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Analysis of Amperometric Enzyme Electrodes in the Homogeneous Mediated Mechanism using Variational iteration Method

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A Mathematical model of amperometric enzyme electrodes is re-studied using variational iteration method. In this paper, He's variational iteration method is implemented to give an approximate and an analytical solution of nonlinear differential equations describing the transport and kinetics of the enzyme and of the mediator in the diffusion layer of the electrode. The variational iteration method produces a simple analytical solution for an enzyme electrode where electron transfer is accomplished by a mediator reacting in a homogeneous solution. These analytical results are compared with available limiting case results and are found to be in good agreement.

Keywords: Mathematical modelling; Homogeneous mechanism; Diffusion and Kinetics; Amperometric enzyme electrode; Variational iteration method.

1. INTRODUCTION

Recently, there has been much interest in the use of mediators to effect electron transfer reactions between biological molecules (enzymes or reduced form of Nicotinamide Adenine Dinucleotide (NADH)) and electrodes [1]. The importance for this work has been focused on two major areas. First the successful transduction of the rate of an enzymatic reaction into a current provides the basis of a selective amperometric enzyme electrode. Second the study of such system provides information about the mechanism of electron transfer in biological system [2 - 14].

John Albery's et al [1] presented a complete theoretical treatment for an enzyme electrode where electron transfer from the enzyme to the electrode is achieved by a mediator reacting in homogeneous solution. John Albery's et al [1] solved the second-order differential equations describing the transport and kinetics of the enzyme and of the mediator in the diffusion layer of the electrode only for the various limiting values of the dimensionless parameters γ, κ_E and κ_M. These

parameters are defined below the eqn. (13). Recently Lyons described the mathematical model of transport and kinetics of substrate and redox mediator within chemically modified electrodes comprising of redox enzymes immobilized in dispersed carbon nanotube meshes dispersed on support electrode surfaces [15].To our knowledge, no general analytical expressions of the concentration of the mediator and the enzyme and current have been reported for all values of parameters [1]. The purpose of this paper is to derive the concentration of the mediator and enzyme for all values of reaction parameters γ, κ_{E} and κ_{M} using variational iteration method [16, 17].

2. MATHEMATICAL FORMULATION OF THE BOUNDARY-VALUE PROBLEM AND ANALYSIS

In biological system, at the electrode

$$M' \rightarrow M$$

homogeneous solution may be expressed by

$$M + E' \xrightarrow{k_M} M' + E$$

$$E \xrightarrow{k_E} E'$$

On the electrode, the mediator redox couple M / M' is converted and reacts with the enzyme in the solution. k_E is the rate constant with which the enzyme reacts with its substrate *S*. k_M is the rate constant with which the enzyme reacts with the mediator. The enzyme is saturated when substrate concentration is sufficiently large. Now the rate constant k_E will be equal to k_{cat}. If the system is unsaturated,

$$k_E = (k_{cat} / K_M)[S] \tag{1}$$

Here we assume that [*S*] is sufficiently large that there is no concentration polarization of *S* in the diffusion layer of the electrode. K_M denotes the Michaelis-Menten constant. Within the diffusion layer of thickness Z_D, the diffusion and kinetics of the four species M, M', E and E' are given by the following differential equations,

$$D_M \partial^2 m / \partial z^2 - k_M e' m = 0 \tag{2}$$

$$D_M \partial^2 m' / \partial z^2 + k_M e' m = 0 \tag{3}$$

$$D_E \partial^2 e' / \partial z^2 - k_M e' m + k_E e = 0 \tag{4}$$

$$D_E \partial^2 e / \partial z^2 + k_M e' m - k_E e = 0 \tag{5}$$

where m, m', e', e represent the concentrations of the various species. D_M is the diffusion coefficient of M and M'. D_E is the diffusion coefficient of E and E'. z is the distance between the electrode and the species. When the electrode is the source of the mediator, on the electrode surface where $z = 0$, the boundary conditions are given by

$$m = m_0,\ m' = 0 \text{ and } (\partial e / \partial z)_{z=0} = (\partial e' / \partial z)_{z=0} = 0 \tag{6}$$

m_0 denote the initial concentration of the mediator. The boundary conditions at the outside edge of the diffusion layer where $z = Z_D$ are

$$m = m' = 0,\ e = 0 \text{ and } e' = e_\Sigma \tag{7}$$

where e_Σ denotes the total concentration of enzyme species. The flux j of electrons from the conversion of M' to M at the electrode surface involving n electrons is given by

$$j = nD_M (\partial m'/\partial z)_{z=0} \tag{8}$$

Integrating the sum of eqns. (2) and (3) gives

$$m + m' = m_0(1 - z/Z_D) \tag{9}$$

Similarly, integrating the sum of eqns. (4) and (5) gives

$$e + e' = e_\Sigma \tag{10}$$

We make the nonlinear differential equations dimensionless by defining the following parameters:

$$u = m/m_0;\ u' = m'/m_0; v = e'/e_\Sigma; \chi = z/Z_D; \kappa_M = k_M Z_D^2 e_\Sigma / D_M;$$

$$\kappa_E = k_M Z_D^2 / D_E \text{ and } \gamma = k_M m_0 / k_E. \tag{11}$$

Here the typical concentration profiles are denoted as u, u', v and 1-v for M, M', E' and E respectively. χ is the normalized distance from the electrode / membrane interface. Now the given two differential equations reduce to the following dimensionless form [1] :

$$\partial^2 u/\partial\chi^2 = \kappa_M uv \tag{12}$$

$$\partial^2 v/\partial\chi^2 = \gamma\kappa_E uv - \kappa_E(1 - v) \tag{13}$$

The parameter κ_M describes the chances of the mediator *M* escaping from the diffusion layer before it reacts with the enzyme. The parameter κ_E describes the chances of the conversion of enzyme *E* and E' by substrate within the diffusion layer. The parameter γ describes the local steady state between the two enzyme forms at the electrode surface. From eqn. (9)

$$u + u' = 1 - \chi \tag{14}$$

These equations must obey the following boundary conditions:

$$u = 1,\ u' = 0 \text{ and } \partial v/\partial\chi = 0 \text{ for } \chi = 0 \tag{15}$$

$$u = u' = 0 \text{ and } v = 1 \text{ for } \chi = 1 \tag{16}$$

The flux of electrons is given by

$$j = (nD_M m_0 / Z_D)(\partial u'/\partial\chi)_{\chi=0} \tag{17}$$

The dimensionless current is given by

$$I = \frac{j}{(nD_M m_0 / Z_D)} = (\partial u'/\partial\chi)_{\chi=0} \tag{18}$$

From eqn. (14) we get

$$I = (\partial u'/\partial\chi)_{\chi=0} = -(\partial u/\partial\chi)_{\chi=0} - 1 \tag{19}$$

When $v = 1$ the eqn. (12) reduces to a simple first order case [18, 19]. However, to the best of author's knowledge no purely complete analytical solution of this problem has been published. In this paper the nonlinear eqns. (12) and (13) are solved for the boundary conditions given by the eqns. (15) and (16) using variational iteration method, proposed by He [16, 17].

3. VARIATIONAL ITERATION METHOD

The Variational iteration method [16, 17, 20, 21] has been extensively worked out over a number of years by numerous authors. Variational iteration method has been favorably applied to various kinds of nonlinear problems [20, 21]. The main property of the method is in its flexibility and ability to solve nonlinear equations [17]. Recently Rahamathunissa and Rajendran [22] implemented variational iteration method to give approximate and analytical solutions of nonlinear reaction diffusion equations containing a nonlinear term related to Michaelis-Menten kinetic of the enzymatic reaction. Besides its mathematical importance and its links to other branches of mathematics, it is widely used in all ramifications of modern sciences [23]. In this method the solution procedure is very simple by means of variational theory and only few iterations lead to high accurate solution which are valid for the whole solution domain. The basic concept of variational iteration method is given in Appendix A.

4. ANALYTICAL SOLUTION OF THE CONCENTRATION AND CURRENT USING VARIATIONAL ITERATION METHOD

Using variational iteration method [16, 17] (refer Appendix A), the concentration of the mediator and the enzyme are

$$u = 1-(a+1)\chi + \frac{\kappa_M}{2}(1+b)\chi^2 - \frac{\kappa_M}{6}(1+b+a+ab)\chi^3 + \frac{\kappa_M}{12}(a+ab-b)\chi^4 + \frac{\kappa_M}{20}(ab+b)\chi^5 - \frac{\kappa_M}{30}ab\chi^6 \tag{20}$$

$$v = 1+b+\frac{\kappa_E}{2}(\gamma+b+\gamma b)\chi^2 - \frac{\gamma\kappa_E}{6}(1+b+ab+a)\chi^3 + \frac{\kappa_E}{12}(\gamma a+\gamma ab-\gamma b-b)\chi^4 + \frac{\gamma\kappa_E b}{20}(a+1)\chi^5 - \frac{\gamma\kappa_E ab}{30}\chi^6 \tag{21}$$

where

$$a = \frac{100}{96\gamma\kappa_E}\begin{bmatrix} 2.16\gamma\kappa_E + 3\kappa_E + 7.2 + 0.6\kappa_M + 0.25\kappa_E\kappa_M - (43.2\kappa_E + 8.64\kappa_M \\ +31.104\gamma\kappa_E + 7.2\kappa_E\kappa_M + 51.84 - 0.84\gamma\kappa_E^2\kappa_M - 2.016\gamma\kappa_E\kappa_M \\ +1.5\kappa_E^2\kappa_M + 0.3\kappa_E\kappa_M^2 + 0.36\kappa_M^2 + 0.0625\kappa_E^2\kappa_M^2 + 4.6656\gamma^2\kappa_E^2 \\ +12.96\gamma\kappa_E^2 + 9\kappa_E^2)^{1/2} \end{bmatrix} \tag{22}$$

$$b = \frac{-5}{2}\left[\frac{12a+\kappa_M a-4\kappa_M}{\kappa_M(2a-9)}\right] \tag{23}$$

