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Nonlinear Reaction-Diffusion and Mediated Electron Transfer Process at Conducting Polymer Modified Ultramicroelectrodes

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Abstract. The primary goal of this article is to present novel analytical solutions for the coupled nonlinear equation found in the mediated electron transfer process at polymer-modified conducting ultramicroelectrodes. Taylor's series method is utilized to obtain approximate analytical solutions for the reaction-diffusion equations, allowing for the determination of the substrate and mediator concentrations and the current response concerning the substrate concentration at the electrode's surface. The impact of different factors on concentration and current is also explored. The derived analytical results are in strong agreement with numerical results and with other analytical outcomes from the literature.

2020 Mathematics Subject Classifications: 4M04, 35B30, 65L10

Key Words and Phrases: Nonlinear reaction-diffusion equations, Polymer-modified ultramicroelectrodes, Taylor's series method, Michaelis–Menten kinetics, Mathematical modeling

1. Introduction

Over the course of more than 30 years, ultramicroelectrodes (UMEs) have been utilized in electrochemistry, resulting in significant theoretical and practical achievements. UMEs are electrodes with dimensions of one micrometre or less [16], providing benefits such as higher current density, reduced cell time constants, and lower ohmic drop. Additionally, ultramicroelectrodes have been used in electrochemical research involving scanning tunnelling, atomic force, and electrochemical microscopy [12, 22, 26]. Furthermore, spherical

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or disc-shaped ultramicroelectrodes exhibit a time-independent current response within relatively brief timeframes, providing practical and theoretical advantages.

Ultramicroelectrodes are also extensively utilized in various fields, such as electro-organic biosynthesis, atomic semiconductors, electroactive indicators, and solar energy conversion and storage. Polymer-modified electrodes have gained significant attention over the past two decades, particularly in electrochemical sensor applications [13, 15, 25, 42]. The working principle of an amperometric polymer sensor is relatively straightforward, and it has been studied via voltammetry, nonlinear impedance, probe beam deviation, photometric, and specific gravity techniques to comprehend the behaviour of paired, solvent, and electronic transit in conducting electroactive molecular thin film materials [6, 11, 20]. This investigation focuses on the alterations in the properties of ultramicrodisc electrodes by incorporating thin polypyrrole films with electrical conductivity. We will also examine the substrate's diffusion and response within an electronically conducting polymer film on a micrometre-sized support surface.

The mathematical modelling of reaction/diffusion processes in a conducting polymer-modified ultramicroelectrode is based on coupled nonlinear reaction-diffusion equations. Adding a chemical reaction term to a Fick diffusion term during differential equation formulation often results in a nonlinear differential equation that is difficult to solve using traditional analytical methods. This is common when a complex rate expression depicts the interaction between the active sensing/mediating group on the polymer chain and the substrate. Therefore, it's necessary to get approximations of the solutions.

Meena and Rajendran [31] discussed the reaction and diffusion processes inside an electroactive polymer film placed on an inlaid microdisc electrode. Meena et al. [32] used the homotopy perturbation approach to provide approximate analytical solutions for the nonlinear equations describing diffusion and reaction within the polymer-modified ultramicroelectrode. Visuvasam et al. [41] employed analytical and numerical solutions of nonlinear diffusion equations to investigate the chronoamperometric limiting current generated by an electrochemical reaction in rotating disc electrodes. Lyons et al. [37] theoretically analyzed the electrochemical behaviour of microdisk electrodes coated with electroactive polymer thin films, considering the radial diffusion and bimolecular chemical reactions within polymer-modified ultramicroelectrodes. Albery and Hillman [7]and Andrieux et al. [8] have conducted theoretical investigations on mediated electron transfer in electroactive polymer films. Lyons et al. [27, 28] recently explored mediated electroanalysis, including charge percolation, electromigration, sensing catalysis, substrate diffusion, and the Michaelis-Menten rate equation. Rebouillat et al. [36] provided concentration and current expressions for only six limiting cases. This communication aims to present analytical solutions for the steady-state concentration and current of a polymer-modified ultramicroelectrode about the substrate concentration at the electrode surface using the Taylor series method.

2. Mathematical modelling of a problem

Standard analytical approaches cannot be used to solve the coupled non-linear reaction/diffusion equations system because of the non-linear chemical reactions. Hence, it is necessary to obtain approximate solutions. As Rebouillat et al. [36] have thoroughly analyzed the underlying assumptions and physical description of the problem, we will only provide a brief overview. Substrate diffusion is anticipated to be high in the solution layer near the microelectrode. In this study, we propose that a conducting polymer film electrodeposited on an ultramicrodisc surface would assume a hemispherical geometry with minimal spillover.

Nomenclature

s^{∞}	Bulk concentration of the substrate (μM)
A	Radius of the electrode (μm)
$C_{\sum}$	Total concentration of reduced and oxidized mediator species (μM)
D_S	Diffusion coefficient of substrate $\left(\frac{\mu\text{m}^2}{s}\right)$
D_E	Diffusion coefficient of oxidized mediator, $\frac{\mu\text{m}^2}{s}$
r	Radial variable (μm)
b	Concentration of oxidized mediator (μM)
s	Concentration of substrate (μM)
k	Bimolecular rate constant for the mediator–substrate reaction (ms)
A	Area of the hemispherical electrode (μm^2)
F	Faraday constant (C/mol)
u	Dimensionless concentration of substrate
v	Dimensionless concentration of mediator
$u(0)$	Dimensionless concentration of substrate at electrode surface
$\rho = \frac{\gamma_s}{\gamma_E}$	Dimensionless parameter
γ_s	Catalytic reaction versus substrate diffusion in the film (Dimensionless diffusion parameters)
γ_E	Catalytic reaction versus electron diffusion in the film (Dimensionless reaction parameters)
ψ	Normalized steady-state current
K	Partition coefficient
I	Net current, None
x	Dimensionless radial distance emanating from the origin of the polymer hemisphere, None
n	Number of the electrode, None

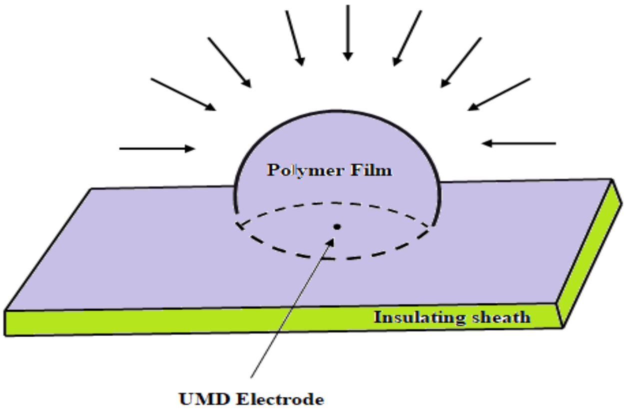


Figure 1: Schematic Representations of the Geometry Modified Electrode.

