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Approximate solution of non-steady concentration and current at a hemispherical microelectrode - Homotopy perturbation approach

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ABSTRACT

The analytical expressions of the steady and non-steady-state concentrations at a hemispherical microelectrode for homogeneous reactions mechanisms are derived in this paper. These simple new approximate expressions are valid for all values of time and possible values of rate constants. The steady state analytical results are compared with the available analytical results and are found to be in good agreement. Moreover, in this work we employ the Homotopy perturbation method (HPM) in Laplace space to solve the boundary value problem.

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KEYWORDS

Homogeneous kinetics;
Non-steady-state;
Microelectrodes;
Mathematical modelling;
Homotopy perturbation
method;
Simulation.

INTRODUCTION

Kinetics of some homogeneous chemical reactions can be measured by electrochemical methods because the chemical disbalance can be maintained at the electrode surface by the electro-consumption of one of the components of the system^[1]. This is called a CE mechanism^[2]. Some examples of the preceding reactions are the dissociation of metal complexes,^[3,4] the dehydration of carbonyl compounds,^[5-7] or the deprotonation of acids^[8]. The theory of CE mechanism was developed for various electrochemical methods, such as chronoamperometry,^[3,8-11] polarography,^[5,12-14] pulse polarography,^[15] cyclic voltammetry,^[1,16] rotating disk² and square-wave voltammetry,^[17,18] using a stationary planar,^[9,18] a stationary spherical,^[3,8,10,11,17] expanding plane,^[12,13] expanding sphere^[14,15] and cylindrical^[16] diffusion mod-

els under the steady-state,^[3,8-12,14] or transient conditions^[13,15-18]. The steady-state models are based on the assumption that the difference between the equilibrium concentrations and the actual concentrations of electroinactive and electroactive forms of the reactant is independent of time.

The purpose of this communication is to derive approximate analytical expressions for the non-steady-state concentrations of the species for all values of parameters m_1 , m_2 , γ_s , γ_E , γ_P and γ_Q using Homotopy perturbation method. These parameters are defined in the Eq.(8).

FORMULATION OF THE PROBLEM AND ANALYSIS

The scheme for a first-order (pseudo-first-order) reaction mechanism can be written as^[10]:



where k_1 and k_{-1} are homogeneous reaction rate constants, P and Q denote non steady-state concentration profiles of isomers. The mathematical model describing the hemispherical (or spherical) diffusion of species P and Q are^[10]:

$$\frac{\partial C_P}{\partial t} = D_P \frac{\partial^2 C_P}{\partial r^2} + \frac{2D_P}{r} \frac{\partial C_P}{\partial r} - k_1 C_P + k_{-1} C_Q \quad (2)$$

$$\frac{\partial C_Q}{\partial t} = D_Q \frac{\partial^2 C_Q}{\partial r^2} + \frac{2D_Q}{r} \frac{\partial C_Q}{\partial r} - k_{-1} C_Q + k_1 C_P \quad (3)$$

where C_P and C_Q denote the concentrations of the species P and Q ; D_P and D_Q are the diffusion coefficients of P and Q respectively. r denotes the radial coordinate; t is the time. All species are considered to have an equal diffusion coefficient ($D_P = D_Q = D$). The initial and boundary conditions are^[10]:

$$t = 0; \quad C_P = C_P^b, \quad C_Q = C_Q^b \quad (4)$$

$$r = a; \quad C_P = C_P^s, \quad C_Q = C_Q^s \quad (5)$$

$$r \rightarrow \infty; \quad C_P \rightarrow C_P^b, \quad C_Q \rightarrow C_Q^b \quad (6)$$

where C_P^b and C_Q^b are the bulk concentrations of the species P and Q , C_P^s and C_Q^s denote the concentrations at electrode surface. The current density is defined as:

$$i = nFAD \left. \frac{\partial C_Q}{\partial r} \right|_{r=a} \quad (7)$$

where n is the number of electrons, A is the area of the hemispherical electrode and F is the Faraday constant. The dimensionless variables are defined as follows:

$$\rho = \frac{r}{a}, \quad \tau = \frac{Dt}{a^2}, \quad u = \frac{C_P}{C_P^b}, \quad v = \frac{C_Q}{C_Q^b},$$

$$\gamma_S = \frac{k_1 a^2}{D}, \quad \gamma_E = \frac{k_{-1} C_Q^b a^2}{C_P^b D}, \quad \gamma_P = \frac{k_{-1} a^2}{D}, \quad (8)$$

$$\gamma_Q = \frac{k_1 C_P^b a^2}{C_Q^b D}, \quad m_1 = \frac{C_P^s}{C_P^b}, \quad m_2 = \frac{C_Q^s}{C_Q^b}$$

After the normalizations, the mathematical model given by Eqs. (2) and (3) become:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial u}{\partial \rho} - \gamma_S u + \gamma_E v \quad (9)$$

$$\frac{\partial v}{\partial \tau} = \frac{\partial^2 v}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial v}{\partial \rho} - \gamma_P v + \gamma_Q u \quad (10)$$