The numerical values of *a* and *b* for various values of γ, κ_E and κ_M are given in Table-3. From eqn. (19), we get dimensionless current

$$I = \left(\frac{\partial u'}{\partial \chi}\right)_{\chi=0} = -\left(\frac{\partial u}{\partial \chi}\right)_{\chi=0} - 1 = a \tag{24}$$

Eqns. (20) and (21) represent the new approximate analytical expressions of the typical concentration profiles for the mediator and the enzyme for all values of γ, κ_E and κ_M. The dimensionless current is given by the eqn. (24).

5. VARIOUS SPECIAL CASES OF JOHN ALBERY'S WORK [1]

Albery's et al. [1] have derived the analytical expressions of concentration of *u* and *v* for number of special cases only. Various expressions of *u* and *v* are given in Table 1. Table 2 indicates the dimensionless current for different limiting cases.

6. RESULTS AND DISCUSSION

Equations (20) and (21) are the new and simple analytical expressions of concentration profiles for the mediator *u* and enzyme *v*. The approximate solutions of second order differential equations describing the transport and kinetics of the enzyme and the mediator in the diffusion layer of the electrode are derived. Albery and co-workers [1] derived the different approximate solutions (eqns. (25)-(36)) for various limiting cases (refer Table. 1) only. By finding the values of constants *a* and *b* (refer Table. 3), we can plot the concentration profiles.

The concentration of mediator in most cases is in the linear form where as the concentration of the enzyme is in the parabolic type. In Figures 1-6 and Table 4-9, our analytical results (eqns. (20) and (21)) are compared with previously available limiting case results. The average relative error between our results and limiting case results [1] are given in Table 10. Since the eqns. (33) and (34) are not satisfying the boundary condition (eqn. (16)), the maximum error 14.43% and 35.12% occurs when $\kappa_E > 1$ and $\kappa_M > 1$. Also in Albery et al [1], equation (31) does not satisfy the boundary condition $u = 0$ when $\chi = 1$.

Equations (37)-(40) derived in Albery et al [1] (refer Table. 2) for current are compared with eqn. (24). Figures 7-10 show the dimensionless current I for various values of κ_M and γ. From Figures 7-10, it is inferred that, the value of the current decreases when γ increases. From the Figures 7- 8, it is known that the value of the current increases when κ_M increases. From the Figures 8- 9 ,it is inferred that the value of the current decreases when κ_E increases.

Table 1. Different analytical approximations proposed in Albery et al [1] for the concentration of u and v

S. No	Cases	Conditions	*U*	*v*	Fig. No.
1.	I & II	$\gamma << 1,$ $\kappa_E < 1$	$u = \cosh(\kappa_M^{1/2}\chi) - \sinh(\kappa_M^{1/2}\chi)\coth(\kappa_M^{1/2})$ (25)	$v = 1$ (26)	Fig. 1 $\gamma = 0.1, \kappa_E = 0.1, \kappa_M = 0.01$
2.	II & III	$\gamma >> 1,$ $\kappa_E << 1,$ $\kappa_M << 1,$ $\gamma\kappa_E \sim 1$	$u = 1 - \chi$ (27)	$v = \dfrac{Bi'(\varphi)Ai(\varphi\chi') - Ai'(\varphi)Bi(\varphi\chi')}{Bi'(\varphi)Ai(0) - Ai'(\varphi)Bi(0)}$ (28) where $\varphi = (\gamma\kappa_E)^{1/3}$, $\chi' = 1 - \chi$	Fig. 2 $\gamma = 100, \kappa_E = 0.01, \kappa_M = 0.1$
3.	V & VI	$\gamma >> 1,$ $\kappa_E >> 1$ $\kappa_M < 2\gamma$	$u = 1 - (1 + \kappa_M / 2\gamma)\chi + \kappa_M \chi^2 / 2\gamma$ (29)	$v = \dfrac{1}{(1 + \gamma u)}$ (30)	Fig. 3 $\gamma = 2,\ \kappa_E = 100,\ \kappa_M = 1$
4.	I & IV	$\kappa_E < 1,$ $\kappa_M > 1$	$u = \exp\left[-(\kappa_M v_0)^{1/2}\chi\right]$ (31) Where $v_0 = (1/2\beta^2)(\kappa_M + 2\beta^2 \pm \sqrt{\kappa_M^2 + 4\kappa_M\beta^2})$ $\beta = \kappa_M / \gamma\kappa_E$	$v = (1/2\beta^2)(\kappa_M + 2\beta^2 \pm \sqrt{\kappa_M^2 + 4\kappa_M\beta^2})$ (32)	Fig. 4 $\gamma = 0.01,\ \kappa_E = 0.01,\ \kappa_M = 5$
5.	I & VII	$\kappa_E > 1,$ $\kappa_M >> 1$	$u = \exp\left[-(\kappa_M v_0)^{1/2}\chi\right]$ (33) Where $v_0^{1/2} = (1+\gamma^2\kappa_E/4\kappa_M)^{1/2} - (\gamma^2\kappa_E/4\kappa_M)^{1/2}$	$v = 1 - (1 - v_0)\{L - M\}/N$ (34) where $L = \kappa_E^{1/2}\exp[-(\kappa_M v_0)^{1/2}\chi]$, $M = (\kappa_M v_0)^{1/2}\exp(-\kappa_E^{1/2}\chi)$, $N = [\kappa_E^{1/2} - (\kappa_M v_0)^{1/2}]$	Fig. 5 $\gamma = 2,\ \kappa_E = 2,\ \kappa_M = 10$
6.	II & V	$\kappa_E >> 1,$ $\kappa_M << 1$	$u = 1 - \chi$ (35)	$v = 1/(1 + \gamma u)$ (36)	Fig. 6 $\gamma = 0.1, \kappa_E = 10, \kappa_M = 0.01$

