Analytical expression of non steady-state concentration profiles at planar electrode for the CE mechanism

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ABSTRACT

The analytical solutions of the non-steady-state concentrations of species at a planar micro-electrode are presented. These simple new approximate expressions of concentrations are valid for all values of time and possible values of rate constants. Analytical equations are given to describe the current when the homogeneous equilibrium position lies heavily in favour of the electroinactive species. Working surfaces are presented for the variation of limiting current with a homogeneous kinetic parameter and equilibrium constant. Moreover, in this work we employ the Homotopy perturbation method to solve the boundary value problem.

Keywords: Planar Electrode; CE Mechanism; Mathematical Modelling; Reaction/Diffusion Equation; Homotopy Perturbation Method

1. INTRODUCTION

One of the major achievements in electroanalytical chemistry in the 1980s was the introduction of micro-electrodes, i.e., electrodes whose characteristic dimension is on the order of a few \( \mu \text{m} \) (the radius in the case of disc and hemispheres, band width in the case of bands, etc.). Microelectrodes have become more commonly used in electrochemistry to probe kinetics of fast chemical reactions [1]. In this work, we are interested in finding the mass transport limiting current response for the CE mechanism at a microelectrode. For each mechanism, the electroinative species \( A \) is in dynamic equilibrium with the electroactive species \( B \) via a homogeneous chemical step. The decay of species \( A \) is described by the first order forward rate constant \( k_f \) and the reverse of this process is described by the rate constant \( k_r \), which is first order for the CE mechanism. All species are considered to have an diffusion coefficient \( D \).

Oldham [2] made use of an analytical expression of CE mechanism at a hemispherical electrode. Lavagnini \textit{et al.} [3] employed the hopscotch method and a conformal map to numerically simulate CE mechanism at a planar electrode. Values of limiting current were analysed for a range of equilibrium constants and rate constants. There have been many previous theoretical descriptions of the diffusion limiting current for the CE mechanism. In Reference [4], Fleischmann \textit{et al.} demonstrate that Neumann’s integral theorem can be used to simulate CE mechanism at a disc electrode. However, to the best of the author’s knowledge, no purely analytical expressions for the non-steady-state concentrations of these CE mechanisms have been reported. The purpose of this communication is to derive approximate analytical expressions for the non-steady-state concentrations of the species for all values of \( m_1, m_2, k_1, k_2, k_3 \) and \( k_4 \) using Homotopy perturbation method.

2. MATHEMATICAL FORMULATION OF THE BOUNDARY VALUE PROBLEM

As a representative example of the reaction-diffusion problems considered, the standard CE mechanism

\[ A \rightleftharpoons 2B \quad \text{products} \]

has been chosen, with initial and boundary conditions corresponding to the potential step for all planar electrodes. Under steady-state conditions, the local concentrations of the species do not change. Therefore the mass transport equations are set equal to zero. We consider the differential equations with diffusion described by the concentration of the two species leads to the following equations [5]

\[
\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - k_f a + k_r b = 0 \quad (1)
\]

\[
\frac{\partial b}{\partial t} = D \frac{\partial^2 b}{\partial x^2} + k_f a - k_r b = 0 \quad (2)
\]

where \( a \) and \( b \) denote the concentration of the species \( A \) and \( B \). \( x \) and \( t \) stand for space and time, respectively. \( k_f \) and \( k_r \) are described the forward and
backward rate constants respectively. The boundary conditions reduce to
\[ t = 0; \quad a = a_0; \quad b = b_0 \quad (3) \]
\[ x = l; \quad a = a'; \quad b = b' \quad (4) \]
\[ x \to \infty; \quad a \to a_0; \quad b \to b_0 \quad (5) \]
where \( a_0 \) and \( b_0 \) are the bulk concentrations of the species \( A \) and \( B \); \( a' \) and \( b' \) denote the concentrations at electrode surface. The flux \( j \) can be described as follows:
\[ j = -D \frac{\partial b}{\partial x} \]  
(6)
The current density is defined as:
\[ i = -nFj \]  
(7)
Where \( n \) is the number of electrons and \( F \) is the Faraday constant. Using the following dimensionless parameters
\[ u = \frac{a}{a_0}; \quad v = \frac{b}{b_0}; \quad X = \frac{x}{l}; \quad T = \frac{Dt}{l^2}; \quad k_1 = \frac{k_1 l^2}{D}; \]
\[ k_2 = \frac{k_2 l^2 b_0}{D a_0}; \quad k_3 = \frac{k_3 l^2 a_0}{D b_0}; \quad k_4 = \frac{k_4 l^2}{D}; \quad m_1 = \frac{a'}{a_0}; \quad m_2 = \frac{b'}{b_0} \]
we obtained the dimensionless non-linear reaction diffusion equations for planar electrode as follows
\[ \frac{\partial u}{\partial T} = \frac{\partial^2 u}{\partial X^2} - k_1 u + k_2 v = 0 \]  
(9)
\[ \frac{\partial v}{\partial T} = \frac{\partial^2 v}{\partial X^2} + k_3 u - k_4 v = 0 \]  
(10)
The initial and boundary conditions becomes:
\[ T = 0; \quad u = 1; \quad v = 1 \quad (11) \]
\[ X = 1; \quad u = m_1; \quad v = m_2 \quad (12) \]
\[ X \to \infty; \quad u \to 1; \quad v \to 1 \quad (13) \]
The dimensionless current is as follows:
\[ \psi = \frac{-nFADb_0}{\partial X} = (\frac{\partial v}{\partial X})_{X=1} \]  
(14)

3. ANALYTICAL SOLUTION OF THE CONCENTRATIONS AND CURRENT USING HOMOTOPY PERTURBATION METHOD

Recently, many authors have applied the Homotopy perturbation method to various problems and demonstrated the efficiency of the Homotopy perturbation method for handling non-linear structures and solving various physics and engineering problems [6-9]. This method is a combination of homotopy in topology and classic perturbation techniques. Ji-Huan He used the Homotopy perturbation method to solve the Lighthill equation [10], the Duffing equation [11] and the Blasius equation [12]. The idea has been used to solve non-linear boundary value problems [13], integral equations [14-16], Klein–Gordon and Sine–Gordon equations [17], Emden–Flower type equations [18] and many other problems. This wide variety of applications shows the power of the Homotopy perturbation method to solve functional equations. The Homotopy perturbation method is unique in its applicability, accuracy and efficiency. The Homotopy perturbation method [19] uses the imbedding parameter \( p \) as a small parameter, and only a few iterations are needed to search for an asymptotic solution. By applying Laplace transformation to the partial differential Eqs.9 and 10 and using the condition Eqs.15-18, the following differential equations in Laplace space are obtained:
\[ \frac{d^2 u}{dx^2} - k_1 u + k_2 v - s u + 1 = 0 \]  
(15)
\[ \frac{d^2 v}{dx^2} + k_3 u - k_4 v - s v + 1 = 0 \]  
(16)
Now the boundary conditions become
\[ X \to \infty; \quad u \to \frac{1}{s}; \quad v \to \frac{1}{s} \]  
(17)
\[ X = 1; \quad u = m_1; \quad v = m_2 \]  
(18)
where \( s \) is the Laplace variable and an overbar indicates a Laplace-transformed quantity. The set of expressions presented in Eqs.15-18 defines the initial and boundary value problem in Laplace space. The Homotopy perturbation method method has overcome the limitations of traditional perturbation techniques, so a considerable deal of research has been conducted to apply the homotopy technique to solve various strong non-linear equations.

The Homotopy perturbation method [20-22] is used to give the approximate analytical solutions of coupled non-linear Eqs.15 and 16. Using this method (see Appendix – A and B) the approximate solutions of the Eqs.9 and 10 are
\[ u(X,T) \approx 1 + (m_1 - 1) \text{erfc} \left( \frac{X-1}{2\sqrt{T}} \right) \]
\[ + \left[ 2 \sqrt{\frac{T}{\pi}} \exp \left( \frac{(X-1)^2}{4T} \right) - (X-1) \text{erfc} \left( \frac{X-1}{2\sqrt{T}} \right) + \left[ \frac{k_3}{2} - \frac{k_4 m_2}{2} \right] \right] \]  
(19)
\[\nu(X,T) \approx 1 + (m_2 - 1) \text{erfc}\left(\frac{X - 1}{2\sqrt{T}}\right) - \left[\frac{\sqrt{T}}{2\pi} \exp\left(-\frac{(X - 1)^2}{4T}\right) - (X - 1) \text{erfc}\left(\frac{X - 1}{2\sqrt{T}}\right) \right] \left[\frac{k_{1}m_{1} - k_{2}m_{2}}{2}\right](1 - X) \tag{20}\]

The Eqs. 19 and 20 satisfies the boundary conditions Eq.11 to Eq.13. These equations represent the new approximate analytical expressions for the concentration profiles \(m_1, m_2, k_1, k_2, k_3\) and \(k_4\). The third term in the Eqs. 19 and 20 are in opposite sign when \(k_1 = k_2\) and \(k_2 = k_4\) or \(a_0 = b_0\). Also the dimensionless concentration \(u\) and \(v\) are equal when \(m_1 = m_2\) (ratio of concentration at electrode surface for bulk concentration) and \(a_0 = b_0\). The current density is

\[\psi \approx \frac{0.56419}{\sqrt{T}} - 0.56419 m_2 \frac{T}{\sqrt{T}} + 2 \frac{T}{\pi} (0.05k_1m_1 - 0.5k_4m_2) \tag{21}\]

4. DISCUSSION

Eqs. 19 and 20 are the new and simple approximate analytical expressions of concentrations of the isomers calculated using Homotopy perturbation method for the initial and boundary conditions Eqs.11-13. The closed analytical expression of current is represented by the Eq.21. The dimensionless concentration profiles of \(u\) and \(v\) versus dimensionless distance \(X\) are given in Figures 1-4 and Figures 5-8 respectively. From these figures, we can see that the value of the concentration \(u\) and \(v\) decreases when \(T\) increases and attains the steady-state value at \(X \geq 40\). When the rate constants are small (less than 1) and \(m_1 = m_2\) the concentration decreases slowly and reaches the minimum value and then increases in Figures 1 and 5. From Figures 2, it is inferred that the concentration \(u\) attains the steady-state value at \(X = 5\). Also, when all the parameters are small and \(T \leq 1\), the concentration attains maximum value at \(X = 4\) in Figures 3 and 4. For large value of parameters \(k_1, k_2, m_1\) and \(m_2\), the concentration \(v\) decreases when \(T\) increases in Figures 6. For the small values of parameter and time \(T\) \((T \leq 1)\), there is no significance different in the concentration. (Refer Figures 7(a,b), Figures 8(a,b).) The dimensionless current \(\psi\) versus \(T\) for various values of \(k_1\) and \(k_4\) is given in Figures 9 and 10. From these figures the value of current decreases as the time \(T\) and \(k_4\) increases. But the value of current increases when \(k_3\) increases.

5. CONCLUSIONS

In this work, the coupled time dependent linear dif-

![Figure 1](http://www.scirp.org/journal/NS/)

**Figure 1.** Normalized concentration \(u\) at microelectrode. The concentrations were computed using Eq. 19 for some value of \(m_1 = 1\), \(m_2 = 1\) and for various values of \(T\) and the reaction/diffusion parameter \(k_1 = 0.001\) and \(k_2 = 0.005\).

![Figure 2](http://www.scirp.org/journal/NS/)

**Figure 2.** Normalized concentration \(u\) at microelectrode. The concentrations were computed using Eq. 19 for some value of \(m_1 = 0.5\), \(m_2 = 1\) and for various values of \(T\) and the reaction/diffusion parameter \(k_1 = 1\) and \(k_2 = 5\).
Figure 3. Normalized concentration $u$ at microelectrode. The concentrations were computed using Eq.19 for some fixed value of $m_1 = 0.1$, $m_2 = 1$ and the reaction/diffusion parameter $k_1 = 1$ and $k_2 = 0.1$ for various values of (a) $T = 0.1$; (b) $T = 1$; (c) $T = 10$.

Figure 4. Normalized concentration $u$ at microelectrode. The concentrations were computed using Eq.19 for some fixed value of $m_1 = 0.001, m_2 = 0.005$ and the reaction/diffusion parameter $k_1 = 0.005$ and $k_2 = 0.001$ for various values of (a) $T = 0.1$; (b) $T = 1$; (c) $T = 10$; (d) $T = 100$.

Figure 5. Normalized concentration $v$ at microelectrode. The concentrations were computed using Eq.20 for some value of $m_1 = 1, m_2 = 1$ and for various values of $T$ and the reaction/diffusion parameter $k_1 = 0.01$ and $k_4 = 0.05$. 
Figure 6. Normalized concentration $v$ at microelectrode. The concentrations were computed using Eq.20 for some value of $m_1 = 1, m_2 = 0.5$ and for various values of $T$ and the reaction/diffusion parameter $k_1 = 5$ and $k_2 = 10$.

Differential equations at planar electrode have been solved analytically. In the first part of the paper, we have derived the analytical expressions of the concentrations of the species for all values of rate constants for planar electrode. In the second part of the paper we have presented approximate analytical expressions corresponding to the species $A$ and $B$ in terms of the kinetic parameters $k_1, k_2, k_3$ and $k_4$ based on the Homotopy perturbation method. In addition, we have also presented an analytical expression for the non-steady state current. The kinetics of this homogeneous step can in principle be studied by observing how the limiting current re-

Figure 7. Normalized concentration $v$ at microelectrode. The concentrations were computed using Eq.20 for some value of $m_1 = 1, m_2 = 0.1$ and the reaction/diffusion parameter $k_3 = 0.1, k_4 = 1$ and for various values of (a) $T = 0.1$; (b) $T = 1$; (c) $T = 10$. 
Figure 8. Normalized concentration $v$ at microelectrode. The concentrations were computed using Eq.20 for some value of $m_2 = 0.001, m_3 = 0.005$ and the reaction/diffusion parameter $k_3 = 0.001, k_4 = 0.005$ and for various values of (a) $T = 0.1$; (b) $T = 1$; (c) $T = 10$; (d) $T = 100$

Figure 9. Plot of the dimensionless current, $\psi$ versus time. The current were calculated using Eq.21 for the fixed value of $k_4 = 1$ and for various values of the reaction/diffusion parameter $k_3$.

