Diffusion at Ultramicro Disk Electrodes: Chronoamperometric Current for Steady-State Ec′ Reaction Using Scattering Analogue Techniques

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An accurate polynomial expression for the steady-state current in the case of first-order EC′ reaction is reported using scattering analogue techniques for ultramicro disk electrodes. When the reaction rate is small, seven terms of diffusion-limited current are reported, and when it is large, five terms of the same are reported. A two-point Padé approximant is derived for all values of reaction rates. By a proper transcription of variables, the methodology is extended to derive chronoamperometric current for diffusion-controlled processes, and excellent agreement with digital simulation data is noticed.

1. Introduction

Microelectrodes are increasingly being used to perform a variety of electrochemical measurements.[1] However, many applications of planar microelectrodes of different shapes are impeded by lack of adequate theoretical description of their behavior. The origin of this difficulty lies in the existence of mixed boundary conditions; i.e., one boundary condition is specified on that part of the boundary comprising the electrode(s), while the other is formulated on the insulating portion of the boundary surrounding the electrode(s).[1] The study of such mixed boundary value problems is a formidable task since standard techniques for solving partial differential equations, such as separation of variables, integral transforms, substitution methods, etc., are no longer valid. Nevertheless, the hitherto available techniques for the study of mixed boundary value problems in various contexts such as electrostatic potential theory,[2] heat tranfer,[3] and soil infiltration[4] fall into three categories: (1) explicit formulas consisting of series or integral representations; (2) asymptotic solutions[5−11] consisting of a formal series which become increasingly accurate at the origin and at the infinity; (3) numerical approaches[12−19] based on multidimensional integral equations, digital simulation procedures, etc.

Ultramicroelectrodes offer several advantages in electrochemical measurements[1] such as lower interfacial capacitance, smaller time constants, reduced ohmic drop, enhanced current density, etc. The most commonly used ultramicroelectrode in analytical and molecular electrochemistry involves disk geometry, because of its easier fabrication as well as feasibility for controlled cleaning of their surfaces through simple grinding/polishing procedures.[20] Further, for quantitative mechanistic investigations, measurement of steady-state current of various radii of disk electrodes is one of the easiest electrochemical methods. The methods to simulate current at microdisk electrodes can also be employed in obtaining current pertaining to scanning electrochemical microscopy.[21−23] In this technique the response of a microdisk electrode is modified by the presence of a substrate within the diffusion layer arising from electrolysis. However, these advantages are earned at the expense of enhanced theoretical difficulties in solving diffusion equations at these electrodes. Thus, it is essential to have analytical expressions to describe the current at electrodes of this geometry.

The relation between disk-shaped and spherical microelectrodes fails in transient techniques such as chronoamperometry[24] and cyclic voltammetry.[25] It also breaks down when chemical kinetic schemes are coupled to electron-transfer reactions.[6,20] The transient response of the ultramicrodisk electrodes has been the subject of many studies.[25] These have employed a wide range of analytical,[6,26−30] semianalytical,[13,19] and finite-difference numerical methods.[17,25 31−33] Further a narrow range of predominantly first-order chemical reactions such as E, CE, EC, EC′, ECE, Disp1, and EC_2E have also been studied.[34,35,40] Some of the range of algorithms such as strongly implicit procedure (SIP),[36] multigrid,[37] hopscotch method,[18,35] alternating direction implicit (ADI) method,[32] successive over-relaxation (SOR) with ADI methods,[38] conformal mapping,[18,30,39] etc., are used to treat electrochemical reactions with coupled homogeneous chemical reactions occurring at ultramicroelectrodes. Recently, Alden and Compton[40] have used ILU (incomplete LU factorization) preconditioned Krylov subspace methods with conformal mapping to simulate the steady-state response of microdisk and hemispherical electrodes when the influence of homogeneous and heterogeneous kinetics is also involved. There are, as yet, no analytical expressions for the steady-state transport-limited current to spherical electrodes for either the EC_2E or DISP2 mechanisms.[40] Also in the EC′ reaction no single analytical expression valid for all reaction rates pertaining to disk electrodes is available.

