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

Vincent Michael Raj Margret PonRani, Lakshmanan Rajendren

Department of Mathematics, The Madura College, Madurai, India; raj_sms@rediffmail.com

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 μm (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 electroinactive 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_b, 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 *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 *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

$$A \rightleftharpoons 2B \quad B \pm e^- \rightarrow products$$
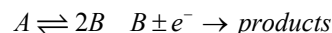
has been chosen, with initial and boundary conditions corresponding to the potential step for all planar electrodes. Under stead-state conditions, the local concentrations of the species do not change. Therefore the mass transport equations are set equal to zero. We consider the differential equations with diffusion described by the concentration of the two species leads to the following equations [5]

$$\frac{\partial a}{\partial t} = D\frac{\partial^2 a}{\partial x^2} - k_f a + k_b b = 0 \qquad (1)$$

$$\frac{\partial b}{\partial t} = D\frac{\partial^2 b}{\partial x^2} + k_f a - k_b b = 0 \qquad (2)$$

where a and b denote the concentration of the species A and B. x and t stand for space and time, respectively. κ_f and κ_b are described the forward and

backward rate constants respectively. The boundary conditions reduce to

$$t = 0; \quad a = a_0; \quad b = b_0 \tag{3}$$

$$x = l; \quad a = a^s; \quad b = b^s \tag{4}$$

$$x \to \infty; \quad a \to a_0; \quad b \to b_0 \tag{5}$$

where a_0 and b_0 are the bulk concentrations of the species A and B, a^s and b^s denote the concentrations at electrode surface. The flux j can be described as follows:

$$j = -D \left. \frac{\partial b}{\partial x} \right|_{x=l} \tag{6}$$

The current density is defined as:

$$i = -nFj \tag{7}$$

Where n is the number of electrons and F is the Faraday constant. Using the following dimensionless parameters

$$u = \frac{a}{a_0}; \quad v = \frac{b}{b_0}; \quad X = \frac{x}{l}; \quad T = \frac{Dt}{l^2}; \quad k_1 = \frac{k_f l^2}{D};$$

$$k_2 = \frac{k_b l^2 b_0}{D a_0}; \quad k_3 = \frac{k_f l^2 a_0}{D b_0}; \quad k_4 = \frac{k_b l^2}{D}; \quad m_1 = \frac{a^s}{a_0}; \quad m_2 = \frac{b^s}{b_0}$$

we obtained the dimensionless non-linear reaction diffusion equations for planar electrode as follows

$$\frac{\partial u}{\partial T} = \frac{\partial^2 u}{\partial X^2} - k_1 u + k_2 v = 0 \tag{9}$$

$$\frac{\partial v}{\partial T} = \frac{\partial^2 v}{\partial X^2} + k_3 u - k_4 v = 0 \tag{10}$$

The initial and boundary conditions becomes:

$$T = 0; \quad u = 1; \quad v = 1 \tag{11}$$

$$X = 1; \quad u = m_1; \quad v = m_2 \tag{12}$$

$$X \to \infty; \quad u \to 1; \quad v \to 1 \tag{13}$$

The dimensionless current is as follows:

$$\psi = \frac{il}{nFADb_0} = (\partial v/\partial X)_{X=1} \tag{14}$$

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 **Eq.11**, the following diffential equations in Laplace space are obtained:

$$\frac{d^2 \bar{u}}{dX^2} - k_1 \bar{u} + k_2 \bar{v} - s \bar{u} + 1 = 0 \tag{15}$$

$$\frac{d^2 \bar{v}}{dX^2} + k_3 \bar{u} - k_4 \bar{v} - s \bar{v} + 1 = 0 \tag{16}$$