Figure 10. Plot of the dimensionless current, $\psi$ versus time. The current were calculated using Eq.21 for the fixed value of $k_4 = 1$ and for various values of the reaction/diffusion parameter $k_3$.

sponds to changes in electrode size. Further, based on the outcome of this work it is possible to calculate the concentration and current at cylindrical and hemispherical electrode for CE mechanism.

REFERENCES


APPENDIX A

Solution of the Eqs. 9 and 10 using Homotopy perturbation method.

In this Appendix, we have used Homotopy perturbation method to solve Eqs. 9 and 10. Furthermore, a Homotopy was constructed to determine the solution of Eqs. 9 and 10. Taking laplace transform Eqs. 9 and 10 we have

\[(1-p) \left[ \frac{d^2 \bar{u}}{dX^2} - s \bar{u} \right] + p \left[ \frac{d^2 \bar{u}}{dX^2} - k_1 \bar{u} + k_3 \bar{v} - s \bar{u} + 1 \right] = 0 \]

(A1)

\[(1-p) \left[ \frac{d^2 \bar{v}}{dX^2} - s \bar{v} \right] + p \left[ \frac{d^2 \bar{v}}{dX^2} + k_1 \bar{u} - k_3 \bar{v} - s \bar{v} + 1 \right] = 0 \]

(A2)

The boundary conditions are

\[ X \to \infty; \quad u = 1; \quad v = 1 \]  

(A4)

The approximate solutions of Eqs. A1 and A2 are

\[ \bar{u} = \bar{u}_0 + p \bar{u}_1 + p^2 \bar{u}_2 + p^3 \bar{u}_3 + \ldots \ldots \]

\[ \bar{v} = \bar{v}_0 + p \bar{v}_1 + p^2 \bar{v}_2 + p^3 \bar{v}_3 + \ldots \ldots \]

(A5)

Substituting Eqs. A5 and A6 into Eqs. A1 and A2 and comparing the coefficients of like powers of \( p \)

\[ p^0 : \quad \frac{d^2 \bar{u}_0}{dX^2} - s \bar{u}_0 = 0 \]

(A7)

\[ p^1 : \quad \frac{d^2 \bar{u}_1}{dX^2} - k_1 \bar{u}_0 + k_3 \bar{v}_0 + 1 = 0 \]

(A8)

\[ p^0 : \quad \frac{d^2 \bar{v}_0}{dX^2} + s \bar{v}_0 = 0 \]

(A9)

\[ p^1 : \quad \frac{d^2 \bar{v}_1}{dX^2} - k_1 \bar{u}_0 - k_3 \bar{v}_0 + 1 = 0 \]

(A10)

Solving the Eqs. A7 to A10, and using the boundary conditions (A3) and (A4), we can find the following results

\[ \bar{u}_0(X,s) = \frac{m_1}{s} e^{-\bar{\mathcal{J}}(X-1)} \]

(A11)

\[ \bar{u}_1(X,s) = \frac{1}{s} + \left[ \frac{k_1 m_1}{2s^{3/2}} e^{\bar{\mathcal{J}}(1-x)} - \frac{k_3 m_2}{2s^{3/2}} e^{\bar{\mathcal{J}}(1-x)} \right] \left( (1-X) - \frac{1}{s} e^{\bar{\mathcal{J}}(1-x)} \right) \]

(A12)

and \( \bar{v}_0(X,s) = \frac{m_2}{s} e^{-\bar{\mathcal{J}}(X-1)} \)

(A13)

\[ \bar{v}_1(X,s) = \frac{1}{s} + \left[ \frac{k_1 m_1}{2s^{3/2}} e^{\bar{\mathcal{J}}(1-x)} - \frac{k_3 m_2}{2s^{3/2}} e^{\bar{\mathcal{J}}(1-x)} \right] \left( (X-1) - \frac{1}{s} e^{\bar{\mathcal{J}}(1-x)} \right) \]

(A14)

According to the Homotopy perturbation method, we can conclude that

\[ \bar{u}_0(X) = \lim_{p \to 1} \bar{u}(X) = u_0 + u_1 + \ldots \]

(A15)

\[ \bar{v}_0(X) = \lim_{p \to 1} \bar{v}(X) = v_0 + v_1 + \ldots \]

(A16)

After putting Eqs. A11 and A12 into Eq. A15 and Eqs. A13 and A14 into Eq. A16. Using inverse Laplace transform, the final results can be described in Eqs. 19 and 20 in the text. The remaining components of \( u_n(x) \) and \( v_n(x) \) can be completely determined such that each term is determined the previous terms.
### APPENDIX B: NOMENCLATURE AND UNITS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Concentration of the species $A$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$b$</td>
<td>Concentration of the species $B$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>Bulk concentration of the species $A$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$b_0$</td>
<td>Bulk concentration of the species $B$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Thickness of the planar electrode</td>
<td>cm</td>
</tr>
<tr>
<td>$\kappa_f$</td>
<td>Forward rate constant</td>
<td>sec$^{-1}$</td>
</tr>
<tr>
<td>$\kappa_b$</td>
<td>Backward rate constant</td>
<td>sec$^{-1}$</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Diffusion coefficient of the species $A$</td>
<td>cm$^2$sec$^{-1}$</td>
</tr>
<tr>
<td>$D_b$</td>
<td>Diffusion coefficient of the species $B$</td>
<td>cm$^2$sec$^{-1}$</td>
</tr>
<tr>
<td>$j$</td>
<td>Flux of the species</td>
<td>mole cm$^{-2}$sec$^{-1}$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons</td>
<td>None</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>sec</td>
</tr>
<tr>
<td>$u$</td>
<td>Normalized concentration of the species $A$</td>
<td>None</td>
</tr>
<tr>
<td>$v$</td>
<td>Normalized concentration of the species $B$</td>
<td>None</td>
</tr>
<tr>
<td>$J$</td>
<td>Dimensionless flux</td>
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<tr>
<td>$T$</td>
<td>Dimensionless time</td>
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<tr>
<td>$k_1$, $k_2$, $k_3$ and $k_4$</td>
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<td>$m_1$, $m_2$</td>
<td>Constant</td>
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</tr>
<tr>
<td>$\psi$</td>
<td>Dimensional current</td>
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Full Paper

Analytical Expression of the Substrate Concentration in Different Part of Particles with Immobilized Enzyme and Substrate Inhibition Kinetics

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Abstract- A mathematical model of enzyme flow calorimetry for the monitoring of hysteresis behaviour of immobilized enzyme is developed. The model is based on diffusion equations containing a non linear term related to substrate inhibition kinetics of the enzymatic reaction. This paper presents an approximate analytical method (He’s Homotopy perturbation method) to solve the non-linear differential equations for spherical, cylindrical and planar particles. Closed and simple analytical expressions for substrate concentration have been derived for all possible values of parameters. These results are compared with numerical results and are found to be in good agreement. The obtained results are valid for the whole solution domain.

Keywords- Immobilized Enzyme, Spherical Particle, Cylindrical Particle, Planar Particle, Homotopy Perturbation Method and Numerical Simulation

1. INTRODUCTION

Immobilization of enzyme is limitation of enzyme mobility achieved by different approaches. Some examples are chemical or physical immobilization on some surface (particles, plates etc.), chemical or physical immobilization inside particle, immobilization on
soluble polymers, cross-linking of enzymes by bi-functional reagents without any carrier and retardation of enzyme in membrane reaction.

There are two cases when enzyme activity is limited by diffusion of substrate to enzyme, such as reaction limitation by external diffusion and reaction limitation by internal diffusion. The second is discussed in this paper.

Enzyme reactions taking part in metabolic pathways, regulation processes, or in “in vitro” conditions often exhibit complicated dynamic behaviour in terms of the relation between the reaction rate and reaction. It can be studied by kinetic nonlinearities resulting from allostERIC interactions, by autocatalytic mechanisms, or by combination of enzyme reaction with mass transfer conditions [1]. This can lead to one of typical effects, the so-called hysteresis, when a retardation of the response between reaction rate and concentration of substrate or other compounds is observed. When the system is repeatedly wiggled back and forth (the concentration is cycled up and down), a hysteresis loop can appear in the reaction rate concentration diagram.

It has been recommended that hysteresis effects in biological systems are adequate to account for short-term memory [2] and the existence of hysteresis was described simply by coupling the enzyme kinetics and diffusion transport. It was also shown that in some cases the changes in conformation of enzyme molecule may give rise to hysteresis [3]. Kernevz and co workers [2] were developed a mathematical model to study hysteresis loop when bulk substrate concentration was progressively increased and decreased and it was explained by combination of the substrate inhibitory effect with diffusion limitation in the membrane. The numerical solution for spherical particles surrounded by a substrate solution with a constant concentration was studied by Malik & Stefuca [4]. However, to the best of our knowledge, till date no general analytical expressions of substrate concentrations in different part of particles with immobilized enzyme for spherical, cylindrical and planar particles have been reported. The purpose of this communication is to derive approximate analytical expression of concentrations for spherical, cylindrical and planar particles by solving the non-linear differential equations using He’s Homotopy perturbation method.

2. EXPERIMENTAL

2.1. Mathematical formulation of the problem and analysis

We consider the non-linear differential equation described by the concentration within the enzymatic layer at steady state conditions as follows [4]:
\( \nabla^2 c_S - \frac{V_m c_S}{K_m + c_S + \frac{c_s^2}{K_i}} = 0 \)  \hspace{1cm} (1)

where \( c_S \) is the substrate concentration, \( K_m \) is the Michaelis constant, \( K_i \) is substrate inhibition constant, \( V_m \) is the maximum reaction rate. Here \( \nabla^2 \) stands for Laplace operator.

Eqn. (1) was combined with the boundary conditions

\[ \frac{\partial c_S}{\partial r} = 0 \quad \text{when} \quad r = 0 \]  \hspace{1cm} (2)

\[ c_S = c_{s0} \quad \text{when} \quad r = R_p \]  \hspace{1cm} (3)

where \( c_{s0} \) is the substrate concentration on the particle surface. We make the non-linear PDE (Eq.1) dimensionless by defining the following parameters:

\[ c = \frac{c_S}{K_m}, \quad x = \frac{r}{R_p}, \quad \Phi = R_p \sqrt{\frac{V_m}{K_m D_e}}, \quad \beta = \frac{K_i}{K_m}, \quad m = \frac{c_{s0}}{K_m} \]  \hspace{1cm} (4)

where \( c \) is the dimensionless substrate concentration, \( x \) is the dimensionless particle radial coordinate, \( \Phi \) is the Thiele modulus, \( \beta \) is the dimensionless kinetic parameter and \( m \) is the dimensionless substrate concentration on the particle surface.

2.1.1. For spherical particle

For this case the Eq.(1) was reduces to the following dimensionless form

\[ \left( \frac{\partial^2 c}{\partial x^2} + \frac{2}{x} \frac{\partial c}{\partial x} \right) - \Phi^2 \frac{c}{1 + c + \frac{c^2}{\beta}} = 0 \]  \hspace{1cm} (5)

whereas the boundary condition reduces to

\[ x = 0, \quad \frac{\partial c}{\partial x} = 0 \]  \hspace{1cm} (6)

\[ x = 1, \quad c = m \]  \hspace{1cm} (7)
2.1.2. For cylindrical particle

For the case of cylindrical particle, the Eq.(1) becomes in dimensionless form as follows:

\[
\frac{\dot{c}^2 c + \frac{1}{x} \frac{\partial c}{\partial x}}{\partial x^2} - \Phi^2 \frac{c}{1 + c + \frac{c^2}{\beta}} = 0
\]  

(8)

2.1.3. For planar particle

For the case of planar particle, the Eq.(1) becomes in dimensionless form as follows:

\[
\frac{\dot{c}^2 c}{\partial x^2} - \Phi^2 \frac{c}{1 + c + \frac{c^2}{\beta}} = 0
\]  

(9)

The boundary conditions for cylindrical and planar particle are same as Eq. (6) and Eq. (7).

3. ANALYTICAL SOLUTION OF SUBSTRATE CONCENTRATION USING HOMOTOPY PERTURBATION METHOD (HPM)

Recently, many authors have applied the Homotopy perturbation method (HPM) to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [5-8]. This method is a combination of homotopy in topology and classic perturbation techniques. Ji-Huan He used the HPM to solve the Lighthill equation [9], the Duffing equation [10] and the Blasius equation [11]. The idea has been used to solve non-linear boundary value problems [12], integral equations [13-15], Klein–Gordon and Sine–Gordon equations [16], Emden-Flower type equations [17] (Chowdhury, & Hashim, 2007) and many other problems. In this paper, the homotopy perturbation method [18-24] is applied and the obtained results show that the HPM is very effective and simple.

3.1. For spherical particle

We can obtain the substrate concentration by solving the Eq. (5) using Homotopy perturbation method (see Appendix A).

\[
c = m + \frac{\Phi^2 \beta m}{3(\beta + \beta m + m^2)}(x^2 - 1)
\]  

(10)
Eq. (10) is the new and simple analytical expression for the dimensionless substrate concentration as a function dimensionless distance $x$, dimensionless kinetic parameter $\beta$, Thiele modulus $\Phi$ and dimensionless substrate concentration at particle surface $m$.

### 3.2. For cylindrical particle

We can obtain the dimensionless substrate concentration for the case of cylindrical particle by solving the Eq. (8):

$$c = m + \frac{\Phi^2 \beta m}{2(\beta + \beta m + m^2)}(x^2 - 1)$$

Eq. (11) is the analytical expressions for the dimensionless substrate concentrations as a function dimensionless distance $x$ for all possible values of parameters. The dimensionless substrate concentration for the case of cylindrical particle differ from the spherical particle only by a constant term in the denominator. The equations (10) and (11) are approximate expression of substrate concentration for spherical and cylindrical particle provided $\Phi^2 \beta m < 3$ $(\beta + \beta m + m^2)$ and $\Phi^2 \beta m < 2$ $(\beta + \beta m + m^2)$.

