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Approximate Solution of Non-Linear Reaction Diffusion Equations in Homogeneous Processes Coupled to Electrode Reactions for CE Mechanism at a Spherical Electrode

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Abstract

A mathematical model of CE reaction schemes under first or pseudo-first order conditions with different diffusion coefficients at a spherical electrode under non-steady-state conditions is described. The model is based on non-stationary diffusion equation containing a non-linear reaction term. This paper presents the complex numerical method (Homotopy perturbation method) to solve the system of non-linear differential equation that describes the homogeneous processes coupled to electrode reaction. In this paper the approximate analytical expressions of the non-steady-state concentrations and current at spherical electrodes for homogeneous reactions mechanisms are derived for all values of the reaction diffusion parameters. These approximate results are compared with the available analytical results and are found to be in good agreement.

Keywords: Non-Linear Reaction/Diffusion Equation, Homotopy Perturbation Method, CE Mechanism, Reduction of Order, Spherical Electrodes

1. Introduction

Microelectrodes are of great practical interest for quantitative in vivo measurements, e.g. of oxygen tension in living tissues [1-3], because electrodes employed in vivo should be smaller than the unit size of the tissue of interest. Microelectrodes having the geometry of a hemisphere resting on an insulating plane are difficult to fabricate, but their behavior is easily predicted [4]. They also have advantages in electrochemical measurements of molten salts with high temperature [5]. Microelectrodes of many shapes have been described [6]. Microelectrodes of simple shapes are experimentally preferable because they are more easily fabricated and generally conformed to simpler voltammetric relationships. Those shapes with restricted size in all superficial dimensions are of special interest because many of these reach true steady-state under diffusion control in a semi infinite medium [7]. Nevertheless, there is interest in microelectrodes of more complicated shapes, only because the shapes of small experimental electrodes may not always be quite as simple as their fabricators intended. Moreover, and ironically, complex shapes may sometimes be more easily modeled than simpler ones [8]. However, many applications of microelectrodes of different shapes are impeded by lack of adequate theoretical description of their behavior.

As far back as 1984, Fleischmann *et al.* [9,10] used microdisc electrodes to determine the rate constant of coupled homogeneous reactions (CE, EC', ECE, and DISPI mechanisms). Fleischmann *et al.* [9] obtained the steady-state analytical expression of the concentration of the species HA and H by assuming the concentration of the specie A is constant. Also measurement of the current at microelectrodes is one of the easiest and yet most powerful electrochemical methods for quantitative mechanistic investigations. The use of microelectrodes for kinetic studies has recently been reviewed [11] and the feasibility demonstrated of accessing nano second time scales through the use of fast scan cyclic voltammetry. However, these advantages are earned at the expense of enhanced theoretical difficulties in solving the reaction diffusion equations at these electrodes. Thus it is essential to have theoretical expressions for non steady state currents at such electrodes for all mechanisms.

The spherical EC' mechanism was firstly solved by Delmastro and Smith [12]. In electrochemical context Diao *et al.* [13] derived the chronoamperometric current

at hemispherical electrode for EC' reaction, whereas Galceran's *et al.* [14] evaluated shifted de facto expression and shifted asymptotic short-time expression for disc electrodes using Danckwerts relation. Rajendran *et al.* [15] derived an accurate polynomial expression for transient current at disc electrode for an EC' reaction. More recently, Molina and coworkers have derived the rigorous analytical solution for EC', CE, catalytic processes at spherical electrodes [16]. Fleischmann *et al.* [17] demonstrate that Neumann's integral theorem can be used to numerically simulate CE mechanism at a disc electrode. Dayton *et al.* [18] also derived the spherical response using Neumann's integral theorem. In this literature steady-state limiting current is discussed in [19]

In general, the characterization of subsequent homogeneous reactions involves the elucidations of the mechanism of reaction, as well as the determination of the rate constants. Earlier, the steady-state analytical expressions of the concentrations and current at microdisc electrodes in the case of first order EC' and CE reactions were calculated [9]. However, to the best of our knowledge, till date there was no rigorous approximate solutions for the kinetic of CE reaction schemes under first or pseudo-first order conditions with different diffusion coefficients at spherical electrodes under non-steady-state conditions for all possible values of reaction/diffusion parameters γ_S, γ_E , γ_{S1}, γ_{E1}, γ_{S2}, ε_1, ε_2 and γ_{E2} have been reported. The purpose of this communication is to derive approximate analytical expressions for the non-steady-state concentrations and current at spherical electrodes for all possible values of parameters using Homotopy perturbation method.

2. Mathematical Formulation of the Problems

At a range of Pt microelectrodes, the electroreduction of acetic acid, a weak acid, is strutinized by as in a usual CE reaction scheme. This reaction is known to proceed via the following reaction sequence [9]:

$$\begin{aligned} &\mathrm{HA} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{H^+ + A^-} \\ &\mathrm{H^+ + e^-} \rightleftharpoons \frac{1}{2}\mathrm{H_2} \end{aligned} \tag{1}$$

where k_1 and k_2 are the rate constants for the forward and back reactiuons respectively and are related to another by the known equilibrium constant for the acid dissociation [9]. The initial boundary value problems for different diffusion coefficients ($D_{\mathrm{HA}}, D_{\mathrm{H}}, D_{\mathrm{A}}$) can be written in the following forms [9]:

$$\frac{\partial c_{\mathrm{HA}}}{\partial t} = D_{\mathrm{HA}} \frac{\partial^2 c_{\mathrm{HA}}}{\partial r^2} + \frac{2D_{\mathrm{HA}}}{r}\frac{\partial c_{\mathrm{HA}}}{\partial r} - k_1 c_{\mathrm{HA}} + k_2 c_{\mathrm{H}} c_{\mathrm{A}} \tag{2}$$

$$\frac{\partial c_{\mathrm{H}}}{\partial t} = D_{\mathrm{H}} \frac{\partial^2 c_{\mathrm{H}}}{\partial r^2} + \frac{2D_{\mathrm{H}}}{r}\frac{\partial c_{\mathrm{H}}}{\partial r} + k_1 c_{\mathrm{HA}} - k_2 c_{\mathrm{H}} c_{\mathrm{A}} \tag{3}$$

$$\frac{\partial c_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \frac{\partial^2 c_{\mathrm{A}}}{\partial r^2} + \frac{2D_{\mathrm{A}}}{r}\frac{\partial c_{\mathrm{A}}}{\partial r} + k_1 c_{\mathrm{HA}} - k_2 c_{\mathrm{A}} c_{\mathrm{H}} \tag{4}$$

