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Mathematical Modelling and Application of Analytical Methods for A Non-Linear EC_2E Mechanism in Rotating Disk Electrode

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ABSTRACT. Rotating disk electrode is the hydrodynamic technique used in the process of analyzing electroanalytic works. This paper deals with the mathematical model describing a non-linear EC_2E mechanism that arises in a rotating disk electrode. This model is based on the system of non-linear reaction-convection-diffusion equations. EC_2E mechanism has an application in finding the shape of current curves in the system of chronoamperometry in addition to steady-state voltammetry. The approximate analytical expression for the concentration of reactant species and current at steady-state condition is obtained using the analytical methods. The attained analytical result is compared with the numerical simulation (MATLAB) result. A satisfactory result is obtained between the series of solutions. The influence of parameters on the concentration of species and current is investigated and presented graphically.

1. Introduction

A Rotating disk electrode (RDE) has numerous applications in electrochemistry. RDE analyses the electrolyte solution where the rotating electrode is placed. The three basic modes of mass transfer are reaction, convection and diffusion [1]. RDE studies the mass transport that

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occurs during the reaction. For the first time, a steady-state expression for the mass transport equation in RDE was computed in Ref [2].

Recently, The ECE mechanism in Rotating disk electrodes has been more considerable. The EC_2E mechanism is described by the second order homogeneous chemical reaction interposed between one-one and half electron transfers. Specific numerical and analytical approaches for RDE mechanisms [3] have been obtained over the years. Daniel Okuoghae used the Galerkin finite element method to model RDE mechanisms such as E, EC′ and ECE reactions [4]. Gulaboski et al provided the mathematical solutions to the complicated redox mechanism in ECE mechanism [5]. Yen et al [6] provides mathematical model for coupled homogeneous and electrochemical reactions for the first time. Chapman et al [7] treated the non-linear problems in Rotating disk electrode involving homogeneous reactions based on Orthogonal collocation method. Hale's transform is used to derive the model and solve them numerically using the implicit method [5]. In [6], the work demonstrated using uniformly accessible RDE and developed the approximate solution to the transient convection-diffusion equation. An analytical solution for the mass transport equation in the reversible homogeneous reaction was obtained in [7]. The expressions for chronoamperometric current and concentrations for linear second-order ECE reaction are obtained in [8]. To the best of our knowledge, there is no approximate analytical expression for non-linear EC_2E problems in rotating disk electrode. This model involves the closed system of reaction-convection-diffusion equations. The paper aims to derive the steady-state analytical expression of concentration and current for the EC_2E mechanism in rotating disk electrodes.

2. Mathematical Formulation of the Problem

Consider the homogeneous reaction that occurs in the EC_2E mechanism [4] as

$$P \pm e^{-} \rightarrow Q \tag{1}$$

$$2Q \overset{K_2}{\rightarrow} R \tag{2}$$

$$R \pm e^{-} \rightarrow D \tag{3}$$

where P, Q and R are the reactant species and K_2 is the reaction rate. Schematic representation is given in Figure 1.

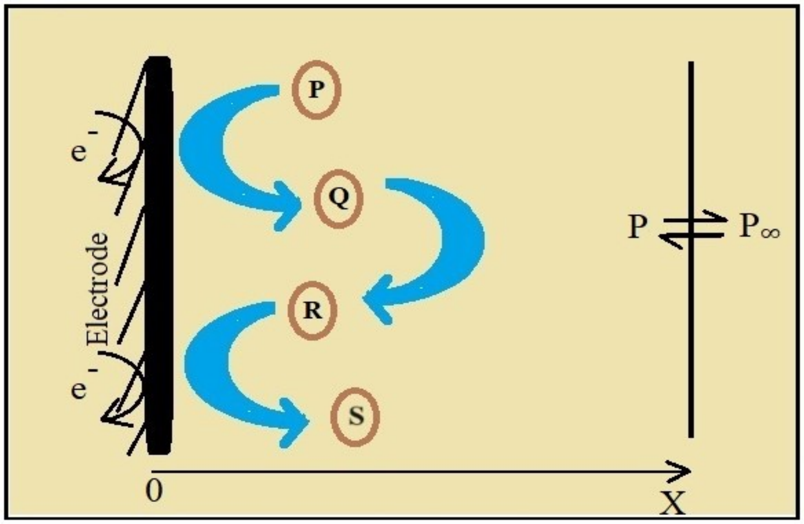

Figure 1: Schematic representation of the reaction

The steady-state mass-transport equation for the species P, Q and R [8] as,

$$-D\frac{d^2P}{dx^2} - Cx^2\frac{dP}{dx} = 0 \tag{4}$$

$$-D\frac{d^2Q}{dx^2} - Cx^2\frac{dQ}{dx} + 2K_2\,Q^2 = 0 \tag{5}$$

$$-D\frac{d^2R}{dx^2} - Cx^2\frac{dR}{dx} - K_2\,Q^2 = 0 \tag{6}$$

Consider the species P, Q and R have equal diffusion coefficient D, and the boundary conditions are,

$$P(0) = 0,\ P(x = X) = P_\infty \tag{7}$$

$$Q'(0) = -P'\,(0),\ Q(x = X) = 0 \tag{8}$$

$$R(0) = 0,\ R(x = X) = 0 \tag{9}$$

Introducing the dimensionless variables as,

$$P = \frac{p}{P_\infty},\ Q = \frac{q}{q_\infty},\ r = \frac{R}{P_\infty},\ \delta = (\frac{C}{D})^{\frac{1}{3}}x,\ k_2 = \frac{K_2}{D}(\frac{C}{D})^{\frac{-2}{3}},\ L = (\frac{C}{D})^{\frac{1}{3}}.X \tag{10}$$