The initial and boundary conditions become:

$$\tau = 0, u = 1; v = 1 \quad (11)$$

$$\rho = 1, u = m_1; v = m_2 \quad (12)$$

$$\rho \rightarrow \infty, u \rightarrow 1; v \rightarrow 1 \quad (13)$$

The dimensionless current is as follows:

$$I = \frac{ia}{nFADC_Q^b} = (\partial v / \partial \rho)_{\rho=1} \quad (14)$$

ANALYTICAL SOLUTIONS OF DIMENSIONLESS CONCENTRATIONS OF THE SPECIES P AND Q UNDER STEADY-STATE

Solving the Eqs. (9) and (10) simultaneously for the steady-state (see Appendix A), we can obtain the following solutions:

$$u = 1 + \left[\frac{\gamma_Q (m_1 - 1) + \gamma_S (m_2 - 1)}{(\gamma_Q + \gamma_S)} \right] \left(\frac{1}{\rho} \right) + \frac{\gamma_S (m_1 - m_2)}{\rho(\gamma_Q + \gamma_S)} \exp \left[-\sqrt{\gamma_S + \gamma_P} (\rho - 1) \right] \quad (15)$$

$$v = 1 + \left[\frac{\gamma_Q (m_1 - 1) + \gamma_S (m_2 - 1)}{\rho(\gamma_Q + \gamma_S)} \right] \left(\frac{1}{\rho} \right) - \frac{\gamma_Q (m_1 - m_2)}{\rho(\gamma_Q + \gamma_S)} \exp \left[-\sqrt{\gamma_S + \gamma_P} (\rho - 1) \right] \quad (16)$$

Eqs. (15) and (16) are the analytical solutions for the dimensionless concentrations as a function dimensionless distance ρ . It satisfies the boundary conditions Eqs. (12) and (13). Knowing the value of m_1 and m_2 , the profiles of concentration of the species can be obtained. Using Eq. (14), the normalized current is given by:

$$I = \frac{\gamma_Q (m_1 - m_2) (1 + \sqrt{\gamma_S + \gamma_P}) + (1 - m_1) \gamma_Q + (1 - m_2) \gamma_S}{\gamma_S + \gamma_Q} \quad (17)$$

COMPARISON WITH OLDHAM'S WORK

Oldham^[10] have derived the analytical expressions of dimensionless steady-state concentrations of the species P and Q as follows:

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$$\mathbf{u} = \left[\frac{\gamma_P}{\gamma_P + \gamma_S} + \frac{\gamma_P \gamma_S}{\gamma_Q (\gamma_P + \gamma_S)} \right] \left(1 - \frac{1}{\rho} \right) + \left[\frac{\gamma_P \mathbf{m}_1}{\gamma_P + \gamma_S} + \frac{\gamma_P \gamma_S \mathbf{m}_2}{\gamma_Q (\gamma_P + \gamma_S)} \right] \left(\frac{1}{\rho} \right) + \left[\frac{\gamma_S \mathbf{m}_1}{\gamma_P + \gamma_S} - \frac{\gamma_P \gamma_S \mathbf{m}_2}{\gamma_Q (\gamma_P + \gamma_S)} \right] \frac{\exp \left[-\sqrt{\gamma_S + \gamma_P} (\rho - 1) \right]}{\rho} \quad (18)$$

$$\mathbf{v} = \left[\frac{\gamma_Q}{\gamma_P + \gamma_S} + \frac{\gamma_S}{\gamma_P + \gamma_S} \right] \left(1 - \frac{1}{\rho} \right) + \left[\frac{\gamma_Q \mathbf{m}_1}{\gamma_P + \gamma_S} + \frac{\gamma_S \mathbf{m}_2}{\gamma_P + \gamma_S} \right] \left(\frac{1}{\rho} \right) + \left[\frac{\gamma_P \mathbf{m}_2}{\gamma_P + \gamma_S} - \frac{\gamma_Q \mathbf{m}_1}{\gamma_P + \gamma_S} \right] \frac{\exp \left[-\sqrt{\gamma_S + \gamma_P} (\rho - 1) \right]}{\rho} \quad (19)$$

The normalized current is given by

$$\mathbf{I} = \frac{(\gamma_Q \mathbf{m}_1 - \gamma_P \mathbf{m}_2) \sqrt{\gamma_S + \gamma_P} + (\gamma_S + \gamma_Q) - \mathbf{m}_2}{(\gamma_S + \gamma_P)} \quad (20)$$

Figure 1a - c represents the normalized concentration u for the species P using Eqs. (15) and (16) for various values of γ_S . From these figures, it is evident that the value of the concentration increases when γ_S increases. Furthermore, Figure 1a - c compares the normalized concentration u obtained in this work with Oldham's work. Upon comparison, it is observed that the results are identical. Figure 2a - c shows the profiles of the concentration v of the species Q for various values of γ_S . In these figures our result is compared with previous result. A satisfactory agreement is noted. From these figures, it is inferred that the concentration of the species decreases abruptly and reaches the steady-state value when $\rho \geq 5$ (see Figure 1 and 2). Figure 3 represents the dimensionless steady-state current versus γ_S . From this figure, we conclude that the current's variation decreases when γ_p increases.