Table 2. Different analytical approximation of dimensionless **c**urrent derived in Albery et al [1].

S.No.	Cases	Conditions	Current	Fig. No.
1.	I & II	$\gamma << 1, \kappa_E < 1$	$I = \kappa_M^{1/2} \coth(\kappa_M^{1/2}) - 1$ (37)	Fig. 7 $\gamma = 0.1, \kappa_E = 0.1$
2.	II & III	$\gamma >> 1, \kappa_E << 1,$ $\kappa_M << 1, \gamma\kappa_E \sim 1$	$I = \beta\{1 - 1/\pi[Ai(0)Bi'(\varphi) - Bi(0)Ai'(\varphi)]\}$ (38)	Fig. 8 $\gamma = 100, \kappa_E = 0.1$
3.	V & VI	$\gamma >> 1, \kappa_E \to \infty$ $\kappa_M < 2\gamma$	$I = \kappa_M / 2\gamma = \beta\kappa_E / 2$ (39)	Fig. 9 $\kappa_M = 5, \kappa_E = 10$
4.	II & V	$\kappa_E >> 1,$ $\kappa_M << 1$	$I = (\kappa_M / \gamma)\left[\frac{1}{2} - \frac{1}{\gamma} + \gamma^{-2}\ln(1+\gamma)\right]$ (40)	Fig. 10 $\kappa_E = 10, \kappa_M = 0.9$

Table 3. The numerical values of the constants *a* and *b* for corresponding values of γ, κ_E, and κ_M calculated using eqns. (22) and (23).

γ	κ_E	κ_M	*a*	*b*
0.1	0.1	0.01	0.0033	-0.0032
100	0.01	0.1	0.0255	-0.2543
2	100	1	0.1362	-0.6385
0.01	0.01	5	1.1765	-0.00002
2	2	10	1.4654	-0.3197
0.1	10	0.01	0.00315	-0.0609

7. CONCLUSIONS

The studies observed in this paper are of theoretical nature. The simple analytical expressions of the concentration of the mediator and the enzyme are reported, for all values of reaction parameters γ, κ_E and κ_M using variational iteration method. These values are compared with previously available limiting case results. A satisfactory agreement with available data for limiting cases is noted. The

extension of this procedure to other reaction mechanism apart from the study of mediated enzyme reaction mechanism in biosensor [24] with complex boundary condition seems possible.

Table 4. Comparison of our results with Albery et al [1] results for the values of $\gamma = 0.1, \kappa_E = 0.1, \kappa_M = 0.01$ (Cases I and II)

χ	u		% deviation of eqn. (20)	v		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (25)		This work eqn. (21)	Albery eqn. (26)	
0	1	1	0	0.9968	1	0.3210
0.2	0.7995	0.7995	0	0.9970	1	0.3009
0.4	0.5994	0.5994	0	0.9975	1	0.2506
0.6	0.3994	0.3994	0	0.9982	1	0.1803
0.8	0.1997	0.1997	0	0.9991	1	0.0901
1.0	0	0	0	1	1	0
	Average deviation		0	Average deviation		0.1905

Table 5. Comparison of our results with Albery et al [1] results for the values of $\gamma = 100, \kappa_E = 0.01, \kappa_M = 0.1$
(Cases II and III)

