv = \frac{du}{d\tau} \quad (6)$$

$$\frac{d^2 v}{d\rho^2} + \frac{2}{\rho} \frac{dv}{d\rho} - \gamma_E uv = \frac{dv}{d\tau} \quad (7)$$

The initial and boundary conditions in the nondimensional form are

$$\tau = 0; u = 0; v = 1 \quad (8a)$$

$$\rho = 0; v = 0; \frac{du}{d\rho} = 0 \quad (8b)$$

$$\rho = 1; \frac{dv}{d\rho} = 0; u = 1 \quad (8c)$$

The nondimensional current (flux) is defined as

$$\psi = \frac{ia}{nFAD_S \kappa s^\infty} = \left( \frac{du}{d\rho} \right)_{\rho=1} \quad (9a)$$

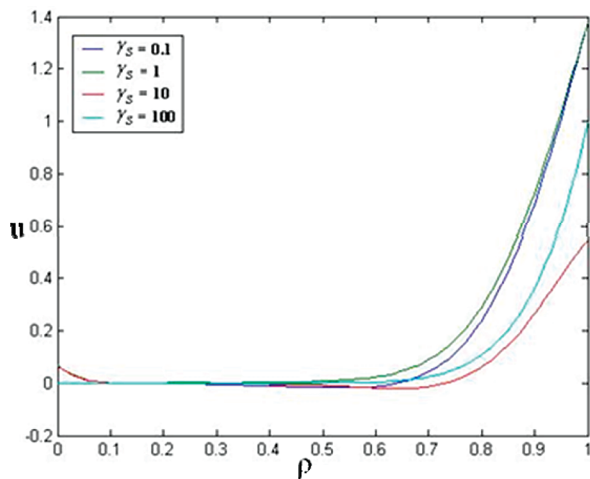
or

$$\psi = \frac{ia}{nFAD_E c_\Sigma} = - \left( \frac{dv}{d\rho} \right)_{\rho=0} \quad (9b)$$

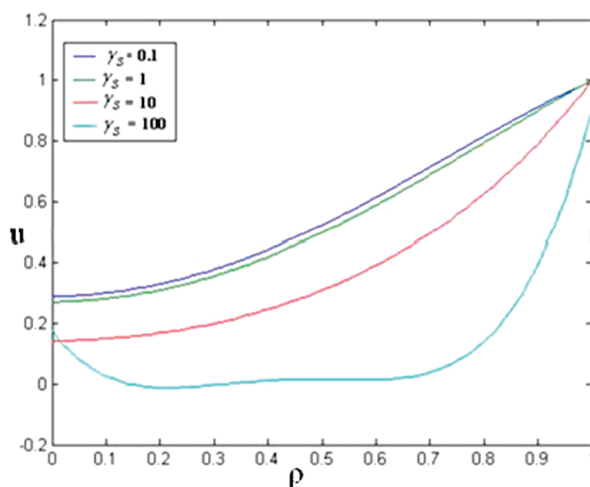
### Approximate Solutions for the Coupled Diffusion Equations

**Electron Percolation through Polymer Layer More Rapid than Substrate Transport.** When  $\gamma_E/\gamma_S \ll 1$ ,  $\kappa D_S s^\infty \ll D_E c_\Sigma$ , or  $\rho \rightarrow \infty$ , the electrons percolate across the layer more readily than substrate. Furthermore, the charge percolation of electrons alongside the polymer chains is considered to be rapid, resulting in a rapid chemical reaction between mediator and substrate. As a result, there will be a little consumption of mediator species across the polymer layer, thereby, we assume that  $v = 1$ ; and, the eq 6 reduces to

$$\frac{d^2 u}{d\rho^2} + \frac{2}{\rho} \frac{du}{d\rho} - \gamma_S u = \frac{du}{d\tau} \quad (10)$$



**Figure 3.** Normalized non-steady-state substrate concentration,  $u$ , at a polymer microelectrode. The concentrations were computed using eq 12 for various values of the reaction diffusion parameters  $\gamma_s$  and time  $\tau = 0.01$ .