ANALYTICAL SOLUTIONS OF DIMENSIONLESS CONCENTRATIONS OF THE SPECIES P AND Q UNDER NON-STEADY-STATE

By applying Laplace transformation to the partial differential Eqs. (9) and (10) and using the condition Eq. (11), the following differential equations in Laplace

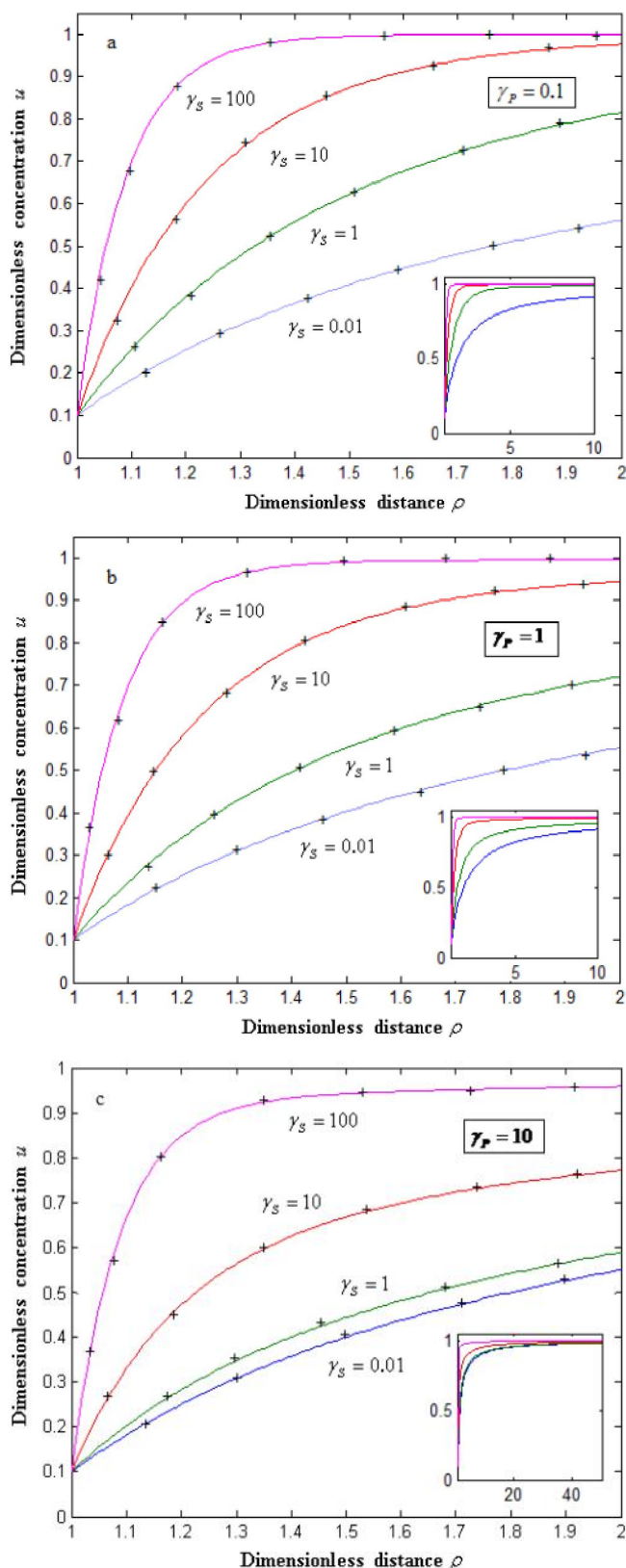


Figure 1 : Plot of the two-dimensional diagram of the concentration u versus the normalized distance ρ for fixed values of $\mathbf{m}_1 = 0.1$, $\mathbf{m}_2 = 1$ and various values of γ_S . _____ is plotted according to Eq. (15), and + is plotted according to Eq. (18).