where D_{HA}, D_{H} and D_{A} are the diffusion coefficient of the species HA, H and A , k_1 and k_2 are the rate constant for the forward and back reactions respectively and $c_{\mathrm{HA}}, c_{\mathrm{H}}$ and c_{A} are the concentration of the species HA, H and A. These equations are solved for the following initial and boundary conditions:

$$t = 0\ ;\ c_{\mathrm{H}} = c_{\mathrm{H}}^{\infty},\ \ c_{\mathrm{HA}} = c_{\mathrm{HA}}^{\infty},\ c_{\mathrm{A}} = c_{\mathrm{A}}^{\infty} \tag{5}$$

$$r = r_S;\ c_{\mathrm{H}} = 0,\ \ dc_{\mathrm{HA}}/dr = 0,\ dc_{\mathrm{A}}/dr = 0 \tag{6}$$

$$r = \infty\ ;\ c_{\mathrm{H}} = c_{\mathrm{H}}^{\infty},\ \ c_{\mathrm{HA}} = c_{\mathrm{HA}}^{\infty},\ c_{\mathrm{A}} = c_{\mathrm{A}}^{\infty} \tag{7}$$

where r_S is the radius of the spherical electrode. We introduce the following set of dimensionless variables:

$$\begin{aligned} &u = \frac{c_{\mathrm{HA}}}{c_{\mathrm{HA}}^{\infty}},\ v = \frac{c_{\mathrm{H}}}{c_{\mathrm{H}}^{\infty}},\ w = \frac{c_{\mathrm{A}}}{c_{\mathrm{A}}^{\infty}},\ \rho = \frac{r}{r_S}, \\ &\tau = \frac{D_{\mathrm{HA}} t}{r_S^2},\ \varepsilon_1 = \frac{D_{\mathrm{H}}}{D_{\mathrm{HA}}},\ \varepsilon_2 = \frac{D_{\mathrm{A}}}{D_{\mathrm{HA}}}, \\ &\gamma_E = \frac{k_1 r_S^2}{D_{\mathrm{HA}}},\ \gamma_S = \frac{k_2 c_{\mathrm{H}}^{\infty} c_{\mathrm{A}}^{\infty} r_S^2}{D_{\mathrm{HA}} c_{\mathrm{HA}}^{\infty}} \\ &\gamma_{E1} = \frac{k_1 c_{\mathrm{HA}}^{\infty} r_S^2}{D_{\mathrm{HA}} c_{\mathrm{H}}^{\infty}},\ \gamma_{\mathrm{S1}} = \frac{k_2 c_{\mathrm{A}}^{\infty} r_S^2}{D_{\mathrm{HA}}}, \\ &\gamma_{E2} = \frac{k_1 c_{\mathrm{HA}}^{\infty} r_S^2}{D_{\mathrm{HA}} c_{\mathrm{A}}^{\infty}},\ \gamma_{\mathrm{S2}} = \frac{k_2 c_{\mathrm{H}}^{\infty} r_S^2}{D_{\mathrm{HA}}} \end{aligned} \tag{8}$$

where u , v, w, ρ and τ represent the dimensionless concentrations and dimensionless radial distance and dimensionless time parameters respectively.

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial u}{\partial \rho} - \gamma_E u + \gamma_S v w \tag{9}$$

$$\frac{\partial v}{\partial \tau} = \varepsilon_1 \frac{\partial^2 v}{\partial \rho^2} + \frac{2\varepsilon_1}{\rho}\frac{\partial v}{\partial \rho} + \gamma_{E1} u - \gamma_{S1} v w \tag{10}$$

$$\frac{\partial w}{\partial \tau} = \varepsilon_2 \frac{\partial^2 w}{\partial \rho^2} + \frac{2\varepsilon_2}{\rho}\frac{\partial w}{\partial \rho} + \gamma_{E2} u - \gamma_{S2} v w \tag{11}$$

where γ_E, γ_S, γ_{E1}, γ_{S1}, γ_{E2} and γ_{S2} are the dimensionless reaction/diffusion parameters and ε_1, ε_2 are dimensionless diffusion coefficients. The initial and boundary conditions are represented as follows:

$$\tau = 0,\ u = 1;\ \ v = 1;\ \ w = 1 \tag{12}$$

$$\rho = 1,\ v = 0;\ \ (\partial u/\partial \rho) = 0;\ \ (\partial w/\partial \rho) = 0 \tag{13}$$

$$\rho \to \infty,\ u = 1;\ v = 1;\ w = 1 \tag{14}$$

The dimensionless current at the microdisc electrode

can be given as follows:

$$I_S = -nFAD_{\mathrm{H}}/r_S\left(dv/d\rho\right)_{\rho=1} \tag{15}$$

3. Analytical Expression of Concentrations and Current Using HPM

Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [20-25]. This method is a combination of homotopy in topology and classic perturbation techniques. The set of expressions presented in Equations (9)-(14) defines the initial and boundary value problem. The homotopy perturbation method [26-32] is used to give the approximate solutions of coupled non-linear reaction/diffusion Equations (9) to (11). The dimensionless reaction diffusion parameters γ_{E}, γ_S, γ_{E1}, γ_{S1}, γ_{E2} and γ_{S2} are related to one another, since the bulk solution is at equilibrium in the non-steady state. Using HPM (see Appendix A and B), we can obtain the following solutions to the Equations (9) to (11).

