Analysis of Steady-State Behavior of EC′ Catalytic Mechanism at Rotating Disk Electrode: Taylor Series Approach

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***Abstract:** Rotating disc electrodes are used to analyze electrochemical reactions in electrochemical cells and various rotating types of machinery. This model contains a system of fully coupled equations. This paper deals with EC′ reaction mechanism arises in Rotating disk electrode. This mathematical model contains system of reaction-convection-diffusion equations. Taylor series method is applied to find the analytical expression of concentration and current. The solutions enable us to obtain the current response in chronoamperometry and steady-state voltammetry and it is beneficial to study the behavior of the system. The obtained results are compared with the numerical simulation. An excellent agreement is observed between the series of solutions obtained by simulation solution. The effect of the parameters on concentration and current are discussed and presented graphically.*

***Keywords:** Rotating disk electrode, convection-diffusion equations, Taylor series method, EC′ reaction, Numerical simulation.*

1. INTRODUCTION:

In recent years, considerable attention has been paid to the EC catalytic mechanism problems at the rotating disk electrodes [1]. The present work is widely used in the experimental study of electrode reaction mechanisms involving homogeneous chemical processes coupled with electro transfers [2]. An equally important general class of mechanistic pathways involves the so-called catalytic (EC) mechanism in which an electrogenerated species (the 'mediator') oxidizes or reduces some other solution species (the 'substrate') with the regeneration of the original electroactive material which can therefore be subjected to further electrode reaction.

There is no closed form solution to the RDE system. Several approaches to obtaining a numerical solution for the RDE system [3] were attempted. For example, Eddowes [4] used finite difference and orthogonal methods of collocation to solve the system of differential equations that explain the state of the rotating disks. Von Karman [5] has presented the steady-state solution for the convective diffusion equation for the RDE system many years ago. Daniel Okuonghae [6] uses a Galerkin finite element approach to solve convection-diffusion equations in the EC′ and ECE reactions for rotating disk electrodes. Compton et.al [1,7,8] conducted an extensive study on the different nuances of the catalytic mechanism (EC')

at a rotating disk electrode. The basics of rotating disk electrodes are thoroughly outlined in [9].

Rotating disk electrode is a powerful electrochemical instrument capable of monitoring the transportation regime of electro-active species to the electrode [10]. Using Pade approximation, Chitra Devi et.al [11] outlines the steady state solution of rotational disk flow and heat transfer of power-law fluid over rotating disk electrode. In [12], it describes convection-diffusion equations in the EC-catalytic pseudo-first - order system at a rotating disk electrode.

In this present work we propose a simple and well-known method of the Taylor series to solve the equations of reaction-convection-diffusion that occur at a rotating disk electrode. For various values of parameters the estimated analytical expression for the concentration and current is obtained. The approach proposed is accurate and available

for the wider community of natural sciences.

The work done in the next sections is summarized as follows. The mathematical formulation of the problem is defined in Section 2, following that the approximate analytical expression is given in Section 3 for the concentrations and the current. In the continued section 4 numerical simulations is provided which is used to check the accuracy of the approximate solution obtained using Taylor series process, complete discussion of the analytical and numerical results is given in section 5, finally in section 6 we draw some concluding remarks.

2. Mathematical formulation of the problem

The EC′ mechanism can be described as follows:

$$A \pm e^- \Leftrightarrow B \tag{1}$$

$$B + S \xrightarrow{k} A + Y \tag{2}$$

Where S and Y represent the electro inactive species and k is the rate of the reaction. The first step is simply a reversible E reaction. The second step represents the species B and S (a substrate molecule) reacts to forms A (the catalytic cycle) and Y (product). This mechanism can be described by the following system of linear convection-diffusion equation [13]:

$$-D_A \frac{d^2 A}{dx^2} - Cx^2 \frac{dA}{dx} - k_s B = 0 \tag{3}$$

$$-D_B \frac{d^2 B}{dx^2} - Cx^2 \frac{dB}{dx} + k_s B = 0 \tag{4}$$

The boundary conditions are

$$A(x = 0) = 0, A(x = L) = A_\infty \tag{5}$$

$$B(x = 0) = A_\infty, B(x = L) = 0 \tag{6}$$

where $C = 0.51023\, v^{-\frac{1}{2}} \omega^{\frac{3}{2}}$.