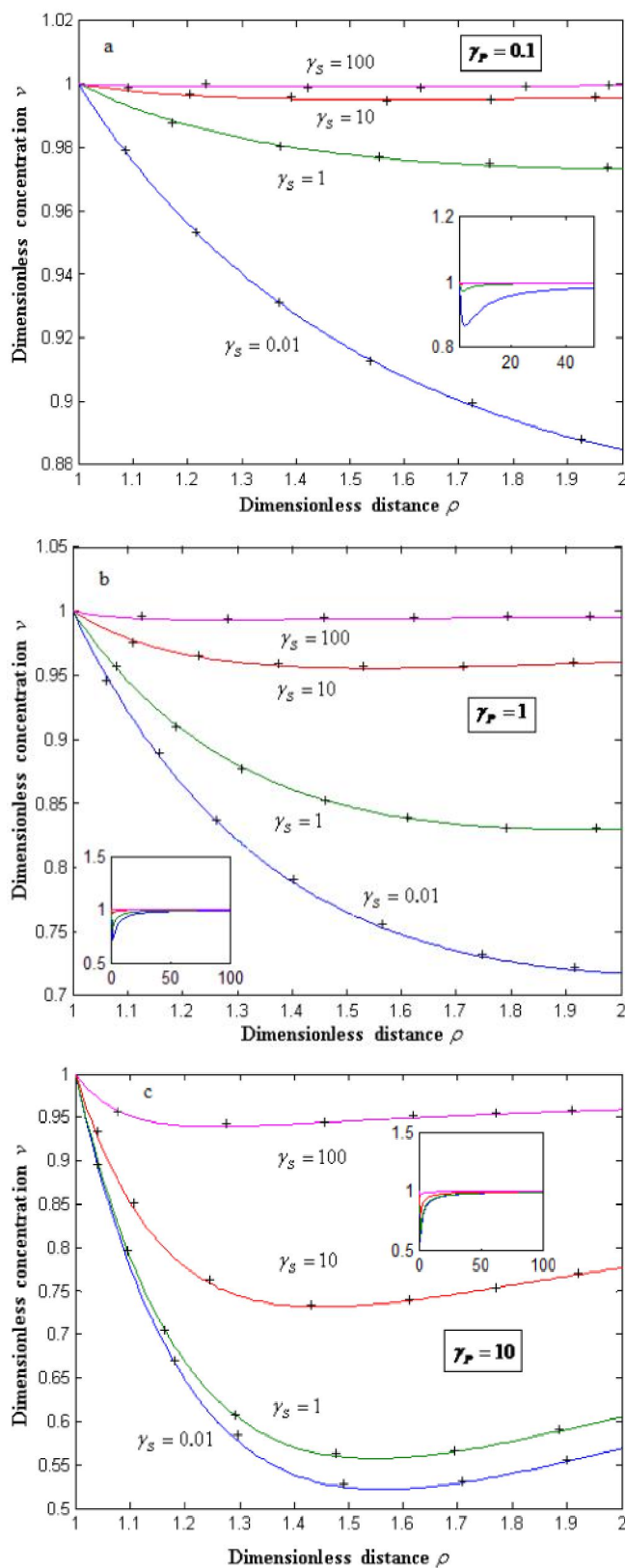


Figure 2 : Plot of the two-dimensional diagram of the concentration ν versus the normalized distance ρ for fixed values of $m_1 = 0.1, m_2 = 1$ and various values of γ_s . _____ is plotted according to Eq. (16), and + is plotted according to Eq. (19).

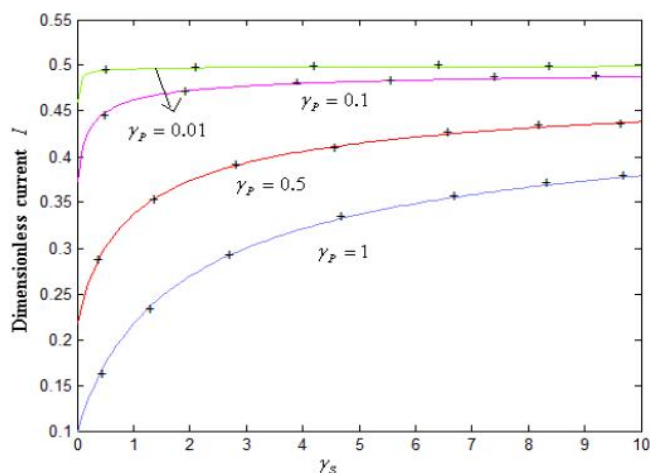


Figure 3 : Comparison of the dimensionless current against γ_s in the range of 0 to 10 for various value of γ_p . _____ is plotted according to Eq. (17), and + is plotted according to Eq. (20).

space are obtained:

$$\frac{d^2 \bar{u}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}}{d\rho} - \gamma_s \bar{u} + \gamma_E \bar{v} - s\bar{u} + 1 = 0 \tag{21}$$

$$\frac{d^2 \bar{v}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{v}}{d\rho} - \gamma_p \bar{v} + \gamma_Q \bar{u} - s\bar{v} + 1 = 0 \tag{22}$$

Now the boundary conditions become

$$\rho = 1, \bar{u} = \frac{m_1}{s}; \bar{v} = \frac{m_2}{s} \tag{23}$$

$$\rho \rightarrow \infty, \bar{u} \rightarrow \frac{1}{s}; \bar{v} \rightarrow \frac{1}{s} \tag{24}$$

where s is the Laplace variable and an overbar indicates a Laplace-transformed quantity. The set of expressions presented in Eqs. (21) - (24) defines the initial and boundary value problem in Laplace space. The HPM method has overcome the limitations of traditional perturbation methods. It can take full advantage of the 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 perturbation method^[14-19] is used to give the approximate analytical solutions of coupled non-linear Eqs. (21) and (22). Using Homotopy perturbation method (see Appendix - A and B) the approximate solutions of the Eqs. (9) and (10) are

$$u(\rho, \tau) = 1 + \left(\frac{m_1 - 1}{\rho}\right) \operatorname{erfc}\left(\frac{\rho - 1}{2\sqrt{\tau}}\right) + \left(\frac{1}{\rho} - 1\right) \left(\frac{\gamma_s m_1 - \gamma_E m_2}{2}\right) \left(\frac{2}{\sqrt{\pi}}\right) \sqrt{\tau} \exp\left(-\frac{(\rho - 1)^2}{4\tau}\right) - (\rho - 1) \operatorname{erfc}\left(\frac{\rho - 1}{2\sqrt{\tau}}\right) \tag{25}$$

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$$v(\rho, \tau) = 1 + \left(\frac{m_2 - 1}{\rho}\right) \operatorname{erfc}\left(\frac{\rho - 1}{2\sqrt{\tau}}\right) + \left(\frac{1}{\rho} - 1\right) \left(\frac{\gamma_P m_2 - \gamma_Q m_1}{2}\right) \left(\frac{2}{\sqrt{\pi}} \sqrt{\tau} \exp\left(-\frac{(\rho - 1)^2}{4\tau}\right) - (\rho - 1) \operatorname{erfc}\left(\frac{\rho - 1}{2\sqrt{\tau}}\right)\right) \quad (26)$$

The Eqs. (25) and (26) satisfies the boundary conditions (11) to (13). These equations represent the new approximate analytical expressions for the concentration profiles for all values of parameters m , γ_E and γ_S and small values of time. The current response is given by

$$I = (1 - m_2) \left[1 + \frac{1}{\sqrt{\pi\tau}} \right] + (\gamma_Q m_1 - \gamma_P m_2) \sqrt{\frac{\tau}{\pi}} \quad (27)$$