χ	u		% deviation of eqn. (20)	v		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (27)		This work eqn. (21)	Albery eqn. (28)	
0	1	1	0	0.7457	0.7421	0.4828
0.2	0.7963	0.8	0.4646	0.7596	0.7560	0.4739
0.4	0.5950	0.6	0.8403	0.7975	0.7942	0.4138
0.6	0.3955	0.4	1.1378	0.8539	0.8513	0.3045
0.8	0.1974	0.2	1.1317	0.9235	0.9220	0.1624
1.0	0	0	0	1	1	0
	Average deviation		0.5957	Average deviation		0.3062

Table 6. Comparison of our results with Albery et al [1] results for the values of $\gamma = 2, \kappa_E = 100, \kappa_M = 1$
(Cases V and VI)

χ	u		% deviation of eqn. (20)	v		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (29)		This work eqn. (21)	Albery eqn. (30)	
0	1	1	0	0.3615	0.3333	7.8008
0.2	0.7795	0.7600	2.5016	0.4453	0.3908	12.2389
0.4	0.5712	0.5400	5.4622	0.5182	0.4668	9.9190
0.6	0.3733	0.3400	8.9204	0.5617	0.5725	1.9227
0.8	0.1840	0.1600	13.0435	0.7023	0.7310	4.0866
1	0	0	0	1	1	0
	Average deviation		4.9880	Average deviation		5.9947

Table 7. Comparison of our results with Albery et al [1] results for the values of $\gamma = 0.01, \kappa_E = 0.01, \kappa_M = 5$ (Cases I and IV)

χ	u		% deviation of eqn. (20)	v		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (31)		This work eqn. (21)	Albery eqn. (32)	
0	1	1	0	1	1	0
0.2	0.6510	0.6394	1.7819	1	1	0
0.4	0.4259	0.4088	4.0150	1	1	0
0.6	0.2659	0.2614	1.6924	1	1	0
0.8	0.1310	0.1672	27.6336	1	1	0
1.0	0	0.1069	_	1	1	0
	Average deviation		7.0246	Average deviation		0

Table 8. Comparison of our results with Albery et al [1] results for the values of $\gamma = 2, \kappa_E = 2, \kappa_M = 10$
(Cases I and VII)

χ	*u*		% deviation of eqn. (20)	*v*		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (33)		This work eqn. (21)	Albery eqn. (34)	
0	1	1	0	0.6803	0.4202	38.2331
0.2	0.6223	0.6637	6.6527	0.7137	0.4383	38.5876
0.4	0.4039	0.4405	9.0616	0.7865	0.4947	37.1011
0.6	0.2603	0.2923	12.2935	0.8679	0.5653	34.8658
0.8	0.1346	0.1940	44.1308	0.9403	0.6371	32.2450
1.0	0	0.1287	_	1	0.7032	29.6800
	Average deviation		14.4277	Average deviation		35.1188

Table 9. Comparison of our results with Albery et al [1] results for the values of $\gamma = 0.1, \kappa_E = 10, \kappa_M = 0.01$ (Cases II and V)

χ	*u*		% deviation of eqn. (20)	*v*		% deviation of eqn. (21)
	This work eqn. (20)	Albery eqn. (35)		This work eqn. (21)	Albery eqn. (36)	
0	1	1	0	0.9391	0.9091	3.1945
0.2	0.7995	0.8	0.0625	0.9445	0.9260	1.9587
0.4	0.5994	0.6	0.1001	0.9568	0.9435	1.3911
0.6	0.3995	0.4	0.1252	0.9715	0.9616	1.0190
0.8	0.1997	0.2	0.1502	0.9862	0.9804	0.5881
1.0	0	0	0	1	1	0
	Average deviation		0.0730	Average deviation		1.3586

Table 10. Value of average relative error when our eqns. (20) and (21) are compared with limiting case results (eqns. (25) to (36))

S. No.	Cases	Conditions	Numerical values taken for γ, κ_E and κ_M	Mediator concentration (u) Percentage error	Enzyme concentration (v) Percentage error
1.	I & II	$\gamma << 1, \kappa_E < 1$	$\gamma = 0.1, \kappa_E = 0.1, \kappa_M = 0.01$	0	0.1905
2.	II & III	$\gamma >> 1, \kappa_E << 1,$ $\kappa_M << 1, \gamma\kappa_E \sim 1$	$\gamma = 100, \kappa_E = 0.01, \kappa_M = 0.1$	0.5957	0.3062
3.	V & VI	$\gamma >> 1,\ \kappa_E >> 1,$ $\kappa_M < 2\gamma$	$\gamma = 2, \kappa_E = 100, \kappa_M = 1$	4.9880	5.9947
4.	I & IV	$\kappa_E < 1, \kappa_M > 1$	$\gamma = 0.01, \kappa_E = 0.01, \kappa_M = 5$	7.0246	0
5.	I & VII	$\kappa_E > 1, \kappa_M >> 1$	$\gamma = 2, \kappa_E = 2, \kappa_M = 10$	14.4277	35.1188
6.	II & V	$\kappa_E >> 1, \kappa_M << 1$	$\gamma = 0.1, \kappa_E = 10, \kappa_M = 0.01$	0.0730	1.3586