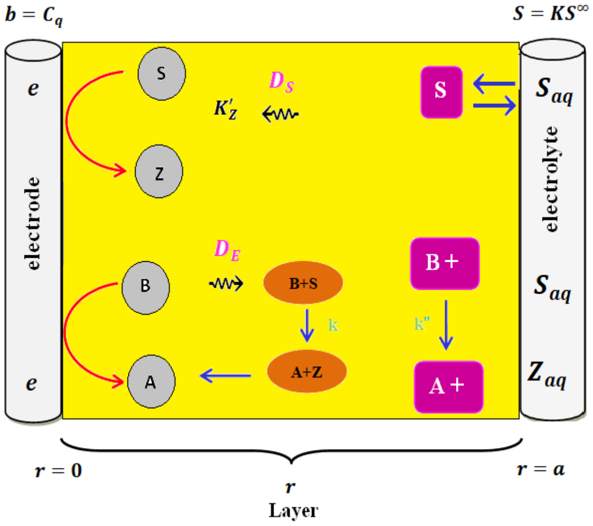


Figure 2: Schematic Representation of Conducting Polymer-Adopted by the Polymer-coatedmicroelectrode.

In Figure 1, a spherical polymer is shown resting on a flat surface. S conducting wire emerges at the hemisphere's center, as represented by a line on the flat insulating surface. Figure 2 illustrates the reaction mechanism model, where r denotes the radial distance from the center of the polymer sphere. The coupled reaction-diffusion equations governing the steady-state conditions in this process can be expressed as follows [36].

$$D_E b''(r) + \frac{2D_E}{r} b'(r) - ks(r)\, b(r) = 0, \tag{1}$$

$$D_S s''(r) + \frac{2D_S}{r} s'(r) - ks(r)\, b(r) = 0, \tag{2}$$

In this system, s refers to the concentration of substrate species present in the film, and b denotes the concentration of the oxidized mediator. The bimolecular rate constant of the mediator-substrate reaction is denoted by k, while r represents the radial coordinate.

The boundary conditions for this system can be described as follows:

$$r = 0,\ b = \mathrm{C}_{\sum},\ \frac{\mathrm{ds}}{\mathrm{dr}} = 0, \tag{3}$$

$$r = a,\ \frac{\mathrm{db}}{\mathrm{dr}} = 0,\ s = \mathrm{ks}^{\infty}, \tag{4}$$

In this context, the total concentration of reduced and oxidized mediator species is represented by $c_{\sum} = s + b$. The electrode's radius is denoted by a, and s^{∞} signifies the bulk concentration of the substrate species in the solution. The net current, denoted by 'I', can be expressed as follows:

$$I = \frac{i}{nFA} = -D_E\left(\frac{db}{dr}\right)_{r=0} = D_S\left(\frac{ds}{dr}\right)_{r=a}, \tag{5}$$

The area of the hemispherical electrode is denoted by A, the Faraday constant is represented by F, and n indicates the charge number of the electrode reaction. To make the non-linear partial differential equations outlined in Eqs. (1) and (2) dimensionless, we introduce the following dimensionless variables [9, 36]:

$$u = \frac{s}{ks^{\infty}},\ v = \frac{b}{c_{\sum}},\ x = \frac{r}{a},\ \gamma_E = \frac{kKs^{\infty}a^2}{D_E},\ \gamma_S = \frac{kc_{\Sigma}a^2}{D_s}, \tag{6}$$

The non-dimensional parameters γ_E and γ_S are used to measure the ratio of chemical reaction rates to charge percolation rates. The resulting system of equations is nonlinear and can be expressed as follows:

$$u''(x) + \frac{2}{x}u'(x) - \gamma_s u(x)v(x) = 0, \tag{7}$$

$$v''(x) + \frac{2}{x}v'(x) - \gamma_E u(x)v(x) = 0, \tag{8}$$

And the dimensionless boundary conditions are

$$\frac{du}{dx} = 0, v = 1 \quad \text{when } x = 0, \tag{9}$$

$$u = 1,\ \frac{dv}{dx} = 0 \quad \text{when } x = 1, \tag{10}$$

The normalized current is given by [36]

$$\psi = \frac{ia}{nFAD_E C_{\sum}} = -\left(\frac{dv}{dx}\right)_{x=0}, \tag{11}$$

or

$$\psi = \frac{ia}{nFAD_s ks^{\infty}} = \left(\frac{du}{dx}\right)_{x=1}. \tag{12}$$

3. Analytical solution of nonlinear differential equations using the Taylor's series method

In many scientific disciplines, nonlinear differential equations are widely used for modelling complex kinetic processes. For nonlinear equations, in general, exact solution are not obtainable and hence approximate numerical solutions are sought.

Numerous nonlinear differential equations in the fields of chemistry and physics can be solved using analytical or semi-analytical methods, such as the Akbari-Ganji [4, 5, 23, 29], variation iteration [1, 35], modified homotopy perturbation [10, 18, 19, 24], Green's function iterative [2, 3], hyperbolic function [14], Adomian decomposition [34], Taylor's series [17, 30, 33, 39, 40], and He-Laplace method [21]. Taylor's series method (TSM) has recently been utilized to solve nonlinear problems in chemical science [17, 30, 33, 39, 40]. TSM does not require a perturbation parameter, unlike perturbation-based approaches or trial functions, such as HAM or HPM. TSM is efficiently simple and cab be easily implemented via various computer algebra programs like Mathematica or Maple. The proposed TSM method generates analytical expressions of the substrate and product concentrations by direct substitution into the nonlinear model (7)-(8) (see details in Appendix A.)