From Eq. (27) it is clearly seen that the expression for the current includes two different terms. The first term

$1 + \frac{1}{\sqrt{\pi\tau}}$ corresponds to the pure diffusive contribution,

whereas the second one is the kinetic-diffusive contribution. When the rate of the preceding chemical reaction is very slow, the current is given as follows:

$$I = (1 - m_2) \left[1 + \frac{1}{\sqrt{\pi\tau}} \right] \quad (27a)$$

DISCUSSION

Eqs. (25) and (26) are the closed and simple approximate analytical expressions of concentrations of the isomers calculated using Homotopy perturbation method for the initial and boundary conditions Eqs. (11), (12) and (13). The closed approximate analytical expression of current is represented by the Eq. (27). The dimensionless concentration profiles of u versus dimensionless distance ρ are given in Figure 4a - c. From these figures, we can see that the value of the concentration decreases when τ and distance ρ increases when $\gamma_S \leq 1$. Also when $\gamma_S > 1$ and $\tau > 1$, the concentration attains the steady-state value. In Figure 5a and b, the normalized concentration profiles of isomers v for various values of parameters are plotted. From these figures, it is inferred that the value of the concentration decreases as τ increases. The dimensionless current I

versus τ for various values of γ_Q is given in Figure 6. It is observed that the variation of the normalized current's variation diminishes with increasing τ .

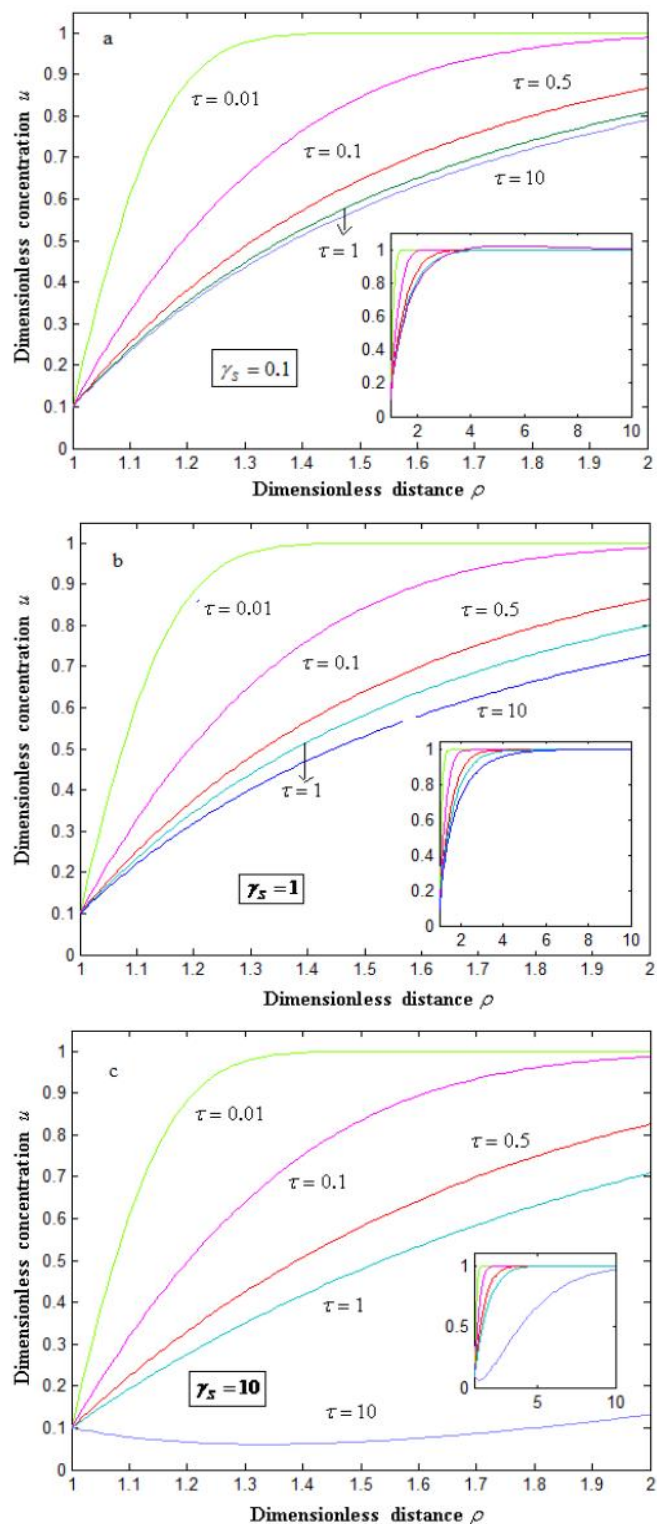


Figure 4 : Normalized concentration u at microelectrode. The concentrations were computed using Eq. (25) for some fixed value of $\gamma_E = 0.5$, $m_1 = 0.1$, $m_2 = 0.5$ and for various values of τ .