Now the boundary conditions become

$$X \to \infty; \quad u \to \frac{1}{s}; \quad v \to \frac{1}{s} \tag{17}$$

$$X = 1; \quad u = \frac{m_1}{s}; \quad v = \frac{m_2}{s} \tag{18}$$

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 perturbtion 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

$$u(X,T) \approx 1 + (m_1 - 1) \ erfc\left(\frac{X-1}{2\sqrt{T}}\right)$$

$$+ \left\{ \left[2\sqrt{\frac{T}{\pi}} \exp\left(-\frac{(X-1)^2}{4T}\right) - (X-1) \ erfc\left(\frac{X-1}{2\sqrt{T}}\right) \right] \right.$$

$$\left. \left[\frac{k_1 m_1}{2} - \frac{k_2 m_2}{2} \right] \right\} \tag{19}$$

$$v(X,T) \approx 1 + (m_2 - 1) \; erfc\left(\frac{X-1}{2\sqrt{T}}\right)$$

$$-\left\{\left[2\sqrt{\frac{T}{\pi}}\exp\left(-\frac{(X-1)^2}{4T}\right) - (X-1)\; erfc\left(\frac{X-1}{2\sqrt{T}}\right)\right]\right.$$

$$\left.\left[\frac{k_3 m_1}{2} - \frac{k_4 m_2}{2}\right]\right\}(1-X) \qquad (20)$$

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 $k_1 = k_3$ 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 the bulk concentration) and $a_0 = b_0$. The current density is

$$\psi \approx \frac{0.56419}{\sqrt{T}} - 0.56419\frac{m_2}{\sqrt{T}} + 2\sqrt{\frac{T}{\pi}}\left(0.05k_3 m_1 - 0.5k_4 m_2\right)$$

$$(21)$$

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_3, k_4, 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 ψ versus T for various values of k_3 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
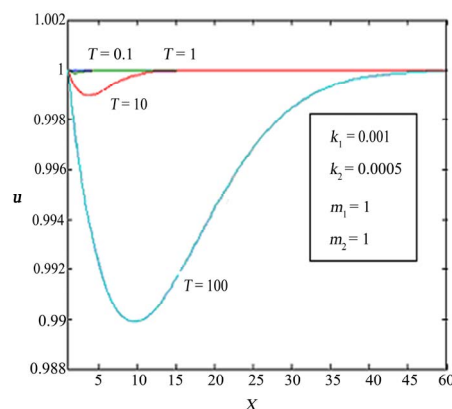
In this work, the coupled time dependent linear dif-

