Chronoamperometric current at ultramicrospheroidal electrodes for steady state EC' reactions - A two-point Pade' approximant

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The steady state chronoamperometric current for EC' reactions pertaining to ultramicroelectrodes is estimated using scattering analogue techniques for different ranges of rate constants. The general results valid for disc, sphere, oblate and prolate spheroidal geometries are reported. The polynomial expressions pertaining to two extreme limits of reaction rates are combined using a two-point Pade' approximant. Numerical estimates for current are reported and compared with existing approximate results, wherever available.

A simple procedure to estimate steady state chronoamperometric current for electron transfer reactions at spheroidal electrodes, using coordinate transformation is also provided.

1. Introduction

The coupling of mass transfer with surface reactions and migration occurs in diverse contexts such as heterogeneous catalysis, electrochemical transport phenomena, protein binding, etc. The theoretical analysis of such processes is rendered difficult on account of the nature of the boundary conditions. Among a variety of mathematical techniques employed to solve such mixed boundary value problems, mention may be made of (i) analysis using dual integral equations involving Bessel functions, (ii) replacing the stipulated exact boundary conditions by approximate versions, (iii) scattering analogue techniques and (iv) multidimensional integral equations and digital simulation procedures.

Ultramicroelectrodes of various geometries and dimensions have become increasingly popular in the past few decades on account of their lower interfacial capacitance, reduction in ohmic resistance, measurement of fast electrochemical reactions, etc. However, the analysis of current response, pertaining to ultramicroelectrodes is not straightforward on account of the mixed nature of the boundary value problem, i.e., one boundary condition is specified on the conducting part of the boundary which comprises the electrode surface while the other restriction is formulated on its insulating portion. In view of this, standard mathematical techniques such as separation of variables, integral transforms, substitutions, etc., become no longer applicable. In electrochemical transport problems involving ultramicroelectrodes, different geometries such as disc, ring, band, hemisphere, etc., have been employed to obtain current response in potential step experiments. However, satisfactory numerical results exist only for disc geometries, even for simple electron transfer reactions. The non-steady state diffusion current for ultramicrodisc electrodes has been estimated using Wiener Hopf factorisation and Pade approximations. Among various numerical techniques proposed to study ultramicroelectrodes, we may mention the Hopscotch algorithm, successive over-relaxation, conformal mapping versions, etc. However, the calculation of steady state current for EC' reactions at spheroidal ultramicroelectrodes has been found formidable and till date, no rigorous analysis is available. We note that spheroidal geometry encompasses disc, whisker, oblate and prolate spheres as special cases.

The purpose of this paper is to (i) derive accurate polynomial expressions pertaining to chronoamperometric current for EC' reactions at spheroidal ultramicroelectrodes, (ii) propose a two-point Pade' approximant for evaluating the same over the entire domain of reaction rates, (iii) indicate the analogy of steady state EC' reactions with non-steady state diffusion versions and (iv) obtain steady state current for simple electron transfer reactions at different ultramicroelectrode geometries using coordinate transformations. Our tour de force consists in employing the scattering analogue techniques, well known in electromagnetic theories and soil infiltration studies.
2 Formulation of the problem

The EC' reaction is represented as

\[ O + n e^{-} \underset{k_f}{\rightarrow} R \underset{k_b}{\rightarrow} \text{Products} \]  

where

\[ k_f \text{ and } k_b \]  

and \[ R + Z \rightarrow O + \text{Products} \]  

Let \( S_e \) and \( S_p \) refer to conducting and insulating regions respectively. The governing transport equation is as follows (cf Appendix A):

\[ \nabla^2 g = \alpha g \]  

where \( g(r) = \frac{1}{k_f C_{e_0}(r) - k_b C_{e_0}(r)} \)  

and \[ \alpha = \frac{a^2 k}{D_k} \]  

\[ \nabla^2 \] refers to the Laplacian operator, \( 'a' \) denotes the characteristic length associated with the geometry under consideration (\( 'a' \) may be identified as the radius for discs and spheres) while \( D_k \) is the diffusion coefficient of species \( R \). The mixed boundary conditions are given by

\[ g = 1 + K \int \frac{dg}{dz}; z = 0; r \in S_e \]  

\[ \frac{dg}{dz} = 0; z = 0; r \in S_p \]  

\[ g = 0 \text{ as } l r l \rightarrow \infty \]  