The purpose of this article is to derive accurate polynomial expressions for diffusion-limited current at disk microelectrodes with a pseudo-first-order EC′ reaction, using the scattering analogue technique[41] originally proposed in soil infiltration studies. A two-point Padé approximant for the steady-state diffusion-limited current is subsequently reported, and excellent agreement with digital simulation data is noticed. By exploitation of the analogy with the non-steady-state diffusion-limited case, expressions for the transient chronoamperometric current at ultramicrodisk electrodes are also provided.

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2. Analysis of Steady-State EC′ Reactions at Ultramicro Disk Electrodes

Consider the steady-state current for a microdisk electrode of radius a wherein the electron-transfer reaction

$$\mathrm{O(soln)} + ne^- \underset{k\mathrm{b}}{\overset{k\mathrm{f}}{\rightleftharpoons}} \mathrm{R(soln)} \tag{1a}$$

occurs at the electrode surface and there is a pseudo-first-order reaction

$$\mathrm{R(soln)} \xrightarrow{k} \mathrm{O(soln)} \tag{1b}$$

regenerating O from R in solution. Let us denote the pseudo-first-order homogeneous rate constant by k and the bulk concentration of species O and R by c_O and c_R and their diffusion coefficients by D_O and D_R. Assume that the bulk concentration of species R is zero, and that of species O is c_O^b. The governing equations and boundary conditions are as follows:

$$D_\mathrm{O}\nabla^2 c_\mathrm{O} = -kc_\mathrm{R} \tag{2a}$$

$$D_\mathrm{R}\nabla^2 c_\mathrm{R} = -kc_\mathrm{R} \tag{2b}$$

$$D_\mathrm{O}\frac{\partial c_\mathrm{O}}{\partial z} = -D_\mathrm{R}\frac{\partial c_\mathrm{R}}{\partial z} = k_\mathrm{f}c_\mathrm{O} - k_\mathrm{b}c_\mathrm{R} \qquad z = 0,\ |\boldsymbol{r}| < a \tag{2c}$$

$$\frac{\partial c_\mathrm{O}}{\partial z} = \frac{\partial c_\mathrm{R}}{\partial z} = 0 \qquad z = 0,\ |\boldsymbol{r}| > \mathrm{a} \tag{2d}$$

$$c_\mathrm{R} \to 0,\ c_\mathrm{O} \to c_\mathrm{O}^\mathrm{b} \text{ as } |\boldsymbol{r}| \to \infty \tag{2e}$$

The chronoamperometric current is given by

$$i = nfD_\mathrm{O}\int_A \frac{\partial c_\mathrm{O}}{\partial z}\,\mathrm{d}S \tag{3}$$

where F is the Faraday constant, A represents the disk $z = 0$, $|\boldsymbol{r}| < a$, and dS is an element of surface area. For convenience, a function f given by

$$f = D_\mathrm{O}c_\mathrm{O} + D_\mathrm{R}c_\mathrm{R} \tag{4}$$

is also introduced. From eqs 2a,b, it is seen that f satisfies Laplace's equation in $z > 0$, while, from eqs 2c,d, $\partial f/\partial z$ is seen to be zero everywhere on $z = 0$, and from eq 2e, $f \to D_\mathrm{O}c_\mathrm{O}^\mathrm{b}$ as $|\boldsymbol{r}| \to \infty$. Thus, we deduce that f equals $D_\mathrm{O}c_\mathrm{O}^\mathrm{b}$ everywhere. Hence

$$D_\mathrm{O}c_\mathrm{O} + D_\mathrm{R}c_\mathrm{R} = D_\mathrm{O}c_\mathrm{O}^\mathrm{b} \tag{5}$$

By defining dimensionless parameters g, α, and K as

$$g = 1 - (k_\mathrm{f}c_\mathrm{O} - k_\mathrm{b}c_\mathrm{R})/k_\mathrm{f}c_\mathrm{O}^\mathrm{b} \tag{6}$$

$$\alpha = a^2k/D_\mathrm{R} \qquad K = (D_\mathrm{O}{}^{-1}k_\mathrm{f} + D_\mathrm{R}{}^{-1}k_\mathrm{b})a \tag{7}$$

we obtain the dimensionless diffusion equation and boundary conditions as

$$\nabla^2 g = \alpha g \tag{8a}$$

$$g = 1 + K^{-1}\frac{\partial g}{\partial z} \qquad z = 0,\ |\boldsymbol{r}| < 1 \tag{8b}$$

