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

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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 \( k_1 \) and the reverse of this process is described by the rate constant \( k_2 \), 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

\[
A \rightleftharpoons 2B \quad B \pm e^- \rightarrow \text{products}
\]

has been chosen, with initial and boundary conditions corresponding to the potential step for all planar electrodes. Under steady-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]

\[
\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - k_1 a + k_2 b = 0 \quad (1)
\]

\[
\frac{\partial b}{\partial t} = D \frac{\partial^2 b}{\partial x^2} + k_1 a - k_2 b = 0 \quad (2)
\]

where \( a \) and \( b \) denote the concentration of the species \( A \) and \( B \); \( x \) and \( t \) stand for space and time, respectively. \( k_1 \) and \( k_2 \) are described the forward and...
backward rate constants respectively. The boundary conditions reduce to
\[ t = 0; \quad a = a_0; \quad b = b_0 \]  \[ x = 1; \quad a = a'; \quad b = b' \]  \[ x \to \infty; \quad a \to a_0; \quad b \to b_0 \]
where \( a_0 \) and \( b_0 \) are the bulk concentrations of the species \( A \) and \( B \), \( a' \) and \( b' \) denote the concentrations at electrode surface. The flux \( j \) can be described as follows:
\[ j = -D \frac{\partial b}{\partial x} \]
The current density is defined as:
\[ i = nFj \]
where \( n \) is the number of electrons and \( F \) is the Faraday constant.

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 differential equations in Laplace space are obtained:
\[ \frac{d^2\tilde{u}}{dx^2} - k_1\tilde{u} + k_2\tilde{v} - s\tilde{u} + 1 = 0 \]  \[ \frac{d^2\tilde{v}}{dx^2} + k_3\tilde{u} - k_4\tilde{v} - s\tilde{v} + 1 = 0 \]

Now the boundary conditions become
\[ X \to \infty; \quad u \to \frac{1}{s}; \quad v \to \frac{1}{s} \]
\[ X = 1; \quad u = m_1; \quad v = m_2 \]

The dimensionless current is as follows:
\[ j = \frac{il}{nFADb_0} = (\partial v/\partial X)_{x=1} \]
\[ \nu(X, T) \approx 1 + (m_2 - 1) \text{erfc} \left( \frac{X - 1}{2\sqrt{T}} \right) \]

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

\[ \left[ \frac{k_1 m_1}{2} - \frac{k_2 m_2}{2} \right](1 - X) \quad (20) \]

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 \( k_1 = k_4 \) and \( k_2 = k_3 \) 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

\[ \psi \approx \frac{0.56419}{\sqrt{T}} \frac{m_2}{\sqrt{T}} + 2 \sqrt{\frac{T}{\pi}} (0.05k_1m_1 - 0.5k_2m_2) \quad (21) \]

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 \( k_1, k_2, m_1 \) 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 \( \psi \) versus \( T \) for various values of \( k_1 \) 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 \( k_4 \) 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 \( k_2 = 0.005 \).](image1)

![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 \( k_2 = 5 \).](image2)
Figure 3. Normalized concentration $u$ at microelectrode. 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) $T = 10$.

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 $k_4 = 0.05$. 

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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 $k_2 = 10$.

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 $k_1 = 0.1, k_2 = 1$ and for various values of (a) $T = 0.1$; (b) $T = 1$; (c) $T = 10$.

differential 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-
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.