**K** is a dimensionless parameter representing the interplay between charge transfer and mass transfer rate constants given by

\[ K = a \left( k_f / D_0 + k_b / D_k \right) \]  

Since the quantity of interest in electrochemistry is in general, the flux vis-a-vis current, we write the latter as

\[ i = -nF D_0 C_{e_0} a \left( 1 + k_b D_0 / k_b D_k \right) \int \frac{dg}{dz} ds \]  

In the diffusion-limited regime, \( K \rightarrow \infty \) and hence

\[ i = -nF C_{e_0} a \int \frac{dg}{dz} ds \]  

while equation (6) becomes

\[ g = 1 \text{ on } z = 0; r \in S_e \]  

The above problem is isomorphic with soil-infiltration from spheroidal cavities of different geometries. Consequently, the expression for current at two extreme values of \( x = \alpha^{(0)} \) is written in a straightforward manner.

2.1 Chronoamperometric current at two limits of reaction rates

For small values of \( x \), the steady state current is given by

\[ i_0 = \sum_{n=0} \alpha_n (\omega) x^n \quad x \to 0 \]  

where \( i_0 \) is given by \( 2 \pi n F D_0 C_{e_0} \) while the aspect ratio \( \omega = b/a \). \( a \) and \( b \) denote respectively the length of the two semi-axis and that of the third axis.

The coefficients \( \alpha_0 \) to \( \alpha_n \) are as follows:

\[ \alpha_0 = \tau; \alpha_1 = \tau^2; \alpha_2 = -\frac{\tau}{3} \left( (\omega^2 - 1) / (\omega - \tau) + \omega + 3\tau \right) \]  

\[ \alpha_3 = \frac{\tau^2}{9} \left[ 4(\omega^2 - 1) - 6 \omega \tau + 9\tau^2 \right] \]  

\[ \alpha_4 = \left( \frac{\tau}{16} \right) \left[ (\omega^2 - 1)^2 \left( 92 - \frac{108\omega^2}{(\omega - \tau)^2} + 16(2\omega^2 + 1) \right) \right] \]  

\[ - 9 (25\omega^2 + 120\omega \tau - 29\omega + 100\tau - 160 (\omega - \tau)^2) \]  

For large values of \( x \), the current is given by

\[ i = -nF D_0 C_{e_0} a \left( 1 + k_b D_0 / k_b D_k \right) \int \frac{dg}{dz} ds \]  

We reiterate that the above coefficients \( \alpha_0 \) to \( \alpha_n \) are dependent in a general manner on the parameters \( \omega \) and
Comparison with existing approaches

The equivalence between steady state diffusion limited current for EC’ reactions and Laplace transformed transient current for disc electrodes has been exploited by Philips28 so as to report the first three terms of Eqs (13) and (15). Fleischmann et al.27 have obtained the first two terms of Eq. (13) by employing an equivalent sphere approximation for disc electrodes. This would imply that the estimation of steady state chronoamperometric current has now been made more accurate due to Eqs (13) and (15). Further, the current expressions for all other geometries (such as sphere, oblate and prolate spheroids, whisker etc.) too have been derived here for the first time spanning all values of dimensionless reaction rates.

2.3. Two-point Pade’ approximation

Pade’ approximants29 are now routinely employed in diverse contexts so as to overcome problems with slowly convergent or divergent power series expressions. In view of the easy implementation of the algorithm, this technique is widely analysed in phase transitions and critical phenomena30, virial equation of state31, quartic anharmonic oscillators32, transient electrochemical techniques39, etc. In the present context, partial information at two extreme values of the dimensionless reaction rates is available. Hence, it is imperative to construct a two-point Pade’ approximant using the coefficients \( \{a_n\} \) and \( \{c_n\} \) of Eqs (13) and (16). Analogous Pade’ approximants can be constructed using Eqs (13) and (15) for disc geometries (\( \omega = 0 \)).