$$u(x)=u(0)+\frac{\gamma_s u(0)}{3}\left(\frac{x^2}{2!}\right)+\frac{\gamma_s}{5}[\gamma_s u(0)+\gamma_E(u(0))^2]\left(\frac{x^4}{4!}\right)+\frac{\gamma_s}{7}[\gamma_s^2 u(0)+\gamma_E(u(0))^2$$
$$+\gamma_s^2(u(0))^2+\gamma_E(u(0))^3+10\gamma_s u(0)+10\gamma_E u(0)]\left(\frac{x^6}{6!}\right), \tag{13}$$

By utilizing the boundary condition Eq. (10), we obtain

$$1=u(0)+\frac{\gamma_s u(0)}{3}\left(\frac{1}{2}\right)+\left(\frac{1}{120}\right)(\gamma_s^2 u(0)+\gamma_E\gamma_s(u(0))^2)$$
$$+\left(\frac{1}{5040}\right)(\gamma_s^3 u(0)+\gamma_s\gamma_E(u(0))^2$$
$$+\gamma_s^3(u(0))^2+\gamma_s\gamma_E(u(0))^3+10\gamma_s^2 u(0)+10\gamma_E\gamma_s u(0)), \tag{14}$$

Some computed values of $u(0)$ for specific parameter values of γ_s and γ_E are given in Table 1. Using Eq. (14), and the relation between $u(x)$ and $v(x)$ (Appendix B), we obtain

$$v(x)=1+\frac{u(x)-u(0)}{\rho}, \tag{15}$$

The expression of the current follows from Eqs. (12) and (13) as follows:

$$\psi=\left(\frac{\mathrm{du}}{\mathrm{dx}}\right)_{\mathrm{x=1}}=u(0)\left[\frac{\gamma_s}{3}+\frac{\gamma_s^2}{420}+\frac{\gamma_s^3}{840}+\frac{\gamma_s\gamma_E}{840}\right]$$
$$+(u(0))^2\left[\frac{29\gamma_s\gamma_E}{420}+\frac{\gamma_s^3}{840}\right]+(u(0))^3\frac{\gamma_s\gamma_E}{840}. \tag{16}$$

4. Previous results

The concentration of substrate and mediator was analytically determined by Senthamarai and Rajendran [38] using the variation iteration method, yielding the following result:

$$u(x) = l + \frac{x^2}{4}(2l - 2 + l\gamma_s) - \frac{x^3}{3}lm\gamma_s + \frac{x^4}{8}(1 - l + lm)\gamma_s + \frac{x^5}{5}(l-1)\gamma_s m + \frac{x^6}{12}m\gamma_s(1-l), \tag{17}$$

$$v(x) = 1 + \frac{x^2}{4}(l\gamma_E - 2m) - \frac{x^3}{3}lm\gamma_E + \frac{x^4}{8}(1 - l + lm)\gamma_E + \frac{x^5}{5}(l-1)\gamma_E m + \frac{x^6}{12}m\gamma_E(1-l), \tag{18}$$

where

$$l = u(0) = \frac{(360 - \gamma_S\gamma_E - 30\gamma_S + 180\gamma_E)}{(360 + 4\gamma_S\gamma_E + 30\gamma_S + 180\gamma_E)} \text{ and } m = \frac{\gamma_E}{\gamma_E + 2}, \tag{19}$$

Additionally, Rebouillat and colleagues [36] employed the variation iteration method to derive the following analytical formulas for the concentration of substrate and mediator:

$$u(x) = \frac{\sinh(\sqrt{\gamma_s}x)}{x\sinh(\sqrt{\gamma_s})}, \tag{20}$$

$$v(x) = \frac{\exp(-\sqrt{\gamma_E})}{\sqrt{\gamma_E}f(\gamma_E)x}\{f(\gamma_E)\exp[-\sqrt{\gamma_E}(1-x)] - \exp[\sqrt{\gamma_E}(1-x)]\}, \tag{21}$$

where

$$F(\gamma_E) = 1 + f(\gamma_E)\exp(-2\sqrt{\gamma_E}) \text{ in which } f(\gamma_E) = \frac{1+\sqrt{\gamma_E}}{1-\sqrt{\gamma_E}}. \tag{22}$$

Senthamarai's result (Eq. (18)) for $v(x)$ is bigger than one for all values of parameters (refer Table 5). However, Rebouillat et al.'s solution (Eq. (21)) is not a valid representation of $v(x)$ (refer Table 5). On the other hand, for all parameter values, our new results (Eqs. (13) and (15)) are less than or equal to one (refer Tables 2–5).

5. Discussion

Eq. (13) presents new analytical formulas that allow for the interpretation of substrate concentration profiles for all values of γ_s and γ_E in a more straightforward manner.

5.1. Validation of analytical results

The validation of analytical findings is a critical objective to ensure the accuracy and reliability of any proposed technique. In this study, we validate our analytical results by comparing them with previous analytical and simulation results. Our analytical findings are compared with prior analytical results in Tables 2 and 3, and with simulation results in Table 4. The comparison in Table 2 reveals that the results reported by Senthamarai et al. [38] are only satisfactory for small values of γ_S and γ_E (in particular when $\gamma_S \leq 1$ and $\gamma_E \leq 1$), while Eq. (20) obtained by Rebouillat et al. [36] is independent of the parameter γ_E (see Eq. (20)). The comparison in Table 4 shows that the maximum average deviation between our analytical results and numerical results (MATLAB) is 0.1. Furthermore, Table 5 indicates that the result of Rebouillat et al. [36] is not an acceptable expression for $v(x)$, while Senthamarai's results [38] for $v(x)$ are greater than one. In contrast, our results are less than or equal to one for all parameter values.

Figure 3(a–d) shows a set of normalized concentration profiles of a substrate, which vary with the reaction/diffusion parameters γ_S and γ_E. By referring to Eq. (13) and the graph, it can be seen that the minimum value of u occurs at $x = 0$, which is denoted by $u(0)$, and the maximum value of u occurs at $x = 1$, with a maximum value of 1. Based on Figure 3(a–d), it can be inferred that u is approximately equal to 1 for all values of γ_E and $\gamma_S \leq 0.1$. Additionally, as γ_S increases, the concentration of substrate at the electrode surface $(u(0))$ decreases.