Using Eqn (10), Eqns (4) – (6) reduces to the dimensionless form as,

$$\frac{d^2p}{d\delta^2} + \delta^2\frac{dp}{d\delta} = 0 \tag{11}$$

$$\frac{d^2q}{d\delta^2} + \delta^2\frac{dq}{d\delta} - 2k_2q^2 = 0 \tag{12}$$

$$\frac{d^2r}{d\delta^2} + \delta^2\frac{dr}{d\delta} + k_2q^2 = 0 \tag{13}$$

where p, q, r represents the dimensionless species concentration and k_2 represents the dimensionless reaction rate for second order homogeneous system.

Now, the corresponding boundary conditions for equation (11) – (13) are,

$$p(\delta = 0) = 0, \qquad p(\delta = L) = 1 \tag{14}$$

$$q'(\delta = 0) = -p'(0), \quad q(\delta = L) = 0 \tag{15}$$

$$r(\delta = 0) = 0, \qquad r(\delta = L) = 0 \tag{16}$$

The expression for dimensionless current is given as,

$$I_{EC_2E} = \frac{\left[\frac{dp}{d\delta}+\frac{dr}{d\delta}\right]_{\delta=0}}{\left[\frac{dp}{d\delta}\right]_{\delta=0}} \tag{17}$$

3. Analytical Observations

Non-linear problems are highly complex to solve analytically. Recently several analytical techniques have been used to solve non-linear equations like Homotopy Perturbation Method(HPM), the Variational iteration method, Taylor's series method(TSM) , the Akbari-Ganji method and the Hyperbolic function method[9-22]. Here we employed two methods HPM and TSM to solve Eqns(11-13).

3.1. Approximate analytical observation using Homotopy Perturbation method (HPM)

Eqns(11-13) with the boundary condition Eqns (14-16) are solved using the HPM method. The dimensionless concentrations p(δ), q(δ) and r(δ) for the species P, Q and R are computed as follows:

$$p(\delta) = \frac{\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{\delta^3}{3}\right)}{\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)} \tag{18}$$

$$q(\delta) = \frac{(3)^{\frac{2}{3}}(L-\delta)}{\left(\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\right)} + \frac{\left(-3L^4\left(6k_2+\sqrt[3]{3}\Gamma\left(\frac{4}{3}\right)\right)+36L^2k_2\delta^2+\sqrt[3]{3}(L^4-\delta^4)\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)-24Lk_2\delta^3+3\delta^3\left(2k_2+\sqrt[3]{3}\Gamma\left(\frac{4}{3}\right)\right)\right)}{4(3^{\frac{2}{3}})\left(\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\right)^2} \tag{19}$$

$$r(\delta) = \frac{27(3)^{\frac{1}{3}}\left(L^2-L\delta+\frac{1}{3}\delta^2\right)(L-\delta)\Gamma\left(\frac{2}{3}\right)^2\delta k_2}{4\left(6.28\sqrt{3}-3\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\Gamma\left(\frac{2}{3}\right)\right)^2} \tag{20}$$

Analytical expression for dimensionless current in EC_2E is given as,

$$I_{EC_2E} = \frac{\left(\frac{3^{\frac{2}{3}}}{\frac{6.28\sqrt{3}}{3\Gamma(\frac{2}{3})}-\Gamma(\frac{1}{3},\frac{L^3}{3})}\right)+\left(\frac{27\sqrt[3]{3}\Gamma(\frac{2}{3})^2k_2L^3}{4\left(3\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\Gamma\left(\frac{2}{3}\right)-6.28\sqrt{3}\right)^2}\right)}{\left(\frac{3^{\frac{2}{3}}}{\frac{6.28\sqrt{3}}{3\Gamma(\frac{2}{3})}-\Gamma(\frac{1}{3},\frac{L^3}{3})}\right)} \tag{21}$$

The detailed solution is given in Appendix A.

3.2. Approximate analytical observation using Taylors series method (TSM)

The non-linear Eqns(12-13) with the boundary condition Eqns (15-16) are solved using the TSM method. The dimensionless concentrations q(δ) and r(δ) for the species Q and R are computed as follows:

$$q(\delta) = h - a\delta + (2k_2h^2)\frac{\delta^2}{2} - (2k_2ah)\frac{\delta^3}{3} + \left(2a - 4k_2a^2 + 8{k_2}^2h^3\right)\frac{\delta^4}{24} - \left(12k_2h^2 + 40{k_2}^2ah^2\right)\frac{\delta^5}{120} + (56k_2ah + 80{k_2}^3h^4 + 48{k_2}^2a^2h)\frac{\delta^6}{720} \tag{22}$$

$$r(\delta) = j\delta - k_2h^2\frac{\delta^2}{2} + k_2ah\frac{\delta^3}{3} + \left(-4h^3{k_2}^2 - 2a^2k_2 - 2j\right)\frac{\delta^4}{24} + \left(20ah^2{k_2}^2 + 6h^2k_2\right)\frac{\delta^5}{120} + (-40h^4{k_2}^3 - 24a^2h{k_2}^2 - 28ahk_2)\frac{\delta^6}{720} \tag{23}$$