$$\frac{\partial g}{\partial z} = 0 \qquad z = 0,\ |\boldsymbol{r}| > 1 \tag{8c}$$

$$g \to 0 \text{ as } |\boldsymbol{r}| \to \infty \tag{8d}$$

In terms of g, the required expression for current is

$$i = -nFc_\mathrm{O}^\mathrm{b}D_\mathrm{O}a(1 + D_\mathrm{O}k_\mathrm{b}/D_\mathrm{R}k_\mathrm{f})^{-1}\int_\mathrm{A}\frac{\partial g}{\partial z}\,\mathrm{d}S \tag{9}$$

where A represents the disk $z = 0$, $|\boldsymbol{r}| < 1$ in nondimensional variables. We restrict attention to the diffusion-limited regime, i.e., K→ ∞, and hence replace the condition (8b) by

$$g = 1 \qquad z = 0,\ |\boldsymbol{r}| < 1 \tag{10}$$

Equations 8c and 10 are the mixed boundary conditions, as they represent different domains of the disk geometry. However, the steady-state diffusion-limited current i_0 for an inlaid microdisk electrode, in the absence of the chemical reaction, i.e., when $\alpha = 0$, is

$$i_0 = 4nFc_\mathrm{O}^\mathrm{b}D_\mathrm{O}a(1 + D_\mathrm{O}k_\mathrm{b}/D_\mathrm{R}k_\mathrm{f})^{-1} \tag{11}$$

Let

$$x = \alpha^{1/2} = a(k/D_\mathrm{R})^{1/2} \tag{12}$$

The application of the scattering analogue technique employed in soil infiltration studies[41] to analyze mixed boundary value problems of identical nature yields highly accurate polynomial expression at two extreme limits of x. The analytical formula for current is then given by (cf. Appendix)

$$i/i_0 \approx \sum_{n=0}^{6} a_n x^n \qquad x \to 0 \tag{13}$$

where i_0 is given by (11) and

$$\begin{gathered} a_0 = 1 \qquad a_1 = 2/\pi \qquad a_2 = 4/\pi^2 - {}^1/_3 \\ a_3 = \frac{2}{\pi}(4/\pi^2 - {}^4/_9) \qquad a_4 = \frac{16}{\pi^4} - \frac{20}{9\pi^2} + \frac{1}{15} \\ a_5 = \frac{2}{\pi}\left(\frac{16}{\pi^4} - \frac{8}{3\pi^2} + \frac{71}{675}\right) \\ a_6 = \frac{64}{\pi^6} - \frac{112}{9\pi^4} + \frac{448}{675\pi^2} - \frac{2}{315} \end{gathered} \tag{14}$$

The numerical values of a_n (n ≥ 1) are as follows:

$$\begin{gathered} a_1 = 0.6366 \qquad a_4 = 0.005\,764 \\ a_2 = 0.071\,95 \qquad a_5 = -0.000\,477 \\ a_3 = -0.024\,93 \qquad a_6 = -0.000\,286 \end{gathered} \tag{15}$$

Similarly, when the dimensionless reaction rate x is large, we obtain

$$i/i0 = \sum_{n=0}^{4} b_n x^{1-n} \qquad x \to \infty \tag{16}$$

TABLE 1: Steady-State Diffusion-Limited Current i/i_0 for Different Reaction Rates in the Case of EC′ Reactions at Ultramicro Disk Electrodes[a]