**Figure 4.** Normalized non-steady-state substrate concentration,  $u$ , at a polymer microelectrode. The concentrations were computed using eq 12 for various values of the reaction diffusion parameters  $\gamma_s$  and time  $\tau = 0.1$ .

The initial and boundary conditions are

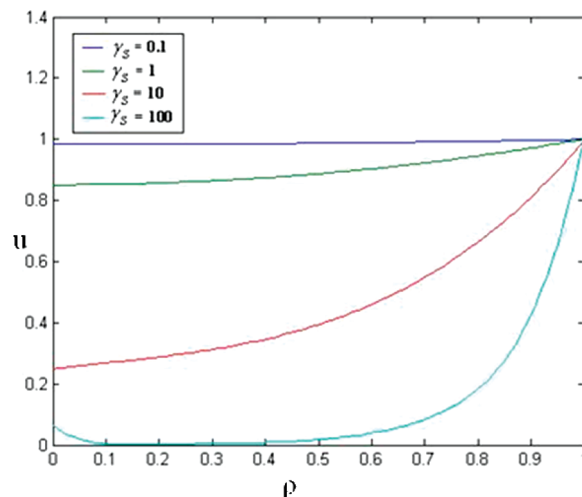
$$\tau = 0; u = 0 \quad (11a)$$

$$\rho = 0; \frac{du}{d\rho} = 0 \quad (11b)$$

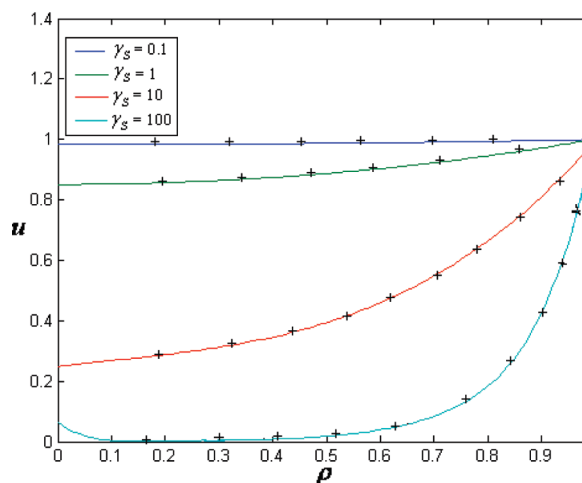
$$\rho = 1; u = 1 \quad (11c)$$

Using the reduction of order method and complex inversion formula (Appendices A and B), the approximate solution of the eq 10 is

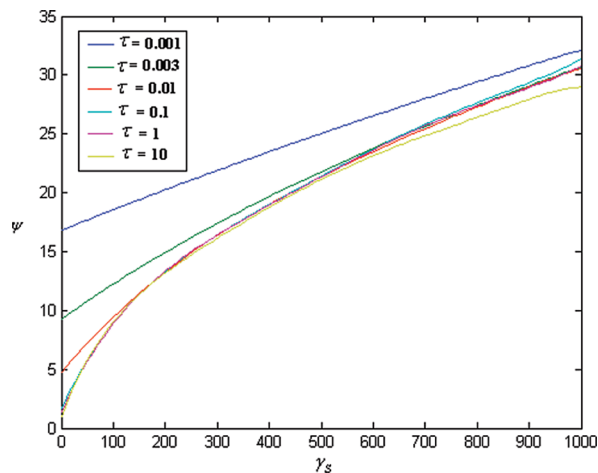
$$u(\rho, \tau) = \frac{\sinh(\sqrt{\gamma_s}\rho)}{\rho \sinh(\sqrt{\gamma_s})} + \frac{2\pi}{\rho} \sum_{n=1}^{\infty} \frac{n \sin(n\pi\rho)}{(-1)^n(n^2\pi^2 + \gamma_s)} \times \exp(-(n^2\pi^2 + \gamma_s)\tau) \quad (12)$$



**Figure 5.** Normalized non-steady-state substrate concentration,  $u$ , at a polymer microelectrode. The concentrations were computed using eq 12 for various values of the reaction diffusion parameters  $\gamma_s$  and time  $\tau = 1$ .

