CHAPTER V

NUMERICAL ANALYSIS OF REACTION/DIFFUSION WITH MICHAELIS–MENTEN KINETICS IN ELECTROACTIVE POLYMER FILMS

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5.1 INTRODUCTION

The development of polymer-based materials for use as electrocatalysis and as chemical and biological sensors operating in the batch amperometric mode [1, 2] was discussed in earlier chapter. The purpose of this chapter is to evaluate numerical solutions for substrate concentration and transient current for non steady state at polymer modified electrodes and interfacial position as a function of time and distance (moving boundary problem) by finite difference method using MS Excel iteration for all values of $\alpha$. Further, to extend the analysis for the case of the coupled reaction diffusion equations [5].

5.2 FORMULATION OF THE BOUNDARY VALUE PROBLEM AND THE ANALYSIS

We assume that the substrate S reacts with the catalyst C via Michaelis–Menten kinetics, according to the following scheme [3].

\[
S + C \xrightleftharpoons[K_m]{k_3}[SC] \rightarrow [PC'] \xrightarrow{k_i} P + C'
\]

\[
C' \xrightarrow{k_b} C + ne^{-}
\]

where $C$ and $C'$ represent the active form of the immobilized enzyme catalyst. S and P denote substrate and product respectively and [SC] is the
enzyme–substrate complex and \([\text{PC}']\) is the product–enzyme complex. \(K_M\) and \(k_c\) denote the Michaelis–Menten constant and catalytic constant respectively [3]. The implicit assumption here is that the amount of substrate which is held bound up in the SC complex in the steady state is insignificant. To demonstrate the problem, a very large concentration of \(C\) within the film is considered so that the concentration of SC present at any time is significant. A full transient treatment for the case where \(S\) diffuses into a film and binds to sites within the film, without undergoing any further reaction can be found in the literature [15]. The partial differential equation quantifying the transport and kinetics within the polymer film may be expressed as

\[
\frac{\partial s}{\partial t} = D_s \frac{\partial^2 s}{\partial x^2} - \frac{k_c c_s s}{K_M + s}
\]  

(1)

where \(s\) denotes the concentration of the substrate at any distance \(x\) in the thin film at any time \(t\), \(D_s\) is the diffusion coefficient of the substrate in the enzyme layer and \(c_s\) denotes the total catalyst concentration in the film. This is a time–dependent non–linear partial differential equation. The left hand side of equation (1) denotes the rate of change of
substrate concentration and right hand side denotes sum of the rates due to reaction and diffusion.

We can write equation (1) in another way by introducing a pseudo-first-order rate constant \( k = k_c c_{\Sigma} / K_M \)

\[
\frac{\partial s}{\partial t} = D_s \frac{\partial^2 s}{\partial x^2} - \frac{ks}{1 + \frac{s}{K_M}}
\]

This equation is solved for the following initial and boundary conditions.

\[
s(x,0) = 0 \quad (3a)
\]

\[
[\frac{\partial s}{\partial x}]_{x=0} = 0 \quad (3a)
\]

\[
s(L, t) = \kappa s^\infty \quad (3a)
\]

where \( \kappa \) and \( L \) denotes the partition coefficient and uniform thickness of the layer and \( s^\infty \) represents the bulk concentration of the substrate in solution. The following parameters have been introduced to express the nonlinear reaction diffusion equation (2) in non dimensional format [2]:

\[
u = \frac{s}{\kappa s^\infty}; \quad \chi = \frac{x}{L}; \quad \tau = \frac{D_s t}{L^2}; \quad \alpha = \frac{\kappa s^\infty}{K_M}; \quad K = \frac{kL^2}{D_s}
\]

where \( \nu, \chi \) and \( \tau \) represent dimensionless concentration, distance and time parameters, respectively. The parameter \( \alpha \) denotes the extent of saturation of the enzyme and \( K \) the reaction diffusion parameter.
\[
\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - \frac{K u}{1 + \alpha u}
\]  \hspace{1cm} (5)

The initial and boundary conditions may be presented as follows

\[
u(\chi, 0) = 0 \hspace{1cm} (6a)
\]

\[
\left[ \frac{\partial u}{\partial \chi} \right]_{\chi=0} = 0 \hspace{1cm} (6b)
\]

\[
u(1, \tau) = 1 \hspace{1cm} (6c)
\]

The first term on the right-hand side of equation (5) is the diffusion term whereas the second one is reaction term. Here the reaction term is a non-linear function of concentration. The parameter \( K \) provides a way of quantifying the influence of substrate diffusion on the reaction kinetics.