Using the following the dimensionless variables[14],

$$a = \frac{A}{A_\infty}; b = \frac{B}{A_\infty}, \xi = \left(\frac{C}{D_A}\right)^{\frac{1}{3}} x, l = \left(\frac{C}{D_A}\right)^{\frac{1}{3}} L, k = \frac{k_s}{D_A}\left(\frac{C}{D_A}\right)^{\frac{-2}{3}}, \mu = \frac{D_A}{D_B} \tag{7}$$

the Eqns. (3) and (4) reduces to the following dimensionless form [14]:

$$\frac{d^2 a}{d\xi^2} + \xi^2 \frac{da}{d\xi} + kb = 0 \tag{8}$$

$$\frac{d^2 b}{d\xi^2} + \mu \xi^2 \frac{db}{d\xi} - k\mu b = 0 \tag{9}$$

The dimensionless boundary conditions are,

$$a(\xi = 0) = 0, a(\xi = l) = 1 \tag{10}$$

$$b(\xi = 0) = 1, b(\xi = l) = 0 \tag{11}$$

The electrode surface is on $\xi = 0$ and the boundary conditions are $b(0) = 1$ and $b(l) = 0$ having an interpretation as that obtained for the *E* reaction. The dimensionless current in this case is

$$I_{EC'} = J = -\frac{db}{d\xi}\Big|_{\xi=0} \tag{12}$$

3. Approximate analytical solution of the Eq. (8-11) using Taylor series method

By solving the Eqns. (8) and (9) using Taylor series method (see Appendix A), the concentration of species $a(\xi)$ and $b(\xi)$ can be obtained as follows:

$$a(\xi) = m\xi - \frac{k\xi^2}{2} - \frac{kn\xi^3}{6} - \frac{(2m+k^2\mu)\xi^4}{24} + \frac{(6-k\mu n)k\xi^5}{120} + \frac{(12n+(2n-\mu^2 k^2))k\xi^6}{720} \tag{13}$$

$$b(\xi) = 1 + n\xi + \frac{\mu k\xi^2}{2} + \frac{\mu k n\xi^3}{6} - \frac{(2n-\mu^2 k^2)\mu\xi^4}{24} - \frac{(6\mu^2 - \mu^2 kn)k\xi^5}{120} - \frac{(14\mu^2 n - \mu^3 k^2)k\xi^6}{720} \tag{14}$$

where,

$$m = -\frac{30l^4 k^2\mu + 360kl^2 + 120kn\,l^3 - 12l^6 kn - 2l^6 \mu kn - 36l^5 k + 6l^5 k^2\mu n + l^6 \mu^2 k^3 + 720}{60l(l^3 - 12)} \tag{15}$$

$$n = -\frac{1}{2}\frac{720 + \mu kl(30\mu k\,l^3 + 360l + \mu^2 k^2 l^5 - 36\mu\,l^4)}{(60\mu k\,l^2 - 30l^3\mu + 3l^4\mu^2 k^2 - 7l^5\mu^2 k)l + 360l} \tag{16}$$

The unknown constant "*m and n*" are obtained using the boundary condition $a(\xi = l) = 1$ and $b(\xi = l) = 0$.

When $D_A = D_B$ or $\mu = 1$, from the above equations, it is observed that $a(\xi) + b(\xi) = 1$. The dimensionless current becomes

$$I_{EC'} = J = -\frac{db}{d\xi}\Big|_{\xi=0} = -n = \frac{1}{2}\frac{720 + \mu kl(30\mu k\,l^3 + 360l + \mu^2 k^2 l^5 - 36\mu\,l^4)}{(60\mu k\,l^2 - 30l^3\mu + 3l^4\mu^2 k^2 - 7l^5\mu^2 k)l + 360l} \tag{17}$$

4. Numerical simulation

MATLAB routine bvp4c/ bvp5c is generated for finding the numerical solution of Eqs. (8-11). This Numerical programme is developed to verifying the accuracy of the approximate analytical solution obtained by Taylor series method. The comparison between numerical and analytical results which are obtained for reaction-convection-diffusion equations in the EC′ mechanism at a rotating disk electrode are shown via figures in the following section.