### 3.3. For planar particle

We can obtain the dimensionless substrate concentration for the case of planar particle by solving the Eq. (9):

$$c = \frac{m \cosh \Phi x}{96 \beta \cosh^2 \Phi} \left(16 \beta \cosh \Phi \cosh 2\Phi - 48 \beta \cosh \Phi + 3m \cosh 3\Phi + 36 \Phi \sinh \Phi\right)$$

$$- \frac{m^2 \Phi^2}{4 \beta \cosh^2 \Phi} \left(\frac{\cosh 3\Phi x}{8 \Phi^2} + \frac{3 \sinh \Phi x}{2 \Phi}\right) - \frac{m \Phi^2}{2 \cosh^2 \Phi} \left(\frac{\cosh 2\Phi x}{3 \Phi^2} - \frac{1}{\Phi^2}\right) + \frac{m \cosh \Phi x}{\cosh \Phi}$$

Eq. (12) is the analytical expressions for the dimensionless concentration as a function dimensionless distance $x$ for all small values of parameters.

### 4. NUMERICAL SIMULATION

The diffusion equations (Eq. (5), (8) and (9)) for the boundary conditions (Eqs. (6)-(7)) are solved by numerical methods. The function pdex4 in Scilab software which is a function of solving the initial-boundary value problems for partial differential equation was used to solve these equations. The Scilab program is also given in APPENDIX B. The numerical results are also compared with our analytical results in Tables 1–2 for spherical and
cylindrical electrode. In all the cases the average relative error between analytical and numerical result is less than 3%.

**Table 1.** Comparison of normalized substrate concentration \( c \) for various values of \( \beta \) when \( m = 800, \Phi = 20 \) (spherical particle)

<table>
<thead>
<tr>
<th>X</th>
<th>( \beta = 20 )</th>
<th>( \beta = 50 )</th>
<th>( \beta = 100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (10)</td>
<td>Eq. (10)</td>
<td>Eq. (10)</td>
</tr>
<tr>
<td></td>
<td>Numerical</td>
<td>Numerical</td>
<td>Numerical</td>
</tr>
<tr>
<td></td>
<td>% deviation of</td>
<td>% deviation of</td>
<td>% deviation of</td>
</tr>
<tr>
<td></td>
<td>Eq. (10)</td>
<td>Eq. (10)</td>
<td>Eq. (10)</td>
</tr>
<tr>
<td>0</td>
<td>792.15</td>
<td>758.18</td>
<td>798.35</td>
</tr>
<tr>
<td></td>
<td>796.00</td>
<td>792.40</td>
<td>799.20</td>
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<tr>
<td></td>
<td>0.4860</td>
<td>0.9195</td>
<td>0.1064</td>
</tr>
<tr>
<td>0.2</td>
<td>792.47</td>
<td>785.77</td>
<td>798.41</td>
</tr>
<tr>
<td></td>
<td>796.10</td>
<td>792.70</td>
<td>799.20</td>
</tr>
<tr>
<td></td>
<td>0.4454</td>
<td>0.8819</td>
<td>0.0989</td>
</tr>
<tr>
<td>0.4</td>
<td>793.41</td>
<td>787.55</td>
<td>798.61</td>
</tr>
<tr>
<td></td>
<td>796.70</td>
<td>793.70</td>
<td>799.30</td>
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<tr>
<td></td>
<td>0.4146</td>
<td>0.7809</td>
<td>0.0864</td>
</tr>
<tr>
<td>0.6</td>
<td>794.98</td>
<td>790.51</td>
<td>798.94</td>
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<tr>
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<td>797.50</td>
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<tr>
<td></td>
<td>0.3169</td>
<td>0.5932</td>
<td>0.0700</td>
</tr>
<tr>
<td>0.8</td>
<td>797.17</td>
<td>797.30</td>
<td>799.40</td>
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<tr>
<td></td>
<td>798.60</td>
<td>797.30</td>
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</tr>
<tr>
<td></td>
<td>0.1793</td>
<td>0.3322</td>
<td>0.0375</td>
</tr>
<tr>
<td>1</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Average deviation 0.3070</td>
<td>Average deviation 0.5846</td>
<td>Average deviation 0.0665</td>
</tr>
</tbody>
</table>

**Table 2.** Comparison of normalized substrate concentration \( c \) for various values of \( \beta \) when \( m = 800, \Phi = 20 \) (cylindrical particle)

<table>
<thead>
<tr>
<th>X</th>
<th>( \beta = 20 )</th>
<th>( \beta = 50 )</th>
<th>( \beta = 100 )</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Eq. (11)</td>
<td>Eq. (11)</td>
<td>Eq. (11)</td>
</tr>
<tr>
<td></td>
<td>Numerical</td>
<td>Numerical</td>
<td>Numerical</td>
</tr>
<tr>
<td></td>
<td>% deviation of</td>
<td>% deviation of</td>
<td>% deviation of</td>
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<td>Eq. (11)</td>
<td>Eq. (11)</td>
<td>Eq. (10)</td>
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<tr>
<td>0</td>
<td>795.12</td>
<td>788.23</td>
<td>777.78</td>
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<td></td>
<td>798.30</td>
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<td></td>
<td>0.1106</td>
<td>0.9857</td>
<td>1.8797</td>
</tr>
<tr>
<td>0.2</td>
<td>795.31</td>
<td>798.70</td>
<td>778.66</td>
</tr>
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<td>798.40</td>
<td>796.10</td>
<td>792.70</td>
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<tr>
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<td>0.0993</td>
<td>0.9832</td>
<td>1.8031</td>
</tr>
<tr>
<td>0.4</td>
<td>795.90</td>
<td>790.11</td>
<td>781.33</td>
</tr>
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<td>793.70</td>
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<td>0.1005</td>
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</tr>
<tr>
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</tr>
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<td>0</td>
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<td></td>
<td>Average deviation 0.0747</td>
<td>Average deviation 0.6249</td>
<td>Average deviation 1.1892</td>
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</table>
5. RESULT AND DISCUSSION

Eq. (10)-(12) are the new and simple approximate analytical expressions of concentrations of substrate \( c(m, \phi^0, \beta) \) for spherical, cylindrical and planar particle respectively. The values of Thiele modulus \( \Phi \) were in the range 20-400 with standard value 160, kinetic parameter \( \beta \) were in the range 10-300 with standard value 128 and substrate concentration on the particle surface \( m \) were in the range 100-1000 (Malik & Stefuca 2002).

The concentration of substrate \( c \) depends upon the three parameters \( \phi, \beta \) and \( m \). The Thiele modulus \( \Phi \) can be varied by changing either the thickness of the enzyme layer or the amount of enzyme immobilized in the matrix. This parameter describes the relative importance of diffusion and reaction in the enzyme layer. When Thiele modulus \( \Phi \) is small, the kinetics is the dominant resistance and the overall uptake of substrate is kinetically controlled. Under these conditions, the substrate concentration profile is essentially uniform. The overall kinetics is governed by the total amount of active enzyme. When \( \Phi \) is large, diffusion limitations are the principal determining factor.

Fig. 1(a) and 2(a) represent the dimensionless steady state substrate concentration for different values of dimensionless Thiele modulus \( \Phi \) for spherical and cylindrical particle. From these figures, it is obvious that the substrate concentration reaches the maximum value \( m \) (Here \( m = 800 \)), when \( x = 1 \). When Thiele modulus \( \Phi < 20 \), the substrate concentration profile is essentially uniform (refer Fig. 1(a) and 2(a)).

![Fig. 1. Plot of normalized concentration profiles for substrate c versus the normalized distance x for the spherical particle. The concentrations are computed using Eq. (10) for (a) various values of \( \Phi \) and some fixed values of \( m \) and \( \Phi \) (\( m = 800, \beta = 20 \)) b) various values of \( \beta \) and some fixed value of \( \Phi \) and \( \beta \) (\( \Phi = 50, m = 800 \)).](image)
Fig. 2. Plot of normalized concentration profiles for substrate \( c \) vs. the normalized distance \( x \) for the cylindrical particle. The concentrations are computed using Eq. (11) for (a) various values of \( \Phi \) and some fixed values of \( m \) and \( \Phi \) (\( m = 800, \beta = 20 \)) (b) various values of \( \beta \) and some fixed value of \( \Phi \) and \( \beta \) (\( \Phi = 50, m = 800 \)).

Fig. 1(b) and 2(b) represent the spherical and cylindrical particle substrate concentration \( c \) for different values of dimensionless kinetic parameter \( \beta \). From these figures it is inferred that the concentration of the substrate \( c \) increases when kinetic parameter \( \beta = K_r / K_m \) decreases. The normalized three-dimensional substrate concentration profiles for spherical, cylindrical and planar particle are plotted in Fig. 3 where the data given by previous figures are verified. The dimensionless substrate concentrations for the spherical, cylindrical and planar particle are plotted in Fig. 4. From these figures it is inferred that the dimensionless substrate concentration for spherical particle is greater than planar and cylindrical particle.
Fig. 3. The three-dimensional normalized substrate concentrations $c$ for (a) spherical particle (Eq. (10)) when $0 \leq \Phi \leq 50$, $\beta = 10$ (b) cylindrical particle (Eq. (11)) when $0 \leq \beta \leq 100$, $\Phi = 50$ (c) planar particle (Eq. (12)) when $0 \leq m \leq 300$, $\beta = 50$
Fig. 4. Plot of the two-dimensional case diagram of the normalized substrate concentration $c$ versus the normalized distance $x$ in the case of spherical, cylindrical, and planar particles. The normalized substrate concentrations were computed using Eq. (10), (11) and (12) when the parameters $\Phi = 50$, $m = 800$ and $\beta = 300$.

APPENDIX A

Solution of the Eq. (5) using Homotopy perturbation method

In this Appendix, we indicate how Eq. (5) in this paper is derived. To find the solution of Eq. (10), we first construct a Homotopy as follows:

$$\left(1-p\right)\left[\frac{\partial^2 c}{\partial x^2} + \frac{2}{x} \frac{\partial c}{\partial x}\right] + p\left[\frac{\partial^2 c}{\partial x^2} + \frac{2}{x} \frac{\partial c}{\partial x} - \left(\frac{\Phi \beta c}{\beta + \beta c + \beta c^2}\right)\right] = 0$$

(A1)

The boundary conditions are

$$x = 0 \quad \frac{\partial c}{\partial x} = 0$$

(A2)

$$x = 1 \quad c = m$$

(A3)

The approximate solutions of (A1) is

$$c = c_0 + pc_1 + p^2c_2 + p^3c_3 + \ldots$$

(A4)

substituting Eq. (A4) into Eq. (A1) and comparing the coefficients of like powers of $p$

$$p^0: \quad \frac{\partial^2 c_0}{\partial x^2} + \frac{2}{x} \frac{\partial c_0}{\partial x} = 0$$

(A5)

The boundary conditions are
\[
\frac{\partial c}{\partial x} = 0 \quad \text{when} \quad x = 0 \tag{A6}
\]
\[
c = m \quad \text{when} \quad x = 1 \tag{A7}
\]
\[
p': \frac{\partial^2 c_1}{\partial x^2} + \frac{2}{x} \frac{\partial c_1}{\partial x} - \frac{\Phi^2 \beta c_0}{(\beta + \beta c_0 + \beta c_0^2)} = 0 \tag{A8}
\]
\[
\frac{\partial c}{\partial x} = 0 \quad \text{when} \quad x = 0 \tag{A9}
\]
\[
c = 0 \quad \text{when} \quad x = 1 \tag{A10}
\]

According to the HPM, we can conclude that
\[
c = c_0 + c_1 + \ldots \tag{A11}
\]

Solving the Eq. (A5), and using the boundary conditions Eqs. (A6) - (A7) we get
\[
c_0 = m \tag{A12}
\]

Solving the Eq. (A8), and using the boundary conditions Eqs. (A9) - (A10) we get
\[
c_1 = \frac{\Phi^2 \beta m}{6(\beta + \beta m + m^2)}(x^2 - 1) \tag{A13}
\]

Adding Eq. (A12) and (A13), we get final results and it can be described in Eq. (10) in the text.

**APPENDIX B**

Scilab program to find the analytical solutions for Eq. (5):

```matlab
function pdex4
m = 2;
x = linspace(0,1);
t=linspace(0,100000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
figure
plot(x,u1(end,:))
title('u1(x,t)')
xlabel('Distance x')
ylabel('u1(x,2)')

%------------------------------------------------------------------
function [c,f,s] = pdex4pde(x,t,u,DuDx)
c = 1;
f = DuDx;
q=0.1;
```

```matlab
end
```
B=10;
F=-q^2*B*u(1)/(B+B*u(1)+u(1)^2);
s=F;

% --------------------------------------------------------------
function u0 = pdex4ic(x);  %create a initial conditions
u0 = 1;
% --------------------------------------------------------------

function [pl,ql,pr,qr]=pdex4bc(xl,ul,xr,ur,t)  %create a boundary conditions
pl = 0;
ql = 1;
pr = ur-1;
qr = 0;

APPENDIX C

Nomenclature

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
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<tr>
<td>A_p</td>
<td>Particle surface area</td>
<td>(m^2)</td>
</tr>
<tr>
<td>c</td>
<td>Dimensionless substrate concentration</td>
<td></td>
</tr>
<tr>
<td>c_s</td>
<td>Substrate concentration</td>
<td>(mole m^{-3})</td>
</tr>
<tr>
<td>c_{s0}</td>
<td>Substrate concentration at particle surface</td>
<td>(mole m^{-3})</td>
</tr>
<tr>
<td>D_e</td>
<td>Particle effective diffusion coefficient</td>
<td>(m^2 s^{-1})</td>
</tr>
<tr>
<td>K_m</td>
<td>Michaelis constant</td>
<td>(mole m^{-3})</td>
</tr>
<tr>
<td>K_i</td>
<td>Substrate inhibition constant</td>
<td>(mole m^{-3})</td>
</tr>
<tr>
<td>r</td>
<td>Particle radial coordinate</td>
<td>(m)</td>
</tr>
<tr>
<td>R_p</td>
<td>Particle diameter</td>
<td>(m)</td>
</tr>
<tr>
<td>v_{obs}</td>
<td>Observed reaction rate</td>
<td>(mole m^{-3} s^{-1})</td>
</tr>
<tr>
<td>v_p</td>
<td>Particle volume</td>
<td>(mole m^{-3} s^{-1})</td>
</tr>
<tr>
<td>V_m</td>
<td>Maximum reaction rate</td>
<td>(mole m^{-3} s^{-1})</td>
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<tr>
<td>V_p</td>
<td>Particle volume</td>
<td>(m^3)</td>
</tr>
<tr>
<td>x</td>
<td>Dimensionless particle radial coordinate</td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>Dimensionless current</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>Dimensionless substrate concentration at particle surface.</td>
<td></td>
</tr>
</tbody>
</table>

Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>β</td>
<td>Dimensionless kinetic parameter</td>
</tr>
<tr>
<td>Φ</td>
<td>Thiele modulus</td>
</tr>
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</table>
6. CONCLUSION
A mathematical model for an immobilized enzyme electrode has been described. In this present paper the particle balance equation have been formulated and solved under steady state conditions subject to defined boundary conditions. In this work, we obtained an analytical expression of the normalized substrate concentration for all possible values of dimensionless kinetic parameters $\beta$ and the Thiele modulus $\Phi$ for spherical, cylindrical, and planar particle. The simple closed forms of analytical solutions have been proposed using Homotopy perturbation method. Furthermore, it gives good agreement with simulation results.