Figure 1. 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 $k_2 = 0.005$.
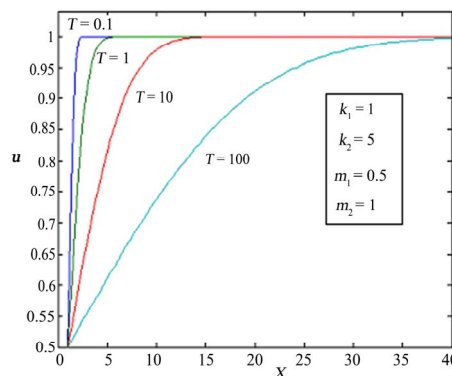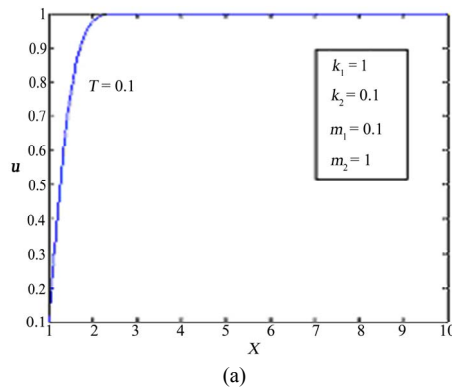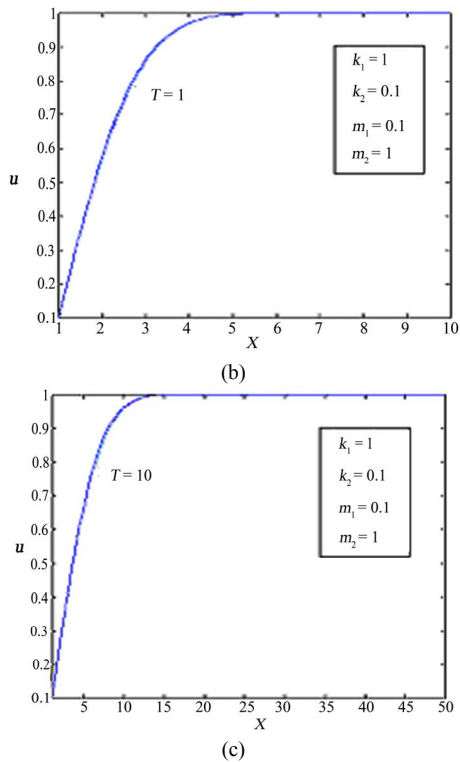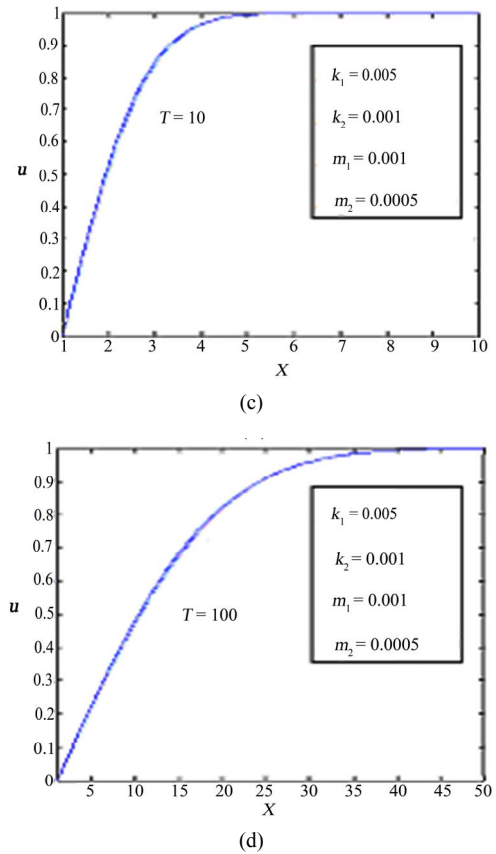

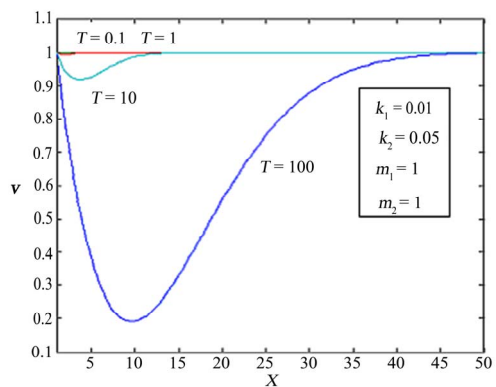
Figure 2. Normalized concentration u at microelectrode. The concentrations were computed using **Eq.19** for some value of $m_1 = 0.5$, $m_2 = 1$ and for various values of T and the reaction/diffusion parameter $k_1 = 1$ and $k_2 = 5$.
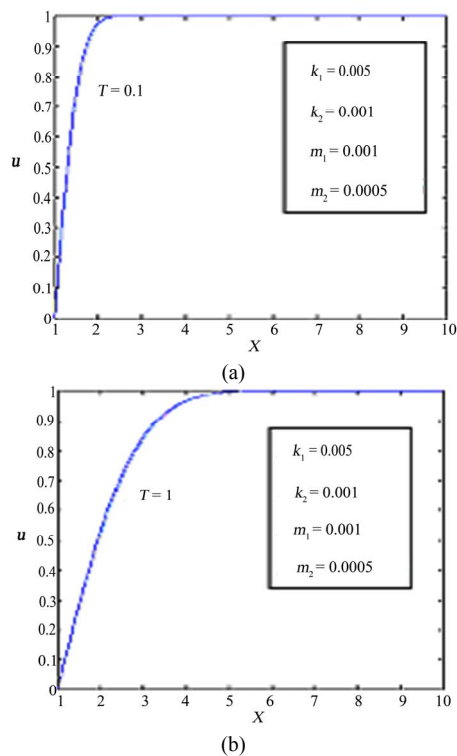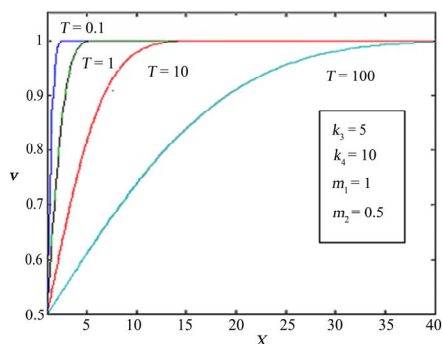