$$\begin{aligned} u(\rho,\tau) = 1 &+ \frac{\gamma_E\sqrt{\varepsilon_1}}{(\varepsilon_1-1)\rho}\left[\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{(\rho-1)^2}{4\tau}\right)\right. \\ &\left. -\exp(\rho-1)\ \exp(\tau)\,erfc\left(\sqrt{\tau}+\frac{\rho-1}{2\sqrt{\tau}}\right)\right] \\ &+ \frac{\gamma_E\varepsilon_1}{(\varepsilon_1-1)\rho}\left[\exp(\rho-1)\ \exp(\tau)\,erfc\left(\sqrt{\tau}+\frac{\rho-1}{2\sqrt{\tau}}\right)\right. \\ &\left. -\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{(\rho-1)^2}{4\tau\ \varepsilon_1}\right)\right] \end{aligned} \tag{16}$$

$$\begin{aligned} v(\rho,\tau) = 1 &- \frac{1}{\rho}erfc\left(\frac{\rho-1}{2\sqrt{\varepsilon_1}\sqrt{\tau}}\right) \\ &- \frac{\gamma_{E1}}{2\sqrt{\varepsilon_1}}\left(\frac{1}{\rho}-1\right)\left[\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{(\rho-1)^2}{4\tau\ \varepsilon_1}\right)\right] \end{aligned} \tag{17}$$

$$\begin{aligned} w(\rho,\tau) = 1 &- \frac{\gamma_{E2}}{\rho(\varepsilon_1-\varepsilon_2)}\left[\sqrt{\varepsilon_1\varepsilon_2}\,\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{(\rho-1)^2}{4\tau\ \varepsilon_2}\right)\right. \\ &\left. -\varepsilon_1\frac{1}{\sqrt{\pi\tau}}\exp\left(-\frac{(\rho-1)^2}{4\tau\ \varepsilon_1}\right)\right] \\ &+ \frac{\gamma_{E2}}{\rho(\varepsilon_1-\varepsilon_2)}\left[\exp(\rho-1)\exp(\varepsilon_2\tau)\right. \\ &\left. \times erfc\left(\sqrt{\varepsilon_2\tau}+\frac{\rho-1}{2\sqrt{\varepsilon_2\tau}}\right)\right]\left(\sqrt{\varepsilon_1}\varepsilon_2-\varepsilon_1\sqrt{\varepsilon_2}\right) \end{aligned} \tag{18}$$

The Equations (16)-(18) satisfies the boundary conditions (12) to (14). These equations represent the new approximate dimensionless solution for the concentration profiles for all possible values of parameters γ_E, γ_S, γ_{E1}, γ_{S1}, γ_{E2}, γ_{S2}, ε_1 and ε_2. From Equations (15) and (17), we can obtain the dimensionless current, which is as follows:

$$\begin{aligned} \psi &= I_S r_S / nFD_{\mathrm{H}}AC_{\mathrm{H}}^{\infty} \\ &= 1 + \frac{0.56419}{\sqrt{\varepsilon_1\tau}} + \frac{0.28217\ \gamma_{E1}}{\sqrt{\varepsilon_1\tau}} \end{aligned} \tag{19}$$

Equation (19) represents the new approximate expression for the current for small and medium of parameters.

4. Comparison with Fleischmann Work [9]

Fleischmann *et al.* [9] have derived the analytical expressions of dimensionless steady-state concentrations *u* and *v* as follows:

$$\begin{aligned} u(\rho) = 1 + \varepsilon_1 &\left[1 - \frac{\gamma_{E1}+\varepsilon_1\gamma_E}{\varepsilon_1\gamma_E+\gamma_{S1}}\right. \\ &\left.\times\left[1-\frac{1}{\rho}\exp\left[-(\rho-1)\sqrt{\gamma_E+\gamma_{S1}/\varepsilon_1}\right]\right]\right] \end{aligned} \tag{20}$$

$$v(\rho) = \frac{\gamma_{E1}+\varepsilon_1\gamma_E}{\varepsilon_1\gamma_E+\gamma_{S1}}\left[1-\frac{1}{\rho}\exp\left[-(\rho-1)\sqrt{\gamma_E+\gamma_{S1}/\varepsilon_1}\right]\right] \tag{21}$$

Fleischmann assumed that the concentration profiles of *w* is constant. So the definite solution for concentration profiles of *w* is not arrived upon in the third specie A. The normalized current is given by

$$\begin{aligned} \psi &= I_S r_S / nFD_{\mathrm{H}}AC_{\mathrm{H}}^{\infty} \\ &= \frac{(\gamma_{E1}+\varepsilon_1\gamma_E)\ \left(1+\sqrt{\gamma_E+\gamma_{S1}/\varepsilon_1}\right)}{(\varepsilon_1\gamma_E+\gamma_{S1})} \end{aligned} \tag{22}$$

When $\gamma_{E1}=\gamma_{S1}$ the above equation becomes

$$u(\rho) = 1+\varepsilon_1\left[\frac{1}{\rho}\exp\left[-(\rho-1)\sqrt{\gamma_E+\gamma_{E1}/\varepsilon_1}\right]\right] \tag{23}$$

$$v(\rho) = \left[1-\frac{1}{\rho}\exp\left[-(\rho-1)\sqrt{\gamma_E+\gamma_{E1}/\varepsilon_1}\right]\right] \tag{24}$$

The normalized current is given by

$$\psi = I_S r_S / nFD_{\mathrm{H}}AC_{\mathrm{H}}^{\infty} = 1+\sqrt{\gamma_E+\gamma_{E1}/\varepsilon_1} \tag{25}$$

Previously, mathematical expressions pertaining to steady-state analytical expressions of the concentrations and current at microdisc electrodes were calculated by Fleischmann *et al.* [9]. In addition, we have also pre-

sented an approximate solution for the non-steady state concentrations and current.

5. Discussions

Equations (16)-(18) are the new and simple approximate solution of the concentrations of the isomers calculated using Homotopy perturbation method for the initial and boundary conditions Equations (12)-(14). The closed approximate solution of current is represented by the Equation (19). The dimensionless concentration profiles of u versus dimensionless distance ρ are expressed in **Figures 1(a)-(d)**. From these figures, we can infer that the value of the concentration decreases when τ and distance ρ increases when $\gamma_E \le 1$. Moreover when $\gamma_E \le 1$ and $\tau > 1$, the concentration attains the steady-state value. In **Figures 2(a)-(d)**, the normalized concentration profiles of isomers v for various values of parameters are plotted. From these figures, it is inferred that the concentration v increases abruptly and reaches the steady-state value when $\rho \ge 5$. In **Figures 1(a)-(d) and 2(a)-(d)**, the values of dimensionless concentrations u and v for various values of γ_E, γ_E and τ and for $\varepsilon_1 < 1$ are reported and a satisfactory agreement with the available [9] estimates of Fleischmann *et al.* is noticed when τ is large. **Figures 3(a)-(d)** show the normalized dimensional concentration profile of w in ρ space calculated using Equation (18). The plot was constructed for various values $\gamma_{E2} = 0.1, 1$ and $\varepsilon_1 < 1$. From these figures it is confirmed that the value of the concentration profile of w increases when τ and γ_{E2} increases. Also from the **Figures 1(a)-(d) and 2(a)-(d)**, it is evident that the concentration of species HA and H increases when the radius of the electrode (r_S) decreases. Therefore, the use of the electrode of the small radius is clearly advangeous for the study of CE reaction mechanism. The concentration of specie A decreases when the radius of the electrode decreases. It reaches the steady state value when $\tau \le 1$. The dimensionless current $\log\psi$ versus τ for various values of γ_{E1} is given in **Figure 4**. From these figure, it is evident that the value of the current ψ decreases abruptly and reaches the steady-state value.