5. Discussion

The effect of the parameters k (reaction rate), μ (ratio of diffusion coefficient) on the concentration of species $a(\xi)$ and $b(\xi)$ using Eqn. (13-14) is shown in Figures 1-4. From the Figures 1-2, it is inferred that concentration decreases slowly when reactant species $a(\xi)$ moves to towards electrode surface for all values of parameters. Also due to mass transport of the electron transfer process, the concentration decreases linearly with l for all values of the other parameters. The concentration $a(\xi)$ increases for the increasing value of the reaction rate rate parameter and for the ratio of the reaction rate, i.e. if species $a(\xi)$ is directly proportional to diffusion coefficient D_A and indirectly proportional to D_B. All the above processes are in the reverse side for the concentration species $b(\xi)$ (refer Fig. 3-4).

Figures 5 and 6 show the current curve for EC′ reaction for different values of the reaction rate constant and rotation rate (ω). From the figures, it is inferred that the peak current is

significantly proportional to the reaction rate inversely proportional to rotation rate. The dependence of current on rotation rate is usually taken as proof that a process is controlled by convection and diffusion.
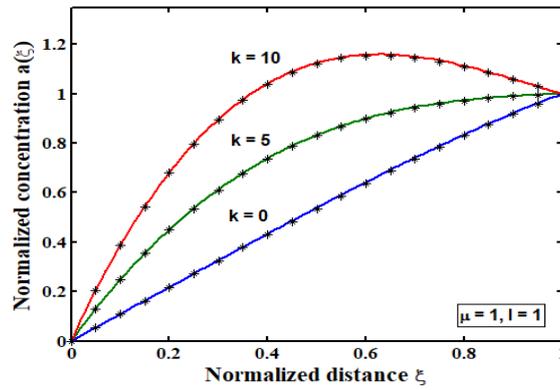
Fig. 1. Effect of the parameter k on concentration profile $a(\xi)$ using Eqn. (13).
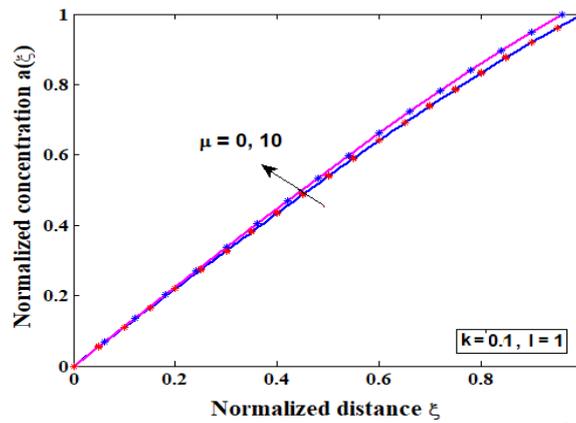
Fig. 2. Effect of the parameter μ on concentration profile $a(\xi)$ using Eqn. (13).
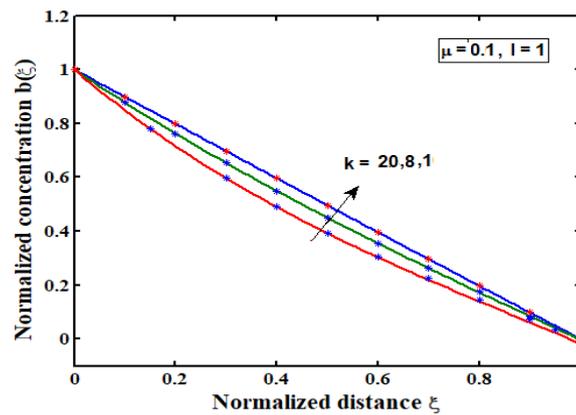
Fig.3. Effect of the parameter k on concentration profile $b(\xi)$ using Eqn. (14).
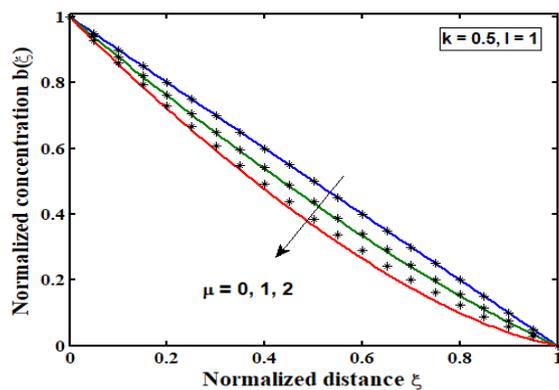
Fig. 4. Effect of the parameter μ on concentration profile $b(\xi)$ using Eqn. (14).
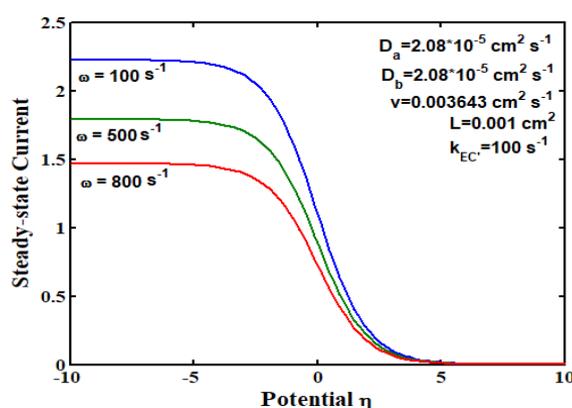
Fig. 5. Steady-state Current versus Potential for various values of rotation rate using Eqn. (17).
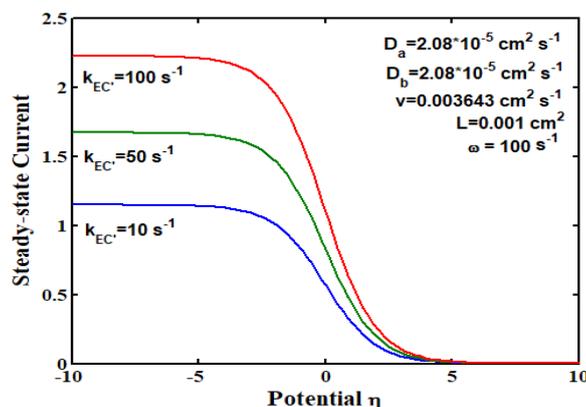
Fig. 6. Steady-state Current versus Potential for various values of reaction rate using Eqn. (17).