APPENDIX

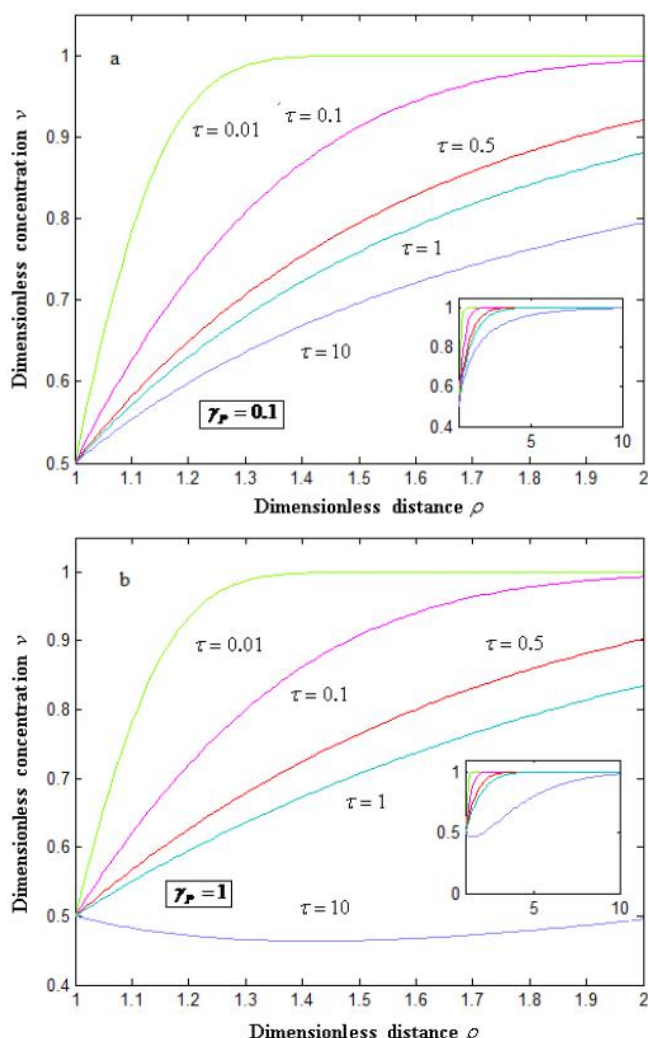


Figure 5 : Normalized concentration ν at microelectrode. The concentrations were computed using Eq. (26) for some fixed value of $\gamma_Q = 0.5, m_1 = 0.1, m_2 = 0.5$ and for various values of τ .

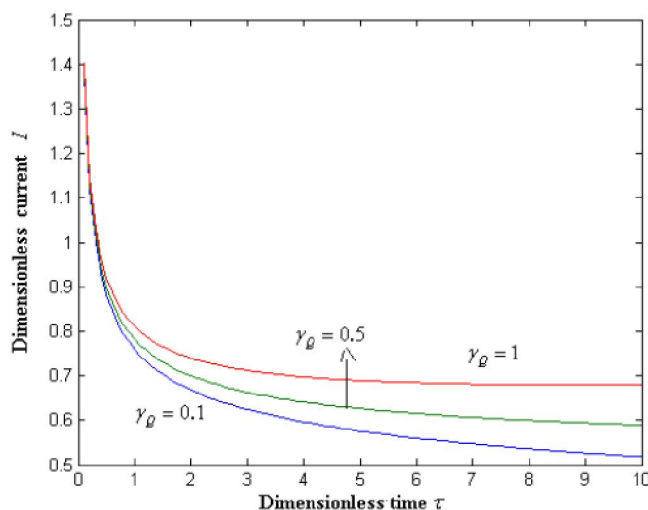


Figure 6 : Variation of normalized non-steady-state current response I as a function of the dimensionless time. The curves were computed using Eq. (27).

Appendix A

Solution of the equations (9) and (10) using Simultaneous equation method

In this appendix we indicate that how Eqs. (15) and (16) are derived. Let us introduce the following variable for transformations

$$c_1 = \rho u \text{ and } c_2 = \rho v \tag{A1}$$

The transformation given by (A1) changes Eqs. (9) and (10) to:

$$\frac{d^2 c_1}{d\rho^2} - \gamma_S c_1 + \gamma_E c_2 = 0 \tag{A2}$$

$$\frac{d^2 c_2}{d\rho^2} - \gamma_P c_2 + \gamma_Q c_1 = 0 \tag{A3}$$

The above equations can be written in the following form.

$$(D^2 - \gamma_S)c_1 + \gamma_E c_2 = 0 \tag{A4}$$

$$(D^2 - \gamma_P)c_2 + \gamma_Q c_1 = 0 \tag{A5}$$

where $D = \frac{d}{d\rho}$. Solving Eqs. (A4) and (A5), we have

$$c_1 = A \exp[\sqrt{\gamma_S + \gamma_P} \rho] + B \exp[-\sqrt{\gamma_S + \gamma_P} \rho] + C\rho + D \tag{A6}$$

$$c_2 = E \exp[\sqrt{\gamma_P} \rho] + F \exp[-\sqrt{\gamma_P} \rho] - \frac{\gamma_Q}{\gamma_S} [C_1 - C\rho - D] + \frac{\gamma_Q}{\gamma_P} [C\rho + D] \tag{A7}$$

Since the highest power of D is 4, the constant must be 4.

$$c_2 = -\frac{\gamma_Q}{\gamma_S} [A \exp[\sqrt{\gamma_S + \gamma_P} \rho] + B \exp[-\sqrt{\gamma_S + \gamma_P} \rho]] + \frac{\gamma_Q}{\gamma_P} [C\rho + D] \tag{A8}$$

Substituting Eqs. (A6) and (A8) in Eq. (A1), we get

$$u = \left[\frac{A \exp[\sqrt{\gamma_S + \gamma_P} \rho] + B \exp[-\sqrt{\gamma_S + \gamma_P} \rho]}{\rho} \right] + C + \frac{D}{\rho} \tag{A9}$$

$$v = -\frac{\gamma_Q}{\gamma_S} \left[\frac{A \exp[\sqrt{\gamma_S + \gamma_P} \rho] + B \exp[-\sqrt{\gamma_S + \gamma_P} \rho]}{\rho} \right] + \frac{\gamma_Q}{\gamma_P} \left[C + \frac{D}{\rho} \right] \tag{A10}$$

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Using the boundary conditions, we can obtain the value of the constants *A*, *B*, *C* and *D*. Substituting the value of the constants in the equations (A9) and (A10), we obtain the Eqs. (15) and (16) in the text.