The \([6/3]\) Pade’ approximant obtained using equations (13) and (16) is

\[
\frac{\frac{d}{dt}}{I_0} = \frac{P_0 + P_1 y + P_2 y^2 + P_3 y^3 + P_4 y^4 + P_5 y^5 + P_6 y^6}{1 + q_1 y + q_2 y^2 + q_3 y^3} \tag{18}
\]

where \( y = x^{\omega} \). The coefficients \( \{p_n\} \) and \( \{q_n\} \) are as follows: \( p_0 = a_0; p_1 = a_1 q_0; p_2 = c_1 c_0 + q_0 c_0; p_3 = c_1 + c_0 + q_0 c_0; p_4 = q_1 + c_0; p_5 = q_1 c_0 + q_0 c_0; p_6 = q_1 c_0 \). The coefficients \( q_1, q_2 \), and \( q_3 \) are obtained from the matrices.

\[
\begin{pmatrix}
q_1 \\
q_2 \\
q_3
\end{pmatrix} =
\begin{pmatrix}
c_1 & -a_0 & 0 \\
0 & -c_1 & a_0 \\
a_1 - c_0 & 0 & -c_1
\end{pmatrix}^{-1}
\begin{pmatrix}
0 \\
0 \\
c_0 - a_1
\end{pmatrix} \tag{19}
\]

The two-point Pade’ approximant given by Eq. 18 is applicable to different geometries of ultramicroelectrodes if appropriate values of \( \omega \) and \( \tau \) are substituted. As a case study, let us consider the hemispherical electrodes wherein \( \omega = 1 \). On account of the singularity behaviour of coefficients \( \{a_n\} \) when \( \omega = \tau = 1 \), we resort to the limits \( \omega \to 1 \) and \( \tau \to 1 \) so as to define
\[ \omega = 1 + \varepsilon \quad \ldots (20) \]

and
\[ \tau = 1 + \varepsilon / 3 - \varepsilon^2 / 45 + O (\varepsilon^3) \quad \ldots (21) \]

Hence the coefficients become
\[ a_0 = a_1 = 0.1; a_2 = -1/3; a_3 = 1/3; a_4 = -16/45; a_5 = 17/45 \]
\[ c_0 = 1/2; c_1 = 0.9961 \quad \ldots (22) \]

Consequently, the steady state current is
\[ \frac{i}{i_0} = 1 + 1.02y + 1.016y^2 + 1.512y^3 + 1.02y^4 + 0.508y^5 + 0.256y^6 \quad \ldots (23) \]

where \[ i_0 = 4\pi n F D C_{\text{hemi}} \] for hemispherical electrodes, \( y \) being equal to \( x^{1/3} \). Table 2 indicates the ratio \( i/i_0 \) estimated at different values of dimensionless reaction rates using Eq. (23) along with the values reported by Fleischmann et al.\(^7\). When the pseudofirst order rate constants are large, marked deviations from the estimate of Fleischmann et al. are noticed. It is interesting to note that the long time time expression (16) is reported in terms of \( x^{1/3} \) whereas the short time Eq. (13) is given in terms of \( x \). Consequently, the lowest order Pade' approximant is as given by Eq. (18) which requires only two terms of the associated power series expansions.

Further, Oldham\(^9\) has reported the ratio \( i/i_0 \) for hemispherical electrodes as
\[ \frac{i}{i_0} = 1 + x \quad \ldots (24) \]

when the dimensionless reaction rate \( x \) is small. For other geometries such as oblate, prolate and whisker electrodes, the coefficients \( p_i, q_i \) along with the coefficients of the given series are reported in Table 3. Table 4 provides steady state chronoamperometric current for EC' reactions pertaining to the above geometries - hitherto unavailable. To place the above analysis in the proper perspective, we reiterate that the calculation of steady state current for spherical electrodes even when the chemical reaction (2) is absent (i.e., simple electron transfer reactions and not EC' mechanism) is rendered difficult. The existing formalisms due to Oldham\(^7\) employing gudermannian functions and Birke\(^35\) using orthogonal curvilinear coordinates are quite tedious. A simple analysis to obtain the steady state current for spherical electrodes, using coordinate transformation is presented in Appendix B. This procedure has been outlined by Phillip\(^35\) in the study of soil infiltration from spheroidal cavities.