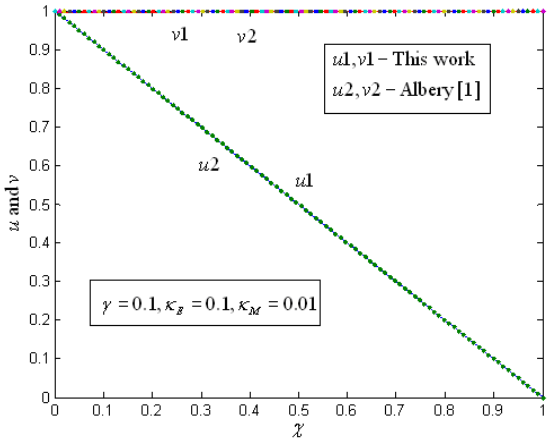

Figure 1. Comparison of dimensionless concentration u and v for cases I and II.

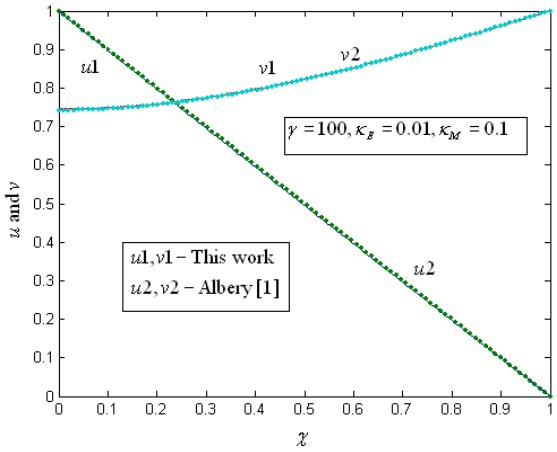

Figure 2. Comparison of dimensionless concentration *u* and *v* for cases II and III.

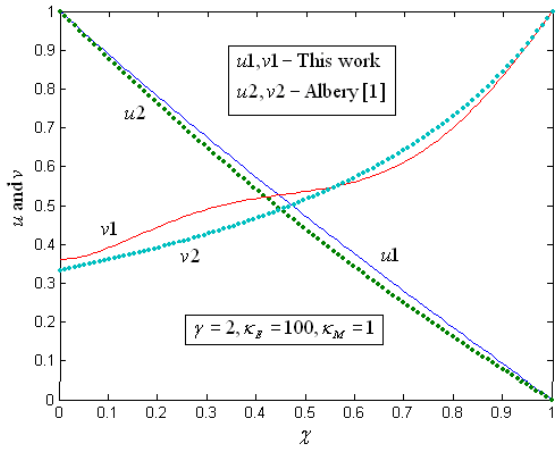

Figure 3. Comparison of dimensionless concentration *u* and *v* for cases V and VI.

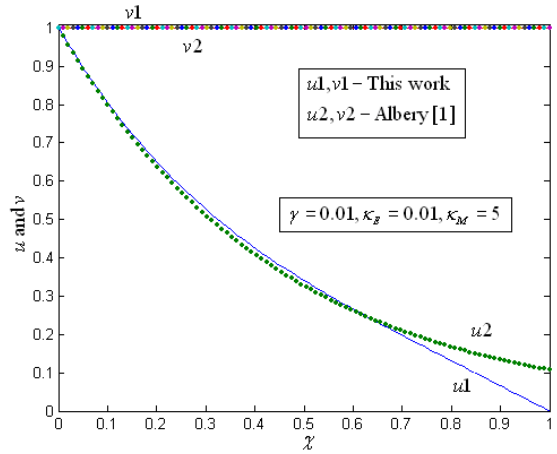

Figure 4. Comparison of dimensionless concentration *u* and *v* for cases I and IV.

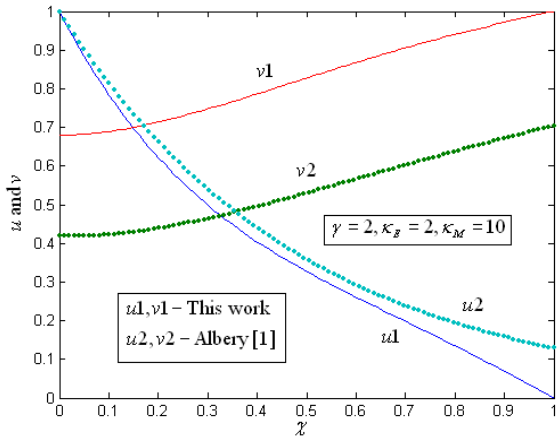

Figure 5. Comparison of dimensionless concentration *u* and *v* for cases I and VII.