$$I_{\mathrm{EC_2E}} = \frac{(a)+j}{(a)} \tag{24}$$

Where $a = p'(0) = \frac{3^{2/3}}{\Gamma(1/3) - \Gamma(1/3, \frac{L^3}{3})}$ (25)

constants h and j can be found by applying the boundary condition at $\delta = L$, and substituting the values for parameters k_2 and L. For example, by taking L=0.2, k_2=1, we can get the expression

$$-1.006648 + 7.111113 * 10^{-6}h^4 + 0.0005246h^3 + 0.039434h^2 + 0.973447h \tag{26}$$

from this expression, we can extract the numeric value of h. In similar way we can find the numeric value of j. The detailed solution is given in Appendix B.

4. Numerical Simulation

Eqns (11)-(13) solved numerically with corresponding boundary conditions using MATLAB software. Here bvp4c solver is used to developing the MATLAB program. Further, to check the efficiency of the method, the numerical solution is compared with the HPM solution and TSM solution given in Eqns (19-20) and Eqns(22-23), and the comparison results are tabulated as follows:

Table 1: Comparison of HPM and TSM solution (Eqn(19) & (22)) for the dimensionless concentration of the species Q ($q(\delta)$) with a numerical solution for different values of the parameter k_2 when L=0.1.

δ	$k_2=7$					$k_2=10$					$k_2=15$				
	Numerical solution	HPM Eqn(19)	% of deviation for HPM	TSM Eqn(22)	% of deviation for TSM	Numerical solution	HPM Eqn(19)	% of deviation for HPM	TSM Eqn(22)	% of deviation for TSM	Numerical solution	HPM Eqn(19)	% of deviation for HPM	TSM Eqn(22)	% of deviation for TSM
0	0.9675	0.9650	0.26	0.9889	2.21	0.9550	0.95	0.52	0.9846	3.10	0.9356	0.925	1.13	0.9776	4.49
0.02	0.7678	0.7654	0.31	0.7794	1.51	0.7562	0.7515	0.62	0.786	3.94	0.7382	0.7283	1.34	0.7805	5.73
0.04	0.5715	0.5696	0.33	0.5927	3.71	0.5621	0.5583	0.68	0.5916	5.25	0.5476	0.5395	1.48	0.5899	7.72
0.06	0.3771	0.3771	0.00	0.3962	5.06	0.3707	0.368	0.73	0.3975	7.23	0.3607	0.3551	1.55	0.3994	10.73
0.08	0.1836	0.1836	0.00	0.1964	6.97	0.1804	0.1791	0.72	0.1985	10.03	0.1755	0.1727	1.60	0.2019	15.04
0.1	0	0	0.00	0	0.00	0	0	0.00	0	0.00	0.00	0	0.00	0	0.00
			0.15		**3.24**			**0.54**		**4.92**			**1.18**		**7.28**

Table 2: Comparison of HPM and TSM solution (Eqn(19) & (22)) for the dimensionless concentration of the species Q ($q(\delta)$) with numerical solution for different values of the parameter L, when k_2=5.

δ	L=0.1					δ	L=0.2					δ	L=0.3				
	Numerical solution	HPM Eqn(19)	% of deviation for	TSM Eqn(22)	% of deviation for		Numerical solution	HPM Eqn(19)	% of deviation for HPM soln	TSM Eqn(22)	% of deviation for TSM soln		Numerical solution	HPM Eqn(19)	% of deviation for HPM soln	TSM Eqn(22)	% of deviation for TSM soln
0	0.9763	0.9750	0.13	0.9920	1.61	0	0.9179	0.8999	1.96	0.9711	5.80	0	0.8472	0.7740	8.64	0.9462	11.69
0.02	0.7760	0.7747	0.17	0.7917	2.02	0.04	0.7217	0.7048	2.34	0.7755	7.45	0.05	0.6560	0.5876	10.43	0.7578	15.52
0.04	0.5781	0.5771	0.17	0.5936	2.68	0.08	0.5341	0.5204	2.57	0.5883	10.15	0.12	0.4809	0.4250	11.62	0.5957	23.87
0.06	0.3817	0.3810	0.18	0.3955	3.62	0.12	0.3514	0.3418	2.73	0.4014	14.23	0.18	0.3146	0.2760	12.27	0.4260	35.41
0.08	0.1858	0.1855	0.16	0.1951	5.01	0.16	0.1708	0.1661	2.75	0.2051	20.08	0.24	0.1525	0.1333	12.59	0.2363	54.95
0.1	0.0000	0.0000	0.00	0.0000	0.00	0.2	0.0000	0.0000	0.00	0.0000	0.00	0.3	0.0000	0.0000	0.00	0.0000	0.00
			0.13		**2.49**				**2.05**		**9.62**				**9.25**		**23.57**

Table 3: Comparison of HPM and TSM solution (Eqn(20)&(23)) for the dimensionless concentration of the species R ($r(\delta)$) with numerical solution for different values of the parameter k_2, when L=0.1.