Appendix B

Solution of the equations (21) and (22) using Homotopy perturbation method

In this Appendix, we indicate how Eqs. (25) and (26) in this paper are derived. To find the solution of Eqs. (21) and (22), we first construct a Homotopy as follows:

$$(1-p) \left[\frac{d^2 \bar{u}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}}{d\rho} - s\bar{u} \right] + p \left[\frac{d^2 \bar{u}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}}{d\rho} - \gamma_s \bar{u} + \gamma_E \bar{v} - s\bar{u} + 1 \right] = 0 \tag{B1}$$

$$(1-p) \left[\frac{d^2 \bar{v}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{v}}{d\rho} - s\bar{v} \right] + p \left[\frac{d^2 \bar{v}}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{v}}{d\rho} - \gamma_P \bar{v} + \gamma_Q \bar{u} - s\bar{v} + 1 \right] = 0 \tag{B2}$$

and the initial approximations are as follows:

$$\rho = 1, \bar{u}_0 = \frac{m_1}{s}; \bar{v}_0 = \frac{m_2}{s} \tag{B3}$$

$$\rho \rightarrow \infty, \bar{u}_0 \rightarrow \frac{1}{s}; \bar{v}_0 \rightarrow \frac{1}{s} \tag{B4}$$

$$\rho = 1, \bar{u}_i = 0, \bar{v}_i = 0 \tag{B5}$$

$$\rho \rightarrow \infty; \bar{u}_i = 0; \bar{v}_i = 0 \quad \forall i = 1, 2, \dots \tag{B6}$$

and

$$\begin{cases} \mathbf{u} = \mathbf{u}_0 + p\mathbf{u}_1 + p^2\mathbf{u}_2 + p^3\mathbf{u}_3 + \dots \\ \mathbf{v} = \mathbf{v}_0 + p\mathbf{v}_1 + p^2\mathbf{v}_2 + p^3\mathbf{v}_3 + \dots \end{cases} \tag{B7}$$

Substituting Eq. (B7) into Eqs. (B1) and (B2), arranging the coefficients of powers *p*, we can obtain the following differential equations.

$$p^0 : \frac{d^2 \bar{u}_0}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}_0}{d\rho} - s\bar{u}_0 = 0 \tag{B8}$$

$$p^1 : \frac{d^2 \bar{u}_1}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}_1}{d\rho} - \gamma_s \bar{u}_0 + \gamma_E \bar{v}_0 - s\bar{u}_1 + 1 = 0 \tag{B9}$$

and

$$p^0 : \frac{d^2 \bar{v}_0}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{v}_0}{d\rho} - s\bar{v}_0 = 0 \tag{B10}$$

$$p^1 : \frac{d^2 \bar{v}_1}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{v}_1}{d\rho} - \gamma_P \bar{v}_0 + \gamma_Q \bar{u}_0 - s\bar{v}_1 + 1 = 0 \tag{B11}$$

Solving equations (B8) to (B11) using reduction of order (see Appendix-C), we can find the following results

$$\bar{u}_0(\rho, s) = \frac{m_1 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \tag{B12}$$

$$\bar{u}_1(\rho, s) = \left(\frac{1}{s} - \frac{m_1 \gamma_s}{2s^{3/2}} + \frac{m_2 \gamma_E}{2s^{3/2}} \right) \left(1 - \frac{1}{\rho} \right) e^{(-\sqrt{s}(\rho-1))} \tag{B13}$$

and

$$\bar{v}_0(\rho, s) = \frac{m_2 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \tag{B14}$$

$$\bar{v}_1(\rho, s) = \left(\frac{1}{s} - \frac{m_2 \gamma_P}{2s^{3/2}} + \frac{m_1 \gamma_Q}{2s^{3/2}} \right) \left(1 - \frac{1}{\rho} \right) e^{(-\sqrt{s}(\rho-1))} \tag{B15}$$

According to the HPM, we can conclude that

$$\mathbf{u}(\rho) = \lim_{p \rightarrow 1} \mathbf{u}(\rho) = \mathbf{u}_0 + \mathbf{u}_1 + \dots \tag{B16}$$

$$\mathbf{v}(\rho) = \lim_{p \rightarrow 1} \mathbf{v}(\rho) = \mathbf{v}_0 + \mathbf{v}_1 + \dots \tag{B17}$$

After putting Eqs. (B12) and (B13) into Eq. (B16) and Eqs. (B14) and (B15) into Eq.(B17) Using inverse Laplace transform, the final results can be described in Eqs. (25) and (26) in the text. The remaining components of *u_n*(*x*) and *v_n*(*x*) be completely determined such that each term is determined by the previous term.