The transient normalized current response \( y \) is given by

\[
y = \frac{iL}{nFAK_M D_S} = \alpha K \int_{0}^{1} u(\chi, \tau) d\chi
\]  \hspace{1cm} (7)

where \( i \) denotes the time dependent amperometric current response and \( n \) is a number of electrons involved in a charge transfer at the electrode surface and \( F \) is Faraday constant and \( A \) is the area of the electrode. \( K_M \) denotes the Michaelis–Menten constant and \( L \) is the uniform thickness of the layer. \( D_S \) is defined below the equation (1). In case of unsaturated (first order) enzyme, the enzyme is not saturated by its substrate, i.e
\( \alpha u \ll 1 \), whereas in saturated (zero order) enzyme case, the enzyme is saturated by its substrate, i.e \( \alpha u \gg 1 \).

Lyons and coworkers have solved the equation (5) subject to the initial and boundary conditions prescribed in equations (6a,6b and 6c) for the limiting situations of \( \alpha u \ll 1 \) and \( \alpha u \gg 1 \) with some restrictions in \( \alpha \) and \( K \) (Refer in Appendix–A).

The non-linear steady state reaction diffusion (spherical) equation of the form as represented by equation (8) is adopted with the boundary condition equations (9a) and (9b) are represented as follows

\[
\frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{d}{d\rho} \right) - \frac{Ku}{1 + \alpha u} = 0 \quad \text{where} \quad 0 \leq \rho \leq 1 \quad \text{and} \quad 0 \leq u \leq 1
\]

\[
\frac{du}{d\rho} = 0 \quad \text{at} \quad \rho = 0
\]

\[
u = 1 \quad \text{at} \quad \rho = 1
\]

The first term in the right hand side of equation (8) is the diffusion (spherical) term whereas the second one is reaction term which is the dimensionless steady state reaction diffusion equation (\( \rho = \frac{r}{a} \),

\[
K = \frac{k_c s^a}{K_M D_S} \quad \text{and} \quad \alpha = \frac{s^w}{K_M}
\]

No analytical result has been presented in Lyons et al.[5]. In this chapter steady state nonlinear spherical diffusion
equation is solved using finite difference method in MS Excel spreadsheet.

In case of unsaturated (first order) enzyme, the enzyme is not saturated by its substrate, i.e, \( \alpha_u << 1 \) in spherical diffusion case i.e the limiting case (first order kinetics \( \alpha_u << 1 \)), reaction diffusion equation (10) and the boundary conditions (11a) and (11b) are represented as follows:

\[
\begin{align*}
\frac{1}{\rho} \frac{d}{d\rho} \left( \rho^2 \frac{du}{d\rho} \right) - Ku &= 0 \quad \text{where } 0 \leq \rho \leq 1 \text{ and } 0 \leq u \leq 1 \\
\frac{du}{d\rho} &= 0 \text{ at } \rho = 0 \\
u &= 1 \text{ at } \rho = 1
\end{align*}
\]  

(10)

(11a)

(11b)

The following solution for limiting case (first order kinetics) is obtained by variable separable method (Lyons [5]).

\[
u(\rho) = \frac{\sinh(\sqrt{K}\rho)}{\rho \sinh(\sqrt{K})} \]  

(12)

The reaction mechanism for the coupled reaction diffusion equations is

\[
S + C \xleftarrow[{K_m}]{k_m} [SC] \xrightarrow{k_p} [PC'] \xrightarrow{b} P + C' \\
C' + M \xrightarrow{b_i} C + M' \\
M' \rightarrow M + ne^-
\]
where \( M \) and \( M' \) represent the oxidized and reduced form of the mediator and the other notations are defined earlier.