Figure 4 represents the concentration of a mediator, denoted as v, for all values of γ_S and γ_E. Figures 4(a) and 4(b) indicate that the mediator concentration (v) is approximately equal to 1 when both γ_S and γ_E are less than or equal to 1. Furthermore, the concentration of $v(x)$ increases as γ_E increases or γ_S decreases, according to Figures 4(a) and 4(b). Referring to Eq. (15) and Figure 4, it can be inferred that the minimum value of the mediator concentration v occurs at $x = 0$, with a minimum value of 1, while the maximum value of v occurs at $x = 1$, with a maximum value of $1 + 1/\rho(1 - u(0))$.

The normalized current response for different values of γ_E and γ_S is depicted in Figure 5(a–c). The figure suggests that an increase in γ_E and γ_S leads to a corresponding increase in current. Furthermore, it can be observed that the current attains a steady-state value when $\gamma_S \gg 100$ and $\gamma_E \gg 100$.

A comparison between our analytical results and the numerical results for the current at all parameter values is presented in Table 6. The table indicates that the average maximum difference between our analytical and numerical results is 0.005.

Table 1: Numerical Values of $u(0)$ for Various Values of γ_s and γ_E using Eq. (14).

Parameter	$\gamma_E = 0.1$			$\gamma_E = 1$			$\gamma_E = 5$			$\gamma_E = 10$		
γ_S	1	5	10	1	5	10	1	5	10	1	5	10
$u(0)$	0.8486	0.4693	0.2531	0.8427	0.4635	0.2508	0.2411	0.2411	0.2411	0.7900	0.4159	0.2305

Table 2: Comparison Between Computed Substrate Concentrations Given by Eq. (13) of Current Work with Other Results in the Literature. A and B refer to Eq. (20) of Ref. [36] and Eq. (17) of Ref. [38], respectively.

x	Substrate concentration $u(x)$														
	$\gamma_s = 1$ and $\gamma_E = 1$			$\gamma_s = 5$ and $\gamma_E = 5$			$\gamma_s = 10$ and $\gamma_E = 10$			$\gamma_s = 20$ and $\gamma_E = 1$			$\gamma_s = 10$ and $\gamma_E = 20$		
	A	B	Current work	A	B	Current work	A	B	Current work	A	B	Current work	A	B	Current work
0.01	0.8496	0.8870	0.8427	0.4835	0.7185	0.4403	0.2682	0.6155	0.2305	0.1022	0.0655	0.0975	0.2682	0.6839	0.2127
0.20	0.8553	0.8929	0.8483	0.4997	0.7427	0.4551	0.2864	0.6572	0.2463	0.1163	0.0622	0.1110	0.2864	0.7309	0.2272
0.40	0.8726	0.9083	0.8655	0.5505	0.7959	0.5026	0.3456	0.7446	0.2986	0.1661	0.0844	0.1588	0.3456	0.8245	0.2766
0.60	0.9020	0.9313	0.8951	0.6421	0.8590	0.5923	0.4607	0.8388	0.4064	0.2773	0.2209	0.2685	0.4607	0.9132	0.3815
0.80	0.9441	0.9613	0.9389	0.7859	0.9248	0.7452	0.6611	0.9212	0.6122	0.5107	0.6086	0.5049	0.6611	0.9704	0.5902
1.00	1.0000	0.9999	1.0000	1.0000	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	1.4443	0.9999	1.0000	1.0000	0.9998

Table 3: Deviation (Absolute Difference) Between Computed Substrate Concentrations Given by Eq. (13) of Current Work and Other Results in the Literature. A Represent Eq. (20) in Ref. [36], B Represents Eq. (17) in Ref. [38], and C Represents the Deviation Between B and the Current Work.

x	Substrate concentration $u(x)$											
	$\gamma_s = 0.1$ and $\gamma_E = 0.1$				$\gamma_s = 1$ and $\gamma_E = 0.1$				$\gamma_s = 10$ and $\gamma_E = 0.1$			
	A	B	Current work	C	A	B	Current Work	C	A	B	Current Work	C
0.0	0.9835	0.9835	0.9834	0.0001	0.8509	0.8509	0.8506	0.0003	0.2682	0.2682	0.2531	0.0151
0.2	0.9842	0.9842	0.9841	0.0001	0.8566	0.8568	0.8563	0.0005	0.2864	0.2953	0.2703	0.025
0.4	0.9862	0.9862	0.9860	0.0002	0.8738	0.8744	0.8735	0.0009	0.3457	0.3694	0.3264	0.043
0.6	0.9894	0.9894	0.9893	0.0001	0.9029	0.9036	0.9027	0.0009	0.4607	0.4891	0.4377	0.0514
0.8	0.9941	0.9941	0.9940	0.0001	0.9446	0.9450	0.9451	0.0001	0.6611	0.6762	0.6395	0.0368
1.0	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000	1.0000	0.0000
	Average			0.0001				0.0005				0.0285

Table 4: Deviation (Absolute Difference) Between Computed Substrate Concentrations Given by Eq. (13) of the Current Work and Numerical Simulations for Various Values of Parameters.