δ	**k_2=1**					**k_2=5**					**k_2=10**				
	Numerical solution	**HPM Eqn(20)**	**% of deviation for HPM**	**TSM Eqn(23)**	**% of deviation for TSM**	**Numerical solution**	**HPM Eqn(20)**	**% of deviation for HPM**	**TSM Eqn(23)**	**% of deviation for TSM**	**Numerical solution**	**HPM Eqn(20)**	**% of deviation for HPM**	**TSM Eqn(23)**	**% of deviation for TSM**
0	0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.00
0.02	0.0003	0.0003	0.00	0.0003	5.72	0.0015	0.0016	3.56	0.0017	8.41	0.0031	0.0033	11.40	0.0033	13.21
0.04	0.0004	0.0004	1.22	0.0004	6.22	0.0018	0.0020	5.79	0.0020	10.07	0.0039	0.0039	11.69	0.0040	15.38
0.06	0.0003	0.0003	0.85	0.0003	7.42	0.0014	0.0015	7.14	0.0016	15.86	0.0030	0.0031	11.85	0.0032	17.38
0.08	0.0002	0.0002	4.34	0.0002	8.42	0.0007	0.0008	7.08	0.0008	13.84	0.0016	0.0016	11.94	0.0017	18.50
0.1	0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.0000	0.00	0.0000	0.00
			1.06		**4.63**			**3.92**		**8.03**			**7.81**		**10.74**

Table 4: Comparison of HPM and TSM solution (Eqns(20)&(23)) for the dimensionless concentration of the species R ($r(\delta)$) with numerical solution for the parameter k_2 =1 and for different values of the parameter L.

δ	**L=0.1**					**δ**	**L=0.2**					**δ**	**L=0.3**				
	Numerical solution	**HPM Eqn(20)**	**% of deviation for**	**TSM Eqn(23)**	**% of deviation for**		**Numerical solution**	**HPM Eqn(20)**	**% of deviation for HPM soln**	**TSM Eqn(23)**	**% of deviation for TSM soln**		**Numerical solution**	**HPM Eqn(20)**	**% of deviation for HPM soln**	**TSM Eqn(23)**	**% of deviation for TSM soln**
0	0.0000	0.0000	0.00	0.0000	0.00	0	0.0000	0.0000	0.00	0.0000	0.00	0	0.0000	0.0000	0.00	0.0000	0.00
0.02	0.0003	0.0003	0.00	0.0003	5.72	0.04	0.0012	0.0013	4.80	0.0013	5.60	0.05	0.0027	0.0030	11.13	0.0029	9.74
0.04	0.0004	0.0004	1.22	0.0004	6.22	0.08	0.0015	0.0016	4.89	0.0016	6.50	0.12	0.0032	0.0035	11.54	0.0035	11.04
0.06	0.0003	0.0003	0.85	0.0003	7.42	0.12	0.0012	0.0012	5.03	0.0013	7.41	0.18	0.0025	0.0028	11.81	0.0028	12.17
0.08	0.0002	0.0002	4.34	0.0002	8.42	0.16	0.0006	0.0006	5.11	0.0007	7.94	0.24	0.0013	0.0014	12.11	0.0014	12.97
0.1	0.0000	0.0000	0.00	0.0000	0.00	0.2	0.0000	0.0000	0.00	0.0000	0.00	0.3	0.0000	0.0000	0.00	0.0000	0.00
			1.06		**4.63**				**3.30**		**4.57**				**7.76**		**5.62**

5. Results and Discussions

Eqns(19-20) and Eqns(22-23) are the approximate analytical expressions for non-linear steady-state reaction-convection-diffusion Eqns(11)-(13) in the EC_2E mechanism obtained using Homotopy Perturbation Method and Taylor's Series Method. The computed numeric values are tabulated to check the efficiency of HPM and TSM solution with numerical result. Table 1-4 shows that the average error percentage of HPM solution is less than 0.62% when $k_2 \leq 15$, and TSM is less than 5.14% when $L \leq 0.3$ for the dimensionless concentration q(δ). The parameters L (dimensionless distance from the electrode) and k_2(dimensionless reaction rate in EC_2E) have the power to influence the species concentration used in the mechanism. Also, it controls the resultant current. The influence of parameters L and k_2(dimensionless reaction rate in EC_2E) on concentration profiles and current is noted and presented graphically. Figure 3, shows that the dimensionless concentration of the reactant species q(δ) is inversely proportional to dimensionless reaction rate(k_2) and the dimensionless distance from the electrode(L). Figure 4 demonstrates the behaviour of the dimensionless concentration of the species r(δ), the concentration increases with increasing dimensionless reaction rate(k_2) and distance(L).

5.1. Influence of parameters L (dimensionless distance from the electrode), k_2 (dimensionless reaction rate) on dimensionless concentration profiles