(a)

(b)

(c)

Figure 3. Normalized concentration u at micro-electrode. 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) $T = 10$.
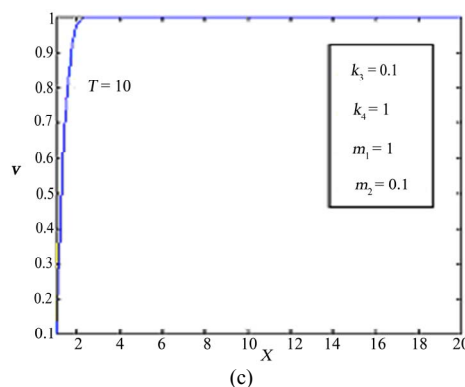

(a)

(b)

(c)

(d)

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 $k_3 = 0.01$ and $k_4 = 0.05$.
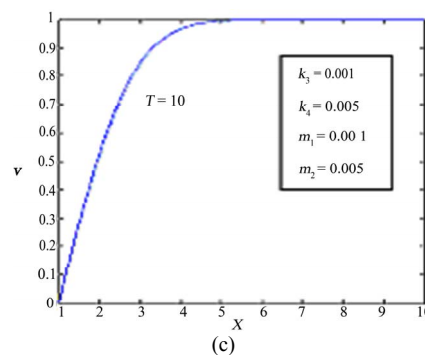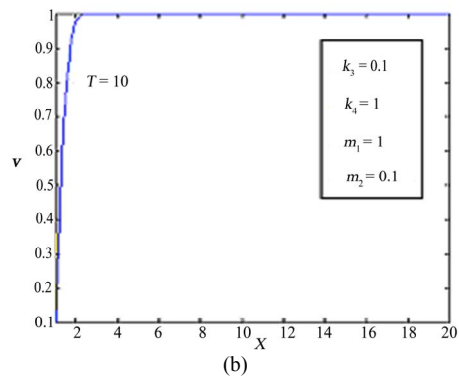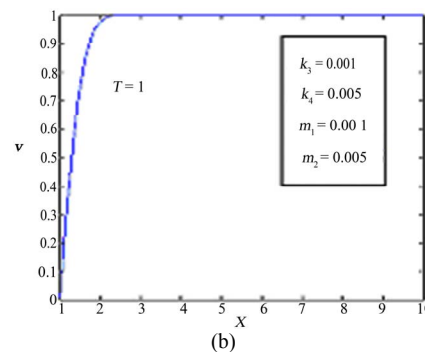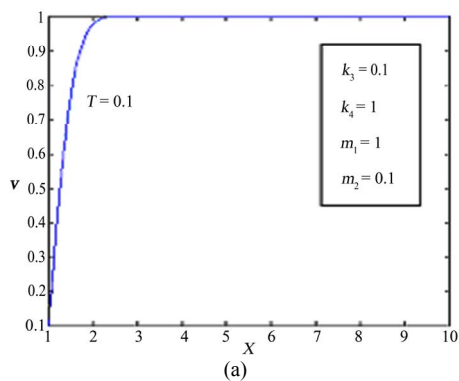
Figure 6. Normalized concentration v at microelectrode. The concentrations were computed using **Eq.20** for some value of $m_1 = 1, m_2 = 0.5$ and for various values of T and the reaction/diffusion parameter $k_1 = 5$ and $k_2 = 10$.