Acknowledgement
This work was supported by the Council of Scientific and Industrial Research (CSIR No.: 01(2442)/10/EMR-II), Government of India. The authors also thank Mr. M.S. Meenakshisundaram, Secretary, The Madura College Board, Dr. R. Murali, The Principal, Madura College, and Madurai, India for their constant encouragement. The author V.Margret PonRani is very thankful to the Manonmaniam Sundaranar University, Tirunelveli for allowing doing the research work.

REFERENCES
**Approximate Solution of Coupled System of Transient Reaction Diffusion Equations for Complexes of Arbitrary Lability**

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**Abstract**

A mathematical model of the finite planar diffusion in lability of complexes is re-studied using the variable separable method and the Homotopy perturbation method (HPM). We also employ the complex inversion formula to solve the boundary value problem. The concentration profiles of metal and complex and current for the non-steady state diffusion limited conditions are described as closed form expressions for small and medium value of parameters. Current is also given in terms of reaction and diffusion layer thickness. When time tends to infinity, the analytical expression of non-steady concentration and current approaches the steady state value, thereby confirming the validity of the mathematical analysis. The exact analytical solution of the reaction-diffusion problem at an active planar surface is also presented for a finite diffusion region for fully labile systems. Furthermore, in this work the non-steady state results are compared with the numerical solution obtained using SCILAB program. They are found to be in satisfactory agreement.

**Keywords:** Heterogeneous catalysis, Lability, Ligands, Mass transport equations, Non-steady state

**Introduction**

Diffusion coupled with chemical reactions in the solution is widely used in electroanalysis and mechanistic electrochemistry for its many favourable attributes in an electrochemical experiment. The understanding of the environmental impact of metal compounds has received a strong attention in recent years [1]. Analytical solutions are very useful in a variety of problems in different scientific areas such as
analytical instrumental measurements, heterogeneous catalysis and electrode reactions. In all of these systems, the responses due to the arrival of the active substance at the surface depend not only on the equilibrium values of its complexation with the ligands [2], but also on the particular values of the various association and dissociation rate constants. The serious pollution hazard of heavy metals demands reliable analytical techniques which are able to measure the flux of metal that reaches micro-organisms, algae, plants and living organisms present in the media. The kinetic contribution of dissociating complexes to the measured currents in polarography was already recognized by Koutecky [3, 4] and other members of the Czechoslovak school.

A very general solution of multicomponent reaction, convection and diffusion (with all components that share a common diffusion coefficient) has been developed by Turner and Whitfield [5]. Galceran and coworkers [6] have extended these procedures. They have considered the diffusion as the only transport phenomenon, and dealt with unequal mobilities for the different complexes [7, 8], so that macromolecular complexation has been realistically modeled. For simplicity, but without losing the generality of the above mentioned applications, they have also used the voltammetric terminology. Salvador et al. [9] presented the analytical solution of the steady state reaction-diffusion problem at an active planar surface for a finite diffusion region using a reaction layer approximation. This principle is deployed in diffusion gradient in thin films (DGT) [10, 11] and permeation liquid membrane (PLM).

However, to the best of the author’s knowledge, no purely analytical expressions of concentrations for the non-steady state planar reaction-diffusion problem of a species that forms a complex have been reported. We adopt the Homotopy perturbation method (HPM) [12-16] to present the approximate analytical expressions for the concentrations of the species of the metal ion and the complex for the non-steady state condition corresponding to small and medium values of the parameters $\kappa_1, \kappa_2$ and $\varepsilon$. These parameters are defined below in Eq. 14. Simple expression of current $\psi$ is also reported.

**Formulation of the Boundary - Value Problem and Analysis**

**Mathematical formulation**

We consider a solution which consists of a free metal ion $M$ with the ligand $L$, according to the scheme. The complexation reaction of the type is written as follows:

\[
M + L \xrightleftharpoons[k_a]{k_d} ML
\]

(1)

where the subscripts $a$ and $d$ indicate association and dissociation respectively. Here we can assume that the ligand is present in the system in a great excess with respect to the metal so that $c_L = c_L^*$ where $c_L^*$ is the bulk concentration of the species. The
equilibrium constant \( K' = K c^*_L = k_c c^*_L / k_d = c^*_M / c^*_M \), \( k'_d = k_d c^*_L \). The mathematical formulation of this scheme corresponds to the following system of linearisation of differential equations [9]:

\[
\frac{\partial c_M}{\partial t} = D_M \frac{\partial^2 c_M}{\partial x^2} + k_d c_M - k'_d c_M \quad (2) \\
\frac{\partial c_{ML}}{\partial t} = D_{ML} \frac{\partial^2 c_{ML}}{\partial x^2} + k'_d c_M - k_d c_{ML} \quad (3)
\]

where \( x \) and \( t \) stand for distance and time respectively. \( c_M(x,t) \) denotes the concentration of the metal and \( D_M \) is its diffusion coefficient. \( c_{ML}(x,t) \) denotes the concentration of the complex and \( D_{ML} \) is its diffusion coefficient. \( k_d \) is described as the association rate constant and \( k'_d \) is that of dissociation. As usual, when the metal is the only one species consumed at the limiting surface, the system of the Eqs. 2 and 3 is solved for the following initial conditions \((t = 0)\):

\[
c_M(x,0) = c^*_M, \quad c_{ML}(x,0) = c^*_M \quad (4)
\]

and the boundary conditions are given by:

\[
c_M(g,t) = c^*_M, \quad c_{ML}(g,t) = c^*_ML \quad (5)
\]

\[
c_M(0,t) = 0, \quad \frac{\partial c_{ML}}{\partial x} \bigg|_{x=0} = 0 \quad (6)
\]

where \( c^*_M \) and \( c^*_ML \) are the concentration of the species in the bulk solution. The flux \( J_M \) can be described as follows:

\[
J_M = D_M \frac{\partial c_M}{\partial x} \bigg|_{x=0} \quad (7)
\]

The current density is defined below as:

\[
i = nF A J_M \quad (8)
\]

where \( n \) is the number of electrons and \( F \) is the Faraday constant. \( A \) is the area of the electrode. The Eqs. 2 and 3 are expressed in the following non-dimensional format:

\[
\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + \kappa_2 (v - u) \quad (9) \\
\frac{\partial v}{\partial \tau} = \varepsilon \frac{\partial^2 v}{\partial \chi^2} + \kappa_1 (u - v) \quad (10)
\]

The dimensionless initial and boundary conditions for the Eqs. 9 and 10 are as follows:

\[
u(\chi,0) = 1, \quad v(\chi,0) = 1 \quad (11)
\]

\[
u(1,\tau) = 1, \quad v(1,\tau) = 1 \quad (12)
\]

\[
u(0,\tau) = 0, \quad \left[\frac{\partial v}{\partial \chi}\right]_{\chi=0} = 0 \quad (13)
\]

The following parameters have been introduced:
\[ u = \frac{c_M^*}{c_M}, \quad v = \frac{c_{ML}^*}{c_{ML}}, \quad \chi = \frac{x}{g}, \quad \tau = \frac{D_M t}{g^2}, \quad \kappa_1 = \frac{k_d g^2}{D_M}, \quad \kappa_2 = \frac{k'_d g^2}{D_M}, \]

\[ \varepsilon = \frac{D_{ML}}{D_M} \quad \text{and} \quad K' = \frac{\kappa_2}{\kappa_1} = \frac{k'_d}{k_d} = \frac{c_{ML}^*}{c_M^*} \]  \hspace{1cm} (14)

where \( u \) represents the dimensionless concentrations of metal M and \( v \) represents the dimensionless concentrations of complex ML. \( \chi \) and \( \tau \) represent the dimensionless distance and time respectively. \( \kappa_1 \) and \( \kappa_2 \) are the dimensionless rate constants and \( \varepsilon \) is the dimensionless diffusion coefficient for the complex ML. \( K' \) is the equilibrium constant. Using Eqs. 7, 8 and 14 the dimensionless current is given by:

\[ \psi = \frac{i}{n FD_M c_M^* g} = \frac{\partial u}{\partial \chi} \bigg|_{\chi=0} \]  \hspace{1cm} (15)

**Approximate analytical solutions of concentrations of the metal and complex under non-steady-state condition**

The advantages of analytical methods [17-19] especially HPM [19], are capable of solving both regular and strong non-linear equations. Also these methods are simple to apply and will not increase complexity. One of the most remarkable features of the HPM is that usually only a few perturbation terms are sufficient to obtain a reasonably accurate solution. Solving the Eqs. 9 and 10 using HPM and simultaneous equation method (see APPENDIX A and B), the steady state and transient contributions to the concentration profiles are given by:

\[ u(\chi, \tau) = \frac{c_M^*}{c_M} = u_{SS}(\chi) + u_{TR}(\chi, \tau) \]  \hspace{1cm} (16)

where

\[ u_{SS}(\chi) = \frac{1}{\beta} \left[ \chi + \frac{K' \varepsilon}{\kappa_1 + \kappa_2} \left[ \tanh \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right) \sinh \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right) (\chi - 1) \right] \right] \]  \hspace{1cm} (17)

\[ u_{TR}(\chi, \tau) = \frac{2 \pi}{\beta} \sum_{n=1}^{\infty} (-1)^n \left[ \frac{K' \varepsilon \tanh \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right) + 1}{\left( \frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon} + n^2 \pi^2 \right) \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right)} \right] \exp \left( -n^2 \pi^2 \tau \sin(n \pi (\chi - 1)) \right) \]  \hspace{1cm} (18)

where

\[ \beta = \left[ 1 + \left( K' \varepsilon \tanh \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right) \right) \left( \sqrt{\frac{K_1}{\varepsilon} + \frac{K_2}{\varepsilon}} \right) \right] \]  \hspace{1cm} (19)
Similarly we can obtain the dimensionless concentration of complex \( v(\xi, \tau) \) as follows:

\[
v(\xi, \tau) = \frac{c_{ML}}{c_{ML}} = v_{SS}(\xi) + v_{TR}(\xi, \tau)
\]  

where

\[
v_{SS}(\xi) = \frac{1}{\beta} \left[ \frac{1}{\sqrt{\kappa_1 + \kappa_2}} \left( \frac{\kappa_1 + \kappa_2}{\epsilon} \right)^{\kappa_1 + \kappa_2} \left( \xi - 1 \right) - \kappa \tan \left( \frac{\kappa_1 + \kappa_2}{\epsilon} \right) \right]
\]  

\[
v_{TR}(\xi, \tau) = \frac{2 \beta}{\sum_{n=1}^{\infty} (-1)^n \left( \frac{1}{4 \pi^2} \left( \kappa_1 + \kappa_2 \right) \left( \kappa_2 \right) - \frac{4}{\pi^2} \right) \left( \exp \left( \frac{(2n-1)^2 \pi^2 \epsilon \tau}{4} \right) \sin \left( \frac{(2n-1)\pi (\xi - 1)}{2} \right) \right)
\]

where \( u_{SS}(\xi) \) and \( v_{SS}(\xi) \) represent a time independent steady state term and \( u_{TR} \) and \( v_{TR} \) denote the time dependent transient component. Eqs. 16 and 20 represent the approximate analytical expressions for the concentration profiles of metal and complex respectively for all small and medium values of parameters \( \kappa_1, \kappa_2 \) and \( \epsilon \). Recently Jose Salvador et al. [9] obtained the steady state concentrations \( u_{SS}(\xi) \) and \( v_{SS}(\xi) \) using d’Alembert methodology. The steady state term will be important at long times as \( \tau \to \infty \). In contrast the transient term will be of importance at short times as \( \tau \to 0 \). The obtained analytical expressions (Eqs. 16 and 20) are compared with the numerical results got using SCILAB program (see APPENDIX C). Using Eqs. 15 and 16 we can obtain the current response as follows:

\[
\psi = \psi_{SS} + \psi_{TR}
\]

where

\[
\psi_{SS} = \frac{(1 + \kappa \epsilon)}{\beta}
\]

\[
\psi_{TR} = \frac{2 \pi^2}{\beta} \sum_{n=1}^{\infty} n^2 \exp(-n^2 \pi^2 \tau) \left( \frac{\kappa \epsilon \tan \left( \frac{\kappa_1 + \kappa_2}{\epsilon} \right) + 1}{\left( \frac{\kappa_1 + \kappa_2 + n^2 \pi^2}{\epsilon} \right)} \right)
\]

Eq. 23 represents the new approximate analytical expression for the current for small and medium values of parameters \( \kappa_1, \kappa_2 \) and \( \epsilon \). \( \psi_{SS} \) represents a time independent steady state current and \( \psi_{TR} \) denotes a time dependent transient component.
**Fully labile system**