6. Conclusions

   A mathematical model describing the process of convection and diffusion of the pseudo-first-order EC-catalytic mechanism at the rotating disc electrode under steady-state is presented. Approximate analytical solutions of the steady-state system of convection-diffusion equations are solved by using homotopy perturbation method. A simple, straight forward and a new method of estimating the radial, tangential, axial velocity components have been reported. The simple closed-form of expressions of concentrations of species and current are derived for EC′ and ECE reaction at the rotating disc electrode for steady-state

conditions. The numerical and analytical results for some of the experimental value of the parameter are plotted. From the figures and tables, it is observed that analytical results are in good agreement with the simulation result. The analytical results obtained help to understand and predict the behavior of the system. This analytical result will be useful to know the behaviour of the reaction system.

Appendix A : Approximate analytical solution of the Eq. (8-11) using Taylor series method

Consider the Maclaurin series (Taylor's series at $\chi = 0$) for dimensionless concentration of $a(\xi)$.

$$a(\xi) = \sum_{p=0}^{q} \left(\frac{d^p a}{d\xi^p} \bigg|_{\xi=0} \right) \frac{\xi^p}{p!} = \sum_{p=0}^{q} A_p \frac{\xi^p}{p!} \qquad \text{(A. 1)}$$

$$b(\xi) = \sum_{p=0}^{q} \left(\frac{d^p b}{d\xi^p} \bigg|_{\xi=0} \right) \frac{\xi^p}{p!} = \sum_{p=0}^{q} B_p \frac{\xi^p}{p!} \qquad \text{(A. 2)}$$

From the boundary conditions (Eq. (10)), we get $a(0) = 0$. Let us consider, $a'(0) = m$ where m is constant and by letting $\frac{d^p a}{d\xi^p}\big|_{\xi=0} = A_p$, $\frac{d^p b}{d\xi^p}\big|_{\xi=0} = B_p$ and from eq. (8 & 9) we can get the followings

$$A_0 = 0, A_1 = m, A_2 = -k, A_3 = -kB_1, A_4 = -2m - kB_2, A_5 = (6 - B_3)k, A_6 = (12B_1 - kB_4)k, A_7 = 40m + (20B_2 - B_5)k. \qquad \text{(A. 3)}$$

$$B_0 = 1, B_1 = n, B_2 = muk, B_3 = \mu kn, B_4 = -2\mu n + \mu^2 k^2, B_5 = -6\mu^2 k + \mu^2 k^2 n, B_6 = -14\mu^2 kn + \mu^3 k^3, B_7 = 40\mu2n - 26\mu^3 k^2 + \mu^3 k^3 n \qquad \text{(A. 4)}$$