2.4. Non-steady state current for diffusion limited electron transfer reactions

The mathematical formalism of steady state current for EC' reactions is equivalent to the Laplace-transformed transient current for diffusion limited electron transfer reactions at ultramicroelectrodes. Consequently, Eqs (13, 15) and (16) become applicable to the estimation of current at ultramicroelectrodes by relating \( \tau \) with Laplace-transformed surface concentrations. Thus, the methodology advocated herein leads to accurate expressions for transient current at spheroidal ultramicroelectrodes, pertaining to simple electron transfer reactions.

3. Perspectives

As indicated earlier, mixed boundary conditions arise naturally in the case of transport at ultramicroelectrodes. Among various geometries of these, disc electrodes have been thoroughly investigated \( \text{albeit} \) for simple electron transfer reaction schemes. For EC' reactions, steady state chronoamperometric current expressions have only recently been derived, even for disc electrodes. However, judicious combinations of numerical and analytical ap-
Table 3 - The coefficients of Pade' approximant in Eq.(18) along with coefficients in Eqs (13) and (16).

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
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<tbody>
<tr>
<td>P₀</td>
<td>0.677</td>
<td>0.716</td>
<td>0.827</td>
<td>1.315</td>
<td>2.137</td>
<td>3.324</td>
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<td>6.231 x 10⁻¹</td>
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<td>8.815</td>
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<td>-13.783</td>
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<td>P₂</td>
<td>-0.045</td>
<td>2.967 x 10⁻¹</td>
<td>0.494</td>
<td>2.214</td>
<td>12.014</td>
<td>-42.269</td>
<td>-18.678</td>
</tr>
<tr>
<td>P₃</td>
<td>+0.486</td>
<td>0.514</td>
<td>0.875</td>
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<td>16.875</td>
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<td>-24.812</td>
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<tr>
<td>P₄</td>
<td>-9.615 x 10⁻¹</td>
<td>4.458 x 10⁻¹</td>
<td>0.538</td>
<td>2.422</td>
<td>18.837</td>
<td>-101.017</td>
<td>-74.645</td>
</tr>
<tr>
<td>P₅</td>
<td>-3.332 x 10⁻¹</td>
<td>2.073 x 10⁻¹</td>
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<td>0.842</td>
<td>2.811</td>
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<td>1.84</td>
<td>3.31</td>
<td>5.32</td>
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<td>2.85</td>
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<tr>
<td>q₂</td>
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<td>q₃</td>
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<td>10.76</td>
<td>12.76</td>
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<tr>
<td>a₀</td>
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<td>1.33</td>
<td>4.57</td>
<td>11.05</td>
<td>29.33</td>
<td>74.65</td>
</tr>
<tr>
<td>a₁</td>
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<td>0.51</td>
<td>0.68</td>
<td>1.73</td>
<td>4.57</td>
<td>11.05</td>
<td>29.33</td>
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<tr>
<td>c₀</td>
<td>0.21</td>
<td>0.34</td>
<td>1.58</td>
<td>2.91</td>
<td>4.62</td>
<td>7.34</td>
<td>12.74</td>
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Table 4 - Dimensionless chronoamperometric steady state current for EC' reactions pertaining to different ultramicrospheroidal electrodes estimated using Eq. (18) and Pade' coefficients of Table 3.

<table>
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<th>x</th>
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<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
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</thead>
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<td>0.8270</td>
<td>1.0000</td>
<td>1.3152</td>
<td>2.1370</td>
<td>3.3241</td>
<td>5.4158</td>
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<td>0.7666</td>
<td>0.8935</td>
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<td>1.5864</td>
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<td>0.9173</td>
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<td>1.9145</td>
<td>3.1995</td>
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<tr>
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<td>1.2269</td>
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<td>50</td>
<td>25.3333</td>
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</tbody>
</table>
proaches have been investigated to make partial breakthroughs in what is essentially a tedious exercise. The most comprehensive approach to the study of diffusion at ultramicroelectrodes is due to Phillips and Janson. An alternate approach is to exploit results known elsewhere in mixed boundary value problems and translate them into electrochemical literature. A particularly illuminating example is the soil infiltration studies wherein accurate polynomial expressions have been reported for transient and steady state EC' reactions using scattering analogue techniques. This mapping enables the analysis of steady state EC' reactions as well as non-steady diffusion limited electron transfer schemes at ultramicroelectrodes. Consequently, scattering analogue technique seems to be a powerful methodology to obtain accurate polynomial expressions for current pertaining to diffusional electrochemical transport studies.