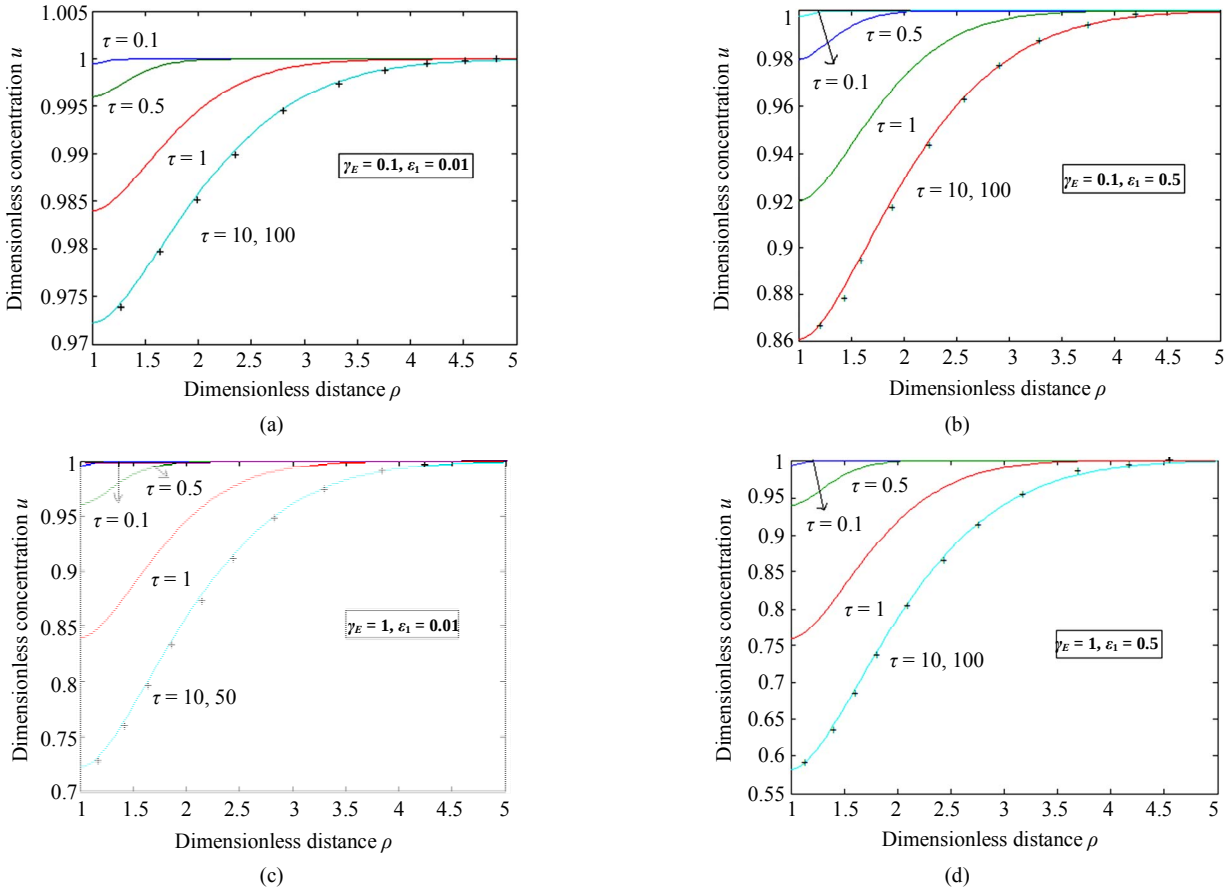


Figure 1. Normalized concentration u at microelectrode. The concentrations were computed using Equation (16) for various values of τ and for some fixed small value of γ_{E1} when the reaction/diffusion parameter and dimensionless diffusion coefficient (a) $\gamma_E = 0.1$, $\varepsilon_1 = 0.01$ (b) $\gamma_E = 0.1$, $\varepsilon_1 = 0.5$ (c) $\gamma_E = 1$, $\varepsilon_1 = 0.01$ (d) $\gamma_E = 1$, $\varepsilon_1 = 0.5$. The key to the graph: (__) represents Equation (16) and (+) represents Equation (23) [9].