a^2k/D_R (=x)	[5/4] Padé approximation eq 21	Phillips et al.[11] small x	Phillips et al.[11] large x	Oldham et al.[46] (adopted to disk electrode)	Fleischmann et al.[47] (equiv sphere approximtn)	simulation of Lavagnini et al.[48] (hopscotch method)
1×10^{-4}	1.006	1.006 (0.00)		1.006 (0.00)	1.008 (0.20)	1.010 (0.40)
1×10^{-3}	1.020	1.020 (0.00)		1.020 (0.00)	1.025 (0.49)	1.023 (0.29)
1×10^{-2}	1.064	1.065 (0.09)		1.064 (0.00)	1.079 (1.41)	1.066 (0.19)
1×10^{-1}	1.208	1.209 (0.08)		1.201 (0.25)	1.248 (3.31)	1.209 (0.08)
1	1.689	1.709 (1.18)	1.767 (4.62)	1.637 (3.08)	1.785 (5.68)	1.689 (0.00)
1×10	3.322		3.331 (0.27)	3.013 (9.30)	3.484 (4.88)	3.320 (0.06)
1×10^2	8.658		8.659 (0.01)	7.366 (14.92)	8.854 (2.26)	8.620 (0.44)
1×10^3	25.628		25.628 (0.00)	21.132 (17.54)	25.836 (0.81)	25.480 (0.58)
1×10^4	79.327		79.327 (0.00)	64.662 (18.49)	79.540 (0.27)	79.088 (0.30)
1×10^6	786.184		786.187 (0.00)	637.620 (18.90)	786.398 (0.30)	788.060 (0.23)
1×10^8	7854.768		7854.767 (0.00)	6367.198 (18.93)	7854.982 (0.00)	7880.280 (0.32)
1×10^{10}	78540.61		78540.602 (0.00)	63662.977 (18.94)	78540.816 (0.00)	78802.730 (0.33)

[a] The number in the parentheses denotes the magnitude of the percentage deviation from the values estimated by eq 21.

where

$$b_0 = \pi/4 \qquad b_1 = \pi/4$$
$$b_2 = \pi/16 \qquad b_3 = -\pi/32 \tag{17}$$
$$b_4 = \pi/64$$

In contrast to all the hitherto known techniques in the context of diffusion at ultramicroelectrodes, the above eqs 13 and 16 represent the most general expressions for steady-state current for the Ec′ reaction. Phillips[11] has reported three terms of eqs 13 and 16 using the equivalence between steady-state diffusion-limited current at disk microelectrodes with a first-order EC′ reaction and the Laplace-transformed current of the transient problem.

3. Two-Point Padé Approximation

The efficacy of the Padé approximation using a partial set of data in diverse contexts such as phase transitions,[43] virial equations of state for hard spheres and disks,[44] cyclic voltammetry,[45] diffusion at ultramicroelectrodes, etc.,[26,27] is well-known. In the present analysis, partial information at two extreme values of reaction rates is available. Hence it is imperative to employ a two-point Padé approximant.

We construct a [5/4] rational function such that the coefficients of eqs 13 and 16 are reproduced. In this case, i/i_0 is given by

$$i/i_0 = \frac{p_0 + p_1x + p_2x^2 + p_3x^3 + p_4x^4 + p_5x^5}{1 + q_1x + q_2x^2 + q_3x^3 + q_4x^4} \tag{18}$$

where

$$p_0 = a_0 \qquad p_1 = b_0 + b_1q_1 + b_2q_2 + b_3q_3 + b_4q_4$$
$$p_2 = b_0q_1 + b_1q_2 + b_2p_3 + b_3q_4$$
$$p_3 = b_0q_2 + b_1q_3 + b_2q_4 \tag{19}$$
$$p_4 = b_0q_3 + b_1q_4 \qquad p_5 = b_0q_4$$

and

$$\begin{bmatrix} q1 \\ q2 \\ q3 \\ q4 \end{bmatrix} = \begin{bmatrix} b_1 - a_0 & b_2 & b_3 & b_4 \\ b_0 - a_1 & b_1 - a_0 & b_2 & b_3 \\ -a_2 & b_0 - a_1 & b_1 - a_0 & b_2 \\ -a_3 & -a_2 & b_0 - a_1 & b_1 - a_0 \end{bmatrix}^{-1} \begin{bmatrix} a_1 - b_0 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \tag{20}$$

The numerical values of p_0−p_5 and q_1−q_4 are $p_0 = 1$, $p_1 = 2.0016$, $p_2 = 1.8235$, $p_3 = 0.96367$, $p_4 = 0.307949$, $p_5 = 4.99248 \times 10^{-2}$, $q_1 = 1.3650$, $q_2 = 0.8826$, $q_3 = 0.32853$, and $q_4 = 6.3566 \times 10^{-2}$. Consequently

$$i/i_0 = [1 + 2.0016x + 1.8235x^2 + 0.96367x^3 + 0.307949x^4 + 4.9925 \times 10^{-2}\, x^5]/[1 + 1.3650x + 0.8826x^2 + 0.32853x^3 + 6.3566 \times 10^{-2}\, x^4] \tag{21}$$