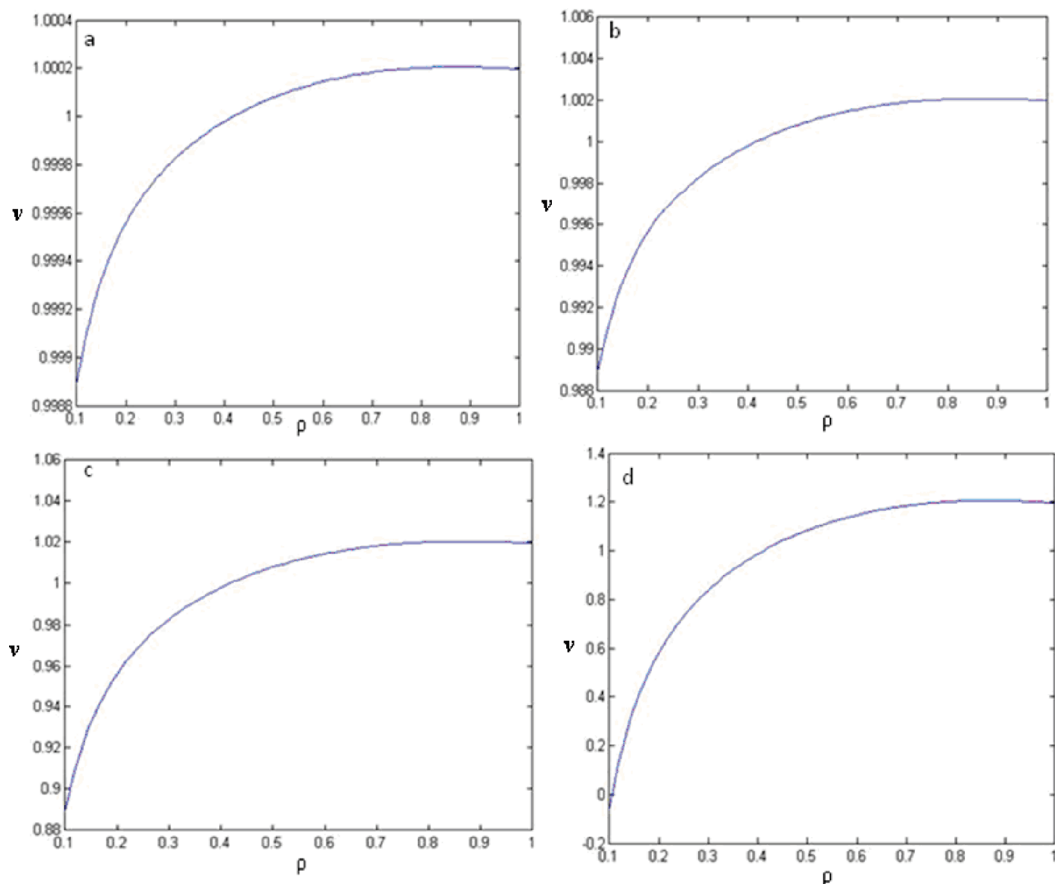


**Figure 6.** Normalized non-steady-state substrate concentration,  $u$ , at a polymer microelectrode. The concentrations were computed using eq 12 for various values of the reaction diffusion parameters  $\gamma_s$  and time  $\tau = 10$  and 100. The key to the graph (—) represents eq 12 and (+) represents eq 13 of ref 21.