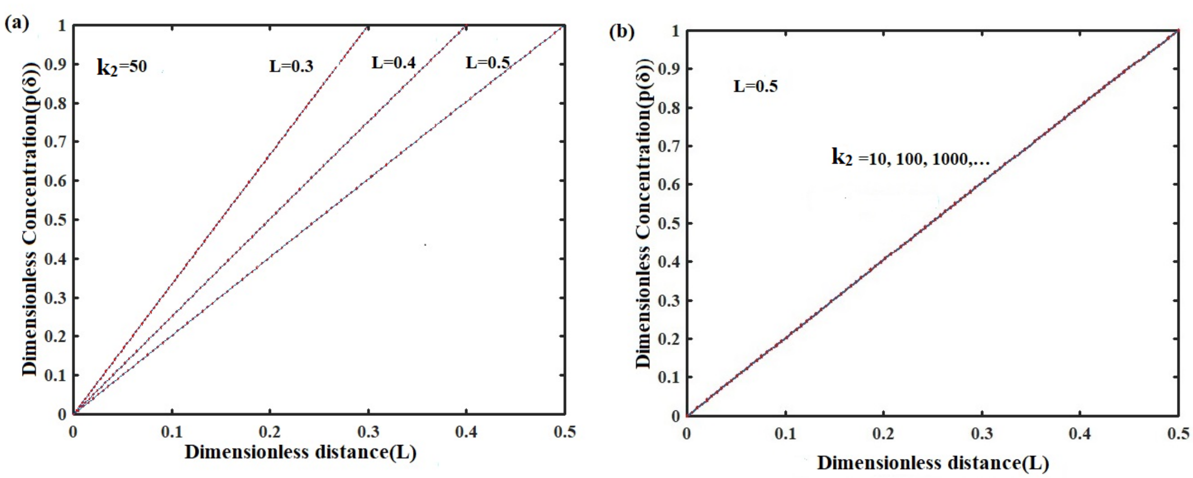

Figure 2. The Plot shows influence of parameter L and k_2 on the dimensionless concentration p(δ) (Eqn(21)). (a) & (b) For different values of parameter L and k_1, when k_2=50 and L=0.5.

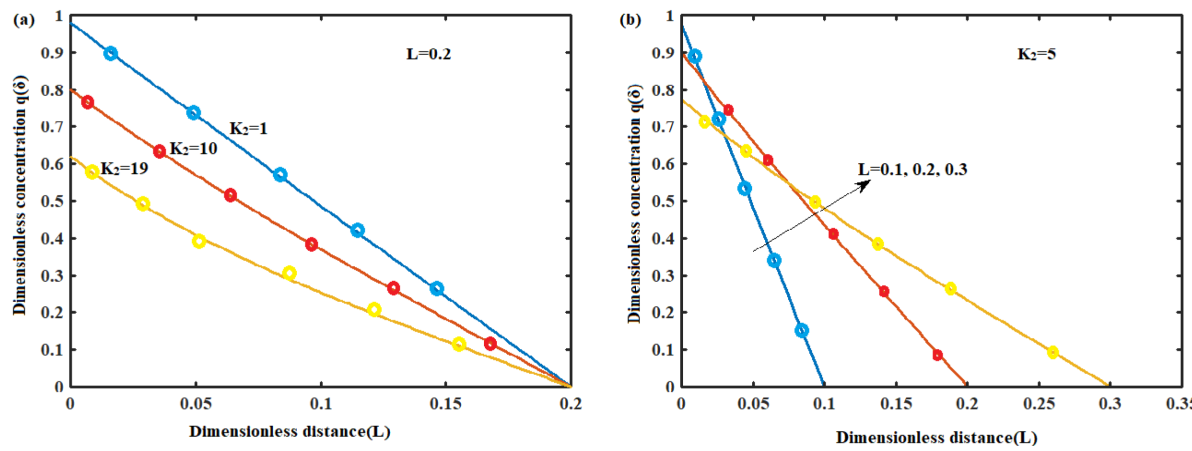

Figure 3: The Plot shows the influence of parameters L and k_2 on the dimensionless concentration q(δ) (Eqn(19)). (a) & (b) For different values of parameter k_2 and L, when L=0.2, k_2=5.

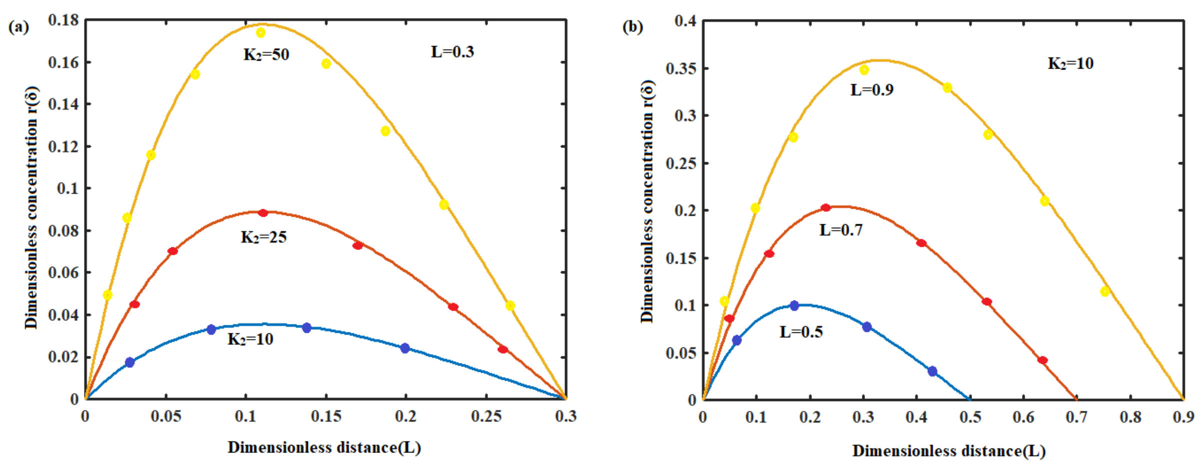

Figure 4: The Plot shows the influence of parameters L and k_2 on the dimensionless concentration r(δ) (Eqn(20)). (a) & (b) For different values of parameter k_2 and L, when L=0.3, k_2=10.