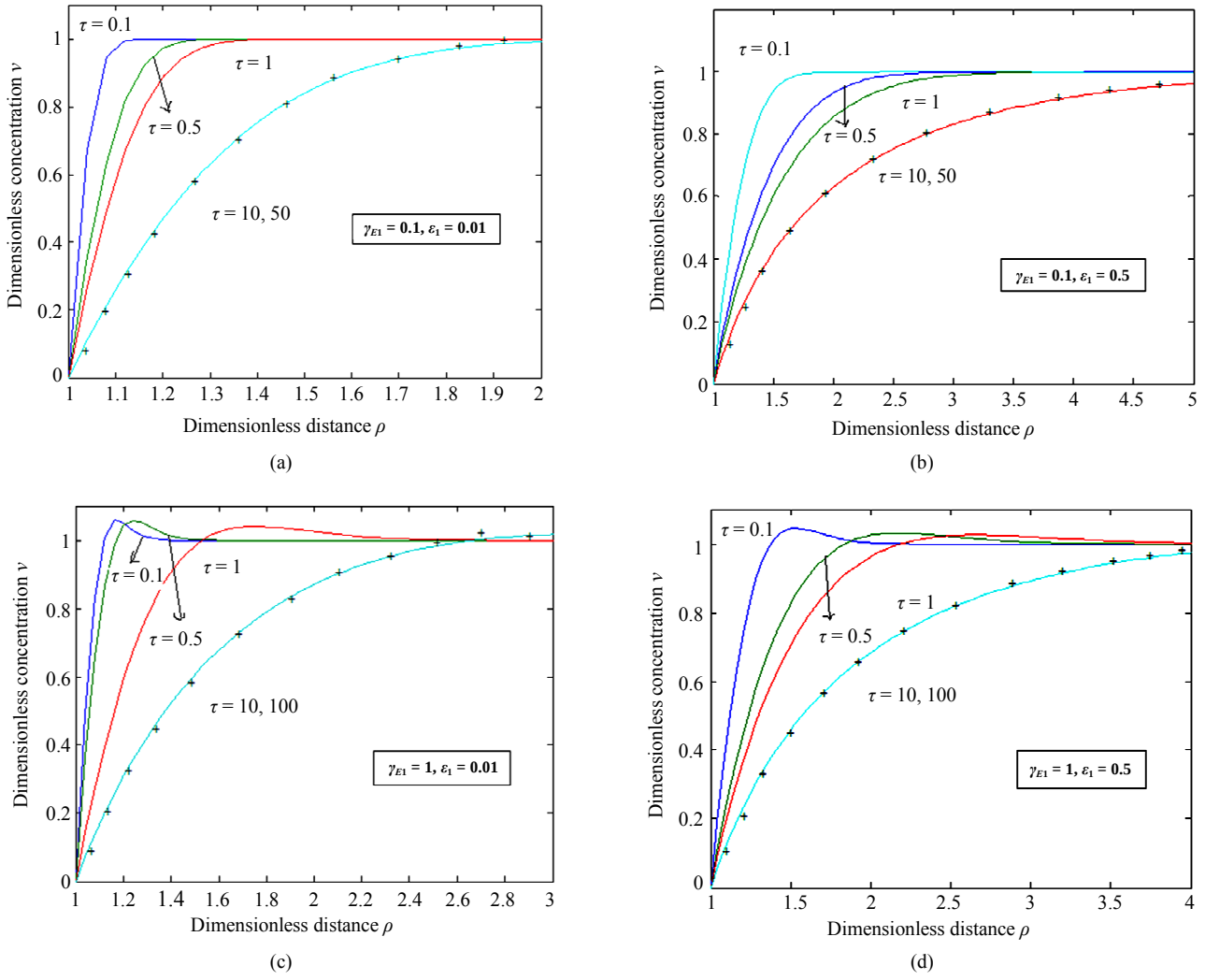
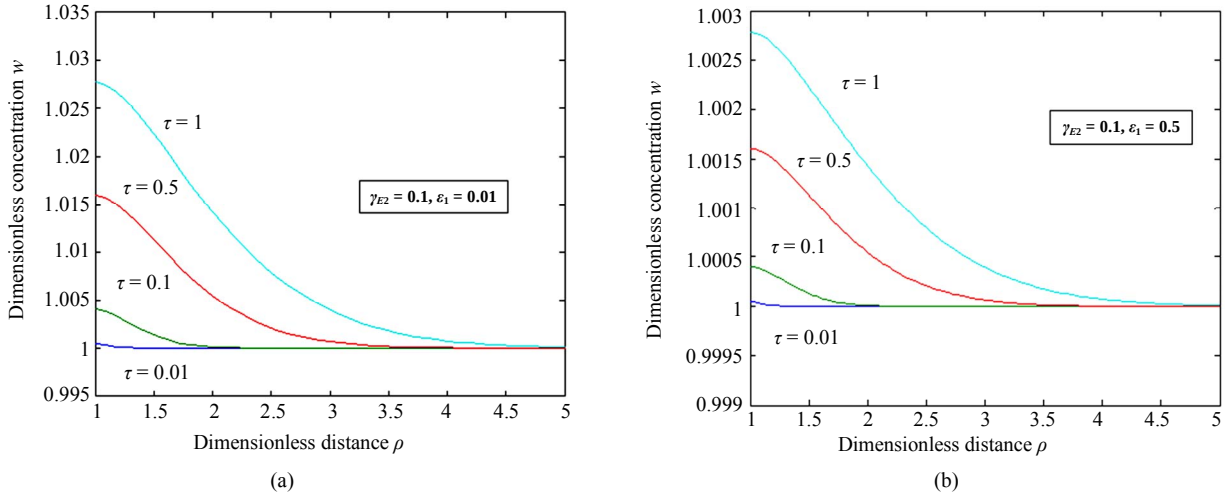


Figure 2. Normalized concentration v at microelectrode. The concentrations were computed using Equation (17) for various values of τ and for some fixed small value of γ_E when the reaction/diffusion parameter and dimensionless diffusion coefficient (a) $\gamma_{E1} = 0.1$, $\varepsilon_1 = 0.01$ (b) $\gamma_{E1} = 0.1$, $\varepsilon_1 = 0.5$ (c) $\gamma_{E1} = 1$, $\varepsilon_1 = 0.01$ (d) $\gamma_{E1} = 1$, $\varepsilon_1 = 0.5$. The key to the graph: (__) represents Equation (17) and (+) represents Equation (24) [9].



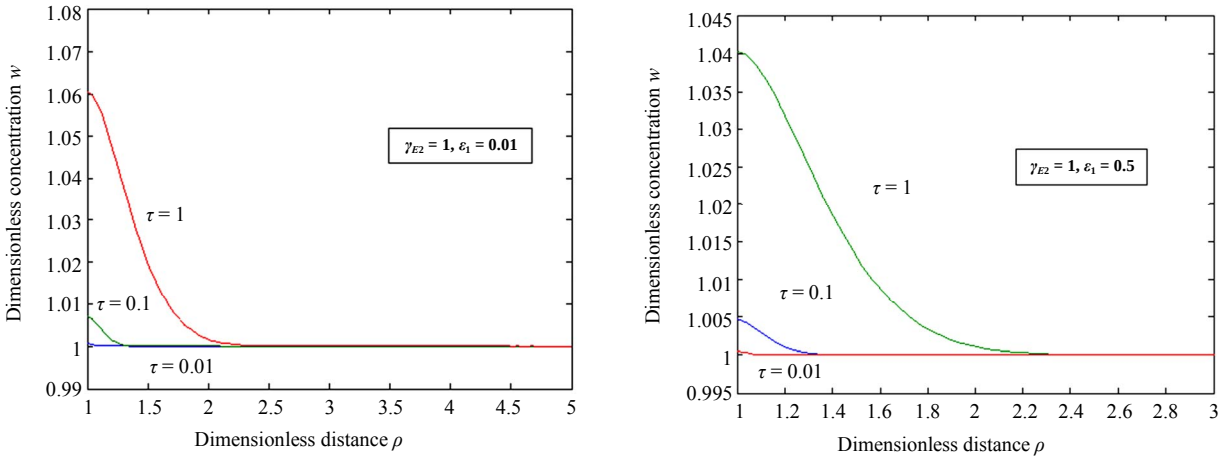


Figure 3. Normalized concentration w at microelectrode. The concentrations were computed using Equation (18) for various values of τ and for some fixed value of the reaction/diffusion parameter and dimensionless diffusion coefficient (a) $\gamma_{E2} = 0.1$, $\varepsilon_1 = 0.01$ (b) $\gamma_{E2} = 0.1$, $\varepsilon_1 = 0.5$ (c) $\gamma_{E2} = 1$, $\varepsilon_1 = 0.01$ (d) $\gamma_{E2} = 1$, $\varepsilon_1 = 0.5$.