ferential 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-
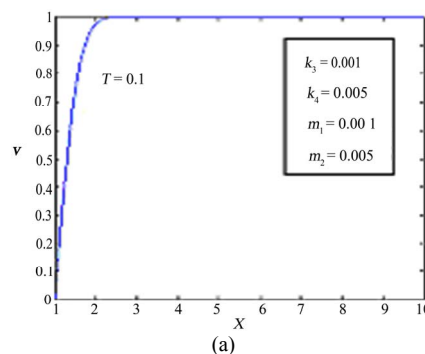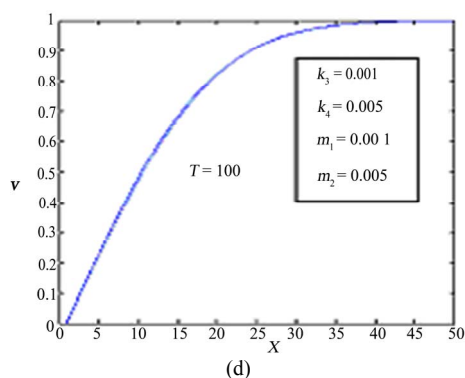

(a)

(b)

(c)

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) $T = 10$.
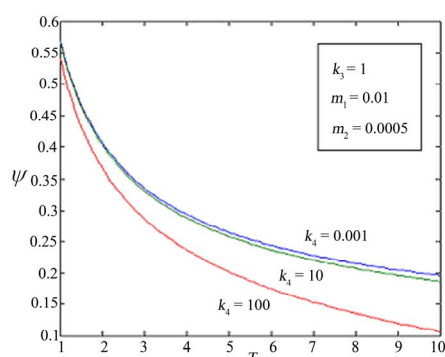

(a)

(b)

(c)

Figure 8. Normalized concentration v at microelectrode. The concentrations were computed using **Eq.20** for some value of $m_1 = 0.001, m_2 = 0.005$ $m_1 = 0.001, m_2 = 0.005$ 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, ψ verses time. The current were calculated using **Eq.21** for the fixed value of $k_3 = 1$ and for various values of the reaction/diffusion parameter k_4.
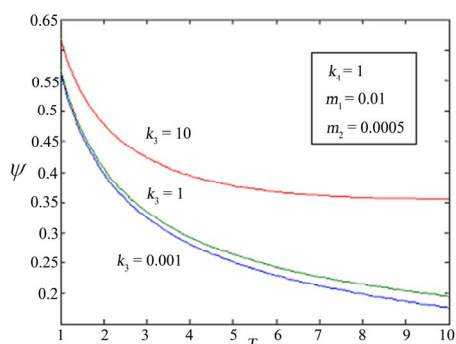
Figure 10. Plot of the dimensionless current, ψ versus time. The current were calculated using **Eq.21** for the fixed value of $k_4 = 1$ and for various values of the reaction/diffusion parameter k_3.

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.

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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

$$(1-p)\left[\frac{d^2\bar{u}}{dX^2} - s\bar{u}\right] + p\left[\frac{d^2\bar{u}}{dX^2} - k_1\bar{u} + k_2\bar{v} - s\bar{u} + 1\right] = 0 \tag{A1}$$

$$(1-p)\left[\frac{d^2\bar{v}}{dX^2} - s\bar{v}\right] + p\left[\frac{d^2\bar{v}}{dX^2} + k_3\bar{u} - k_4\bar{v} - s\bar{v} + 1\right] = 0 \tag{A2}$$