Table 1 indicates the ratio of steady-state current in the presence of the chemical reaction to that in its absence for disk electrodes, and satisfactory agreement with the other estimates may be noticed. Figures 1−4 show the Padé approximant of EC′ working curves at a disk electrode for a^2/D_R values of 0.1, 1, 10, and 100, respectively. In addition, the simulation results of the pseudo-first-order expressions of Phillips,[11] Oldham,[46] Fleischmann et al.[47] (adapted to the disk electrode), and Lavagnini et al.[48] are also plotted. From Table 1 and Figures 1−4 it is inferred that Oldham's result is within 18% and the Fleischmann et al.[47] expression is within 5%, whereas computed values using eq 21 are accurate to within 0.5% of the digital simulation results.[48] The equation reported by Phillips[11] furnishes the disk response quite well (except at intermediate region near $x = 1$) better than the equivalent spherical expression. The methodology of ref 11 consists of exploiting the equivalence between the Laplace transform of the current in transient problems and the steady-state diffusion-limited current with a pseudo-first-order EC′ reaction. Oldham[46] and Fleischmann et al.[47] have derived current for pseudo-first-order EC′ behavior at a microdisk using the "equivalent sphere" approximation. The EC′ mechanism has been simulated numerically at a microdisk electrode under pseudo-first-order conditions by Lavagnini et al.[48] using the hopscotch method and under second-order conditions by Tutty[49] using ADI. Recently Alden and Compton[40] have simulated the steady-state response of microdisk and hemispherical electrodes with the influence of homogeneous and heterogeneous using ILU preconditioned Krylov subspace

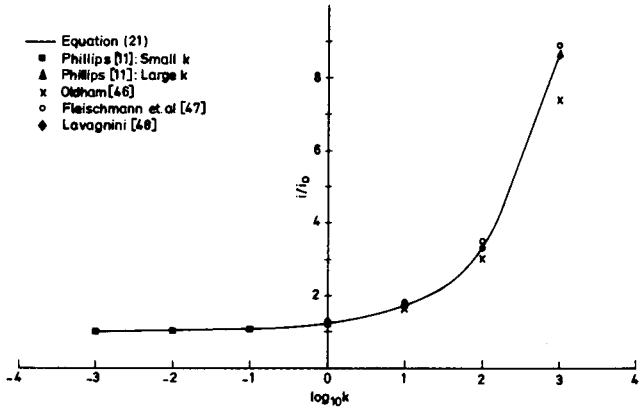

Figure 1. Comparison of eq 21 with digital simulation data and other approaches ($a^2/D_R = 0.1$).

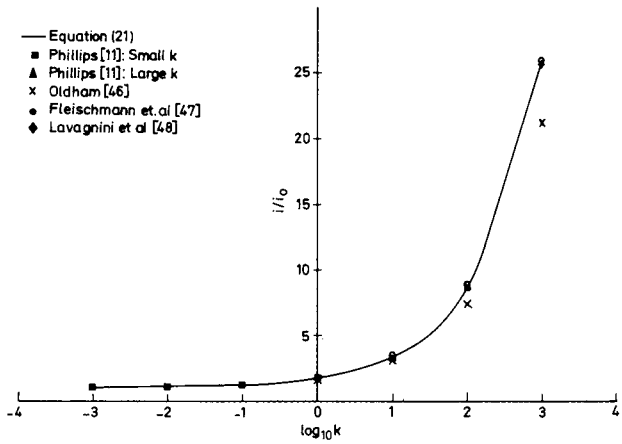

Figure 2. Comparison of eq 21 with digital simulation data and other approaches ($a^2/D_R = 1$).