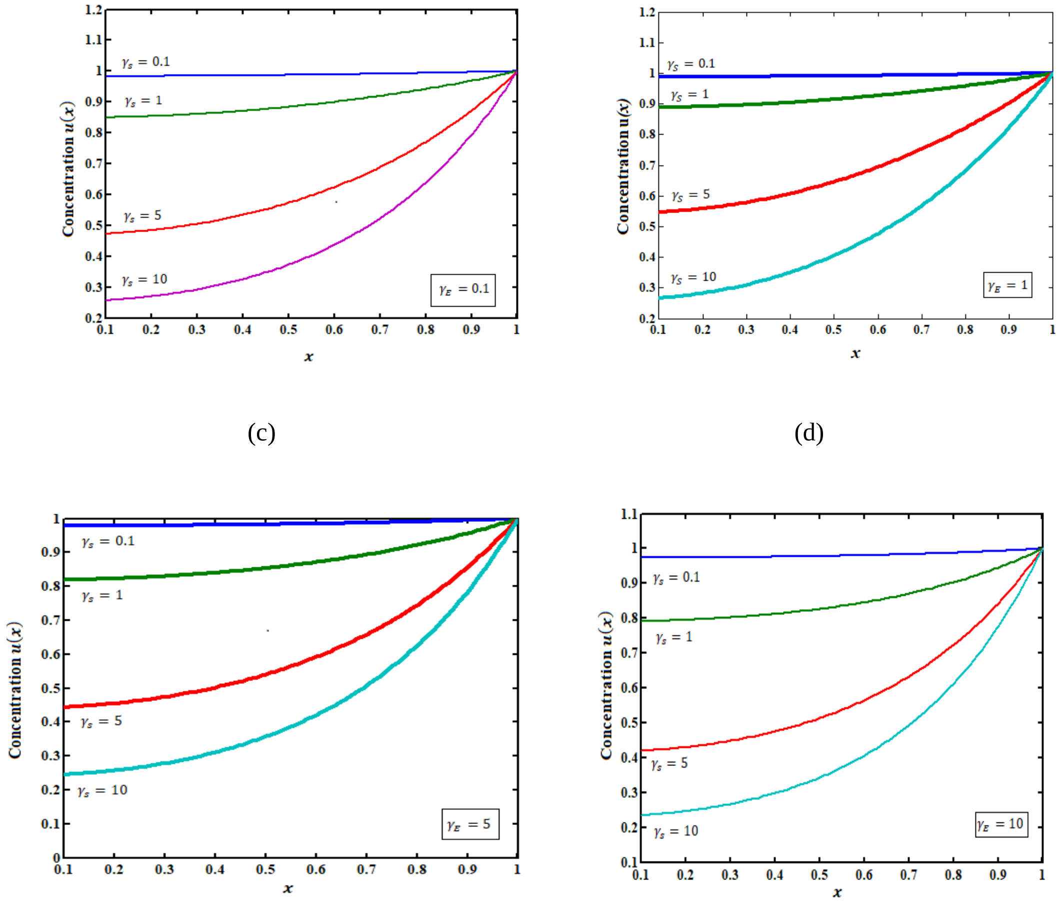
x	Substrate concentration $u(x)$											
	$\gamma_s = 0.1$ and $\gamma_E = 0.1$			$\gamma_s = 1$ and $\gamma_E = 1$			$\gamma_s = 5$ and $\gamma_E = 5$			$\gamma_s = 10$ and $\gamma_E = 10$		
	Numerical results	Current work	Absolute difference	Numerical results	Current work	Absolute difference	Numerical results	Current work	Absolute difference	Numerical results	Current work	Absolute difference
0.0	0.9831	0.9836	0.0005	0.9145	0.8441	0.0704	0.2970	0.4440	0.1470	0.1154	0.2344	0.1190
0.3	0.9842	0.9849	0.0007	0.9132	0.8554	0.0578	0.3211	0.4744	0.1533	0.1351	0.2671	0.1320
0.5	0.9869	0.9875	0.0006	0.9297	0.8787	0.0510	0.3967	0.5412	0.1445	0.2029	0.3464	0.1435
0.7	0.9911	0.9914	0.0003	0.9528	0.9151	0.0377	0.5439	0.6590	0.1151	0.3584	0.4930	0.1346
0.9	0.9967	0.9968	0.0001	0.9825	0.9670	0.0155	0.8047	0.8565	0.0518	0.6988	0.7760	0.0772
1.0	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000
Average			0.0004			0.0387			0.1019			0.1011

Table 5: Deviation (Absolute Difference) Between Computed Mediator Concentrations Given by Eq. (15) of Current Work and Other Results in the Literature. A Represent Eq. (21) in Ref. [36], B Represents Eq. (18) in Ref. [38], and C Represents the Deviation Between B and the Current Work.

x	Mediator Concentration $v(x)$								
	$\gamma_s = 1$ and $\gamma_E = 1$			$\gamma_s = 5$ and $\gamma_E = 5$			$\gamma_s = 10$ and $\gamma_E = 10$		
	A	B	Current Work	A	B	Current Work	A	B	Current Work
0.10	−664.3	1.0007	0.9968	−2.5410	1.0050	0.9974	−4.4370	1.0182	0.9999
0.20	−283.7	1.0026	0.9873	−1.0060	1.0160	0.9894	−1.6120	1.0628	0.9995
0.30	−159.7	1.0049	0.9715	−0.5274	1.0290	0.9760	−0.7790	1.0209	0.9988
0.40	−99.53	1.0074	0.9491	−0.3082	1.0430	0.9572	−0.4213	1.0822	0.9979
0.50	−64.61	1.0097	0.9201	−0.1890	1.0540	0.9328	−0.2407	1.2387	0.9967
0.60	−42.13	1.0116	0.8844	−0.1174	1.0630	0.9025	−0.1405	1.2850	0.9952
0.70	−26.62	1.0129	0.8418	−0.0714	1.0670	0.8663	−0.0811	1.3182	0.9935
0.80	−15.34	1.0137	0.7920	−0.0400	1.0680	0.8237	0.0437	1.3378	0.9915
0.90	−6.766	1.0141	0.7347	−0.0173	1.0660	0.7746	0.0185	1.3456	0.9893
1.00	0.0000	1.0141	0.6697	0.0000	1.0650	0.7189	0.0000	1.3472	0.9862

Table 6: Comparison of Current Values (Ψ) Between the Analytical Solution (Current Work) and Numerical Simulations for Various Values of Parameters.

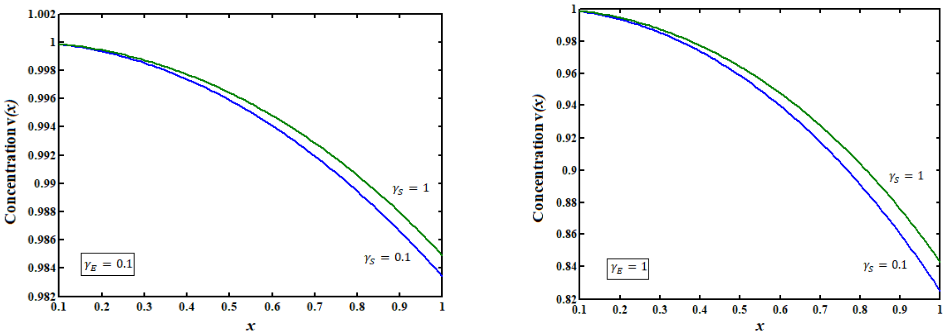
γ_E	Current Ψ											
	$\gamma_s = 0.1$			$\gamma_s = 1$			$\gamma_s = 10$			$\gamma_s = 100$		
	Current Work	Numerical results	Absolute Error	Current Work	Numerical results	Absolute Error	Current Work	Numerical results	Absolute Error	Current Work	Numerical results	Absolute Error
0	0.0000	0.0000	0.0000	0.0000	0.0013	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
20	0.1218	0.1210	0.0008	0.8506	0.8454	0.0052	2.7999	2.8202	0.0203	5.2608	5.2620	0.0012
40	0.2044	0.2067	0.0023	1.2122	1.2254	0.0132	3.0974	3.0990	0.0016	5.2694	5.2690	0.0004
60	0.2819	0.2852	0.0033	1.4856	1.474	0.0116	3.3235	3.3260	0.0025	5.2781	5.2780	0.0001
80	0.3547	0.3680	0.0133	1.7043	1.7140	0.0097	3.5047	3.5120	0.0073	5.2964	5.2870	0.0094
100	0.4235	0.4330	0.0095	1.8862	1.8850	0.0012	3.6552	3.6550	0.0002	5.2945	5.2950	0.0005
Average			0.00436			0.00103			0.00530			0.00137