Acknowledgement
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Appendix A

For the EC' reaction sequence represented by

\[ O + ne^+ \overset{k_i}{\rightleftharpoons} R \overset{k_{th}}{\rightarrow} \text{O+Products} \]  

\[ \text{with } R+Z \overset{k}{\rightarrow} O+\text{Products} \]  

the diffusion equation is given as

\[ D_o \nabla^2 C_o = -k C_r \]  

\[ D_r \nabla^2 C_r = k C_r \]  

along with the boundary conditions

\[ D_o \ell \frac{\partial C_o}{\partial z} = -D_r \frac{\partial C_r}{\partial z} = k_{i} C_{o} - k_{th} C_{r} \text{ at z=0, r}\in S_k \]  

\[ \frac{\partial C_o}{\partial z} = -\frac{\partial C_r}{\partial z} = 0 \text{ at r=0, z}\in S_{r} \]  

\[ C_o \rightarrow C_{o}^{i(0)} \text{ and } C_r \rightarrow 0 \text{ as } r\rightarrow \infty \]  

The heterogeneous electron transfer rate constants \( k_i \) and \( k_{th} \) are potential-dependent via Butler-Volmer equation. The dimensionless concentration \( g(r) \) is defined as

\[ g(r) = 1 - \left[ \frac{k_{i} C_{o} - k_{th} C_{r}(r)}{k_{i} C_{o}^{i(0)}} \right] \]

with

\[ \alpha = a^2 k/D_{r} \]

We further define the ratio of charge transfer and mass transfer rate constants via \( K \) as

\[ K = a (k_{i}/D_{o} + k_{th}/D_{r}) \]

where \( a \) denotes the characteristic length of the geometry (a denotes radius for discs and spheres and equatorial radius for prolate and oblate spheroids)

\[ D_{o} C_{o}(r) + D_{r} C_{r}(r) = D_{o} C_{o}^{i(0)} \]

The above considerations lead to Eqs (6) - (8) of the text. The parameter \( \alpha \) indicates the rate of regeneration of the bulk species relative to the time constant of diffusion over distance 'a'.

Appendix B

In this Appendix, we report a simple method of deriving steady state diffusion limited current at spheroidal electrodes, using co-ordinate transformation. (This procedure is identical with that demonstrated by Philip for soil infiltration). In this case, \( \alpha = 0 \) since the chemical reaction is absent and \( g=1 \), \( K \) being \( \infty \). Consequently, the transport equation and the boundary conditions are:

\[ \nabla^2 g = 0 \]

\[ g = 1 \quad z = 0; \quad r\in S_{r} \]

\[ g = 0 \quad r\rightarrow \infty \]

The spheroidal electrodes have two semi-axes of length \( a \) and another third semi-axis of length \( b \). The
aspect ratio \( \omega = b/a \) takes values depending upon the particular spheroid geometry under consideration. The spheroid surface is represented in cylindrical coordinates as

\[
\frac{r^2}{a^2} + \frac{z^2}{b^2} = 1
\]  

... (B4)

The prolate spheroidal co-ordinates \( \eta, \phi \) are related as

\[ r = \lambda \sinh \eta \sin \phi \]  

... (B5)

\[ z = \lambda \cosh \eta \cos \phi \]  

... (B6)

and

\[ \lambda^2 = b^2 - a^2 \]  

... (B7)

By using separation of variables, (B1) becomes

\[
\frac{d^2 g}{d\eta^2} + \left( \coth r \right) \frac{dg}{d\eta} = 0
\]  

... (B8)

whose solution is

\[ g = C_1 + C_2 \ln \coth (\eta/2) \]  

... (B9)

where \( C_1 \) and \( C_2 \) are integration constants whose values follow from the Eqs (B2) and (B3) as

\[ C_1 = 0 \quad \text{and} \quad C_2 = 1/\cosh^1 (b/a) \]  

... (B10)

Further, \( \eta \to \infty \) as \( \rho \to \infty \) being \( (r^2 + z^2)^{1/2} = \rho \). Hence \( \rho^2 = \lambda^2 \cosh^2 \eta \) and \( d\eta/d\rho = \rho^{-1} \).