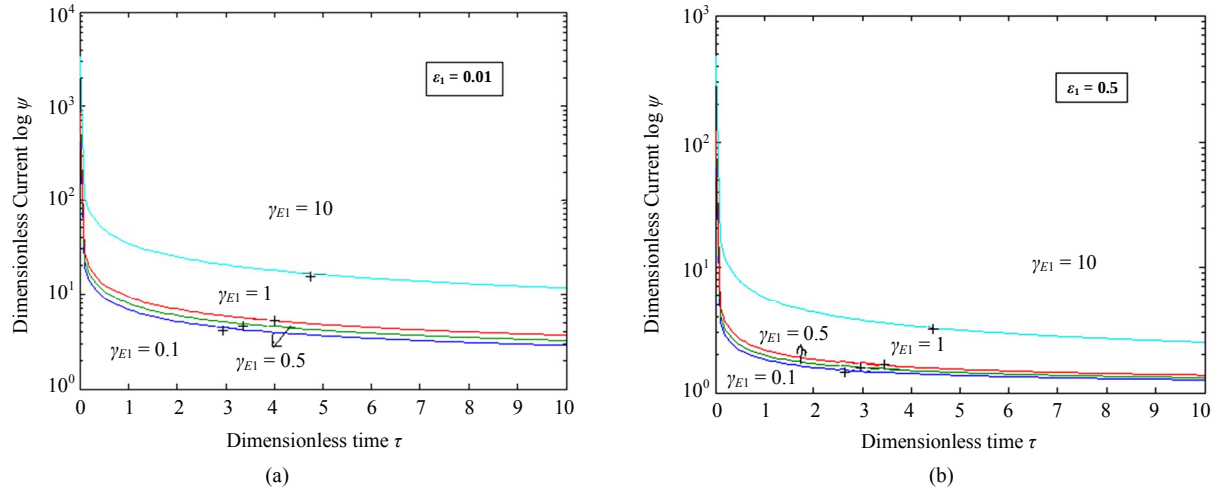


Figure 4. Variation of normalized non-steady-state current response $\log\psi$ as a function of the dimensionless time τ for various values of γ_{E1} and for the fixed values of (a) $\varepsilon_1 = 0.01$ (b) $\varepsilon_1 = 0.5$. The curves were computed using Equation (19). The key to the graph: (__) represents Equation (19) and (+) represents Equation (25) [9].

when the values of $\gamma_{E1} \geq 0.1$. Also, the value of the current ψ increases when the reaction diffusion parameter γ_{E1} increases

6. Conclusions

The time dependent non-linear reaction/diffusion equations for spherical microelectrodes for CE mechanism has been formulated and solved using HPM. The primary result of this work is simple approximate calculation of concentration profiles and current for all values of fundamental parameters. We have presented approximate solutions corresponding to the species HA, H and A in terms of the parameters of γ_E, γ_S, γ_{E1}, γ_{S1}, γ_{E2}, γ_{S2}, ε_1, ε_2 and τ based on the Homotopy perturbation method. This method can be easily extended to find the concentrations and current for all mechanism for all microelectrodes for various complex boundary conditions.

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Appendix A: Solution of the Equations (9) to (11) Using Homotopy Perturbation Method

In this Appendix, we indicate how Equations (16) to (18) in this paper are derived. To find the solution of Equations (9) to (11) we first construct a Homotopy as follows:

$$(1-p)\left[\frac{d^2u}{d\rho^2}+\frac{2}{\rho}\frac{du}{d\rho}-\frac{du}{d\tau}\right] + p\left[\frac{d^2u}{d\rho^2}+\frac{2}{\rho}\frac{du}{d\rho}-\frac{du}{d\tau}-\gamma_E u+\gamma_S vw\right]=0 \quad \text{(A1)}$$

$$(1-p)\left[\varepsilon_1\frac{d^2v}{d\rho^2}+\frac{2\varepsilon_1}{\rho}\frac{dv}{d\rho}-\frac{dv}{d\tau}\right] + p\left[\varepsilon_1\frac{d^2v}{d\rho^2}+\frac{2\varepsilon_1}{\rho}\frac{dv}{d\rho}-\frac{dv}{d\tau}+\gamma_{E1}u-\gamma_{S1}vw\right]=0 \quad \text{(A2)}$$

$$(1-p)\left[\varepsilon_2\frac{d^2w}{d\rho^2}+\frac{2\varepsilon_2}{\rho}\frac{dw}{d\rho}-\frac{dw}{d\tau}\right] + p\left[\varepsilon_2\frac{d^2w}{d\rho^2}+\frac{2\varepsilon_2}{\rho}\frac{dw}{d\rho}-\frac{dw}{d\tau}+\gamma_{E2}u-\gamma_{S2}vw\right]=0 \quad \text{(A3)}$$

and the initial approximations are as follows:

$$\tau=0;\ u_0=1;\ v_0=0;\ w_0=1 \quad \text{(A4)}$$

$$\rho=1;\ v_0=0;\ \left(du_0/d\rho\right)=0,\ dw_0/d\rho=0 \quad \text{(A5)}$$

$$\rho\to\infty;\ u_0=1;\ v_0=0;\ w_0=1 \quad \text{(A6)}$$

$$\tau=0;\ u_i=0;\ v_i=0;\ w_i=0 \quad \text{(A7)}$$

$$\rho=1;\ v_i=0;\ \left(du_i/d\rho\right)=0,\ \left(dw_i/d\rho\right)=0 \quad \text{(A8)}$$

$$\rho\to\infty;\ u_i=0;\ v_i=0;\ w_i=0 \qquad \forall i=1,2,\cdots \quad \text{(A9)}$$

and

$$\begin{cases} u=u_0+pu_1+p^2u_2+p^3u_3+\cdots \\ v=v_0+pv_1+p^2v_2+p^3v_3+\cdots \\ w=w_0+pw_1+p^2w_2+p^3w_3+\cdots \end{cases} \quad \text{(A10)}$$

