CHAPTER- 1

INTRODUCTION

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1.1 INTRODUCTION

1.1.1 NON LINEAR PHENOMENA

Non linear phenomena play a crucial role in applied mathematics and chemistry. Exact (closed-form) solution of non linear reaction diffusion equations plays an important role in the proper understanding of qualitative features of many phenomena and processes in various areas of natural science. But it is difficult for us to obtain the exact solution for these problems. The investigation of exact solution of nonlinear equation is interesting and important. Non–Linear reaction–diffusion models and their study arise in various contexts. Polymer modified ultra–micro–electrodes, Homogeneous mediated enzyme catalyzed reaction, Electrodes modified with multi layered enzyme system, Electrodes modified with nano–structured porous film. The dimensionless non –linear reaction diffusion equation is

\[
\frac{\partial C}{\partial T} = \nabla^2 C - \Phi(C) \tag{1}
\]

where \( C \) represents the dimensionless concentration of the active species, \( T \) represents the dimensionless time. The first term on the right
hand side of equation (1) accounts for active species (substrate) diffusion, whereas the second term \( \phi(C) \) represents the homogenous reaction term, generally polynomial in the concentration (which is non-linear function in concentration \( C \)).

1.1.2 MODELLING

Modelling is an essential and inseparable part of all scientific activity, and many scientific disciplines have their own ideas about specific types of modelling. A model is a simplified abstract view of the complex reality. A scientific model represents empirical objects, phenomena, and physical processes in a logical way. A kinetic model of biosensor provides a link between the experimental factors, the concentration of the analyte, the sensor response and the model provides a mathematical description of the physical processes occurring within the system. The developed kinetic model provides the scientists with the tools to design future experiments or to rationally improve the enzyme electrode’s performance for a specific application. In the subsequent chapters, the behaviour of the system is considered with a Michaelis–Menten type mechanism.
1.1.3 NON–LINEAR REACTION DIFFUSION EQUATION

Considerable advances have been made during the last decade in the development of polymer–based materials for use as electrocatalysts and as chemical and biological sensors operating in the batch amperometric model [1, 2]. Albery et al [3] and Lyons and co–workers [1] developed the theoretical models of steady state current of a polymer modified electrode which exhibits a rate law described by the Michaelis–Menten equation. Building upon earlier work for this mechanism, Lyons and co–workers [2] presented a concise discussion of boundary value problem for modified electrodes and quantifying the transport and kinetics within the polymer film expression as dimensionless form of non–linear partial differential equation with the initial and boundary conditions may be written as

\[
\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} - \frac{K u}{1 + \alpha u} \quad (2)
\]

\[u(\chi,0) = 0 \quad (2a)\]

\[\left[ \frac{\partial u}{\partial \chi} \right]_{\chi=0} = 0 \quad (2b)\]

\[u(1,\tau) = 1 \quad (2c)\]
where $u$, $\chi$ and $\tau$ represent dimensionless concentration, distance and time parameters, respectively. The parameter $\alpha$ denotes the extent of saturation of the enzyme and $\kappa$ the reaction diffusion parameter. Lyons and co-workers [2] have calculated the transient current for the above mechanisms for the limiting cases of $\alpha << 1$ and $\alpha >> 1$. The first term on the right-hand side of equation (2) is the diffusion term whereas the second one is reaction term. Here the reaction term is a non-linear function of concentration. In this thesis the above problem was solved analytically using Danckwerts' relation [4] and variable and separable method and numerically using Microsoft excel spread sheet.

1.1.4 REACTION DIFFUSION MODELS WITH LINEAR AND NONLINEAR BOUNDARY CONDITIONS

Electrochemistry has come a long way from the classical areas of physical chemistry. During the second half of the century, especially in electroanalytical chemistry, one can visualize two major contributing factors for this development. One is, the advances made in the electronic instrumentation, the second factor is the advances in mathematical
modelling of the electrochemical processes, coupled with the numerical calculations and simulation.

Chronopotentiometry, an electroanalytical technique in which the current is controlled and potential becomes the dependent variable, which is determined as a function of time. This technique enables the study of the kinetics of electrode processes with or without chemical kinetics and of adsorption at the electrode surface.