For the case of fully labile system, we have $k_d \to \infty$ or $\kappa_1 \to \infty$. By adding $\kappa_1$ times Eq. 9 and $\kappa_2$ times Eq. 10, we can obtain the following equation:

$$\frac{\partial (\kappa_1 u + \kappa_2 v)}{\partial \tau} = \frac{\partial^2 (\kappa_1 u + \kappa_2 v)}{\partial \chi^2}$$

(26)

Now, full lability means that we can use the equilibrium relationship given in Eq. 14, not only for the bulk, but also for any point and time [9]. Now we can obtain,

$$K' = \frac{\kappa_2}{\kappa_1} = \frac{c_{ML}^*}{c_M^*} = \frac{c_{ML}}{c_M}$$

(27)

$$\nu = \frac{c_{ML}^*}{c_{ML}} = \frac{c_M^*}{c_M}$$

(28)

Now the differential Eq. 26 becomes

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} = \frac{1 + \kappa_1 / \kappa_1}{1 + \kappa_2 / \kappa_1} \frac{\partial^2 u}{\partial \chi^2} = \frac{1 + \kappa_1 / \kappa_1}{1 + K'} \frac{\partial^2 u}{\partial \chi^2}$$

(29)

The resulting differential equation is physically interpreted as a continuity equation for the (normalized) total metal because:

$$u = \frac{c_{ML}^* u + c_{ML}^* v}{c_M^* + c_{ML}^*} = \frac{c_{ML}^* u + c_{ML}^* \nu}{c_M^* + c_{ML}^*} = \frac{c_{T,M}^*}{c_{T,M}}$$

(30)

so that

$$\frac{\partial}{\partial \tau}\left(\frac{c_{T,M}^*}{c_{T,M}}\right) = \frac{1 + \kappa_1 / \kappa_1}{1 + K'} \frac{\partial^2}{\partial \chi^2}\left(\frac{c_{T,M}^*}{c_{T,M}}\right)$$

(31)

Assuming $\left(\frac{c_{T,M}^*}{c_{T,M}}\right) = u_{FS}$, we get

$$\frac{\partial u_{FS}}{\partial \tau} = \frac{1 + \kappa_1 / \kappa_1}{1 + K'} \frac{\partial^2 u_{FS}}{\partial \chi^2}$$

(32)

Solving the above equation (see APPENDIX D) using the boundary conditions given by the Eqs. 11 to 13 we obtain

$$u_{FS}(\chi, \tau) = \frac{c_{T,M}^*}{c_{T,M}} = \chi + \frac{2}{\pi} \sum_{n=1}^{\infty} (-1)^n \sin(n \pi (\chi - 1)) \exp(-n^2 \pi^2 \tau(1 + K' \epsilon)/(1 + K'))$$

(34)

The current also has a component arising from the gradient of ML:
Coupled System of Transient Reaction Diffusion Equations

\[ I = nFA \left( D_M \left. \frac{\partial c_{ML}}{\partial x} \right|_{t=0} + D_{ML} \left. \frac{\partial c_{ML}}{\partial x} \right|_{t=0} \right) = nFA \left( \left. D_M \frac{\partial c_{ML}}{\partial x} \right|_{t=0} + D_{ML} K' \left. \frac{\partial c_{ML}}{\partial x} \right|_{t=0} \right) \]

\[ = nFAD_M (1 + \varepsilon K') \left. \frac{\partial c_{ML}}{\partial x} \right|_{t=0} = FAD_M \left( 1 + \varepsilon K' \right) \left. \frac{\partial u}{\partial x} \right|_{t=0} \]

\[ \psi_{FS}(\chi, \tau) = \frac{I}{nFD_M c_{ML} / g} = (1 + \varepsilon K') \left. \frac{\partial u_{FS}}{\partial x} \right|_{t=0} \]

\[ = (1 + K'\varepsilon) + 2(1 + K'\varepsilon) \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \tau (1 + K'\varepsilon)/(1 + K')) \]  

(35)

In the case of only metal in the system \( K' = 0 \), then Eq. 36 becomes

\[ \psi_{inert}(\chi, \tau) = 1 + 2 \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \tau) \]

(36)

Eq. 34 represents the simple and accurate expression of concentration in the fully liable system. The current response in this system is given by the Eq. 36.

Results and Discussion

The approximate analytical expressions of concentration of metal \( u(\chi, \tau) \) and complex \( v(\chi, \tau) \) (solutions of Eqs. 9 and 10) are given in the Eqs. 16 and 20. The Eqs. 9 and 10 are also solved by numerical methods. The function pde23 in SCILAB software is used for solving the initial-boundary value problems for parabolic-elliptic partial differential equations. The obtained analytical results are compared with the numerical results for various values of equilibrium constant \( K' \) (Tables 1 and 2) and time \( \tau \) (Fig. 1). In all the cases the concentration of the metal and complex gives good agreement with the numerical results.

From the Table 1, we infer that in all the cases, the variation of concentration of the metal \( u \) is very small due to variation of equilibrium constant \( K' = \kappa_z / \kappa_z \). Table 2 illustrates that the concentration of the complex \( v(\chi, \tau) \) increases when \( K' \) and \( \chi \) increases. The average relative error of the concentration of the metal (analytical result) and the simulation result is less than 0.3% whereas it is less than 0.5% in case of complex for small and medium values of equilibrium constant \( K' \).

Typical time dependent concentration profiles of metal \( u(\chi, \tau) \) (Eq. 16) and complex \( v(\chi, \tau) \) (Eq. 20) are illustrated in Figs. 1A and B respectively. From these figures it is inferred that the concentration of the metal reaches the steady state value when \( \tau \geq 1 \), whereas the concentration of the complex reaches the steady state value, only when \( \tau \geq 5 \). Both the concentration of the metal and the complex are inversely proportional to time \( \tau \).
Table 1: Comparison of concentration of the metal $u(\chi, \tau)$ for various values of equilibrium constant $K$ when $\tau = 0.1, \varepsilon = 0.07, \kappa_2 = 0.1$

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/10 = 0.01$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.1 = 0.1$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.01 = 0.1$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.001 = 0.1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. 16</td>
<td>Numerical deviation of Eq. 16</td>
<td>Eq. 16</td>
<td>Numerical deviation of Eq. 16</td>
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<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3454</td>
<td>0.3490</td>
<td>1.0423</td>
<td>1.0497</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6293</td>
<td>0.6316</td>
<td>0.3655</td>
<td>0.3672</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8220</td>
<td>0.8209</td>
<td>0.1338</td>
<td>0.1323</td>
</tr>
<tr>
<td>0.8</td>
<td>0.9337</td>
<td>0.9315</td>
<td>0.2356</td>
<td>0.2356</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Average deviation: 0.2962</td>
<td>Average deviation: 0.3119</td>
<td>Average deviation: 0.2192</td>
<td>Average deviation: 0.2241</td>
</tr>
</tbody>
</table>

Table 2. Comparison of concentration of the complex $v(\chi, \tau)$ for various values of equilibrium constant $K$ when $\tau = 2, \varepsilon = 0.7$.

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/10 = 0.01$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.1 = 0.1$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.01 = 0.1$</th>
<th>$K' = \frac{k_2}{k_1} = 0.1/0.001 = 0.1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. 20</td>
<td>Numerical deviation of Eq. 20</td>
<td>Eq. 20</td>
<td>Numerical deviation of Eq. 20</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.7058</td>
<td>0.6996</td>
<td>0.7068</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7234</td>
<td>0.7169</td>
<td>0.8985</td>
<td>0.7244</td>
</tr>
<tr>
<td>0.4</td>
<td>0.7697</td>
<td>0.7638</td>
<td>0.7665</td>
<td>0.7706</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8359</td>
<td>0.8316</td>
<td>0.5144</td>
<td>0.8367</td>
</tr>
<tr>
<td>0.8</td>
<td>0.9141</td>
<td>0.9126</td>
<td>0.2514</td>
<td>0.9153</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Average deviation: 0.5515</td>
<td>Average deviation: 0.5505</td>
<td>Average deviation: 0.5376</td>
<td>Average deviation: 0.3873</td>
</tr>
</tbody>
</table>
Figure 1: Influence of time on the concentration profiles of (A) metal \( u = c_M / c_M^* \) (B) complex \( v = c_{ML} / c_{ML}^* \) obtained from our transient approximate solution (solid line) presented in this work (Eqs. 16 and 20 respectively), and from the numerical simulation (dotted line).

The analytical expression of the current (Eq. 23) may be decomposed into two parts. Eq. 24 represents the steady state solution \( \psi_{SS} \), which pertains as \( \tau \to \infty \). The Eq. 25 involving the infinite series describes the transient contribution to the current expression. Normalized total current response \( \psi \) versus dimensionless time \( \tau \) is plotted in Fig. 2. From this figure it is observed that the total current increases when \( K' \) increases. The total current reaches the steady state value when \( \tau \geq 1 \).

Figure 2: Influence of excess-ligand equilibrium constant \( K' = c_{ML}^* / c_M^* \) on the current response \( \psi = i / (nF \Delta M c_{ML}^* g) \) obtained from our transient approximate solution presented in this work (Eq. 23). The values of parameters are \( \varepsilon = 0.07 \) for \( \kappa_1 = 1 \).
When $\varepsilon = 1$, from Eq. 23, the current $\psi$ in terms of diffusion layer thickness $\delta_d(=\sqrt{\pi Dt})$ and reaction layer thickness $\delta_r(=\sqrt{D_M/(k_d + k_r)})$ is given as follows:

$$\psi = \frac{1}{1 + K\frac{\tanh(g/\delta_r)}{(g/\delta_r)^2}} \left[ 1 + K\sum_{n=1}^{\infty} \frac{\tanh(g/\delta_r)/(g/\delta_r)^2}{(g/\delta_r)^2 + n^2\pi^2} \right]$$

(28)

When $\delta_d/g \to 0$ and $\delta_r/g \to \infty$, the current $\psi = 3$ for various values of $K'$. In Fig. 3 we illustrate the normalised current $\psi = i/\sqrt{nFD_Mc_{M_0}}$ for various values of the diffusion and reaction layer thickness. The value of the current decreases when both $\delta_r/g$ and $\delta_d/g$ increases or the reaction thickness $g$ increases (Fig. 3A and B).

![Figure 3](image)

**Figure 3:** Normalised current response $\psi$ plotted using Eq. 38 for various values of the dimensionless (A) reaction layer thickness and (B) diffusion layer thickness when $K' = 10$

As outlined in Fig. 4, we note that for a given ratio diffusion coefficient for the complex ($\varepsilon$) and time $\tau$, the concentration $u_{FS}$ increases in a regular manner with increasing value of the equilibrium constant $K'$. Eq. 36 gives the analytical expression of the current in the fully liable system. Eq. 37 denotes the inert current in the fully liable system. The analytical expression of current (Eq. 36) in the fully liable system gives rise to a quantification of the lability degree of the system. The lability degree can be used to determine the thickness of the diffusion layer of sensors like DGT or PLM.
Figure 4: Influence of excess-ligand equilibrium constant $K'(c_{ML}^*/c_M^*)$ on the concentration profiles in the fully liable system $u_{FS}(c_{TM}^*/c_{TM}^*)$ obtained in this work (Eq. 34). The values of parameters are $\varepsilon = 0.07$ and $\tau = 0.05$.

Fig. 5 describes the variation of normalized current response $\psi_{FS}$ for various values of $K'$. This figure shows that the current $\psi_{FS}$ is directly proportional to $K'$. $\psi_{FS}$ decreases as $\tau$ increases and finally achieves a time independent value when $\tau$ is large. In the case of only metal in the system (i.e. no ligand is present), $K' = 0$, Eq. 23 successfully merges with the inert current (Eq. 37) in the fully liable system. And also in the case of $\kappa_1$ and $\kappa_2$ tend to 0, Eq. 23 successfully merges with Eq. 37.

Figure 5: Influence of excess-ligand equilibrium constant $K'(c_{ML}^*/c_M^*)$ on the current response in the fully liable system $\psi_{FS}$ obtained in this work (Eq. 36) when $\varepsilon = 0.07$. 
Conclusions
In this work, the coupled system of time dependent differential equations for the finite planar diffusion-reaction has been formulated and solved analytically using the new separation of variables and HPM method. We have presented an analytical solution of the reaction-diffusion problem of a species that forms a complex in solution and disappears at an active planar surface for a finite diffusion region. Moreover, we have also presented an approximate analytical expression of concentration profiles of metal and complex and current for various for small and medium values of the parameters $\kappa_1, \kappa_2$ and $\varepsilon$ for non-steady state conditions. The exact analytical solution (Eq. 34) of the reaction-diffusion problem at an active planar surface is also presented for a finite diffusion region for fully labile systems. The extension of the procedure to mixture of ligands under non-steady state condition seems possible [6]. The model may be applied to discrete mixtures of ligands, either arising from the mixing of a number of different real species or from the consideration of sites in macromolecules as formal species.