5.2. Influence of parameters X (distance from the electrode), K_2 (reaction rate) on limiting current

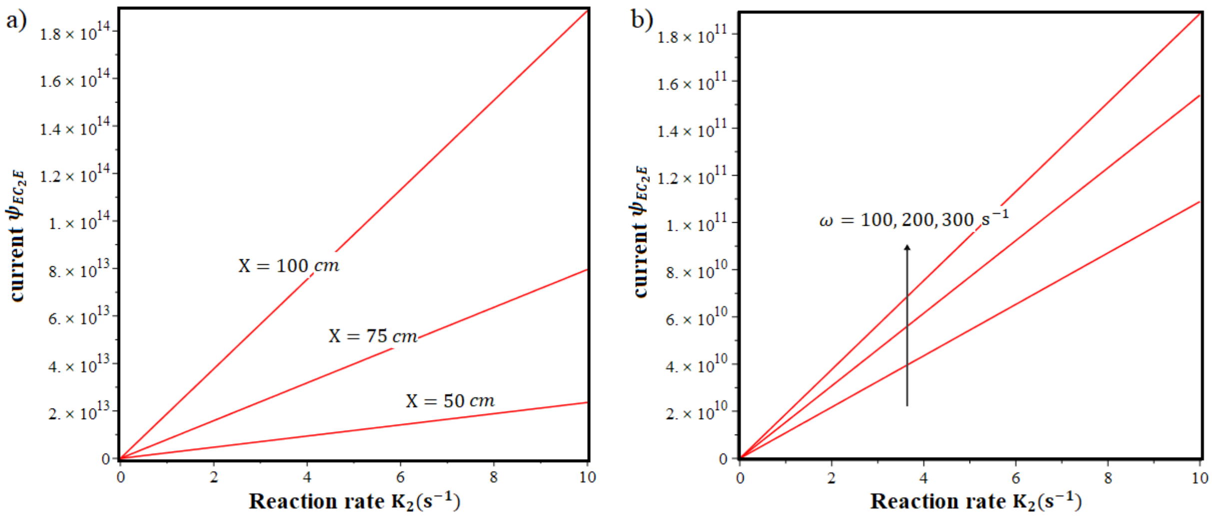

Figure 5: Influence of parameter X (distance from the electrode) and ω (rotating speed of the disk) on limiting current for various values of X and ω using Eqn(21). a)$\mathcal{V} = 0.003643, D = 1.48x10^{-5}, \omega = 300$. b)$\mathcal{V} = 0.003643, D = 1.48x10^{-5}, X = 10$.

The impact caused by the dimensional parameters distance from the electrode(X) and the rotating speed of the rotating disk electrode is observed and a graph is plotted between the Reaction rate (k_2) and limiting current. It is observed that current increases for increasing reaction rate and rotating speed are depicted in Figure 5. Also, the sensitive measure is carried for current and given in Figure 6, it is noted that for the particular value $k_2 = 5$ & $L = 10$. Dimensionless distance(L) has more impact on limiting current than dimensional reaction rate.