The theoretical analysis for the evaluations of expressions for potential transient in case of the charge transfer and coupled electrochemical reactions (at the boundary) taking into consideration for the interplay of the three following possible conditions [5]:

(a) Potential transient response due to the effects of activation and diffusion obtained from the linear faradaic form,

(b) Potential transient response due to the interaction of double layer effect with activation and diffusion obtained from the complex faradaic form,
A large number of possible mechanisms involving both chemical and electrochemical steps can be envisaged. The response (potential transient) of an electrode – electrolyte interface by the redox reaction

\[ \text{O} + \text{n} \; \text{e} \leftrightarrow \text{R} \]

to a current perturbation \( i(t) = \Delta i \exp(-t/\tau) \), where \( \tau \) is the characteristic life of the pulse) is considered with and without double layer effect. The diffusion of reactant ‘O’ and product ‘R’ occur in the bulk of electrolyte. Hence the species of reactant ‘O’ and product ‘R’ obeys the following diffusion equations

\[
\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2} \quad (3a)
\]

\[
\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (3b)
\]

with the initial and boundary conditions

\[
t = 0, \; x \geq 0: \; C_o = C_o^b, \; C_R = C_R^b \quad (4a)
\]

\[
t \geq 0, \; x \to \infty: \; C_o \to C_o^b, \; C_R \to C_R^b \quad (4b)
\]

\[
t \geq 0, \; x = 0: \; D_o \frac{\partial C_o}{\partial x} = -D_R \frac{\partial C_R}{\partial x} = \frac{i}{nFA} \quad (4c)
\]
Equation (4a) represents initial boundary condition and equation (4b) represents the concentration of the species in the bulk of electrolyte. Equation (4c) is an important interphase boundary condition whereas current perturbation \( \dot{i}(t) = \Delta i \exp(-t/\tau) \), (\( \tau \) is the characteristic life of the pulse) is considered and the case of a simple reversible charge transfer reaction with double layer effect, the only change is in the boundary value problem. The boundary condition equation (4c) takes the following form

\[
t \geq 0, x = 0 : D_O \frac{\partial C_O}{\partial x} = -D_R \frac{\partial C_R}{\partial x} = \frac{i}{nFA} + \frac{\partial n}{\partial t} \frac{C_d}{nFA}
\]

The diffusion equations (3a) and (3b) were solved numerically by finite difference method using Microsoft excel spread sheet to study the variation of the potential \( \eta(t) \) with time upon a controlled current for all the possible chemical/electrochemical processes under activation–diffusion conditions. The phenomenological relation between current and potential (linear, nonlinear or differential equation) as shown Table 1 enters through the boundary condition equation (4c). This poses a great problem in obtaining the solution of PDE (equation (3a) and (3b)) through
conventional method. They are solved in finite difference method using Microsoft excel spread sheet.

Table 1

**Contribution of input current for a system involving a charge transfer with and without double layer charging**

<table>
<thead>
<tr>
<th>Activation and Diffusion (Linear form)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ i(t) = i_0 \left{ \frac{\Delta C_o - \Delta C_R}{C_o^b - C_R^b} + \frac{nF\eta(t)}{RT} \right} ]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activation, Diffusion and Double layer effect (Complex form)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ i(t) = i_0 \left{ \frac{\Delta C_o - \Delta C_R}{C_o^b - C_R^b} + \frac{nF\eta(t)}{RT} \right} + C_d \frac{d\eta(t)}{dt} ]</td>
</tr>
</tbody>
</table>

Where \( \Delta C_o = C_o - C_o^b \) (Concentration of the reactant \( O \)), \( C_o^b \) (bulk concentration), \( C_d \) (double layer capacitance), \( i_0 \) (exchange current density) and \( \alpha \) (transfer coefficient), \( n \) (number of electrons involved in charge transfer step), \( F \) (faraday constant), \( R \) (gas constant) and \( T \) (temperature) viz.
1.2 OBJECTIVES AND SCOPE OF THE PRESENT INVESTIGATION

The objectives of the present investigation are as follows:

(i) To derive the transient chronoamperometric current for a catalytic reaction (EC’ reaction) mechanism at cylindrical ultramicroelectrodes using Danckwerts’ expression for a short duration and lower reaction rate and to solve an initial boundary value problem using Danckwerts’ expression.