When the conductivity of the layer is not assumed to be rapid, now the equation (5) is transformed into a set of dimensionless coupled non-linear differential equations (13a) and (13b) are as shown below:

\[
\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - \frac{K_{uv}}{1 + \alpha u}
\]

(13a)

\[
\frac{\partial v}{\partial \tau} = \frac{\partial^2 v}{\partial \chi^2} - \frac{K_{uv}}{1 + \alpha u}
\]

(13b)

\[
\chi = 0; \quad \frac{\partial u}{\partial \chi} = 0, \quad v = 1
\]

(14a)

\[
\chi = 1; \quad u = 1, \quad \frac{\partial v}{\partial \chi} = 0
\]

(14b)

\[
\tau = 0; \quad u = 0, \quad v = 0
\]

(14c)

The coupled non-linear steady state reaction diffusion (spherical form) equations (16a) and (16b) will adopt the following form:

\[
\frac{1}{\rho} \frac{d}{d\rho} \left[ \rho \frac{d u}{d\rho} \right] - \frac{K_{uv}}{1 + \alpha u} = 0
\]

(16a)

\[
\frac{1}{\rho} \frac{d}{d\rho} \left[ \rho \frac{d v}{d\rho} \right] - \frac{K_{uv}}{1 + \alpha u} = 0
\]

(16b)

\[
\rho = 0, \quad v = 1, \quad \frac{du}{d\rho} = 0
\]

(17a)

\[
\rho = 1, \quad \frac{dv}{d\rho} = 0, \quad u = 1
\]

(17b)
In this chapter, steady state nonlinear coupled diffusion (spherical form) equation is solved using finite difference method in MS Excel spreadsheet.

5.3 CALCULATION FOR CONCENTRATION AND CURRENT (NON-STeady STATE) USING NUMERICAL TECHNIQUE (FINITE DIFFERENCE METHOD)

In finite difference method, the continuous differential equation is replaced with discrete approximation formulae. So the solution is known only at the cross of a rectangular grid (mesh). Each intersection point (knot) has a numeric value. Translating in the language of the spreadsheet we can say that each cell represents a knot of the mesh and the all range corresponds to the mesh itself. Each cell contains the discrete solution of the correspondent knot. As we can see, for rectangular mesh, the similarity is very tight, so it is natural to think to apply the power of the spreadsheet tool to the finite difference method. In this context the word “discrete” means that the numerical solution is known only at a finite number of points in the physical domain. The number of those points can be chosen by the user. In general, increasing the number of points not only increases the resolution (i.e., detail), but
also the accuracy of the numerical solution. The mesh is a set of location points where the discrete solution is computed. These points are called nodes or knots. The key parameters of the mesh are $\Delta x$ the local distance between adjacent points in space, and $\Delta \tau$, the local distance between adjacent time steps. The difference equation for the equation (5) can be written as,

$$u(i, j+1) = \left( \frac{h^2 m}{h^2 + m} \right) \left[ \frac{1}{2h^2} (u(i-1, j)+u(i+1, j)+u(i-1, j+1)+u(i+1, j+1)) + \frac{h^2 - m}{h^2 m} u(i, j) - \frac{Ku(i, j+1)}{1+\alpha u(i, j+1)} \right]$$

(18)

The comparisons of values obtained by Lyons series [2] and equation (18) for concentration for various values of $\alpha$ and $K$ are given in figures (2a–2f) and performing the numerical integration, we obtain the numerical values for current as indicated in the figures (3a–3b) and (4a–4b).

The difference equations for the coupled non-linear reaction diffusion equations ((13a) and (13b)) are given by,

$$u(i, j+1) = \left( \frac{h^2 m}{h^2 + m} \right) \left[ \frac{1}{2h^2} (u(i-1, j)+u(i+1, j)+u(i-1, j+1)+u(i+1, j+1)) + \frac{h^2 - m}{h^2 m} u(i, j) - \frac{Ku(i, j+1)\nu(i, j+1)}{1+\alpha u(i, j+1)} \right]$$

(19a)
\[ v(i, j+1) = \left( \frac{h^2m}{h^2 + m} \right) \left[ \frac{1}{2h^2} (v(i-1, j) + v(i+1, j) + v(i-1, j+1) + v(i+1, j+1)) \right. \]

\[ + \left( \frac{h^2 - m}{h^2m} \right) v(i, j) - \frac{Ku(i, j+1)v(i, j+1)}{(1 + \alpha u(i, j+1))} \]  

(19b)

Using the above equations ((19a) and (19b)), the concentration for various values of \( \alpha \) and \( K \) are given in Figures 5a to 5d.