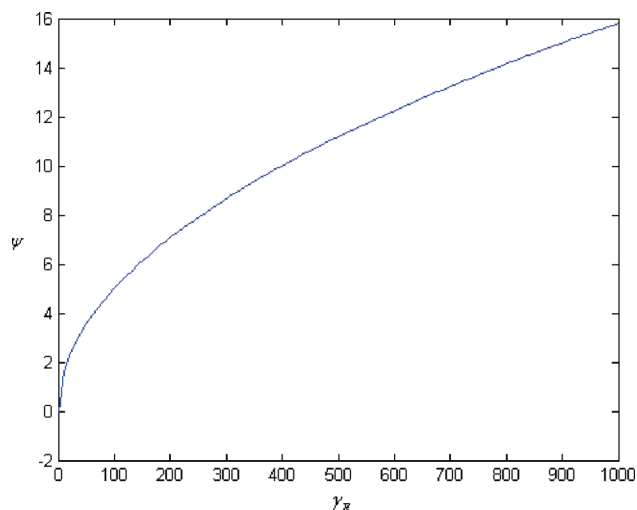


**Figure 7.** Normalized non-steady-state current  $\psi$  versus  $\gamma_s$  at a polymer microelectrode. The current was calculated using eq 13 for various  $\tau$  values.

The non-steady-state current will be given by



**Figure 8.** Normalized non-steady-state substrate concentration  $v$  versus  $\rho$  calculated using eq 16 at a polymer microelectrode for  $\gamma_E =$  (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1.



**Figure 9.** Normalized non-steady-state current  $\psi$  versus  $\gamma_E$  calculated eq 17 at a polymer microelectrode for various values of  $\tau$  (0.2, 0.5, 0.8, 1, 10, and 100).

$$\psi = \left( \frac{du}{d\rho} \right)_{\rho=1} = \sqrt{\gamma_S} \coth(\sqrt{\gamma_S}) - 1 + 2\pi^2 \sum_{n=1}^{\infty} \frac{n^2}{(n^2\pi^2 + \gamma_S)} \exp[-(n^2\pi^2 + \gamma_S)\tau] \quad (13)$$

Equation 12 represents the dimensionless concentration of substrate. When  $\tau \rightarrow \infty$ , eq 12 takes the form  $u_{ss} = \sinh((\gamma_S)^{1/2}\rho)/\rho \sinh((\gamma_S)^{1/2})$ . This steady-state result is identical to eq 13,<sup>21</sup> and the normalized non-steady-state current is represented by eq 13. When  $\tau \rightarrow \infty$ , from eq 13, we obtained

the steady-state current  $\psi_{ss} = (\gamma_S)^{1/2} \coth(\gamma_S) - 1$ . This is the same as eq 14 described elsewhere.<sup>21</sup>

**Substrate Diffusion through the Polymer Layer Is More Rapid than Electron Diffusion.** When  $\gamma_E/\gamma_S \gg 1$ ,  $\kappa D_{sS}^\infty \gg D_{EC\Sigma}$ , or  $\rho \rightarrow 0$ , the substrate diffusion through the polymer layer is more rapid than the electron diffusion. As a result of rapid substrate diffusion through the layer, a small amount of substrate was considered to be consumed during the passage across the layer, and it can be assumed that  $u = 1$ , thereby eq 7 reduces to

$$\frac{d^2v}{d\rho^2} + \frac{2}{\rho} \frac{dv}{d\rho} - \gamma_E v = \frac{dv}{d\tau} \quad (14)$$

The initial and boundary conditions are

$$\tau = 0; v = 1 \quad (15a)$$

$$\rho = 0; v = 1 \quad (15b)$$

$$\rho = 1; \frac{dv}{d\rho} = 0 \quad (15c)$$

Using reduction of order method, complex inversion formula (Appendices A and B), heaviside expansion theorem for repeated roots eq 8.3.22,<sup>22</sup> and the eigenvalues of a regular Sturm–Liouville problem,<sup>23</sup> the approximate solution of the eq 14 is

$$\begin{aligned}
v(\rho, \tau) = & \frac{\exp(\sqrt{\gamma_E}\rho)}{\rho\sqrt{\gamma_E}} + \\
& \frac{(1 - \gamma_E) \exp(\sqrt{\gamma_E}) \cosh(\sqrt{\gamma_E}\rho)}{\rho\sqrt{\gamma_E}(\sqrt{\gamma_E} \sinh(\sqrt{\gamma_E}) - \cosh(\sqrt{\gamma_E}))} \\
& - 2 \frac{\gamma_E \tau^2}{\rho} \sum_{n=1}^{\infty} \frac{(n-1)^2 \cos((n-1)\pi\rho)}{((n-1)^2\pi^2 + \gamma_E)} \times \\
& \exp(-((n-1)^2\pi^2 + \gamma_E)\tau)
\end{aligned} \quad (16)$$