Substituting Equation (A10) into Equations (A1) and (A2) and (A3) and arranging the coefficients of powers p, we can obtain the following differential equations.

$$p^0:\frac{d^2u_0}{d\rho^2}+\frac{2}{\rho}\frac{du_0}{d\rho}-\frac{du_0}{d\tau}=0 \quad \text{(A11)}$$

$$p^1:\frac{d^2u_1}{d\rho^2}+\frac{2}{\rho}\frac{du_1}{d\rho}-\frac{du_1}{d\tau}-\gamma_E u_0+\gamma_S v_0w_0=0 \quad \text{(A12)}$$

and

$$p^0:\varepsilon_1\frac{d^2v_0}{d\rho^2}+\frac{2\varepsilon_1}{\rho}\frac{dv_0}{d\rho}-\frac{dv_0}{d\tau}=0 \quad \text{(A13)}$$

$$p^1:\varepsilon_1\frac{d^2v_1}{d\rho^2}+\frac{2\varepsilon_1}{\rho}\frac{dv_1}{d\rho}-\frac{dv_1}{d\tau}+\gamma_{E1}u_0-\gamma_{S1}v_0w_0=0 \quad \text{(A14)}$$

and

$$p^0:\varepsilon_2\frac{d^2w_0}{d\rho^2}+\frac{2\varepsilon_2}{\rho}\frac{dw_0}{d\rho}-\frac{dw_0}{d\tau}=0 \quad \text{(A15)}$$

$$p^1:\varepsilon_2\frac{d^2w_1}{d\rho^2}+\frac{2\varepsilon_2}{\rho}\frac{dw_1}{d\rho}-\frac{dw_1}{d\tau}+\gamma_{E2}u_0-\gamma_{S2}v_0w_0=0 \quad \text{(A16)}$$

Subjecting Equations (A11) to (A16) to Laplace transformation with respect to τ results in

$$\frac{d^2\overline{u_0}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{u_0}}{d\rho}-s\overline{u_0}+1=0 \quad \text{(A17)}$$

$$\frac{d^2\overline{v_0}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{v_0}}{d\rho}-\frac{s}{\varepsilon_1}\overline{v_0}+\frac{1}{\varepsilon_1}=0 \quad \text{(A18)}$$

$$\frac{d^2\overline{w_0}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{w_0}}{d\rho}-\frac{s}{\varepsilon_2}\overline{w_0}+\frac{1}{\varepsilon_2}=0 \quad \text{(A19)}$$

$$\frac{d^2\overline{u_1}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{u_1}}{d\rho}-s\overline{u_1}-\frac{\gamma_E}{s}+\gamma_S\left(\frac{1}{s}-\frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho}\right)=0 \quad \text{(A20)}$$

$$\frac{d^2\overline{v_1}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{v_1}}{d\rho}-\frac{s}{\varepsilon_1}\overline{v_1}+\frac{\gamma_{E1}}{\varepsilon_1 s}-\frac{\gamma_{S1}}{\varepsilon_1}\left(\frac{1}{s}-\frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho}\right)=0 \quad \text{(A21)}$$

$$\frac{d^2\overline{w_1}}{d\rho^2}+\frac{2}{\rho}\frac{d\overline{w_1}}{d\rho}-\frac{s}{\varepsilon_2}\overline{w_1}+\frac{\gamma_{E2}}{\varepsilon_2 s}-\frac{\gamma_{S2}}{\varepsilon_2}\left(\frac{1}{s}-\frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho}\right)=0 \quad \text{(A22)}$$

Now the initial and boundary conditions become

$$\tau=0;\ u_0=1;\ v_0=0;\ w_0=1 \quad \text{(A23)}$$

$$\rho=1;\ v_0=0;\ \left(du_0/d\rho\right)=0,\ \left(dw_0/d\rho\right)=0 \quad \text{(A24)}$$

$$\rho\to\infty;\ u_0=1/s;\ v_0=1/s;\ w_0=1/s \quad \text{(A25)}$$

$$\tau=0;\ u_i=0;\ v_i=0;\ w_i=0 \quad \text{(A26)}$$

$$\rho=1;\ v_i=0;\ \left(du_i/d\rho\right)=0,\ \left(dw_i/d\rho\right)=0 \quad \text{(A27)}$$

$$\rho\to\infty;\ u_i=0;\ v_i=0;\ w_i=0 \qquad \forall i=1,2,\cdots \quad \text{(A28)}$$

where s is the Laplace variable and an overbar indicates a Laplace-transformed quantity. Solving equations (A17) to (A22) using reduction of order (see Appendix-B) for

solving the Equation (A20), and using the initial and boundary conditions (A26) to (A28), we can find the following results

$$u_0(\rho) = 1/s \tag{A29}$$

$$u_1(\rho) = \frac{\gamma_S \sqrt{\varepsilon_1} e^{\left(-\sqrt{s}(\rho-1)\right)}}{(\varepsilon_1 - 1)\rho\left(\sqrt{s}+1\right)} - \frac{\gamma_E}{s^2} + \frac{\gamma_S}{s^2} - \frac{\gamma_S \varepsilon_1 e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{\rho\sqrt{s}(\varepsilon_1 - 1)} + \frac{\gamma_S \varepsilon_1 e^{\left(-\sqrt{s}(\rho-1)\right)}}{(\varepsilon_1 - 1)\rho\sqrt{s}\left(\sqrt{s}+1\right)} \tag{A30}$$

and

$$v_0(\rho) = \frac{1}{s} - \frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho} \tag{A31}$$

$$v_1(\rho) = \frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{\rho}\left(\frac{\gamma_{S1}}{s^2} - \frac{\gamma_{E1}}{s^2}\right) + \frac{\gamma_{E1}}{s^2} - \frac{\gamma_{S1}}{s^2} - \frac{\gamma_{S1} e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{2\sqrt{\varepsilon_1}\sqrt{s}}(1/\rho - 1) \tag{A32}$$