The difference equations for (spherical diffusion under steady state) the limiting case (equation (10)), steady state non-linear (equation (8)) and coupled nonlinear (equation (16a) and (16b)) reaction diffusion equation are presented as follows

\[ u(i) = \left( \frac{h^2}{2(h + \rho(i))} \right) \left[ \frac{\rho(i)u(i-1)}{h^2} + \left( \frac{2h + \rho(i)}{h^2} \right) u(i+1) - Ku(i) \right] \]  

(20)

\[ u(i) = \left( \frac{h^2}{2(h + \rho(i))} \right) \left[ \frac{\rho(i)u(i-1)}{h^2} + \left( \frac{2h + \rho(i)}{h^2} \right) u(i+1) - \frac{Ku(i)v(i)}{1 + \alpha u(i)} \right] \]  

(21)

\[ u(i) = \left( \frac{h^2}{2(h + \rho(i))} \right) \left[ \frac{\rho(i)u(i-1)}{h^2} + \left( \frac{2h + \rho(i)}{h^2} \right) u(i+1) - \frac{Ku(i)v(i)}{1 + \alpha u(i)} \right] \]  

(22a)

\[ v(i) = \left( \frac{h^2}{2(h + \rho(i))} \right) \left[ \frac{\rho(i)v(i-1)}{h^2} + \left( \frac{2h + \rho(i)}{h^2} \right) v(i+1) - \frac{Ku(i)v(i)}{1 + \alpha u(i)} \right] \]  

(22b)

where \( h = \Delta \chi \) (local distance between adjacent points in space) and \( m = \Delta \tau \) (the local distance between adjacent time steps); \( \alpha \), the saturation of the enzyme parameter and \( K \) the reaction diffusion parameter, are same as
defined in earlier equation (4). The detailed derivation of equation (18) was presented in Appendix – B.

Using the above equations (20), (21), (22a) and (22b), the concentrations were computed for various values of $\alpha$ and $K$ are given in Figures (6a), (6b), (7a), (7b), (8a) and (8b).

5.4 RESULTS AND DISCUSSION

We have obtained numerical solution of finite difference equation (18) for all values of $K$ and $\alpha$ using MS Excel iteration as shown in excel spreadsheet (Figure 1a) to evaluate concentration as well as current and its the solution for equation (5) and equation (7) for typical values of $\alpha=0.5$ and $K=0.01$ and further the moving boundary problem was solved effortlessly and represented in the Figure 1b for the typical case $\alpha=10$ and $K=50$ which covers $\alpha \ll 1$ and $\alpha \gg 1$. Lyons and coworkers [1, 2] have solved the equation (5) and presented the non-steady state concentration (refer [2] Equations (9) and (24)) and current (refer [2] Equations (15) and (26)) for limiting cases i.e., $\alpha \ll 1$ and $\alpha \gg 1$. The comparisons of values obtained by Lyons series [2] and equation (18) for concentration for various values of $\alpha$ and $K$ are given in figures (2a–2f).
and performing the numerical integration, we obtain the numerical values for current as indicated in the figures (3a–3b) and figures (4a–4b). The difference equations for coupled transient nonlinear (equations (13a) and 13b)), (spherical diffusion) the limiting case (equation (10)), non-linear (equation (8)) and coupled nonlinear (equations (16a and 16b)) reaction diffusion equation was obtained for all values of K and $\alpha$ using MS Excel iteration in excel spreadsheet (refer Figures 5a to 5d, (6a), (6b), (7a), (7b), (8a) and (8b). These graphs indicate that it is possible to obtain accurate results in a short duration by finite difference when processed in MS Excel iteration (The maximum number of iteration is 1000 and the maximum change is 0.001).