The boundary conditions are

$$X = 1; \quad u = \frac{m_1}{s}; \quad v = \frac{m_2}{s} \tag{A3}$$

$$X \to \infty; \quad u = 1; \quad v = 1 \tag{A4}$$

The approximate solutions of **Eqs.A1** and **A2** are

$$\bar{u} = \bar{u}_0 + p\bar{u}_1 + p^2\bar{u}_2 + p^3\bar{u}_3 + \dots \tag{A5}$$

$$\bar{v} = \bar{v}_0 + p\bar{v}_1 + p^2\bar{v}_2 + p^3\bar{v}_3 + \dots \tag{A6}$$

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

$$p^0: \quad \frac{d^2\bar{u}_0}{dx^2} - s\bar{u}_0 = 0 \tag{A7}$$

$$p^1: \quad \frac{d^2\bar{u}_1}{dX^2} - s\bar{u}_1 - \kappa_1\bar{u}_0 + k_2\bar{v}_0 + 1 = 0 \tag{A8}$$

$$p^0: \quad \frac{d^2\bar{v}_0}{dX^2} + s\bar{v}_0 = 0 \tag{A9}$$

$$p^1: \quad \frac{d^2\bar{v}_1}{dX^2} - s\bar{v}_1 + k_3\bar{u}_0 - k_4\bar{v}_0 + 1 = 0 \tag{A10}$$

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

$$\bar{u}_0(X,s) = \frac{m_1}{s}e^{-\sqrt{s}(X-1)} \tag{A11}$$

$$\bar{u}_1(X,s) =$$
$$\frac{1}{s} + \left[\frac{k_1 m_1}{2s^{3/2}}e^{\sqrt{s}(1-X)} - \frac{k_2 m_2}{2s^{3/2}}e^{\sqrt{s}(1-X)}\right](1-X) - \frac{1}{s}e^{\sqrt{s}(1-x)} \tag{A12}$$

$$\text{and } \bar{v}_0(X,s) = \frac{m_2}{s}e^{-\sqrt{s}(X-1)} \tag{A13}$$

$$\bar{v}_1(X,s) =$$
$$\frac{1}{s} + \left[\frac{k_3 m_1}{2s^{3/2}}e^{\sqrt{s}(1-X)} - \frac{k_4 m_2}{2s^{3/2}}e^{\sqrt{s}(1-X)}\right](X-1) - \frac{1}{s}e^{\sqrt{s}(1-x)} \tag{A14}$$

According to the Homotopy perturbation method, we can conclude that

$$\bar{u}_0(X) = \lim_{p\to1}\bar{u}(X) = u_0 + u_1 + \dots \tag{A15}$$

$$\bar{v}_0(X) = \lim_{p\to1}\bar{v}(X) = \bar{v}_0 + \bar{v}_1 + \dots \tag{A16}$$

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 $v_n(x)$ be completely determined such that each term is determined the previous terms.

APPENDIX B: NOMENCLATURE AND UNITS

Symbol	Meaning	Usual dimension
a	Concentration of the species A	mole cm^{-3}
b	Concentration of the species B	mole cm^{-3}
a_0	Bulk concentration of the species A	mole cm^{-3}
b_0	Bulk concentration of the species B	mole cm^{-3}
l	Thickness of the planar electrode	cm
κ_f	Forward rate constant	sec^{-1}
κ_b	Backward rate constant	sec^{-1}
D_a	Diffusion coefficient of the species A	cm^{2}sec^{-1}
D_b	Diffusion coefficient of the species B	cm^{2}sec^{-1}
j	Flux of the species	mole cm^{-2} sec^{-1}
F	Faraday constant	C
n	Number of electrons	None
t	Time	sec
u	Normalized concentration of the species A	None
v	Normalized concentration of the species B	None
J	Dimensionless flux	None
T	Dimensionless time	None
k_1, k_2, k_3 and k_4	Dimensionless rate constants	None
m_1 m_2	Constant	None
ψ	Dimensional current	None