Furthermore, the non-steady-state current is given by

$$\begin{aligned}
\psi = -\left(\frac{dv}{d\rho}\right)_{\rho=0} = & -\frac{\sqrt{\gamma_E}}{2} - \frac{\sqrt{\gamma_E}(1 - \sqrt{\gamma_E}) \exp(\sqrt{\gamma_E})}{2(\sqrt{\gamma_E} \sinh(\sqrt{\gamma_E}) - \cosh(\sqrt{\gamma_E}))} \\
& - \gamma_E \tau^4 \sum_{n=1}^{\infty} \frac{(n-1)^4}{((n-1)^2\pi^2 + \gamma_E)} \exp(-((n-1)^2\pi^2 + \gamma_E)\tau)
\end{aligned} \quad (17)$$

Equations 16 and 17 represent the dimensionless non-steady-state concentration of mediator and current for all values of parameters. When  $\tau \rightarrow \infty$ , the steady-state concentration of mediator and current were obtained from eqs 16 and 17. This steady-state concentration of mediator and current are same as the results of Rebouillat et al.<sup>21</sup> (See eqs 22 and 25.)

By solving the above eq 14, Rebouillat et al.<sup>21</sup> obtained the expression for the mediator concentration for the steady state, which is shown below

$$v(\rho) = \frac{\exp(-\sqrt{\gamma_E})}{\sqrt{\gamma_E} F(\gamma_E) \rho} \{f(\gamma_E) \exp[-\sqrt{\gamma_E}(1 - \rho)] - \exp[\sqrt{\gamma_E}(1 - \rho)]\} \quad (18)$$

where

$$F(\gamma_E) = 1 + f(\gamma_E) \exp(-2\sqrt{\gamma_E}) \quad (19)$$

and

$$f(\gamma_E) = (1 + \sqrt{\gamma_E})/(1 - \sqrt{\gamma_E}) \quad (20)$$

## Discussion

Figure 3 represents the normalized non-steady-state substrate concentration  $u$  for different values of dimensionless diffusion parameter,  $\gamma_s$ , and for time  $\tau = 0.01$ . From this Figure, it is evident that the value of substrate concentration gradually increases when  $\rho \geq 0.5$ . Figure 4 indicates the substrate concentration,  $u$ , for various values of  $\gamma_s$  and for  $\tau = 0.1$ . From Figure 4, it is obvious that the substrate concentration,  $u$ , reaches the maximum value 1 when  $\rho = 1$ . Figure 5 represents a series of normalized non-steady-state substrate concentration,  $u$ , for various values of  $\gamma_s$  and for time  $\tau = 1$ . Figure 6 represents the substrate concentration,  $u$ , for all values of  $\gamma_s$  and for  $\tau = 10, 100$ . From this Figure, it is evident that the concentration of substrate  $u$  attains the steady state when  $\tau \geq 1$ . Figure 7 is the normalized non-steady-state current response  $\psi$  for various values of  $\gamma_s$ . From this Figure, we conclude that the value of current reported in Rebouillat et al.<sup>21</sup> and our work eq 13 were identical.

Figure 8a–d represents the normalized non-steady-state mediator concentration,  $v$ , at a polymer electrode. The concentration of mediator was calculated for various values of dimensionless diffusion parameter  $\gamma_E < 1$  (0.0001, 0.001, 0.01, and 0.1). From these Figures, it is obvious that the values of the mediator concentration reach the maximum value of 1. Figure 9 shows the normalized non-steady-state current of the mediator concentration for various values of  $\gamma_E$  and  $\tau$ . Furthermore, upon comparing the mediator concentration “ $v$ ” of eq 18 derived by Rebouillat et al.<sup>21</sup> with our result of eq 16, as shown in Table 1, we noticed an excellent agreement.