5.5 CONCLUSION

The studies reported in this chapter are of theoretical nature. A non-linear time dependent partial differential equation was formulated and solved numerically. The whole non-linear term (reaction term) was taken into account and solved numerically using finite difference method. The moving boundary problem was also solved. Concentration and current were calculated using Microsoft excel. Lyons and his co-workers
presented series solution for limiting cases and they have imposed restrictions for $\alpha$ and $K$, but the solution for whole non linear case was obtained by MS Excel iteration.

**APPENDIX–A**

Lyons and coworkers [2] have presented the concentration and current for limiting cases ($\alpha u << 1$ and $\alpha u >> 1$) as follows,

For $\alpha u << 1$ the equation (5) becomes,

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - K u$$  \hspace{1cm} (A1)

The concentration and current is

$$u(\chi, \tau) = \cosh(\sqrt{K} \chi) \text{sech}(\sqrt{K})$$

$$- 2\pi \sum_{n=0}^{\infty} (-1)^n \left\{ \frac{(n+1/2) \cos\left((n+1/2)\pi \chi\right)}{(n+1/2)^2 \pi^2 + K} \right\} \exp\left[ - \left(\frac{(n+1/2)^2 \pi^2 + K}{2}ight) \tau \right]$$  \hspace{1cm} (A2)

$$y(\tau) = \alpha \sqrt{K} \tanh(\sqrt{K}) - 2\alpha K \sum_{n=0}^{\infty} \left\{ \exp\left[ - \left(\frac{(n+1/2)^2 \pi^2 + K}{2}ight) \tau \right] \right\}$$  \hspace{1cm} (A3)

For $\alpha u >> 1$ the equation (5) becomes,

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - \frac{K}{\alpha}$$  \hspace{1cm} (A4)

The concentration (only when $K < 2\alpha$) and current is

$$u(\chi, \tau) = 1 + \frac{K}{2\alpha} \left(\chi^2 - 1\right)$$

$$- \sum_{n=1}^{\infty} (-1)^n \left\{ \frac{4}{\pi} \left(\frac{4K}{\pi^2 \alpha (2n-1)^2} - \frac{1}{(2n-1)}\right) \right\} \cos\left[ \frac{(2n-1)\pi \chi}{2} \right] \exp\left[ - \left(\frac{(2n-1)^2 \pi^2 \tau}{4}\right) \right]$$  \hspace{1cm} (A5)
\[ y(\tau) = K - \frac{K^2}{3\alpha} + \sum_{n=1}^{\infty} \left\{ \frac{8K}{\pi^2 (2n - 1)^2} \left( \frac{4K}{\pi^2 \alpha (2n - 1)^2} - 1 \right) \right\} \exp \left[ -\frac{(2n - 1)^2 \pi^2 \tau}{4} \right] \]  

(A6)

**APPENDIX-B**

The difference equation for the equation (5) was formulated as follows,

\[ u(\chi, \tau_j) = u(i, j) \quad \text{where} \quad \chi_i = (i - 1) \Delta \chi, \quad i = 1, 2, 3, \ldots, M \quad \text{and} \]

\[ \tau_j = (j - 1) \Delta \tau, \quad j = 1, 2, 3, \ldots, N \]

\[ \frac{\partial u}{\partial \tau} = \frac{u(i, j+1) - u(i, j)}{m} \quad \text{where} \quad m = \Delta \tau \]  

(B1)

\[ \frac{\partial^2 u}{\partial \chi^2} = \frac{1}{2h^2} \left( u(i - 1, j) - 2u(i, j) + u(i + 1, j) + u(i - 1, j + 1) \right) - 2u(i, j + 1) + u(i + 1, j + 1) \]

Where \( h = \Delta \chi \)  

(B2)

\[ u(i, j+1) = \left( \frac{h^2 m}{h^2 + m} \right) \left[ \frac{1}{2h} (u(i - 1, j) + u(i + 1, j) + u(i - 1, j + 1) + u(i + 1, j + 1)) + \left( \frac{h^2 - m}{h m} \right) u(i, j) - \frac{K u(i, j+1)}{1 + au(i, j+1)} \right] \]  

(B3)
REFERENCES