The steady state current for prolate spheroidal geometry is

\[
i = \frac{i}{\eta \cosh \omega^0} \left( \lim_{\eta \to \infty} 4\pi \left( \frac{dg}{d\eta} \right) \right)
\]  

... (B11)

Equation (B9) leads to

\[
\left( \frac{dg}{d\eta} \right) = -\frac{\lambda\rho^{-1}}{\cosh^{-1} (b/a)}
\]  

... (B12)

Hence

\[
i = \frac{i}{\eta \cosh \omega^0} \left( \lim_{\eta \to \infty} 4\pi \left( \frac{dg}{d\eta} \right) \right) = \frac{4\pi (b^2 - a^2)^{1/2}}{\cosh^{-1/2} (b/a)}
\]  

... (B13)

Eq. (B13) is identical with Eq. (21) of Oldham et al.\(^{37} \)

and is consistent with Eq. (19) of Birke\(^{35} \)

Oblate spheroids

The co-ordinates \( \eta, \phi \) are now given as

\[ r = \lambda \cosh \eta \sin \phi \]  

... (B14)

\[ z = \lambda \sinh \eta \cos \phi \]  

... (B15)

As in the earlier prolate case, we obtain

\[
d^2 g + (\tanh \eta) \frac{dg}{d\eta} = 0
\]  

... (B16)

whose solution, taking into account the boundary conditions is

\[ g = \cot^1 (\sinh \eta)/\cos^1 (b/a) \]  

... (B17)

The steady state current becomes

\[ i = \frac{4\pi n F D C_o^{(b)}}{\ln (2\omega)} \]  

... (B18)

where \( i \) is \( 4\pi n F D C_o^{(b)} a \) for oblate spheroidal geometries.

(B18) is identical with Eq. (21) of Oldham et al.\(^{37} \).

Disc and whisker electrodes

For disc electrodes \( \omega = 0 \) and Eq. (B18) yields \( i = 8n F D a \) – a well-known result. Whisker electrodes refer to prolate hemispheroidal geometries in which the aspect ratio exceeds 6.3 and \( \omega \to \infty \). Noting that \( \cosh^{-1} (b/a) = \ln [(\omega + \omega^2 - 1)^{1/2}] \), we obtain from Eq. (B13)

\[ i = \frac{4\pi n F D C_o^{(b)}}{b} b \ln (2\omega) \]  

... (B19)

which is identical with equation (27) of Oldham et al.\(^{37} \).

List of symbols:

\[ a \] = Characteristic length of the geometrical shape; equals radius for discs and spheres; for oblate and prolate geometries a denotes the horizontal equatorial radius.

\[ b \] = Length of the vertical third semi-axis.

\[ C_o, C_n \] = Surface concentrations of O and R.

\[ C_\infty \] = Concentration of O.

\[ D_C, D_R \] = Diffusion coefficient of O and R.

\[ g \] = Dimensionless concentration.

\[ k, k_n \] = Forward and backward electron transfer rate constants.
k = Pseudo first order rate constant for the bulk reaction
K = Dimensionless ratio of mass transfer and charge transfer rate constants
\( p_1, p_2 \) = Coefficients of Pade' approximant
r = Radial distance in cylindrical co-ordinates
S_k, S_r = Conducting electrode surface and insulating planar region
z = Direction normal to the plane
\( \alpha \) = Dimensionless bulk reaction coefficient.
\( \omega \) = Aspect ratio (b/a)
\( \tau \) = Steady state limit
\( \eta, \theta \) = Spheroidal co-ordinates

References