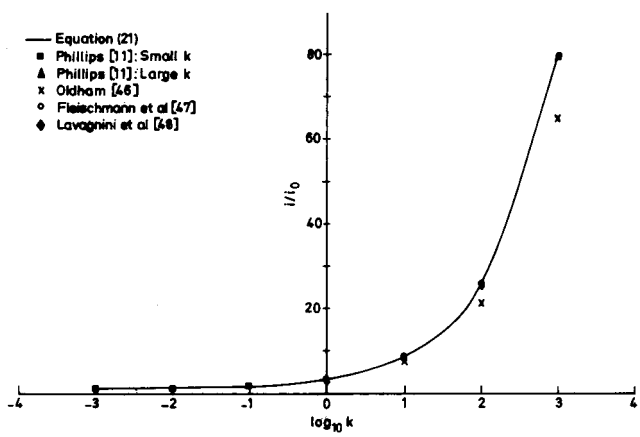

Figure 3. Comparison of eq 21 with digital simulation data and other approaches ($a^2/D_R = 10$).

methods. Denuault et al.[50] derived an analytical expression for steady-state current at spherical electrodes due to a second-order EC′ process. Delmastro and Smith[51] solved mass transport equations at a dropping mercury electrode for the pseudo-first-order case. Fleischmann et al.[47] adapted this to give an expression for a spherical electrode. Dayton et al.[52] also derived the spherical response using Neumann's integral theorem.

The approximate equivalence between microdisk and (hemi) spherical electrodes has been investigated[40] for homogeneous ECE, ECE, DISP1, DISP2, and EC′ reactions, and for the former four mechanisms, the relations $a_{hemi} = \pi a_{disk}/4$ and $k_{hemi} = \pi k_{disk}/4$ can be used to estimate the disk response with

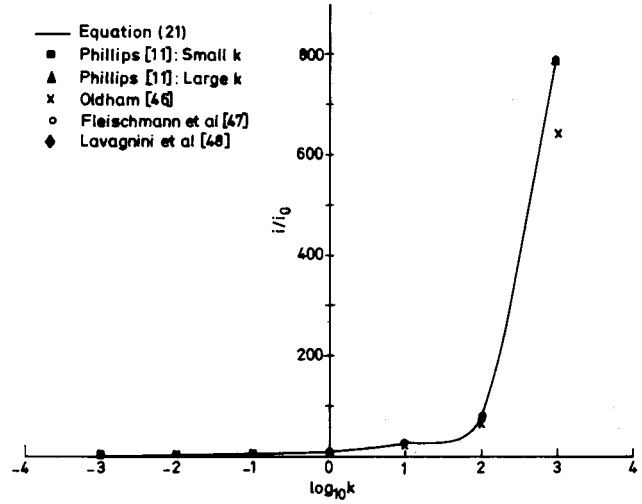

Figure 4. Comparison of eq 21 with digital simulation data and other approaches ($a^2/D_R = 100$).

maximum error of 1% (k_{disk} represents the rate constant for the disk electrode). This equivalence is not however uniformly valid. For the EC′ reaction, this equivalence approximation breaks down for increasing k. Hence, the analytical expressions derived[47,50] for this case using the above "equivalent sphere" approximation is significantly in error unless the reaction rate is very small. Philips[11] derived three terms of current expression for the pseudo-first-order EC′ behavior at a microdisk without resorting to a spherical approximation.

4. Analogy with Non-Steady-State Problems

The analysis of steady-state current pertaining to EC′ reaction is mathematically equivalent to the Laplace transformed transient current.[11] Therefore, from the above steady-state current for a pseudo-first-order EC′ reactions, non-steady-state diffusion-limited current for disk electrodes can be easily obtained.

The non-steady-state dimensionless diffusion equation governing the transport of electroactive species along with the boundary condition is as follows:

$$\frac{\partial h}{\partial t} = \nabla^2 h = \frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r} + \frac{\partial^2 h}{\partial z^2} \tag{22}$$

where h is a dimensionless concentration given by $h = 1 - c/c_0$, c_0 being the bulk concentration.

The initial condition is given by

$$h = 0 \text{ at } t = 0 \tag{23}$$

The mixed boundary conditions are given by $h(r,0,t) = 1$ on the electrode surface and $\partial h/\partial z|_{z=0} = 0$ on the other regions. The Laplace transform of eq 22 yields

$$\nabla^2 \bar{h} = \frac{\partial^2 \bar{h}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{h}}{\partial r} + \frac{\partial^2 \bar{h}}{\partial z^2} = \alpha \bar{h} \tag{24}$$

where α is the Laplace variable. The above equation and (8a) become isomorphic if $\bar{h}$ is related to g as $\bar{h} = g/\alpha$. Consequently, current pertaining to steady-state Ec′ reactions can be converted into Laplace-transformed non-steady-state diffusion-controlled current.[11]