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References


Appendix A: Transformation and steady state solution

In this appendix we indicate that how the analytical expression for the boundary value problem in the text can be obtained by using a new separation of variables method. Let us introduce the following variables transformation:

\[ u(\chi, \tau) = u_{ss}(\chi) + u_{tr}(\chi, \tau) \]  
\[ v(\chi, \tau) = v_{ss}(\chi) + v_{tr}(\chi, \tau) \]  

Using this transformation in Eqs. 9 and 10 and separating the variables, we get:

\[ \frac{\partial^2 u_{ss}}{\partial \chi^2} + \kappa_2 (v_{ss} - u_{ss}) = 0 \]  
\[ \varepsilon \frac{\partial^2 v_{ss}}{\partial \chi^2} + \kappa_1 (u_{ss} - v_{ss}) = 0 \]  

and

\[ \frac{\partial u_{tr}}{\partial \tau} = \frac{\partial^2 u_{tr}}{\partial \chi^2} + \kappa_2 (v_{tr} - u_{tr}) \]  
\[ \varepsilon \frac{\partial v_{tr}}{\partial \tau} = \varepsilon \frac{\partial^2 v_{tr}}{\partial \chi^2} + \kappa_1 (u_{tr} - v_{tr}) \]

Here \( u_{ss}(\chi) \) satisfies the inhomogeneous boundary conditions:

\[ \chi = 1; \quad u_{ss} = 1; \quad v_{ss} = 1 \]  
\[ \chi = 0; \quad u_{ss} = 0; \quad \partial v_{ss} / \partial \chi = 0 \]

The variables \( u_{tr}(\chi, \tau) \) and \( v_{tr}(\chi, \tau) \) satisfies the homogeneous boundary conditions and the initial condition as follows:

\[ \chi = 1; \quad u_{tr} = 0; \quad v_{tr} = 0 \]  
\[ \chi = 0; \quad u_{tr} = 0; \quad \partial v_{tr} / \partial \chi = 0 \]  
\[ \tau = 0; \quad u_{tr} = 1 - u_{ss}; \quad v_{tr} = 1 - v_{ss} \]

Now \( u_{ss}(\chi) \) and \( v_{ss}(\chi) \) can be solved by using simultaneous equation method. 
Steady state solution of the equations using simultaneous equation method:
Eqs. A3 and A4 can be written in the following forms:
Coupled System of Transient Reaction Diffusion Equations

\( (D^2 - \kappa_2)u_{SS} + \kappa_2 v_{SS} = 0 \) \hspace{1cm} (A12)

\( (\varepsilon D^2 - \kappa_1)v_{SS} + \kappa_1 u_{SS} = 0 \) \hspace{1cm} (A13)

Solving Eqs. A12 and A13, we have

\( (\varepsilon D^4 - (\kappa_2 \varepsilon + \kappa_1) D^2) u_{SS} = 0 \) \hspace{1cm} (A14)

Solving the Eq. A14 for \( u_{SS} \) and substituting in Eq. A12, we get \( v_{SS} \). Using the boundary conditions given by the Eqs. A7 and A8 we can obtain \( u_{SS}(\chi) \) (Eq. 17) and \( v_{SS}(\chi) \) (Eq. 21) as in the text.

**Appendix B: Non-steady state solution of the Equations (A5) and (A6) using the HPM**

Taking the Laplace transform to the partial differential Eqs. A5 and A6 and using the initial conditions given by Eq. A11, we get,

\[ \frac{d^2 \overline{u}_{TR}}{d\chi^2} + \kappa_2 (\overline{v}_{TR} - \overline{u}_{TR}) - s \overline{u}_{TR} + 1 - u_{SS} = 0 \] \hspace{1cm} (B1)

\[ \frac{d^2 \overline{v}_{TR}}{d\chi^2} + \frac{\kappa_1}{\varepsilon} (\overline{u}_{TR} - \overline{v}_{TR}) - \frac{s}{\varepsilon} \overline{v}_{TR} + \frac{(1 - v_{SS})}{\varepsilon} = 0 \] \hspace{1cm} (B2)

where \( s \) is the Laplace parameter. In Laplace space the boundary conditions are as follows:

\[ \chi = 1; \quad \overline{u}_{TR} = 0; \quad \overline{v}_{TR} = 0 \] \hspace{1cm} (B3)

\[ \chi = 0 \quad \overline{u}_{TR} = 0; \quad \overline{v}_{TR} / \partial \chi = 0 \] \hspace{1cm} (B4)

and an overbar indicates a Laplace-transformed quantity. We construct the Homotopy [19] for the Eqs. B1 and B2 as follows:

\[ (1 - p) \left[ \frac{d^2 \overline{u}_{TR}}{d\chi^2} - s \overline{u}_{TR} \right] + p \left[ \frac{d^2 \overline{u}_{TR}}{d\chi^2} + \kappa_2 (\overline{v}_{TR} - \overline{u}_{TR}) - s \overline{u}_{TR} + 1 - u_{SS} \right] = 0 \] \hspace{1cm} (B5)

\[ (1 - p) \left[ \frac{d^2 \overline{v}_{TR}}{d\chi^2} - \frac{s}{\varepsilon} \overline{v}_{TR} \right] + p \left[ \frac{d^2 \overline{v}_{TR}}{d\chi^2} + \frac{\kappa_1}{\varepsilon} (\overline{u}_{TR} - \overline{v}_{TR}) - \frac{s}{\varepsilon} \overline{v}_{TR} + \frac{(1 - v_{SS})}{\varepsilon} \right] = 0 \] \hspace{1cm} (B6)

The approximate solutions of Eqs. B5 and B6 obtained are:

\[ \overline{u}_{TR} = \overline{u}_{TR,0} + p \overline{u}_{TR,1} + p^2 \overline{u}_{TR,2} + \ldots \] \hspace{1cm} (B7)

\[ \overline{v}_{TR} = \overline{v}_{TR,0} + p \overline{v}_{TR,1} + p^2 \overline{v}_{TR,2} + \ldots \] \hspace{1cm} (B8)

The boundary conditions are as follows:

\[ \chi = 1; \quad \overline{u}_{TR,0} = 0; \quad \overline{v}_{TR,0} = 0 \] \hspace{1cm} (B9)
\[ \chi = 1; \quad \bar{u}_{TR,j} = 0; \quad \bar{v}_{TR,j} = 0 \quad i = 1, 2 \ldots \]  
(B10)

\[ \chi = 0; \quad \bar{u}_{TR,0} = 0; \quad \partial \bar{v}_{TR,0} / \partial \chi = 0 \]  
(B11)

\[ \chi = 0; \quad \bar{u}_{TR,j} = 0; \quad \partial \bar{v}_{TR,j} / \partial \chi = 0 \quad i = 1, 2 \ldots \]  
(B12)

Substituting Eqs. B7 and B8 in Eqs. B5 and B6 we have,

\[
(1 - p) \left[ \frac{d^2}{d\chi^2} (\bar{u}_{IR,0} + p \bar{u}_{IR,1} + p^2 \bar{u}_{IR,2} + \ldots) - s(\bar{v}_{IR,0} + p \bar{v}_{IR,1} + p^2 \bar{v}_{IR,2} + \ldots) \right] + \\
\frac{1}{s} \left[ \frac{d}{d\chi} (\bar{u}_{IR,0} + p \bar{u}_{IR,1} + p^2 \bar{u}_{IR,2} + \ldots) - \frac{s}{e} (\bar{v}_{IR,0} + p \bar{v}_{IR,1} + p^2 \bar{v}_{IR,2} + \ldots) \right] = 0
\]  
(B13)

Comparing the coefficients of like powers of \( p \) in Eq. B13, we get

\[
p^0 : \quad \frac{d^2 \bar{u}_{IR,0}}{d\chi^2} - s \bar{u}_{IR,0} = 0 \]  
(B15)

\[
p^1 : \quad \frac{d^2 \bar{u}_{IR,1}}{d\chi^2} - s \bar{u}_{IR,1} + \kappa_2 (\bar{v}_{IR,0} - \bar{u}_{IR,0}) + 1 - u_{SS} = 0
\]  
(B16)

Comparing the coefficients of like powers of \( p \) in Eq. B14, we have

\[
p^0 : \quad \frac{d^2 \bar{u}_{TR,0}}{d\chi^2} - s \bar{u}_{TR,0} = 0 \quad (B17) \quad p^1 : \\
\frac{d^2 \bar{u}_{TR,1}}{d\chi^2} - s \bar{v}_{TR,1} + \frac{\kappa_1}{e} (\bar{u}_{TR,0} - \bar{v}_{TR,0}) + \frac{(1 - u_{SS})}{e} = 0
\]  
(B18)

Solving the Eqs. B15 to B18 by using the boundary conditions given in Eqs. B9 to B12 we can obtain

\[
\bar{u}_{TR,0} = 0
\]  
(B19)

\[
\bar{u}_{TR,1} = A_1 \cosh \sqrt{s} \chi + B_1 \sinh \sqrt{s} \chi + \\
\frac{1}{\beta} \left[ 1 / s - \chi / s + \left[ \kappa \sinh \left( \frac{\kappa_1}{e} + \kappa_2 (\chi - 1) \right) \right] \left[ \frac{\kappa_1}{e} + \kappa_2 - s \right] \left[ \frac{\kappa_1}{e} + \kappa_2 \right] \cosh \left( \frac{\kappa_1}{e} + \kappa_2 \right)^{-1} \right]
\]  
(B20)

where
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\[
A_1 = \frac{1}{\beta} \left( \frac{K \varepsilon \tanh \left( \frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon} \right)}{\sqrt{\frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon} - \frac{s}{\varepsilon}}} \right) - \frac{1}{s} \right) \tag{B21}
\]

and

\[
B_1 = -\frac{A_1 \cosh \sqrt{s}}{\sinh \sqrt{s}} \tag{B22}
\]

\[
\bar{v}_{TR,0} = 0 \tag{B23}
\]

\[
v_{TR,1} = A_2 \cosh \sqrt{s/\varepsilon} \chi + B_2 \sinh \sqrt{s/\varepsilon} \chi + \frac{1}{\beta} \left( \frac{e/s(1-\chi)}{s} - \left[ \sinh \left( \frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon} (\chi-1) \right) \right] \frac{1}{\sqrt{\frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon} - \frac{s}{\varepsilon}}} \right) \cosh \left( \frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon} \right) \tag{B24}
\]

where

\[
B_2 = \frac{1}{\beta \sqrt{s \varepsilon}} \left( \frac{e}{s} + \frac{1}{s} \right) \tag{B25}
\]

and

\[
A_2 = -B_2 \frac{\sinh \sqrt{s/\varepsilon}}{\cosh \sqrt{s/\varepsilon}} \tag{B26}
\]

According to the HPM, we can conclude that

\[
u_{TR} (\chi, s) = \lim_{p \to 1} u_{TR} (\chi, s) = u_{TR,0} + u_{TR,1} + \ldots \tag{B27}
\]

\[
v_{TR} (\chi, s) = \lim_{p \to 1} v_{TR} (\chi, s) = v_{TR,0} + v_{TR,1} + \ldots \tag{B28}
\]

Put Eqs. B19 and B20 into Eq. B27 and Eqs. B23 and B24 into Eq. B28. Then using inverse Laplace transform (see APPENDIX E), the final results can be described by Eqs. 18 and 22 in the text. The remaining components of \( u_{TR,n} (\chi) \) and \( u_{TR,n} (\chi) \) can be completely determined such that each term is determined by the previous term.

Appendix C: SCILAB program to find the numerical solution of Eqs. 9 and 10 function pdex4

```scilab
m = 0;
x = [0 0.2 0.4 0.6 0.8 1];
```

\[ t = [0 0.4 0.8 1.2 1.6 2]; \]
\[ \text{sol} = 
\text{pdepe}(m, @(x,t,u,DuDx), @(x), @(x,t), @pdex4ic); \]
\[ u1 = \text{sol}(; ; , 1); \]
\[ u2 = \text{sol}(; ; , 2); \]

```matlab
figure
plot(x, u1(end, :))
title('u1(x)')
figure
plot(x, u2(end, :))
title('u2(x)')
```

% ------------------------------------------------------------

```matlab
function [c, f, s] = pdex4pde(x, t, u, DuDx)
k1=1;
k2=0.5;
E=0.7;
c = [1; 1];
f = [1; E].* DuDx;
F1 = k2*(u(2) - u(1));
F2 = k1*(u(1)-u(2));
s = [F1; F2];
```

% ------------------------------------------------------------

```matlab
function u0 = pdex4ic(x);
u0 = [1; 1];
```

% ------------------------------------------------------------

```matlab
function [pl, ql, pr, qr] = pdex4bc(xl, ul, xr, ur, t)
k1=1;
k2=0.5;
n=k2/k1;
E=100;
pl = [ul(1); 0];
ql = [0; 1];
pr = [ur(1)-1; ur(2)-1];
qr = [0; 0];
```

**Appendix D: Solution for the case of fully liable system ( Eq. 33 )**

Taking the Laplace transform to the partial differential Eq. 33 and using the initial conditions given by Eqs. 11-13 we get,

\[
s\bar{u}_{fs} - 1 = \left(\frac{1 + K^e}{1 + K}\right) \frac{d^2\bar{u}_{fs}}{d\chi^2} \tag{D1}
\]

where \( s \) is the Laplace parameter. In Laplace space the boundary conditions are as follows:

\[
\chi = 1; \quad \bar{u}_{fs} = 1/s \tag{D2}
\]
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\[ \chi = 0; \quad \overline{\tau}_{FS} = 0 \]  \hspace{1cm} (D3)

and an overbar indicates a Laplace-transformed quantity. Solving the Eq. D1 for \( \overline{u}_{FS} \) we get,

\[ \overline{u}_{FS} = P \cosh \left( \frac{s(1 + K')}{1 + K' \varepsilon} \chi \right) + Q \sinh \left( \frac{s(1 + K')}{1 + K' \varepsilon} \chi \right) + \frac{1}{s} \]  \hspace{1cm} (D4)

Using the boundary conditions given by Eqs. D2 and D3 in Eq. D4 we get,

\[ P = -\frac{1}{s} \]  \hspace{1cm} (D5)

\[ Q = \frac{\cosh \left( \frac{s(1 + K')}{1 + K' \varepsilon} \right)}{s \sinh \left( \frac{s(1 + K')}{1 + K' \varepsilon} \right)} \]  \hspace{1cm} (D6)

Using Eqs. D5 and D6 in Eq. D4 we get,

\[ \overline{u}_{FS} = \frac{\sinh \left( \frac{s(1 + K')}{1 + K' \varepsilon} (\chi - 1) \right)}{s \sinh \left( \frac{s(1 + K')}{1 + K' \varepsilon} \right)} + \frac{1}{s} \]  \hspace{1cm} (D7)

Then using inverse Laplace transform (see APPENDIX E), the final results can be described by Eq. 34 in the text.