(a) (b)

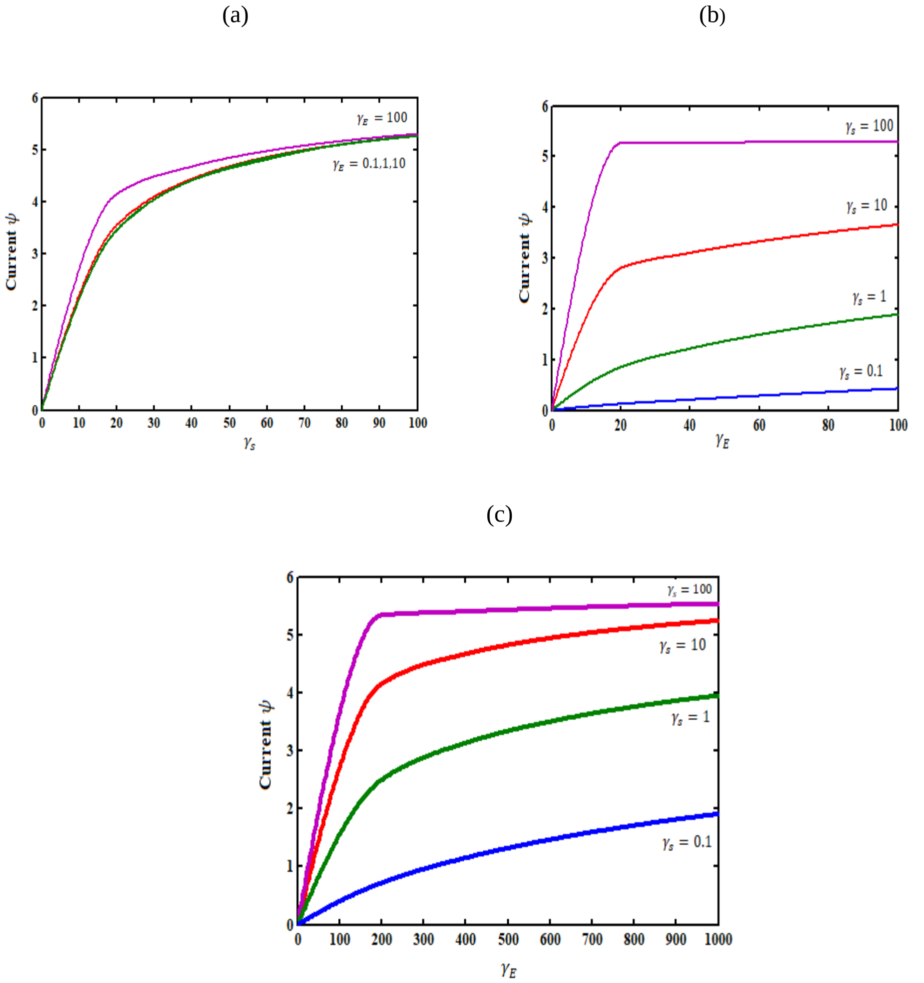
(c) (d)

Figure 3: Normalized Substrate Concentration u at a Polymer Microelectrode. The Concentrations Were Computed Using Eq. (13), for Various Values of the Reaction/Diffusion Parameters γ_E and γ_s.



(a) (b)

Figure 4: Normalized Mediator Concentration v at a Polymer Microelectrode Using Eq. (15), for Various Values of the Reaction/Diffusion Parameters γ_E and γ_s.


(a)

(b)

(c)

Figure 5: Variation of Normalized Steady-State Current Response ψ for Various Values of γ_E Using Eq. (16).

6. Conclusions

This study aims to estimate the concentrations of the mediator, substrate, and current for the non-linear Michaelis-Menten kinetic scheme. To achieve this, we utilized Taylor's series method to derive analytical expressions for the substrate concentration and the mediated profiles within the polymer film. The steady-state substrate and mediator concentrations, as well as the steady-state current, were also expressed analytically in simple closed forms. Furthermore, we evaluated the transport and kinetics based on the polymer's fundamental reaction/diffusion parameters, γ_S and γ_E. Our method is straightforward and holds promise for solving other non-linear equations. The analytical results demonstrate the reliability of Taylor's series method in solving this type of non-linear differential equation. It is possible to extend this analytical procedure to other spillover models for various electrode geometries, among others, in addition to the amperometric biosensor study.

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References

[1] M Abukhaled. Variational iteration method for nonlinear singular two-point boundary value problems arising in human physiology. *Journal of Mathematics*, 2012, 2013.

[2] M Abukhaled. Green's function iterative method for solving a class of boundary value problems arising in heat transfer. *Applied Mathematics & Information Sciences*, 11:229–234, 2017.

[3] M Abukhaled. Green's function iterative approach for solving strongly nonlinear oscillators. *Journal of Computational and Nonlinear Dynamics*, 12:051021, 2017.

[4] MR Akbari, S Akbari, E Kalantari, and DD Ganji. Akbari-Ganj's method "AGM" to chemical reactor design for non-isothermal and non-adiabatic of mixed flow reactors. *Journal of Materials Science and Chemical Engineering*, 11(1):1–9, 2020.