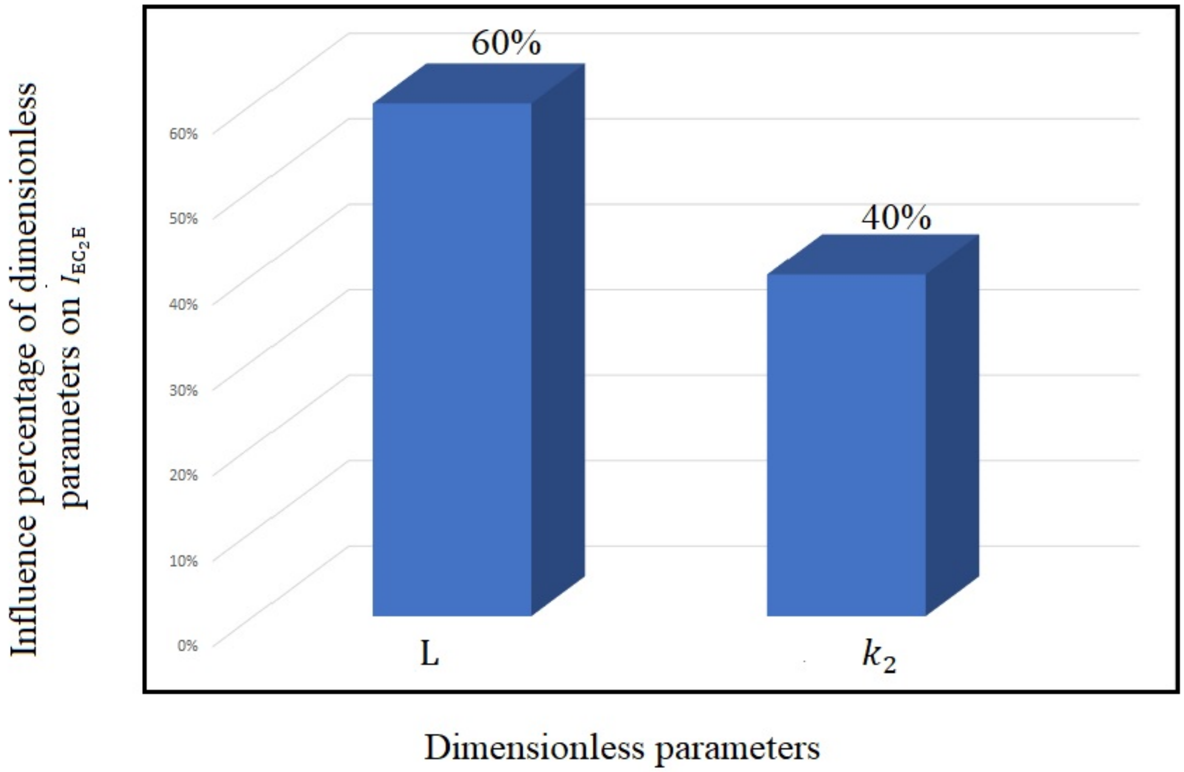

Figure 6: Sensitivity measure of dimensionless parameters L and k_2 on dimensionless current. For the particular values $L = 10$ and $k_2 = 5$.

6. Conclusion

The Mathematical modelling of the EC_2E mechanism on Rotating Disk Electrode is discussed. An approximate analytical expression for non-linear convection-reaction-diffusion equations at steady-state conditions is derived using HPM and TSM. HPM provides the most straightforward and exact convergent solution series for the non-linear case while comparing it with Taylor's series method. The exact capable result is obtained between analytical and numerical solutions. Further, this work may extend to transient conditions with a corresponding electrochemical mechanism.

Appendix A: Approximate analytical solution for Eqns(19)-(20) using Homotopy Perturbation method

Consider the non-linear coupled Eqns(18) - (20) as follows,

$$\frac{d^2p}{d\delta^2}+\delta^2\frac{dp}{d\delta}=0 \tag{A1}$$

$$\frac{d^2q}{d\delta^2}+\delta^2\frac{dq}{d\delta}-2k_2q^2=0 \tag{A2}$$

$$\frac{d^2r}{d\delta^2}+\delta^2\frac{dr}{d\delta}+k_1q^2=0 \tag{A3}$$

With the boundary conditions

$$p(\delta=0)=0, \qquad p(\delta=L)=1 \tag{A4}$$

$$q'(\delta=0)=-p'(0), \quad q(\delta=L)=0 \tag{A5}$$

$$r(\delta=0)=0, \qquad r(\delta=L)=0 \tag{A6}$$

The dimensionless concentration from Eqn(A1) is easily obtained using worlfram computational software as,

$$p(\delta)=\frac{\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{\delta^3}{3}\right)}{\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)} \tag{A7}$$

For Eqn(A2) & (A4), construct the homotopy as,

$$(1-s)\left(\frac{d^2q}{d\delta^2}\right)+s\left(\frac{d^2q}{d\delta^2}+\delta^2\frac{dq}{d\delta}-2k_2q^2\right)=0 \tag{A8}$$

$$(1-s)\left(\frac{d^2r}{d\delta^2}\right)+s\left(\frac{d^2r}{d\delta^2}+\delta^2\frac{dr}{d\delta}+k_2q^2\right)=0 \tag{A9}$$

where s is the embedding parameter and s ϵ [0,1].

Now assuming the approximate solutions for (A2) and (A3) as the series,

$$q=q_0+sq_1+s^2q_2+\cdots \tag{A10}$$

$$r=r_0+sr_1+s^2r_2+\cdots \tag{A11}$$

Substituting Eqn(A10) in Eqn(A11) and comparing the like powers of s^0, s^1,…

we get,

$$s^0:\frac{d^2q_0}{d\delta^2}=0 \tag{A12}$$

$$s^1:\frac{d^2q_1}{d\delta^2}+\delta^2\frac{dq_0}{d\delta}-2k_2{q_0}^2=0 \tag{A13}$$

with corresponding boundary conditions

$$q_0'(0)=-p_0'(0), q_0(L)=0 \tag{A14}$$

$$q_0'(0)=0, q_0(L)=0 \tag{A15}$$

Substituting Eqn(A11) in Eqn(A3) and comparing the like powers of s^0, s^1,…

we get,

$$s^0 : \frac{d^2 r_0}{d\delta^2} = 0 \tag{A16}$$

$$s^1 : \frac{d^2 r_1}{d\delta^2} + \delta^2 \frac{dr_0}{d\delta} + k_2 {q_0}^2 = 0 \tag{A17}$$

with corresponding boundary conditions

$$r_0(0) = 0, r_0(L) = 0 \tag{A18}$$

$$r_1(0) = 0, r_1(L) = 0 \tag{A19}$$

Solving Eqns(A12) & (A13) using boundary conditions Eqns(A14) & (A15), and substituting the solutions in Eqn(A10). we get,

$$\mathrm{q}(\delta) = \frac{(3)^{\frac{2}{3}}(L-\delta)}{(\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right))} + \frac{(-3L^4\left(6k_2+\sqrt[3]{3}\Gamma\left(\frac{4}{3}\right)\right)+36L^2k_2\delta^2+\sqrt[3]{3}(L^4-\delta^4)\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)-24Lk_2\delta^3+3\delta^3(2k_2+\sqrt[3]{3}\Gamma\left(\frac{4}{3}\right))}{4(3^{\frac{2}{3}})(\Gamma\left(\frac{1}{3}\right)-\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right))^2}$$

(A20)