**Appendix E: Inverse Laplace transform using Complex inversion formula**

In this appendix we indicate that how Eqs. B20, B24 and D7 may be inverted using complex inversion formula [20]. If \( \bar{y}(s) \) represents the Laplace transform of a function \( y(\tau) \), then according to the complex inversion formula we can state that

\[ y(\tau) = \frac{1}{2\pi i} \lim_{C \to \infty} \int_{C-i\infty}^{C+i\infty} \exp[s \tau] \overline{y}(s) ds = \frac{1}{2\pi i} \lim_{C \to \infty} \int_{C-i\infty}^{C+i\infty} \exp[s \tau] \overline{y}(s) ds \]  \hspace{1cm} (E1)

where the integration in Eq. E1 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 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. E1, which is evaluated using the so-called Bromwich contour [21]. The contour integral is then evaluated using the residue theorem [22] which states for any
analytic function $F(z)$.

$$\oint F(z)dz = 2\pi i \sum_{n} \text{Res}[F(z)]_{z=z_{n}}$$  \hspace{1cm} (E2)$$

where the residues are computed at the poles of the function $F(z)$. Hence from Eq. E2 we note that:

$$y(\tau) = \sum_{n} \text{Res}[\exp[s\tau]y(s)]_{s=s_{n}}$$  \hspace{1cm} (E3)$$

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:

$$\text{Res}[F(z)]_{z=a} = \text{Lim}_{z \to a} (z-a)F(z)$$  \hspace{1cm} (E4)$$

Hence in order to invert Eq. B20, we need to evaluate $\text{Res}\left[\frac{\sinh s(1-\chi)}{s \sinh \sqrt{s}}\right]$ at the poles. Now the poles are obtained from $s \sinh \sqrt{s} = 0$. Hence there is a simple pole at $s = 0$ and there are infinitely many poles given by the solution of the equation $s \sinh \sqrt{s} = 0$ and so $s_{n} = -n^{2}\pi^{2}\tau$ with $n = 1, 2, \ldots$. Hence we note that:

$$S(\chi, \tau) = \text{Res}\left[\frac{\sinh s\chi}{s \sinh \sqrt{s}}\right]_{s=0} + \text{Res}\left[\frac{\sinh s\chi}{s \sinh \sqrt{s}}\right]_{s=s_{n}}$$

$$= \text{Lim}_{s \to 0} (s \sinh \sqrt{s}) \left[\exp(s\tau) \frac{\sinh s\chi}{s \sinh \sqrt{s}}\right]_{s=0} + \text{Lim}_{s \to s_{n}} (s \sinh \sqrt{s}) \left[\exp(s\tau) \frac{\sinh s\chi}{s \sinh \sqrt{s}}\right]_{s=s_{n}}$$  \hspace{1cm} (E5)$$

The first residue in Eq. E5 is given by

$$\text{Res}\left[\frac{\sinh s\chi}{s \sinh \sqrt{s}}\right]_{s=0} = \text{Lim}_{s \to 0} (s \sinh \sqrt{s}) \left[\exp(s\tau) \frac{\sinh s\chi}{s \sinh \sqrt{s}}\right] = 1 - \chi$$  \hspace{1cm} (E6)$$

The second residue in Eq. E5 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 $g(s_{n}) = 0$ while $g'(s_{n}) \neq 0$ and $f(s_{n}) \neq 0$. Then it becomes

$$\text{Res}[F(z)]_{s=s_{n}} = \sum_{n=0}^{\infty} \frac{f(s_{n})}{g'(s_{n})} \exp[s_{n}\tau].$$

Hence we can show that:

$$\text{Lim}_{s \to s_{n}} (s \sinh \sqrt{s}) \left[\exp(s\tau) \frac{\sinh s\chi}{s \sinh \sqrt{s}}\right] = \text{Lim}_{s \to s_{n}} (s \sinh \sqrt{s}) \left[\frac{2\sqrt{s} \sinh s\chi}{s_{n} \cosh \sqrt{s}}\right]$$

$$= 2 \sum_{n=1}^{\infty} \frac{(-1)^{n}}{n} e^{-n^{2}\pi^{2}\tau} \sin(n\pi(1-\chi)) \quad n = 0, 1, 2, \ldots$$  \hspace{1cm} (E7)$$
Similarly we can take the inverse Laplace transform to Eqs. B24 and D7 also.

Appendix F: Nomenclature

Symbol | Meaning | Usual dimension
--- | --- | ---
$c_M$ | Concentration of the metal M | mole m$^{-3}$
$c_{ML}$ | Concentration of the complex ML | mole m$^{-3}$
$c'_M$ | Bulk concentration of the metal M | mole m$^{-3}$
$c'_{ML}$ | Bulk concentration of the complex ML | mole m$^{-3}$
$D_M$ | Diffusion coefficient of the metal M | m$^2$ s$^{-1}$
$D_{ML}$ | Diffusion coefficient of the complex ML | m$^2$ s$^{-1}$
$F$ | Faraday constant | C
$g$ | Thickness of the diffusion domain | m
$J_M$ | Flux of the species | mole m$^{-2}$ s$^{-1}$
$K'$ | Excess-ligand equilibrium constant | None
$n$ | Number of electrons | None
$t$ | Time | s
$u$ | Normalized concentration of the metal M | None
$v$ | Normalized concentration of the complex ML | None
$k_a$ | Association rate constant | s$^{-1}$
$k_d$ | Dissociation rate constant | s$^{-1}$
$k'_a$ | Effective association rate constant | s$^{-1}$
$\varepsilon$ | Dimensionless diffusion coefficient for the complex ML | None
$\psi$ | Dimensionless flux | None
$\kappa_1$, $\kappa_2$ | Dimensionless rate constants | None
$\tau$ | Dimensionless time | None
$u_{FS}$ | Normalised concentration in fully liable system | None
$\psi_{FS}$ | Dimensionless current in fully liable system | None
$\delta_d$ | Diffusion layer thickness | m
$\delta_r$ | Reaction layer thickness | m

Authors Biography

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Mathematical modelling of steady-state concentration in immobilized glucose isomerase of packed-bed reactors

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Abstract The theoretical model of the steady-state immobilized enzyme electrodes is discussed. This model is based on diffusion equation containing a non-linear term related to Michaelis–Menten kinetics of the enzymatic reaction. Homotopy perturbation method (HPM) is employed to solve the non-linear diffusion equation for the steady-state condition. Simple and approximate polynomial expression of concentration and flux are derived for all small values of parameters \( \phi_p \) (Theiele modulus) and \( \beta \) (kinetic parameter). Furthermore, in this work the numerical solution of the problem is also reported using SCILAB/MATLAB program. The analytical results are compared with the numerical results and found to be in good agreement.

Keywords Glucose isomerase · Mathematical modelling · Diffusion · Homotopy perturbation method · Simulation · Packed bed

List of symbols

\[
\begin{align*}
G & \quad \text{Reaction of glucose} \\
E & \quad \text{Reaction of enzyme} \\
F & \quad \text{Reaction of fructose} \\
G_0 & \quad \text{Initial concentration} \\
D_p & \quad \text{Pore diffusivity} \\
R & \quad \text{Reaction rate} \\
X & \quad \text{Complex intermediate} \\
K_{mf} & \quad \text{Michaelis–Menten constant} \\
v_{mf} & \quad \text{Maximum velocity of the forward reaction}
\end{align*}
\]
1 Introduction

Pore networks are frequently used in the modelling of transport and reactions in porous materials. This has been reviewed recently Sahimi et al. [1]. By representing the void space with a pore of idealised geometry, usually a cylindrical pore, the equations for diffusion and reaction may be solved. Marshall and Kooi [2] discovered glucose isomerase using enzymatic isomerization (EI). This discovery, which made it possible to produce fructose by EI of glucose isomerase [3–5]. The process was originally carried out in batch reactors with soluble enzymes. It was later extended to one involving immobilized glucose isomerase (IGI); Melkote and Jensen [6] used the percolation properties of a bethe lattice to model deactivation of glucose isomerase. Reyes and Jensen [7] calculate the effective diffusivity of the pore networks. A probabilistic approach was adopted by Forment et al. [8–10] to describe the pore network of the catalyst. Mann et al. [11] simulated fouling within individual catalyst particles using a two-dimensional square pore network. For example, Ching and Chu [12] studied the effect of desperation and flow on the performance of the reactor. Vasic-Racki et al. [13] carried out experimental studies and computer modelling of glucose isomerization. Houng et al. [14] carried out experimental studies of the problem using both a differential and a packed-bed reactor. They also studied the effect of a variety of factors on the reactor’s performance. Park et al. [15] and Faqir [16] investigated the effect of the temperature on the performance of the reactor and developed criteria for optimizing the reactor.

Recently, Mitra Dadvar et al. [17] studied deactivation of the microporous particles as a percolation process by developing a network model. However, to the best of our knowledge, no general analytical results for the steady-state substrate concentration and current for all values of parameters $\phi_p$, $\beta$, $\alpha_1$ and $\alpha_2$ have been reported. The purpose of this communication is to derive expression for the steady-state substrate concentration and the current in closed form for small values of parameters using the Homotopy perturbation method.

2 Mathematical formulation of the problem and analysis

The model describes the mechanism by which glucose enzyme moves from the intermediate complex form to the fructose and back to the intermediate to the complex glucose enzyme. This can be written as

$$G + E \xrightleftharpoons[k_{-1}]{k_1} X \xrightleftharpoons[k_{-2}]{k_2} F + E,$$

(1)
where $k_1, k_2$ are the kinetic constants for the forward direction and $k_{-1}, k_{-2}$ are the kinetic constants for the backward direction. The non-linear reaction diffusion equation for this model can be represented as follows [17]

$$D_p(\lambda) \frac{d^2 G}{dx^2} - \frac{2}{r \alpha} R = 0$$

(2)

where $\lambda = R_M / r (R_M$ is the molecular radius and $r$ is the pore radius) and $D_p$ is the pore diffusivity. To proceed further, we make the non-linear differential equation outlined in the Eq. (2) dimensionless by introducing the following parameters:

$$R = \frac{v_m \overline{G}}{K_m + \overline{G}} = G - G_e, \quad v_m = \frac{K_{mr} v_{mr}(1 + K^{-1})}{K_{mr} - K_{mf}},$$

$$K_m = \frac{K_{mf} K_{mr}}{K_{mr} - K_{mf}} \left[ 1 + \left( \frac{K_{mr}}{K_{mf}} \right) \frac{G_0}{1 + K} \right]$$

(3)

Now the Eq. (2) becomes,

$$D_p \frac{d^2 \overline{G}}{dx^2} - \frac{2}{r} \frac{v_m \overline{G}}{K_m + \overline{G}} = 0$$

(4)

By introducing the following dimensionless quantities

$$C = \frac{\overline{G}}{(G_0 - G_e)}, \quad z = \frac{x}{l_p}, \quad \beta = \frac{C_0}{K_m}, \quad \phi_p^2 = \frac{2l_p^2 v_m}{r D_p K_m}$$

(5)

the Eq. (4) becomes, [17]

$$\frac{d^2 C}{d z^2} - \phi_p^2 \frac{C}{1 + \beta C} = 0$$

(6)

The boundary conditions may be presented as follows:

$$C = \alpha_1 \text{ at } z = 0$$

(7)

$$C = \alpha_2 \text{ at } z = 1$$

(8)

The dimensionless current is given by

$$J_{ij} = \left[ \frac{\partial C}{\partial z} \right]_{z=1}$$

(9)
3 Analytical solution of the concentration and current using Homotopy perturbation method (HPM)

Recently, various analytical methods are applied to solve non-linear equations. Lesnic [18] used the Adomian decomposition method, He [19], Ozis et al. [20] used Homotopy perturbation method and Zhu [21,22] used exp-function method. The homotopy algorithm might be improved, if Rentoul and Ariel algorithm is adopted [23]. In this paper, the Homotopy perturbation method is applied [24,25]. This method is very effective and simple. Using this method, we obtain the analytical expression of substrate concentration (see Appendix A), as follows:

\[
C = \frac{1}{6A(B^2 - 1)} \times \left[ \begin{array}{c}
2\beta a_1 a_2 A B \cosh(2\phi p) + 6\alpha_2 \sinh(\phi p) \cosh^2(\phi p) - 2\beta a_1^2 AB^2 \cosh(2\phi p) \\
+ \cosh(2\phi p) \sinh(\phi p) \left[ 2\beta a_1^2 B^2 - 2\beta a_1 \phi B - \beta a_1 \right] + \sinh(2\phi p) \sinh(\phi p) \left[ 2\beta a_1 a_2 A - 2\beta a_1^2 B \right] \\
\end{array} \right] \\
+ \sinh(2\phi p) \left[ 2\beta a_1 a_2 - 2\beta a_1^2 B - 2\beta a_1 \phi B^2 + 2\beta a_1^2 B^3 \right] \\
+ \sinh(\phi p) \left[ 6\alpha_1 B - 4\beta a_1 a_2 B^2 + 18\beta a_1 a_2 B - 6\beta a_2 B^2 + 4\beta a_2^2 B^3 - 2\beta a_1 B - 6\alpha_1 B^3 - 6\alpha_2 \right] \\
+ \cosh(\phi p) \left[ 2\beta a_1 a_2 A - 6\alpha_1 A + 12\alpha_1 a_2 \beta A - 4\alpha_1^2 A B^2 + 4\beta a_1 a_2 AB + 6\alpha_1 A B^2 \right] + 12\alpha_1 a_2 \beta A \\
- 6\beta a_1 a_2 AB + 6\beta a_1 A B^2 - 3\beta a_1 A \\
\right]
\]

(10)

where

\[
A = \sinh(\phi p) \text{ and } B = \cosh(\phi p)
\]

Equation (10) is the new analytical expressions for the dimensionless substrate concentration in terms dimensionless kinetic parameter \( \beta \) and Thiele modulus \( \phi p \). Using Eq. (9), the current density is

\[
J_{ij} = \left[ \begin{array}{c}
0.1666 \\
\end{array} \right] \\
\begin{array}{c}
+ 6\alpha_2 B^2 \phi_p - 6\alpha_2 B - 6\alpha_1 A^2 \phi_p + 6\alpha_1 B^2 \phi_p - 4\alpha_1 a_2 B^2 \phi_p + 18\alpha_1 a_2 B^2 \phi_p + 2a_1 \beta A^2 \phi_p \\
- 12a_1 a_2 B^2 \phi_p - 6\alpha_2 \beta B^2 \phi_p + 4\alpha_1^2 B^2 \phi_p - 4\alpha_1 a_2 B^2 \phi_p + 4a_1 A^2 B^2 \phi_p \\
\times \left[ 6a_1 B^2 \phi_p + 3a_1 B \phi_p - 6a_1 B^2 \phi_p + 6a_1 A^2 B^2 \phi_p - 12a_1 a_2 B \phi_p \right] \\
+ \cosh(2\phi p) \left[ 6a_1 B^2 \phi_p - a_1 B \phi_p - 4a_1 a_2 \beta B \phi_p - 4a_1 a_2 \beta B \phi_p \right] \\
+ \sinh(2\phi p) \left[ 2a_1 a_2 \beta \phi_p + 6a_1 B^2 \phi_p \right]
\end{array}
\]