[5] MR Akbari, DD Ganji, M Nimafar, and AR Ahmadi. Significant progress in solution of nonlinear equations at displacement of structure and heat transfer extended surface by new AGM approach. *Frontiers of Mechanical Engineering*, 9(4):390–401, 2014.

[6] WJ Albery, Z Chen, BR Horrocks, AR Mount, PJ Wilson, D Bloor, AT Monkman, and CM Elliott. Spectroscopic and electrochemical studies of charge transfer in modified electrodes. *Faraday Discuss Chem Soc*, 88:247–259, 1989.

[7] WJ Albery and AR Hillman. Transport and kinetics in modified electrodes. *Journal of Electroanalytical Chemistry*, 170:27–49, 1984.

[8] CP Andrieux, JM Dumas-Bouchiat, and JM Saveant. Kinetics of electrochemical reactions mediated by redox polymer films. new formulation and strategies for analysis and optimization. *Journal of Electroanalytical Chemistry*, 169:9–21, 1984.

[9] CP Andrieux, JM Dumas-Bouchiat, and JM Saveant. Catalysis of electrochemical reactions at redox polymer electrodes: Kinetic model for stationary voltammetric techniques. *Journal of Electroanalytical Chemistry*, 131:1–35, 1992.

[10] N Anjum, JH He, QT Ain, and D Tian. Li-He modified homotopy perturbation method for doubly-clamped electrically actuated microbeams-based microelectromechanical system. *Facta Universitatis Series Mechanical Engineering*, 19(4):601–612, 2021.

[11] C Barbero, MC Mirasa, O Haas, and R Kotz. Direct in situ evidence for proton/anion exchange in polyaniline films by means of probe beam deflection. *Journal Electrochemical Society*, 138:669–672, 1991.

[12] AJ Bard and MV Mirkin. Scanning electrochemical microscopy. *Journal Electrochemical Society*, 2001.

[13] PN Bartlett, PR Birkin, and EKN Wallace. Oxidation of β-nicotinamide adenine dinucleotide (NADH) at poly(aniline)-coated electrodes. *J. Chem Soc Faraday Trans*, 93:1951–1960, 1997.

[14] M Chitra Devi, P Pirabaharan, L Rajendran, and M Abukhaled. An efficient method for finding analytical expressions of substrate concentrations for different particles in an immobilized enzyme system. *Reaction Kinetics, Mechanisms and Catalysis*, 130:35–53, 2020.

[15] DJ Fermin, J Mostany, and BR Scharifker. Electronically conducting polymers: Synthesis and electrochemical properties of polypyrrole. *Current Topic in Electrochemistry*, 2:131–144, 1993.

[16] M Fleishmann, S Pons, D Rolison, and PP Schmidt. *Ultramicroelectrodes.* Datatech Systems & Technology, Morganton, NC, 1987.

[17] JH He. Taylor series solution for a third order boundary value problem arising in architectural engineering. *Ain Shams Engineering Journal*, 11(4):1411–1414, 2022.

[18] JH He and YO El-Dib. The enhanced homotopy perturbation method for axial vibration of strings. *Facta Universitatis Series Mechanical Engineering*, 19(4):735–750, 2021.

[19] JH He and YO El-Dib. A heuristic review on the homotopy perturbation method for non-conservative oscillators. *Journal of Low Frequency Noise Vibration and Active Control*, 41(2):572–603, 2022.

[20] SJ Higgins, PA Christensen, A Hamnett, and MEG Lyons. *Electroactive Polymer Electrochemistry: Part II. Methods and Applications.* Plenum Press, New York, Springer, 1996.

[21] J.H. He and G. M. Moatimid and D.R. Mostapha. Nonlinear instability of two streaming-superposed magnetic Reiner-Rivlin Fluids by He-Laplace method. *Journal of Electroanalytical Chemistry*, 895:115388, 2021.

[22] JP Hornak. *Encyclopedia of Imaging Science and Technology.* A Wiley Interscience Publication, 2002.

[23] P Jeyabarathi, L Rajendran, MEG Lyons, and M Abukhaled. Theoretical analysis of mass transfer behavior in fixed-bed electrochemical reactors: Akbari-Ganji's method. *Electrochem*, 3:699–712, 2022.

[24] QP Ji, J Wang, LX Lu, and CF Ge. Li-He's modified homotopy perturbation method coupled with the energy method for the dropping shock response of a tangent nonlinear packaging system. *Journal of Low Frequency Noise Vibration and Active Control*, 40(2):675–682, 2021.

[25] AA Karyakin, OA Bobrova, and EE Karyakina. Electroreduction of NAD+ to enzymatically active NADH at poly (neutral red) modified electrodes. *Journal of Electroanalytical Chemistry*, 399:179–184, 1995.

[26] DM Kolb, RJ Nichols, and RJ Behm. The application of scanning tunneling microscopy to electrochemistry. In R. Guidelli, editor, *Electrified Interfaces in Physics, Chemistry and Biology.*, volume 355. NATO ASI Series, Springer, 1992.

[27] MEG Lyons, T Bannon, G Hinds, and S Rebouillat. Reaction/diffusion with Michalis–Menten kinetics in electroactive polymer films. Part 2. the transient amperometric response. *Analyst*, 123:1947–1959, 1998.

[28] MEG Lyons, JC Greer, CA Fitzgerald, T Bannon, and PN Bartlett. Reaction/diffusion with Michaelis–Menten kinetics in electroactive polymer films. Part 1. the steady-state amperometric response. *Analyst*, 121:715–731, 1996.

[29] B Manimegalai, MEG Lyons, and L Rajendran. A kinetic model for amperometric immobilized enzymes at planar, cylindrical and spherical electrodes: The Akbari-Ganji method. *Journal of Electroanalytical Chemistry*, 880:114921, 2021.

[30] M. Lilly Clarance Mary, A. Meena M. C. Devi, L. Rajendran, and M. Abukhaled. A reliable taylor series solution to the nonlinear reaction-diffusion model representing the steady-state behaviour of a cationic glucose-sensitive membrane. *J. Math. Comput. Sci*, 11:8354–8381, 2021.

[31] A Meena and L Rajendran. Analytical solution of system of coupled non-linear reaction diffusion equations. Part I: Mediated electron transfer at conducting polymer ultramicroelectrodes. *Journal of Electroanalytical Chemistry*, 647(2):103–116, 2010.