Solving Eqn(A16) & (A17) using boundary conditions Eqn(A18) & (A19), and substituting the solutions in Eqn(A11). we get,

$$\mathrm{r}(\delta) = \frac{27(3)^{\frac{1}{3}}(L^2-L\delta+\frac{1}{3}\delta^2)(L-\delta)\Gamma\left(\frac{2}{3}\right)^2\delta k_2}{4(6.28\sqrt{3}-3\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\Gamma\left(\frac{2}{3}\right))^2} \tag{A21}$$

The dimensionless expression for current for EC₂E mechanism is given as,

$$I_{\mathrm{EC_2E}} = \frac{\dfrac{3^{\frac{2}{3}}}{\frac{6.28\sqrt{3}}{3\Gamma(\frac{2}{3})}-\Gamma(\frac{1}{3},\frac{L^3}{3})} + \dfrac{27\sqrt[3]{3}\Gamma(\frac{2}{3})^2k_2L^3}{4(3\Gamma\left(\frac{1}{3},\frac{L^3}{3}\right)\Gamma\left(\frac{2}{3}\right)-6.28\sqrt{3})^2}}{\dfrac{3^{\frac{2}{3}}}{\frac{6.28\sqrt{3}}{3\Gamma(\frac{2}{3})}-\Gamma(\frac{1}{3},\frac{L^3}{3})}} \tag{A22}$$

Appendix B: Approximate analytical solution for Eqns(19)-(20) using Taylor's series method

Considering the nonlinear Eqns(A2)-(A3) .

Consider the Taylor's series solution at $\delta = 0$ for the Eqns(A2)-(A3) as follows:

$$\mathrm{q}(\delta) = q(0) + q'(0)\frac{\delta}{1!} + q''(0)\frac{\delta^2}{2!} + q^{(3)}(0)\frac{\delta^3}{3!} + q^{(4)}(0)\frac{\delta^4}{4!} + \cdots \tag{B1}$$

$$r(\delta) = r(0) + r'(0)\frac{\delta}{1!} + r''(0)\frac{\delta^2}{2!} + r^{(3)}(0)\frac{\delta^3}{3!} + r^{(4)}(0)\frac{\delta^4}{4!} + \cdots \tag{B2}$$

from the condition given in Eqn(A5-A6),

For Eqn(A2), consider $q(0) = h$ (constant)

and from boundary condition Eqn (A5), we get $q'(0) = -p'(0) = -a$, $q''(0) = 2k_2h^2$

$q^{(3)}(0) = -4k_2ah$, $q^{(4)}(0) = 2a - 4k_2a^2 + 8{k_2}^2h^3$, $q^{(5)}(0) = -12k_2h^2 - 40{k_2}^2ah^2$,

$q^{(6)}(0) = 56k_2ah + 80{k_2}^3h^4 + 48{k_2}^2a^2h, \ldots$ (B3)

Substituting Eqn(B3) in Eqn(B1), we get the analytical expression of dimensionless concentration q(δ) as follows,

$$q(\delta) = h - a\delta + (2k_2h^2)\frac{\delta^2}{2} - (2k_2ah)\frac{\delta^3}{3} + \left(2a - 4k_2a^2 + 8{k_2}^2h^3\right)\frac{\delta^4}{24} - \left(12k_2h^2 + 40{k_2}^2ah^2\right)\frac{\delta^5}{120} + (56k_2ah + 80{k_2}^3h^4 + 48{k_2}^2a^2h)\frac{\delta^6}{720} \quad \text{(B4)}$$

the constant h can be obtained using the boundary condition $q(\delta = L) = 0$ and substituting values for all parameters. For example, substitute $a = \frac{3^{2/3}}{\Gamma(1/3) - \Gamma(1/3, \frac{L^3}{3})}$, L=0.2, $k_2 = 1$ in Eqn(B4), we get the expression

$$-1.006648 + 7.111113 * 10^{-6}h^4 + 0.0005246h^3 + 0.039434h^2 + 0.973447h \quad \text{(B5)}$$

Further solving Eqn(B5) using wolfram software, we can extract the possible value of h($\approx$ 0.994069).

The analytical expression for dimensionless concentration r(δ) is,

$$r(\delta) = j\delta - k_2h^2\frac{\delta^2}{2} + k_2ah\frac{\delta^3}{3} + \left(-4h^3{k_2}^2 - 2a^2k_2 - 2j\right)\frac{\delta^4}{24} + \left(20ah^2{k_2}^2 + 6h^2k_2\right)\frac{\delta^5}{120} + (-40h^4{k_2}^3 - 24a^2h{k_2}^2 - 28ahk_2)\frac{\delta^6}{720} \quad \text{(B6)}$$

constant j can be extracted using the same argument.

Nomenclature

Symbol	**Name**	**Unit**
P, Q, R	Concentration of reactant species involved in ECE mechanism	$mol\ cm^{-3}$
p_∞, q_∞	Bulk concentration of the species P, Q.	$mol\ cm^{-3}$
D	Diffusion rate	$cm^2 s^{-1}$
ω	Rotating speed of the disk	s^{-1}
K_2	Reaction rate	s^{-1}
X	Distance from the electrode	cm
p, q, r	Normalised concentration of the species P, Q, R	none
L	Normalised distance from the electrode	none
k_2	Normalised reaction rate in EC_2E mechanism	none

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