and

$$w_0(\rho) = 1/s \tag{A33}$$

$$w_1(\rho) = \frac{\gamma_{E2}}{s^2} - \frac{\gamma_{S2}}{s^2} - \frac{\gamma_{S2}\,\varepsilon_1 e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{\rho\sqrt{s}\left(\varepsilon_2 - \varepsilon_1\right)} + \frac{\gamma_{S2}\sqrt{\varepsilon_1}\sqrt{\varepsilon_2}\; e^{\left(-\sqrt{s/\varepsilon_2}(\rho-1)\right)}}{\rho\left(\sqrt{s}+\sqrt{\varepsilon_2}\right)\left(\varepsilon_2 - \varepsilon_1\right)} + \frac{\gamma_{S2}\varepsilon_1\sqrt{\varepsilon_2}\; e^{\left(-\sqrt{s/\varepsilon_2}(\rho-1)\right)}}{\rho\left(\sqrt{s}+\sqrt{\varepsilon_2}\right)\sqrt{s}\left(\varepsilon_2 - \varepsilon_1\right)} \tag{A34}$$

According to the HPM, we can conclude that

$$u(\rho) = \lim_{p\to 1} u(\rho) = u_0 + u_1 + \cdots \tag{A35}$$

$$v(\rho) = \lim_{p\to 1} v(\rho) = v_0 + v_1 + \cdots \tag{A36}$$

$$w(\rho) = \lim_{p\to 1} w(\rho) = w_0 + w_1 + \cdots \tag{A37}$$

After putting Equations (A29) and (A30) into Equation (A35) and Equations (A31) and (A32) into Equation (A36) and Equations (A33) and (A34) into Equation (A37). Using inverse Laplace transform [33], the final results can be described in Equations (16) to (18) 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 B

In this Appendix, we derive the solution of Equation (A20) by using reduction of order. To illustrate the basic concepts of reduction of order, we consider the equation

$$\frac{\mathrm{d}^2 c}{\mathrm{d}\rho^2} + P\frac{\mathrm{d}c}{\mathrm{d}\rho} + Qc = R \tag{B1}$$

where P, Q, R are function of r. Equation (A20) can be simplified to

$$\frac{\mathrm{d}^2\overline{u_1}}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}\overline{u_1}}{\mathrm{d}\rho} - s\overline{u_1} - \frac{\gamma_E}{s} + \gamma_S\left(\frac{1}{s} - \frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho}\right) = 0 \tag{B2}$$

Using reduction of order, we have

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

and

$$R = \frac{\gamma_E}{s} - \gamma_S\left(\frac{1}{s} - \frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s\rho}\right) \tag{B3}$$

Let $$u = cv \tag{B4}$$

Substitute (B4) in (B1), if u is so chosen that

$$2\frac{\mathrm{d}c}{\mathrm{d}\rho} + Pc = 0 \tag{B5}$$

Substituting the value of P in the above Equation (A7) become

$$c = 1/\rho \tag{B6}$$

The given Equation (B3) reduces to

$$v'' + Q_1 v = R_1 \tag{B7}$$

where

$$Q_1 = Q - \frac{P^2}{4} - \frac{P'}{2} = 0,\;\; R_1 = \frac{R}{c} \tag{B8}$$

Substituting (B8) in (B7) we obtain,

$$v'' - sv = \frac{\gamma_E\rho}{s} - \frac{\gamma_S\rho}{s} + \gamma_S\left(\frac{e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{s}\right) \tag{B9}$$

Integrating Equation (B9) twice, we obtain

$$v = A\, e^{\sqrt{s}\rho} + B\, e^{-\sqrt{s}\rho} - \frac{\gamma_E\rho}{s^2} + \frac{\gamma_S\rho}{s^2} - \gamma_S\left(\frac{\varepsilon_1 e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{\sqrt{s}\left(\varepsilon_1 - 1\right)}\right) \tag{B10}$$

Substituting (B6) and (B10) in (B4) we have,

$$u = \frac{A\, e^{\sqrt{s}\rho}}{\rho} + \frac{B\, e^{-\sqrt{s}\rho}}{\rho} - \frac{\gamma_E}{s^2} + \frac{\gamma_S}{s^2} - \gamma_S \left(\frac{\varepsilon_1 e^{\left(-\sqrt{s/\varepsilon_1}(\rho-1)\right)}}{\rho\sqrt{s}\left(\varepsilon_1 - 1\right)} \right) \quad \text{(B11)}$$

Using the boundary conditions Equations (A27) and (A28), we can obtain the value of the constants A and B. Substituting the value of the constants A and B in the Equation (B11) we obtain the Equation (A30). Similarly we can solve the other differential Equations (A17), (A18), (A19), (A21) and (A22) using the reduction of order method.

Appendix C

Nomenclature

Symbols

c_{HA}	Concentration of the species HA (mole·cm^{-3})
c_{H}	Concentration of the species H (mole·cm^{-3})
c_{A}	Concentration of the species A (mole·cm^{-3})
c_{HA}^{∞}	Bulk concentration of the species HA (mole·cm^{-3})
c_{H}^{∞}	Bulk concentration of the species H (mole·cm^{-3})
c_{A}^{∞}	Bulk concentration of the species A (mole·cm^{-3})
D_{HA}	Diffusion coefficient of the species HA (cm^2·sec^{-1})
D_{H}	Diffusion coefficient of the species H (cm^2·sec^{-1})
D_{A}	Diffusion coefficient of the species A (cm^2·sec^{-1})
D	Diffusion coefficient (cm^2·sec^{-1})
R	Radial distance(cm)
T	Time (s)
k_1	Rate constant for the forward reactions (cm^3/mole·sec)
k_2	Rate constant for the backward reactions (cm^3/mole·sec)
r_S	Radius of spherical electrode (cm)
r	Distance in the radial direction (cm)
u, v, w	Dimensionless concentrations (dimensionless)
ρ	Dimensionless radial distance (dimensionless)
τ	Dimensionless time (dimensionless)
I_S	Current density at a sphere (ampere/cm^2)
A	Area of the spherical electrode (cm^2)
F	Faraday constant (C·mole^{-1})
n	Number of the electron (dimensionless)

Greek symbols

ε_1	Dimensionless diffusion coefficient (dimensionless)
ε_2	Dimensionless diffusion coefficient (dimensionless)
γ_E, γ_S, γ_{E1}, γ_{S1}, γ_{E2}, γ_{S2}	Dimensionless reaction/diffusion parameters (dimensionless)