[32] A Meena and L Rajendran. Analytical solution of system of coupled non-linear reaction diffusion equations. Part II: Direct reaction of substrate at underlying microdisc surface. *Journal of Electroanalytical Chemistry*, 650(1):143–151, 2010.

[33] KL Narayanan, R Shanthi, R Usha Rani, and MEG Lyons. Mathematical modelling of forced convection in a porous medium for a general geometry: Solution of thermal energy equation via Taylor's series with ying buzu algorithms. *Int. Journal of Electrochemical Science*, 17:220623, 2020.

[34] S Noeiaghdam, D Sidorov, AM Wazwaz, N Sidorov, and V Sizikov. The numerical validation of the adomian decomposition method for solving volterra integral equation with discontinuous kernels using the CESTAC method. *Mathematics*, 9(3):1–15, 2021.

[35] L Rajendran and G Rahamathunissa. Application of he's variational iteration method in nonlinear boundary value problems in enzyme – substrate reaction diffusion processes: Part 1. the steady-state amperometric response. *Journal of Mathematical Chemistry*, 44:849–861, 2008.

[36] S Rebouillat, MEG Lyons, and A Flynn. Heterogeneous redox catalysis at conducting polymer ultramicroelectrodes. *Analyst*, 124:1635–1644, 1999.

[37] S Rebouillat, MEG Lyons, and A Flynn. Mediated electron transfer at conducting. *Analyst*, 125:1611–1628, 2000.

[38] R Senthamarai and L Rajendran. System of coupled non-linear reaction diffusion processes at conducting polymer-modified ultramicroelectrodes. *Electrochimica Acta*, 55:3223–3235, 2010.

[39] F Shiraishi, M Egashira, and M Iwata. Highly accurate computation of dynamic sensitivities in metabolic reaction systems by a Taylor series method. *Mathematical Biosciences*, 233(1):59–67, 2011.

[40] S Vinolyn Sylvia, R Joy Salomi, L Rajendran, and M Abukhaled. Solving nonlinear reaction–diffusion problem in electrostatic interaction with reaction-generated pH change on the kinetics of immobilized enzyme systems using Taylor series method. *Journal of Mathematical Chemistry*, 59(5):1332–1347, 2021.

[41] J Visuvasam, A Meena, and L Rajendran. New analytical method for solving nonlinear equation in rotating disk electrodes for second-order ECE reactions. *Journal of Electroanalytical Chemistry*, 856:114106, 2010.

[42] SA Wring and JP Hart. Chemically Modified, Carbon-based Electrodes and Their Application as Electrochemical Sensors for the Analysis of Biologically Important Compounds: A Review. *Analyst*, 119:1215–1229, 1992.

Appendix

Appendix A. Approximate analytical solution of nonlinear Eq. (7) using Taylor's series method

Assume the solution of Eq. (7) is expressed in the following Taylor's series expansion

$$u(x) = u(0) + u'(0)x + u''(0)\frac{x^2}{2!} + u'''(0)\frac{x^3}{3!} + u^{(4)}(0)\frac{x^4}{4!} + \cdots , \tag{A1}$$

Take the derivate of the Eq. (7), we get

$$xu'''(x) + 3u''(x) - \gamma_s[xu^{'(x)}v(x) + xu(x)v'(x) + u(x)v(x)] = 0, \tag{A2}$$

Put $x = 0$ in Eqn. (A2) and using the boundary condition given in Eq. (9), we get

$$u''(0) = \frac{\gamma_s u(0)}{3}, \tag{A3}$$

Differentiating Eq. (A2) again, with respect to x, gives

$$xu^{(4)}(x) + 4u'''(x) - \gamma_s[xv(x) + xu''(x)v''(x) + 2u'(x)v^{'(x)} + 2u'(x)v(x) + 2u(x)v^{'(x)}] = 0, \tag{A4}$$

Substituting $x = 0$ in Eq. (A4) and using boundary conditions (Eq. (9)) implies

$$u'''(0) = 0, \tag{A5}$$

Continuing with another derivative of Eq. (A4) and using the boundary condition (Eq. (9)) gives

$$\begin{aligned} xu^{(5)}(x) + 5u^{(4)}(x) - \gamma_s[xu'''(x)v(x) + xu(x)v'''(x) + 3xu''(x)(x)v^{'(x)} + 3u^{''(x)}v(x) \\ + 3xu'(x)v(x) + 3u(x)v(x) + 6u(x)v'(x)] = 0, \end{aligned} \tag{A6}$$

Now when $x = 0$, Eq. (A6) becomes

$$u^{(4)}(0) = \frac{\gamma_s}{5}[\gamma_s u(0) + \gamma_E(u(0)^2], \tag{A7}$$

By similar technique, the following are readily obtained:

$$u^{(5)}(0) = 0, \tag{A8}$$

$$u^{(6)}(0) = \frac{\gamma_s}{7}[\gamma_s^2 u(0) + \gamma_E\gamma_s(u(0))^2 + \gamma_s^2(u(0))^2 + \gamma_s\gamma_E(u(0))^3 + 10\gamma_s u(0) + 10\gamma_E u(0)]. \tag{A9}$$

When we substitute Eqs. (A3), (A5), (A7), (A8) and (A9) into Eq. (A1), we obtain Eq. (13).

Appendix B. Relation between $u(x)$ and $v(x)$

From Eqs. (7) and (8), we have

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

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

$$\frac{d}{dx}\left(x^2\frac{du(x)}{dx}\right) = \rho\frac{d}{dx}\left(x^2\frac{dv\,(X)}{dx}\right), \tag{B3}$$

where $\rho = \frac{\gamma_s}{\gamma_E}$

Integrating (B3) gives

$$\frac{du(x)}{dx} = \rho\frac{dv(x)}{dx} + \frac{1}{x^2}, \tag{B4}$$

And integrating (B4) gives

$$xu(x) = x\rho v(x) - c_1 + xc_2, \tag{B5}$$

Letting $x = 0$ in Eq. (B5) gives $c_1 = 0$, and hence Eq. (B5) becomes

$$u(x) = \rho v(x) + c_2, \tag{B6}$$

Letting $x = 0$ again leads to $c_2 = u(0) - \rho$. Solving Eq. (B6) for $v(x)$ gives

$$v(x) = 1 + \frac{u(x) - u(0)}{\rho}. \tag{B7}$$