Substituting the above values in eq. (18 & 19) we get

$$a(\xi) = m\xi - \frac{k\xi^2}{2} - \frac{kn\xi^3}{6} - \frac{(2m+k^2\mu)\xi^4}{24} + \frac{(6-k\mu n)k\xi^5}{120} + \frac{(12n+(2n-\mu^2 k^2))k\xi^6}{720} = 1 \qquad \text{(A. 5)}$$

$$b(\xi) = 1 + n\xi + \frac{\mu k\xi^2}{2} + \frac{\mu kn\xi^3}{6} - \frac{(2n-\mu^2 k^2)\mu\xi^4}{24} - \frac{(6\mu^2-\mu^2 kn)k\xi^5}{120} - \frac{(14\mu^2 n-\mu^3 k^2)k\xi^6}{720} = 0 \qquad \text{(A. 6)}$$

Using the boundary conditions $a(\xi = l) = 1$, $b(\xi = l) = 0$ we can find the unknown constant "m and n".

$$a(l) = ml - \frac{kl^2}{2} - \frac{knl^3}{6} - \frac{(2m+k^2\mu)l^4}{24} + \frac{(6-k\mu n)kl^5}{120} + \frac{(12n+(2n-\mu^2 k^2))kl^6}{720} \qquad \text{(A. 7)}$$

$$b(l) = 1 + nl + \frac{\mu kl^2}{2} + \frac{\mu knl^3}{6} - \frac{(2n-\mu^2 k^2)\mu l^4}{24} - \frac{(6\mu^2-\mu^2 kn)kl^5}{120} - \frac{(14\mu^2 n-\mu^3 k^2)kl^6}{720} \qquad \text{(A. 8)}$$

By solving the above equations we get,

$$m = -\frac{30l^4 k^2\mu + 360kl^2 + 120knl^3 - 12l^6 kn - 2l^6\mu kn - 36l^5 k + 6l^5 k^2\mu n + l^6\mu^2 k^3 + 720}{60l(l^3-12)}, \qquad \text{(A. 9)}$$

$$n = -\frac{1}{2}\frac{720+\mu kl(30\mu kl^3+360l+\mu^2 k^2 l^5-36\mu l^4)}{(60\mu kl^2-30l^3\mu+3l^4\mu^2 k^2-7l^5\mu^2 k)l+360l}. \qquad \text{(A. 10)}$$

The current is

$$I_{ECl} = J = -\frac{db}{d\xi}\bigg|_{\xi=0} = -n = \frac{1}{2}\frac{720 + \mu kl(30\mu kl^3 + 360l + \mu^2 k^2 l^5 - 36\mu l^4)}{(60\mu kl^2 - 30l^3\mu + 3l^4\mu^2 k^2 - 7l^5\mu^2 k)l + 360l} \qquad \text{(A. 11)}$$

Appendix B : Nomenclature and units

Symbols	Name	Unit
A, B	Concentration of species A, B	$mol\ cm^{-3}$
A_∞	Bulk concentration of species A	$mol\ cm^{-3}$
D_A, D_B	Diffusion coefficients of species A and B	$cm^2 s^{-1}$
ω	Rotation speed	s^{-1}
v	Kinematic viscosity	$cm^2 s^{-1}$
C	Parameter	$1/(cm.s)$
μ	Ratio of diffusion coefficient	none
k_s	The standard rate constant of the electrode reaction	s^{-1}
L	Distance from the electrode surface where $A = A_\infty$	cm
x	Distance normal to the electrode surface	cm
$k_{EC'}$	Reaction rate	s^{-1}
$I_{EC'lim}$	The dimensionless current when $k=0$	
$\psi_{EC'lim}$	The limiting current	none
$I_{EC'}$	Dimensionless current	none
$\psi_{SVEC'}$	Dimensionless current for steady state voltamatery	
η	Potential	V
R	The universal gas constant	$Jm^{-1}K^{-1}$
F	Faraday constant	cm^{-1}
T	Temperature	K
n	Number of moles of electrons transferred in the balanced equation	*none*
E	Electrode potential	V
E^0	Standard potential of the electrode reaction	V
a, b	Dimensionless concentration of the species A and B respectively	none
k	Dimensionless reaction rate	none
ξ	Dimensionless distance from the electrode surface	none
l	Dimensionless distance from the electrode surface when $a(\xi) = 1$	none

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