(ii) To derive analytical solutions for substrate concentration and transient current for both steady and non steady state using Danckwerts’ relation and variable separable method and to derive a two-point Padé approximation for the non–steady state current for all values of saturation parameter \( \alpha \).

(iii) To give approximate and analytical solutions of non-linear reaction diffusion equations containing a non linear term related to Michaelis–Menten kinetics of the enzymatic reaction using variational iteration method.
(iv) To give numerical solutions for substrate concentration and transient current for non steady state by finite difference method using MS Excel iteration and to obtain a general simple numerical evaluation of current for all values of enzyme saturation parameter ($\alpha$) and a moving boundary problem is also solved in MS Excel spreadsheet.

(v) To obtain the potential time response under Tafel polarization conditions with double layer charging, a nonlinear ordinary differential equation was solved analytically.

(vi) To evaluate the expressions for potential transient the diffusion equations with linear and non–linear boundaries and, with and without double layer effect were solved using finite difference method in Microsoft excel sheet.
1.3 ORGANIZATION OF THE THESIS

In chapter 2, the transient chronoamperometric current for a catalytic reaction mechanism at cylindrical ultra-micro-electrodes is derived using Danckwerts’ expression [4] for short duration and lower reaction rate. The transient current at cylindrical microelectrodes for whole duration and all reaction rates is also reported. The primary result of this work is the first accurate calculation of non-steady state current at cylindrical ultra-micro-electrode (for an EC’ mechanism over significant time intervals and reaction rates). The theory of the catalytic electrode processes at cylindrical microelectrodes was presented.

In chapter 3, a non-linear time dependent partial differential equation was solved analytically. The analytical solutions for substrate concentration and transient current for both steady and non steady state are obtained using Danckwerts’ relation [4] and variable separable method. A two-point Padé approximation is also derived for the non-steady state current for all values of saturation parameter $\alpha$.

In chapter 4, a mathematical model of amperometric biosensors is developed and variational iteration method is implemented to give
approximate and analytical solutions of non-linear reaction diffusion equations containing a non linear term related to Michaelis–Menten kinetics of the enzymatic reaction. The variational iteration method produces the solutions in terms of convergent series, requiring no linearization or small perturbation. These analytical results are compared with available limiting case result and are found to be in good agreement.

In chapter 5, a numerical analysis of amperometric response for a polymer–modified electrode system has been carried out for the reaction/diffusion model. The situations of catalytic site unsaturation and site saturation are considered. The numerical solutions for substrate concentration and transient current for non steady state are obtained by finite difference method using MS Excel iteration. An excellent agreement with the previous analytical results is noted. A general simple numerical evaluation of current for all values of enzyme saturation parameter ($\alpha$) is obtained and a moving boundary problem is also solved in MS Excel spreadsheet. The whole non-linear term (reaction term) is taken into account and solved numerically using finite difference method. The
moving boundary problem is also solved. Concentration and current were calculated using Microsoft excel.

**In chapter 6,** analytical solution for nonlinear ordinary differential equation [5] is obtained which is applicable for certain input parameters. The numerical solution for the same equation is also obtained. This numerical solution gives good result for all input parameters. An analytical solution of the equation is derived and experimental and simulated data are fit and the results are analyzed.

**In chapter 7,** simulation scheme for the calculation of theoretical chronopotentiograms at planar electrodes is presented based on the relaxation technique and finite difference method for all possible mechanisms involving both chemical and electrochemical steps. A detailed analysis of the simulated potential–time response obtained under varied conditions of the input parameters as well as the system parameters were undertaken to investigate the factors responsible for the observed transition time effects on the kinetic data. The interaction of double layer charging is also considered. A large number of possible mechanisms involving both chemical and electrochemical steps can be
envisaged. The problems are solved for few of the schemes in MS Excel spreadsheet.

REFERENCES

[5] Rangarajan SK, Electroanalytical chemistry and Interfacial  
   Electrochemistry, 41:459, 1953.