## Conclusions

In this work, the coupled time-dependent nonlinear reaction/diffusion equations have been formulated and solved analytically. We have presented analytical expression corresponding to the substrate concentration and mediated concentration profiles within the polymer film in terms of  $\gamma_s$  and  $\gamma_E$  based on the reduction of order method. Moreover, we have also presented an analytical expression for the non-steady-state current. Furthermore, on the basis of the outcome of this work, it is possible to calculate the approximate amounts of substrate concentrations, mediator concentrations, and current corresponding to a nonlinear Michaelis–Menten kinetic scheme. In addition, the transport and kinetics are quantified

**TABLE 1: Normalized Mediator Concentration,  $v$ , by Using Equations 16 and 18 for Various Values of  $\rho$  and Some Values of  $\gamma_E$  (0.0001, 0.001, 0.01, 0.1)**

$\rho$	concentration $v$							
	$v$ (when $\gamma_E = 0.0001$ )		$v$ (when $\gamma_E = 0.001$ )		$v$ (when $\gamma_E = 0.01$ )		$v$ (when $\gamma_E = 0.1$ )	
	Serge Rebouillat et. al. <sup>21</sup> (eq 18)	this work (eq 16)	Serge Rebouillat et. al. <sup>21</sup> (eq 18)	this work (eq 16)	Serge Rebouillat et. al. <sup>21</sup> eq (18)	this work (eq 16)	Serge Rebouillat et. al. <sup>21</sup> (eq 18)	this work (eq 16)
0.10	1.0003333	1.000333	1.0033370	1.0033371	1.03355310	1.03355311	1.35521218	1.35521216
0.20	1.0001673	1.0001668	1.00167439	1.0016745	1.01683740	1.01683736	1.178455814	1.17845580
0.30	1.0001126	1.0001126	1.00112687	1.0011269	1.01133328	1.01133327	1.120322727	1.12032272
0.40	1.0000860	1.0000860	1.00086057	1.00086058	1.00865708	1.00865706	1.092096497	1.092096496
0.50	1.00007083	1.0000707	1.00070882	1.00070882	1.007132062	1.00713206	1.076034508	1.076034509
0.60	1.00006156	1.0000615	1.00061601	1.00061603	1.006199306	1.00619930	1.066223288	1.066223283
0.70	1.00005573	1.0000556	1.00055827	1.00055825	1.005619291	1.00561928	1.060129254	1.060129252
0.80	1.00005235	1.0000524	1.00052372	1.00052373	1.005272276	1.00527227	1.056486418	1.056486417
0.90	1.00005054	1.0000506	1.00050575	1.00050578	1.005091733	1.00509173	1.054592277	1.054592279
1.00	1.00005004	1.0000500	1.000500381	1.00050037	1.005037759	1.00503775	1.054026179	1.054026179



in terms of fundamental reaction/diffusion polymer parameters  $\gamma_E$ ,  $\gamma_S$ , and  $\rho$ .

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## Appendix A

In this Appendix, we derive the general solution of linear eq 1 by using reduction of order. Using Laplace transform eqs 11a–11c become

$$\frac{d^2 U}{d\rho^2} - \frac{2dU}{\rho d\rho} - (\gamma_S + s)U = 0 \quad (A1)$$

where  $s$  is Laplace variable. Now the boundary conditions become

$$\rho = 0, \frac{dU}{d\rho} = 0 \quad (A2)$$

$$\rho = 1, U = \frac{1}{s} \quad (A3)$$

To illustrate the basic concepts of reduction of order, we consider the equation

$$\frac{d^2 U}{d\rho^2} + P \frac{dU}{d\rho} + QU = R \quad (A4)$$

where  $P$ ,  $Q$ , and  $R$  are function of  $\rho$ . Using reduction of order, from eq A1, we have

$$P = \frac{2}{\rho}; \quad Q = -(\gamma_S + s); \quad \text{and} \quad R = 0 \quad (A5)$$

$$\text{Let } U = v w \quad (A6)$$

be the general solution of eq A4.