Appendix C

In this Appendix, we derive the solution of equation (B9) by using reduction of order. To illustrate the basic concepts of reduction of order, we consider the equation

$$\frac{d^2 c}{d\rho^2} + P \frac{dc}{d\rho} + Qc = R \tag{C1}$$

where P, Q, R are function of ρ . Eq. (B9) can be simplified to

$$\frac{d^2 \bar{u}_1}{d\rho^2} + \frac{2}{\rho} \frac{d\bar{u}_1}{d\rho} - s\bar{u}_1 + 1 - \gamma_s \left(\frac{m_1 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \right) + \gamma_E \left(\frac{m_2 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \right) = 0 \tag{C2}$$

Using reduction of order, we have

$$P = \frac{2}{\rho}; Q = -s$$

and

$$R = -1 + \gamma_s \left(\frac{m_1 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \right) - \gamma_E \left(\frac{m_2 e^{(-\sqrt{s}(\rho-1))}}{s\rho} \right) \quad (C3)$$

$$\text{Let } u_1 = cv \quad (C4)$$

Substitute (C4) in (C1), if u is so chosen that

$$2 \frac{dc}{d\rho} + Pc = 0 \quad (C5)$$

Substituting the value of P in the above equation (C5) becomes

$$c = \frac{1}{\rho} \quad (C6)$$

The given equation (C2) reduces to

$$v'' + Q_1 v = R_1 \quad (C7)$$

where

$$Q_1 = Q - \frac{P^2}{4} - \frac{P'}{2} = 0, R_1 = \frac{R}{c} \quad (C8)$$

Substituting (C8) in (C7) we obtain,

$$v'' - sv = -\rho + \gamma_s \left(\frac{m_1 e^{(-\sqrt{s}(\rho-1))}}{s} \right) - \gamma_E \left(\frac{m_2 e^{(-\sqrt{s}(\rho-1))}}{s} \right) \quad (C9)$$

Integrating equation (C9) twice, we obtain

$$v = A e^{\sqrt{s}\rho} + B e^{-\sqrt{s}\rho} + \frac{\rho}{s} - \gamma_s \left(\frac{m_1 e^{(-\sqrt{s}(\rho-1))} \rho}{2s^{3/2}} \right) + \gamma_E \left(\frac{m_2 e^{(-\sqrt{s}(\rho-1))} \rho}{2s^{3/2}} \right) \quad (C10)$$

Substituting (C6) and (C10) in (C4) we have,

$$u_1 = \frac{A e^{\sqrt{s}\rho}}{\rho} + \frac{B e^{-\sqrt{s}\rho}}{\rho} + \frac{1}{s} - \gamma_s \left(\frac{m_1 e^{(-\sqrt{s}(\rho-1))}}{2s^{3/2}} \right) + \gamma_E \left(\frac{m_2 e^{(-\sqrt{s}(\rho-1))}}{2s^{3/2}} \right) \quad (C11)$$

Using the boundary conditions, we can obtain the value of the constants A and B . Substituting the value of the constants A and B in the equation (C11) we obtain the equation (B13). Similarly we can solve the other differential Eqs. (B12), (B14) and (B15) using the reduction of order method.

Appendix D

Nomenclature and Units

Symbol	Meaning	Usual dimension
C_P	Concentration of the species P	mole cm^{-3}
C_Q	Concentration of the species Q	mole cm^{-3}
a	radius of spherical microelectrode	Cm
C_P^b	Bulk concentration of the species P	mole cm^{-3}
C_Q^b	Bulk concentration of the species Q	mole cm^{-3}
C_P^s	Concentration of the species P at electrode surface	mole cm^{-3}
C_Q^s	Concentration of the species Q at electrode surface	mole cm^{-3}
k_1	Rate constant for the forward direction	sec^{-1}
k_{-1}	Rate constant for the backward direction	sec^{-1}
D_P	Diffusion coefficient of the species P	$\text{cm}^2 \text{sec}^{-1}$
D_Q	Diffusion coefficient of the species Q	$\text{cm}^2 \text{sec}^{-1}$
R	Radial coordinate	Cm
j_P	Flux of the species P	mole $\text{cm}^{-2} \text{sec}^{-1}$
j_Q	Flux of the species Q	mole $\text{cm}^{-2} \text{sec}^{-1}$
A	Area of the hemisphere	Cm^2
E	Electrode potential	Volt
E_2^0	Conditional potential of 2 nd reaction	Volt
R	Gas constant	$\text{K}^{-1} \text{mol}^{-1}$
T	Temperature	K
F	Faraday constant	C
n	Number of electrons	None
τ	Time	Sec
u	Normalized concentration of the species P	None
v	Normalized concentration of the species Q	None
ρ	Dimensionless radial distance	None
$\gamma_s, \gamma_E, \gamma_P$ and γ_Q	Dimensionless rate constants	None
m_1	Ratio of concentration of species P and bulk concentration for the species P	None
m_2	Ratio of concentration of species Q and bulk concentration for the species Q	None
I	Dimensionless current	None

CONCLUSIONS

In this work, the coupled time dependent linear differential equations has been restudied and solved analytically. In the first part of the paper, we have derived the steady-state analytical expressions of the concentrations of the species for all values of rate constants.

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Moreover, it is compared with available analytical results. It gives an excellent agreement. In the second part of the paper we have presented an approximate analytical expression corresponding to the species P and Q in terms of the kinetic parameters γ_S , γ_E , γ_P and γ_Q based on the Homotopy perturbation method for non-steady-state. 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 responds to changes in electrode size. Further, based on the outcome of this work it is possible to calculate the current for the various mechanisms (CE, EC, ECE and EC') and various electrode geometries.

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