(12)

4 Numerical Simulation

The diffusion equation, Eq. (6) for the boundary conditions Eqs. (7–8) is solved by numerical methods. The function pde4 in Scilab software which is a function of solving the initial-boundary value problems for partial differential equation is used to solve these equations. Its numerical solution is compared with our analytical results in Tables 1, 2, 3, 4 and it gives good agreement between them. The SCILAB/MATLAB program is also given in Appendix B.
Table 1  Comparison of the analytical result Eq. (10) with the numerical result of concentration $C$ when $\phi_p = 2$, $\alpha_1 = 0.5$, $\alpha_2 = 1$ and for various values of $\beta$

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\beta = 0.01$</th>
<th>$\beta = 1$</th>
<th>$\beta = 2.5$</th>
<th>$\beta = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (10) Numerical % deviation of Eq. (10)</td>
<td>Eq. (10) Numerical % deviation of Eq. (10)</td>
<td>Eq. (10) Numerical % deviation of Eq. (10)</td>
<td>Eq. (10) Numerical % deviation of Eq. (10)</td>
</tr>
<tr>
<td>0</td>
<td>0.5000 0.5000 0.00</td>
<td>0.4999 0.5000 0.02</td>
<td>0.5000 0.5000 0.00</td>
<td>0.5000 0.5000 0.00</td>
</tr>
<tr>
<td>0.2</td>
<td>0.4411 0.4383 0.63</td>
<td>0.4799 0.4851 1.08</td>
<td>0.5231 0.5387 2.98</td>
<td>0.6367 0.5514 13.40</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4534 0.4492 0.93</td>
<td>0.5020 0.5234 4.26</td>
<td>0.5827 0.5756 1.22</td>
<td>0.6982 0.6263 10.30</td>
</tr>
<tr>
<td>0.6</td>
<td>0.5390 0.5347 0.80</td>
<td>0.5780 0.6175 6.83</td>
<td>0.6805 0.6370 6.39</td>
<td>0.7355 0.7255 1.36</td>
</tr>
<tr>
<td>0.8</td>
<td>0.7118 0.7087 0.44</td>
<td>0.7298 0.7735 5.99</td>
<td>0.8187 0.7573 7.50</td>
<td>0.8098 0.8498 5.84</td>
</tr>
<tr>
<td>1</td>
<td>1.0000 1.0000 0.00</td>
<td>1.0000 1.0000 0.00</td>
<td>1.0000 1.0000 0.00</td>
<td>1.0000 1.0000 0.00</td>
</tr>
</tbody>
</table>

Average deviation 0.47  Average deviation 3.03  Average deviation 3.02  Average deviation 5.15
Table 2 Comparison of the analytical result Eq. (10) with the numerical result of concentration $C$ when $\beta = 0.01$, $\alpha_1 = 0.1$, $\alpha_2 = 1$ and for various values of $\phi_p$

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\phi_p = 0.01$</th>
<th>$\phi_p = 0.1$</th>
<th>$\phi_p = 1$</th>
<th>$\phi_p = 3$</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Eq. (10)</td>
<td>Numerical</td>
<td>% deviation of</td>
<td>Eq. (10)</td>
</tr>
<tr>
<td>0</td>
<td>0.1000</td>
<td>0.1000</td>
<td>0.00</td>
<td>0.1000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2799</td>
<td>0.2800</td>
<td>0.04</td>
<td>0.2789</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4589</td>
<td>0.4600</td>
<td>0.24</td>
<td>0.4584</td>
</tr>
<tr>
<td>0.6</td>
<td>0.6398</td>
<td>0.6400</td>
<td>0.03</td>
<td>0.6383</td>
</tr>
<tr>
<td>0.8</td>
<td>0.8199</td>
<td>0.8200</td>
<td>0.01</td>
<td>0.8188</td>
</tr>
<tr>
<td>1</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.00</td>
<td>1.0000</td>
</tr>
<tr>
<td></td>
<td>Average deviation</td>
<td>0.05</td>
<td></td>
<td>Average deviation</td>
</tr>
</tbody>
</table>
Table 3  Comparison of the analytical result Eq. (10) with the numerical result of concentration $C$ when $\beta = 0.01$, $\phi_p = 2$, $\alpha_2 = 1$ and for various values of $\alpha_1$

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\alpha_1 = 0.01$</th>
<th>$\alpha_1 = 0.1$</th>
<th>$\alpha_1 = 0.5$</th>
<th>$\alpha_1 = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (10)</td>
<td>Numerical</td>
<td>Eq. (10)</td>
<td>Numerical</td>
</tr>
<tr>
<td>0</td>
<td>0.0099</td>
<td>0.0100</td>
<td>0.9999</td>
<td>0.1000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1197</td>
<td>0.1184</td>
<td>0.1786</td>
<td>0.1772</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2490</td>
<td>0.2466</td>
<td>0.2863</td>
<td>0.2838</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4186</td>
<td>0.4157</td>
<td>0.4405</td>
<td>0.4375</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6561</td>
<td>0.6538</td>
<td>0.6662</td>
<td>0.6639</td>
</tr>
<tr>
<td>1</td>
<td>0.9999</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Average deviation | 0.69 | 0.33 | 0.47 | 0.65
Table 4  Comparison of the analytical result Eq. (10) with the numerical result of concentration $C$ when $\beta = 0.01, \phi_p = 2, \alpha_1 = 1$ and for various values of $\alpha_2$.

<table>
<thead>
<tr>
<th>X</th>
<th>$\alpha_2 = 0.01$</th>
<th>$\alpha_2 = 0.1$</th>
<th>$\alpha_2 = 0.5$</th>
<th>$\alpha_2 = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (10)</td>
<td>Numerical % deviation of Eq. (10)</td>
<td>Eq. (10)</td>
<td>Numerical % deviation of Eq. (10)</td>
</tr>
<tr>
<td>0</td>
<td>0.9999</td>
<td>1.0000</td>
<td>0.01</td>
<td>0.9999</td>
</tr>
<tr>
<td>0.2</td>
<td>0.6562</td>
<td>0.6538</td>
<td>0.82</td>
<td>0.6693</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4499</td>
<td>0.4157</td>
<td>3.30</td>
<td>0.4448</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2531</td>
<td>0.2466</td>
<td>2.57</td>
<td>0.2904</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1225</td>
<td>0.1184</td>
<td>3.35</td>
<td>0.1814</td>
</tr>
<tr>
<td>1</td>
<td>0.0999</td>
<td>0.0100</td>
<td>1.01</td>
<td>0.1000</td>
</tr>
<tr>
<td></td>
<td>Average deviation</td>
<td>1.84</td>
<td>Average deviation</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Fig. 1 Plot of the concentration $C$ versus the normalised distance $z$ for various values of $\phi_p$ and some fixed values of $\alpha_1$, $\alpha_2$ and $\beta$. The concentrations were computed using Eq. (10). The key to the graph: (dotted line) represents the Eq. (10) and (+) represents the numerical simulation.

Fig. 2 Plot of the concentration $C$ versus the normalised distance $z$ for various values of $\beta$ and some fixed value of $\alpha_1$, $\alpha_2$ and $\phi_p$. The concentrations were computed using Eq. (10). The key to the graph: (dotted line) represents the Eq. (10) and (+) represents the numerical simulation.

5 Result and discussion

Equation (10) represents the closed and simple approximate analytical expression of the concentration of substrate for small values of parameters $\phi_p$, $\beta$, $\alpha_1$ and $\alpha_2$. Equation (12) represents new simple analytical expression of flux. The concentration of
substrate depends upon the values parameters $\phi_p$, $\beta$, $\alpha_1$ and $\alpha_2$. The parameter Thiele modulus $\phi_p$ can be varied by changing either the thickness of the enzyme layer or the amount of enzyme immobilized in the matrix. This parameter describes the relative importance of diffusion and reaction in the enzyme layer. Figures 1 and 2 represent the dimensionless steady state concentration $C$ for different values of the Thiele modulus $\phi_p$ and dimensionless kinetic parameter $\beta$. From these figures, it is obvious that the substrate concentration $C$ reaches the maximum value 1, when $x = 1$. Figure 3a–d represent the dimensionless flux $J_{ij}$ versus dimensionless kinetic parameter $\beta$ for various values of Thiele modulus $\phi_p$. From this figure, it is evident that the flux value increases as the dimensionless kinetic parameter $\beta$ and Thiele modulus $\phi_p$ increases. In Tables 1, 2, 3 and 4 our result is compared with numerical result for small values of parameters. The substrate concentration $C$ is compared numerically for various values of the dimensionless kinetic parameter $\beta$ (Table 1), Thiele modulus $\phi_p$ (Table 2), $\alpha_1$
Thenormalizedthree-dimensional normalizedconcentration profile Eq. (10) when 0 ≤ \( \beta \leq 1, \phi_p = 0.01, \alpha_1 = 1 \) and \( \alpha_2 = 1 \). b The normalized three-dimensional normalized concentration profile Eq. (10) when 0 ≤ \( \alpha_1 \leq 1, \beta = 0.01, \phi_p = 1 \) and \( \alpha_2 = 0.1 \). c The normalized three-dimensional normalized concentration profile Eq. (10) when 0 ≤ \( \alpha_2 \leq 1, \beta = 0.01, \phi_p = 1 \) and \( \alpha_1 = 1 \)  

(Table 3) and \( \alpha_2 \) (Table 4). In all the cases average relative error is less than 3%. From these tables we conclude that there is no significant difference found in the substrate concentration \( C \) when the value of all parameters is less than 0.1. The normalized three-dimensional substrate concentration profile \( C \) is plotted in Fig 4a–c where the data given by Figs. 1 and 2 are verified.

6 Conclusion

In this work, system of coupled, steady-state non-linear reaction/diffusion equation in pore network model has been solved analytically. Approximate analytical expressions for the concentration and flux in packed-bed reactor for kinetic reactions with diffusion coefficients at a planar microelectrode under steady-state conditions are obtained using the Homotopy perturbation method. The primary result of this work is simple approximate calculation of concentration profiles and flux for small values of the fundamental parameters. The small variation in Thiele modulus caused a significant change in both the magnitude of the current response and the general behavior of the system. The Homotopy perturbation method is extremely simple and promising to solve other non-linear equations. This method can be easily extended to find the solution of all other non-linear reaction diffusion equations in kinetic reactions for all microelectrodes for various complex boundary conditions.
Acknowledgments  This work was supported by the University Grants Commission (F. No. 39-58/2010(SR)), New Delhi, India. The authors are thankful to Dr. R. Murali, The Principal, The Madura College, Madurai and Mr. M. S. Meenakshisundaram, The Secretary, Madura College Board, Madurai for their encouragement. The author V. Margret PonRani is very thankful to the Manonmaniam Sundaranar University, Tirunelveli for allowing to do the research work.

Appendix A

Solution of the Eq. (6) using Homotopy perturbation method

In this Appendix, we indicate how Eq. (10) in this paper are derived. To find the solution of Eq. (10) we first construct a Homotopy as follows:

\[ (1 - p) \left[ \frac{d^2 C}{dz^2} - \phi_p^2 C \right] + p \left[ \frac{d^2 C}{dz^2} - \phi_p^2 C + \beta C \frac{d^2 C}{dz^2} \right] = 0 \]  \hspace{1cm} (A1)

The boundary conditions are

\[ C = \alpha_1 \text{ at } z = 0 \] \hspace{1cm} (A2)
\[ C = \alpha_2 \text{ at } z = 1 \] \hspace{1cm} (A3)

The approximate solutions of Eq. (A1) is

\[ C = C_0 + pC_1 + p^2C_2 + p^3C_3 + \cdots \cdots \]. \hspace{1cm} (A4)

Substituting Eq. (A4) into (A1) and comparing the coefficients of like powers of \( p \)

\[ p^0: \frac{d^2 C_0}{dz^2} - \phi_p^2 C_0 = 0 \] \hspace{1cm} (A5)

The boundary conditions are

\[ C_0 = \alpha_1 \text{ at } z = 0 \] \hspace{1cm} (A6)
\[ C_0 = \alpha_2 \text{ at } z = 1 \] \hspace{1cm} (A7)

\[ p^1: \frac{d^2 C_1}{dz^2} - \phi_p^2 C_1 + \beta C_0 \frac{d^2 C_0}{dz^2} = 0 \] \hspace{1cm} (A8)

The boundary conditions are

\[ C_1 = 0 \text{ at } z = 0 \] \hspace{1cm} (A9)
\[ C_1 = 0 \text{ at } z = 1 \] \hspace{1cm} (A10)

According to the HPM, we can conclude that

\[ C = C_0 + C_1 + \cdots \cdots \]. \hspace{1cm} (A11)
Solving the Eqs. (A5) and (A8), using the boundary conditions Eqs. (A6, A7, A9, A10) and substituting into Eq. (A11), and we can obtain Eq. (10) in the text.

Appendix B

SCILAB/MATLAB program to find the numerical solutions for Eq. (6):

```matlab
function pdex4
m=0;
x=linspace(0,1);
t=linspace(0,100000);
sol=pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
figure
plot(x,u1(end,:))
title('u1(x,t)')
xlabel('Distance x')
ylabel('u1(x,2)')
end

function [c,f,s]=pdex4pde(x,t,u,DuDx)
c=1;
f=DuDx;
q=0.1;
B=10;
F=-q^2*u(1)/(1+B*u(1));
s=F;
end

function u0=pdex4ic(x) %create a initial conditions
u0=1;
end

function [pl,ql,pr,qr]=pdex4bc(xl,ul,xr,ur,t) %create a boundary conditions
pl=0;
ql=1;
pr=ur-1;
qr=0;
end
```

References