If  $v$  is so chosen that

$$2 \frac{dv}{d\rho} + P v = 0 \quad (A7)$$

substituting the value of  $P$  in the above eq A7, we get

$$v = \frac{1}{\rho} \quad (A8)$$

Then, eq A4 reduces to

$$w'' + Q_1 w = R_1 \quad (A9)$$

where

$$Q_1 = Q - \frac{1}{2} \frac{dP}{d\rho} - \frac{P^2}{4}; \quad R_1 = \frac{R}{v} \quad (A10)$$

from eqs A9 and A8 reduces to

$$w'' - (\gamma_S + s)w = 0 \quad (A11)$$

Integrating eq A10 twice, we obtain

$$w = c_1 \exp(\sqrt{\gamma_S + s}) + c_2 \exp(-\sqrt{\gamma_S + s}) \quad (A12)$$

Substituting A8 and A12 in A6, we have

$$U(\rho, s) = \frac{1}{\rho} (c_1 \exp(\sqrt{\gamma_S + s}) + c_2 \exp(-\sqrt{\gamma_S + s})) \quad (A13)$$

Using the boundary conditions eqs A2 and A3, we can obtain the value of the constants

$$c_1 = \frac{1}{2s \sinh(\sqrt{\gamma_S + s})} \quad \text{and} \quad c_2 = -\frac{1}{2s \sinh(\sqrt{\gamma_S + s})} \quad (A14)$$

Substituting A14 in eq A13, we obtain

$$U(\rho, s) = \frac{\sinh(\sqrt{\gamma_S + s}\rho)}{\rho s \sinh(\sqrt{\gamma_S + s})} \quad (A15)$$

By applying the same procedure for  $V$ , we can get

$$V(\rho, s) = \frac{\gamma_E \sqrt{s + \gamma_E} \exp(\sqrt{s + \gamma_E}\rho)}{\rho s (s + \gamma_E)^2} + \frac{\frac{1}{\rho} \gamma_E (1 - \sqrt{s + \gamma_E}) \sqrt{s + \gamma_E} \exp(\sqrt{s + \gamma_E}\rho) \cosh(\sqrt{s + \gamma_E}\rho)}{s (s + \gamma_E)^2 [\sqrt{s + \gamma_E} \sinh(\sqrt{s + \gamma_E}) - \cosh(\sqrt{s + \gamma_E})]} + \frac{1}{s + \gamma_E} \quad (A16)$$

Using the complex inverse formula (refer to Appendix B), we can obtain the concentrations of substrate and mediator.

## Appendix B

In this Appendix, we indicate that how eq A15 may be inverted using complex inversion formula. If  $\bar{y}(s)$  represents the Laplace transform of a function  $y(\tau)$ , then according to the complex inversion formula, we can state that

$$y(\tau) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \exp[s\tau] \bar{y}(s) ds = \frac{1}{2\pi i} \oint_c \exp[s\tau] \bar{y}(s) ds \quad (B1)$$

where the integration in eq B1 is to be performed along a line  $s = c$  in the complex plane where  $s = x + iy$ . The real number  $c$  is chosen such that  $s = c$  lies to the right of all of the

singularities but is otherwise assumed to be arbitrary. In practice, the integral is evaluated by considering the contour integral presented on the right-hand side of eq B1, which is evaluated using the so-called Bromwich contour. The contour integral is then evaluated using the residue theorem that states for any analytic function  $F(z)$

$$\oint_c F(z) dz = 2\pi i \sum_n \operatorname{Re} s[F(z)]_{z=z_n} \quad (\text{B2})$$

where the residues are computed at the poles of the function  $F(z)$ . Therefore, from eq B2, we note that

$$y(\tau) = \sum_n \operatorname{Re} s[\exp[s\tau]\bar{y}(s)]_{s=s_n} \quad (\text{B3})$$

From the theory of complex variables, we can show that the residue of a function  $F(z)$  at a simple pole at  $z = a$  is given by

$$\operatorname{Re} s[F(z)]_{z=a} = \lim_{z \rightarrow a} \{(z - a)F(z)\} \quad (\text{B4})$$