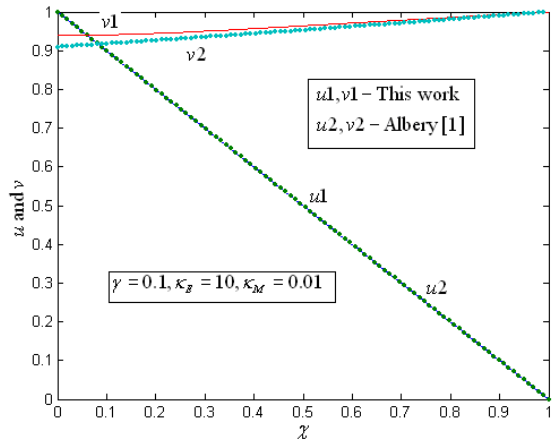

Figure 6. Comparison of dimensionless concentration *u* and *v* for cases II and V.

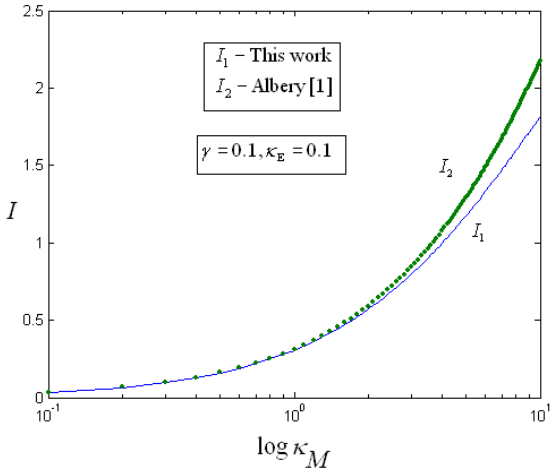

Figure 7. Comparison of current for cases I and II.

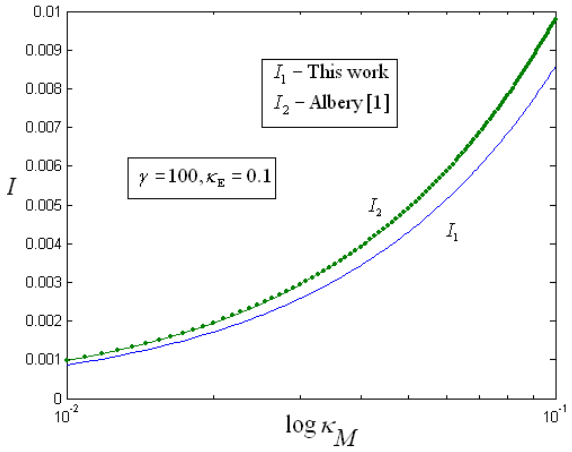

Figure 8. Comparison of current for cases II and III.

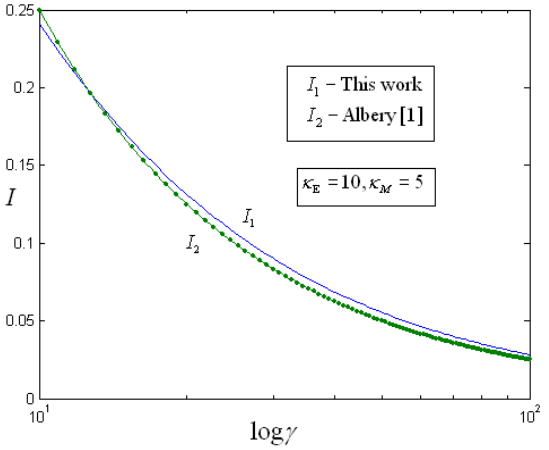

Figure 9. Comparison of current for cases V and VI.

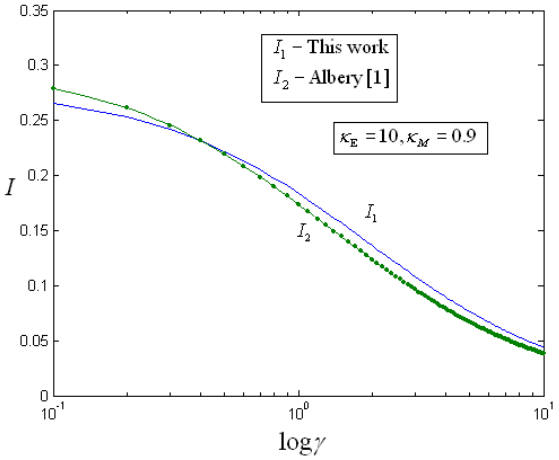

Figure 10. Comparison of current for cases II and V.