REFERENCES


The approximate solutions of Eqs.A1 and A2 are

$$\begin{align*}
\bar{u} & = \bar{u}_0 + p\bar{u}_1 + p^2\bar{u}_2 + p^3\bar{u}_3 + \ldots \quad (A5) \\
\bar{v} & = \bar{v}_0 + p\bar{v}_1 + p^2\bar{v}_2 + p^3\bar{v}_3 + \ldots \quad (A6)
\end{align*}$$

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

$$\begin{align*}
p^0 : & \quad \frac{d^2\bar{u}_0}{dx^2} - s\bar{u}_0 = 0 \quad (A7) \\
p^1 : & \quad \frac{d^2\bar{u}_1}{dx^2} - s\bar{u}_1 - k_1\bar{u}_0 + k_2\bar{v}_0 + 1 = 0 \quad (A8) \\
p^0 : & \quad \frac{d^2\bar{v}_0}{dx^2} + s\bar{v}_0 = 0 \quad (A9) \\
p^1 : & \quad \frac{d^2\bar{v}_1}{dx^2} - s\bar{v}_1 + k_3\bar{u}_0 - k_5\bar{v}_0 + 1 = 0 \quad (A10)
\end{align*}$$

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

$$\begin{align*}
\bar{u}_0(X,s) & = \frac{m_1}{s} e^{-s\bar{J}(x-1)} \quad (A11) \\
\bar{u}_1(X,s) & = \frac{1}{s} + \left[ k_2m_1 \int_{x}^{\bar{J}(x-1)} 2s^{3/2} e^{s\bar{J}(1-x)} \right] (1-X) - \frac{1}{s} e^{s\bar{J}(1-x)} \quad (A12) \\
\bar{v}_0(X,s) & = \frac{m_2}{s} e^{-s\bar{J}(x-1)} \quad (A13) \\
\bar{v}_1(X,s) & = \frac{1}{s} + \left[ k_5m_1 \int_{x}^{\bar{J}(x-x)} 2s^{3/2} e^{s\bar{J}(1-x)} \right] (X-1) - \frac{1}{s} e^{s\bar{J}(1-x)} \quad (A14)
\end{align*}$$

According to the Homotopy perturbation method, we can conclude that

$$\begin{align*}
\bar{u}_0(X) & = \lim_{p\to 1} \bar{u}(X) = \bar{u}_0 + \bar{u}_1 + \ldots \quad (A15) \\
\bar{v}_0(X) & = \lim_{p\to 1} \bar{v}(X) = \bar{v}_0 + \bar{v}_1 + \ldots \quad (A16)
\end{align*}$$

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 $u_i(x)$ and $v_i(x)$ be completely determined such that each term is determined the previous terms.
### APPENDIX B: NOMENCLATURE AND UNITS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Concentration of the species $A$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$b$</td>
<td>Concentration of the species $B$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>Bulk concentration of the species $A$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$b_0$</td>
<td>Bulk concentration of the species $B$</td>
<td>mole cm$^{-3}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Thickness of the planar electrode</td>
<td>cm</td>
</tr>
<tr>
<td>$\kappa_f$</td>
<td>Forward rate constant</td>
<td>sec$^{-1}$</td>
</tr>
<tr>
<td>$\kappa_b$</td>
<td>Backward rate constant</td>
<td>sec$^{-1}$</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Diffusion coefficient of the species $A$</td>
<td>cm$^2$sec$^{-1}$</td>
</tr>
<tr>
<td>$D_b$</td>
<td>Diffusion coefficient of the species $B$</td>
<td>cm$^2$sec$^{-1}$</td>
</tr>
<tr>
<td>$j$</td>
<td>Flux of the species</td>
<td>mole cm$^{-2}$sec$^{-1}$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons</td>
<td>None</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>sec</td>
</tr>
<tr>
<td>$u$</td>
<td>Normalized concentration of the species $A$</td>
<td>None</td>
</tr>
<tr>
<td>$v$</td>
<td>Normalized concentration of the species $B$</td>
<td>None</td>
</tr>
<tr>
<td>$J$</td>
<td>Dimensionless flux</td>
<td>None</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Dimensionless time</td>
<td>None</td>
</tr>
<tr>
<td>$k_1$, $k_2$, $k_3$ and $k_4$</td>
<td>Dimensionless rate constants</td>
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</tr>
<tr>
<td>$m_1$, $m_2$</td>
<td>Constant</td>
<td>None</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Dimensional current</td>
<td>None</td>
</tr>
</tbody>
</table>