Therefore, to invert eq A15, we need to evaluate  $\operatorname{Re} s[\sinh((\gamma_s + s)^{1/2}\rho)/s \sinh((\gamma_s + s)^{1/2})]$ . Now the poles are obtained from  $s \sinh((\gamma_s + s)^{1/2}\rho) = 0$ . Therefore, there is a simple pole at  $s = 0$ , and there are infinitely many poles given by the solution of the equation  $\sinh((\gamma_s + s)^{1/2}) = 0$ , and so  $s_n = -n^2\pi^2 - \gamma_s$  with  $n = 1, 2, \dots$ . Therefore, we note that

$$\begin{aligned} S(X, T) &= \operatorname{Re} s \left[ \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} \right]_{s=0} + \\ &\quad \operatorname{Re} s \left[ \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} \right]_{s=s_n} = \\ &\quad \lim_{s \rightarrow 0} (s - 0) \left\{ \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} \right\} + \\ &\quad \lim_{s \rightarrow s_n} (s - s_n) \left\{ \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} \right\} \quad (\text{B5}) \end{aligned}$$

The first residue in eq B5 is given by

$$\begin{aligned} \operatorname{Re} s \left[ \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} \right]_{s=0} &= \\ \lim_{s \rightarrow 0} \left\{ \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{\sinh(\sqrt{\gamma_s + s})} \right\} &= \frac{\sinh(\sqrt{\gamma_s}\rho)}{\sinh(\sqrt{\gamma_s})} \quad (\text{B6}) \end{aligned}$$

The second residue in eq B5 can be evaluated as follows. It is established that if  $F(z)$  can be expressed as  $F(z) = f(z)/g(z)$ , where the functions  $f$  and  $g$  are analytic at  $s = s_n$  and  $g(s_n) = 0$ , whereas  $g'(s_n) \neq 0$  and  $f(s_n) \neq 0$ . Then,  $\operatorname{Re} s[F(z)]_{s=s_n} = \sum_{n=0}^{\infty} (f(s_n))/(g'(s_n)) \exp[s_n\tau]$ . Therefore, we can show that

$$\begin{aligned} \lim_{s \rightarrow s_n} \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{s \sinh(\sqrt{\gamma_s + s})} &= \\ \lim_{s \rightarrow s_n} \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)(2\sqrt{\gamma_s + s})}{s_n \cosh(\sqrt{\gamma_s + s})} &= \\ \frac{2 \exp[-(n^2\pi^2 + \gamma_s)T](n\pi i) \sinh(n\pi\rho)}{-(n^2\pi^2 + \gamma_s) \cosh(n\pi i)}, \quad n = 1, 2, \dots \quad (\text{B7}) \end{aligned}$$

Using  $\cosh(i\theta) = \cos(\theta)$  and  $\sinh(i\theta) = i \sin(\theta)$

$$\begin{aligned} \lim_{s \rightarrow s_n} \exp(sT) \frac{\sinh(\sqrt{\gamma_s + s}\rho)}{\sinh(\sqrt{\gamma_s + s})} &= 2\pi \sum_{n=1}^{\infty} (-1)^n \left\{ \frac{n \sin(n\pi\rho)}{(n^2\pi^2 + \gamma_s)} \right\} \times \\ &\quad \exp[-(n^2\pi^2 + \gamma_s)T] \quad (\text{B8}) \end{aligned}$$

Similarly, we can invert eq A16.

## Appendix C

Matlab program to find the sum of the series of eq 12

function  $u = u(p)$

$k = 0.1$ ;

$t = 0.01$ ;

$p = \text{linspace}(0.1, 1)$ ;

$s1 = 0$ ;

$N = 100$ ;

for  $n = 0:1:N + 1$ ;

$s1 = s1 + ((-1)^n * \sin(n * \pi * p) * \exp(-(n^2 * \pi^2 * t - k * t)) / ((n^2 * \pi^2 + k)))$ ;

end

$u = ((2 * \pi) * s1) ./ p$ ;

$u1 = \sin(h * (k^{1/2} * p) ./ (p * \sinh(k^{1/2})))$ ;

$u2 = u + u1$ ;

plot( $p, u2$ )

Similarly, we can find the sum of the series of eqs 13, 16, and 17.

## References and Notes

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