Appendix A

In this appendix we outline the basic concept and solution of equations (12) and (13) using variational iteration method. To illustrate the basic concept of variational iteration method [16] we consider the following nonlinear partial differential equation:

$$L\,[u(x)] + N\,[u(x)] = \mathrm{g}(x) \tag{A1}$$

where L is a linear operator, N is a nonlinear operator and $g(x)$ is a given continuous function. According to the variational iteration method, we can construct a correction functional as follows

$$u_{n+1}(x) = u_n(x) + \int_0^x \lambda \left[L[u_n(s)] + N[\tilde{u}_n(s)] - g(s) \right] ds \tag{A2}$$

where λ is a general Lagrange multiplier which can be identified optimally via variational theory, u_n is the nth approximate solution, $\tilde{u}_n$ denotes a restricted variation, i.e., $\delta \tilde{u}_n = 0$. Using variational iteration method, we can write the correction functional of eqn. (12) as follows

$$u_{n+1}(\chi) = u_n(\chi) + \int_0^{\chi} \lambda_1 \left[u_n''(s) - \overbrace{\kappa_M u_n(s) v_n(s)}^{\sim} \right] ds \tag{A3}$$

and eqn. (13) as follows

$$v_{n+1}(\chi) = v_n(\chi) + \int_0^{\chi} \lambda_2 \left[v_n''(s) - \overbrace{\gamma \kappa_E u_n(s) v_n(s)}^{\sim} + \overbrace{\kappa_E (1 - v_n(s))}^{\sim} \right] \mathrm{d}s \tag{A4}$$

Taking variation with respect to the independent variable u_n in (A3) and v_n in (A4), we get

$$\delta u_{n+1}(\chi) = \delta u_n(\chi) + \delta \int_0^{x} \lambda_1 \left[u_n''(s) - \overbrace{\kappa_M u_n(s) v_n(s)}^{\sim} \right] ds \tag{A5}$$

and

$$\delta v_{n+1}(\chi) = \delta v_n(\chi) + \delta \int_0^{\chi} \lambda_2 \left[v_n''(s) - \overbrace{\gamma \kappa_E u_n(s) v_n(s)}^{\sim} + \overbrace{\kappa_E (1 - v_n(s))}^{\sim} \right] ds \tag{A6}$$

where λ_1 and λ_2 are general Lagrange multipliers, u_0 and v_0 are initial approximations or trial functions, $\overbrace{\kappa_M u_n(s) v_n(s)}^{\sim}$, $\overbrace{\gamma \kappa_E u_n(s) v_n(s)}^{\sim}$ and $\overbrace{\kappa_E (1 - v_n(s))}^{\sim}$ are considered as restricted variations [17] i.e $\delta \tilde{v}_n = 0$ and $\delta \tilde{u}_n \tilde{v}_n = 0$. Making the above correction functional (A5) and (A6) stationary, noticing that $\delta v_n(0) = 0$ and $\delta u_n(0) v_n(0) = 0$, we obtain

$$\delta u_n : 1 - \lambda_1'(s)\,|_{s=\chi} = 0 \tag{A7}$$

$$\delta u_n' : \lambda_1(s)\,|_{s=\chi} = 0 \tag{A8}$$

$$\delta u_{\mathrm{n}} : \lambda_1''(s)\,|_{s=\chi} = 0 \tag{A9}$$

The Lagrange multiplier can be identified as

$$\lambda_1(s) = s - \chi \tag{A10}$$

Similarly we can obtain the Lagrange multiplier $\lambda_2(s) = s - \chi$ for eqn. (A6). Assuming the initial approximate solution of eqn. (12) and eqn. (13) has of the form

$$u_0(\chi) = 1 - (a+1)\chi + a\chi^2 \tag{A12}$$

$$v_0(\chi) = 1 + b - b\chi^2 \tag{A13}$$

where *a* and *b* are constants which are to be determined using the boundary conditions. Substituting the Lagrange multiplier in the iteration formula eqns. (A5) and (A6) we get the approximations,

$$u_1 = 1 - (a+1)\chi + \frac{\kappa_M}{2}(1+b)\chi^2 - \frac{\kappa_M}{6}(1+b+a+ab)\chi^3 + \frac{k_M}{12}(a+ab-b)\chi^4 + \frac{\kappa_M}{20}(ab+b)\chi^5 - \frac{\kappa_M}{30}ab\chi^6 \tag{A14}$$

and

$$v_1 = 1 + b + \frac{\kappa_E}{2}(\gamma + b + \gamma b)\chi^2 - \frac{\gamma\kappa_E}{6}(1+b+ab+a)\chi^3 + \frac{\kappa_E}{12}(\gamma a + \gamma ab - \gamma b - b)\chi^4 + \frac{\gamma\kappa_E b}{20}(a+1)\chi^5 - \frac{\gamma\kappa_E ab}{30}\chi^6 \tag{A15}$$

respectively. By using the boundary conditions at $\chi = 1$, $u = 0$ and $v = 1$ in the eqns. (A14) and (A15), we obtain two nonlinear equations. By solving these non linear equations using Scilab software, we obtain the values of *a* and *b* (eqns. (22) and (23)). First iteration is enough. Furthermore the obtained result is of higher accuracy. Therefore by considering $u = u_1$ and $v = v_1$ we get the eqns. (20) and (21) in the text.

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