Asymptotic expansions are known for the total flux rate when $\alpha(\alpha = x^2)$ is large and small from scattering analogue techniques. From eqs 9 and 11 we obtain

$$-\int_A \frac{\partial g}{\partial z} ds = 4i/i_0 \quad (25)$$

When $\alpha = x^2 \rightarrow \infty$, eq 16 becomes

$$-\int_A \frac{\partial g}{\partial z} ds = \pi[\alpha^{1/2} + 1 + {}^1/_4\alpha^{-1/2} - {}^1/_8\alpha^{-1} + {}^1/_{16}\alpha^{-3/2} + O(\alpha^{-5/2})] \quad (26)$$

Dividing by α and applying the inverse Laplace transform, we obtain

$$-\int_A \frac{\partial h}{\partial z} ds = [\pi/t]^{1/2} + \pi + {}^1/_2(\pi t)^{1/2} - {}^1/_8(\pi t) + {}^1/_{12}(\pi^{1/3}t)^{3/2} + O(t^2) \quad (27)$$

Similarly when $\alpha = x^2 \rightarrow O$, eq 13 becomes

$$-\int_A \frac{\partial g}{\partial z} ds = 4[a_0 + a_1\alpha^{1/2} + a_2\alpha + a_3\alpha^{3/2} + a_4\alpha^2 + a_5\alpha^{5/2} + a_6\alpha^3 + O(\alpha^{7/2})] \quad (28)$$

where the constants $a_0 - a_4$ are as in eq 13. Dividing all the terms of (28) by α^4, applying inverse Laplace transform, and differentiating subsequently, we obtain

$$-\int_A \frac{\partial h}{\partial z} ds = 4\left[a_0 + \frac{a_1}{\pi^{1/2}}t^{-1/2} - \frac{a_3}{2\pi^{1/2}}t^{-3/2} + \frac{3a_5}{4\pi^{1/2}}t^{-5/2} + O(t^{-7/2})\right] = 4\left[1 + 2\pi^{-3/2}t^{-1/2} - 4\pi^{-3/2}\left(\frac{1}{\pi^2} - \frac{1}{9}\right)t^{-3/2} + \frac{3}{2}\pi^{-3/2}\left(\frac{16}{\pi^4} - \frac{8}{3\pi^2} + \frac{71}{675}\right)t^{-5/2} + O(t^{-7/2})\right] \quad (29)$$

Let us define τ as $4t$ and identify i_0 as $4nFD_0c_0{}^ba$. Equation 27 can now be rewritten as

$$i/i_0 = \frac{\pi^{1/2}}{2}\tau^{-1/2} + \frac{\pi}{4} + \frac{\pi^{1/2}}{16}\tau^{1/2} - \frac{\pi}{128}\tau + \frac{\pi^{1/2}}{384}\tau^{3/2} + O(\tau^2) = 0.88623\tau^{-1/2} + 0.7854 + 0.11078\tau^{1/2} - 0.0245\tau + 0.00462\tau^{3/2} + O(\tau^2)(\tau \rightarrow 0) \quad (30)$$

Similarly when $\tau \rightarrow \infty$, eq 29 becomes

$$i/i_0 = 1 + 4\pi^{-3/2}\tau^{-1/2} - 32\left(\frac{1}{\pi^2} - \frac{1}{9}\right)\pi^{-3/2}\tau^{-3/2} + 48\left(\frac{16}{\pi^4} - \frac{8}{3\pi^2} + \frac{71}{675}\right)\pi^{-3/2}\tau^{-5/2} + O(\tau^{-7/2}) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2} + O(\tau^{-7/2}) \quad (31)$$

We reiterate here that eqs 30 and 31 represent the most accurate expression hitherto known for diffusion-limited current at ultramicro disk electrodes. As described elsewhere,[26,27] eqs 30 and 31 can also be combined into a [5/4] Padé approximant as

$$i/i_0 = \frac{1 + 2.5929x + 3.9686x^2 + 4.51506x^3 + 3.47861x^4 + 1.34989x^5}{1 + 1.87459x + 2.62197x^2 + 2.57529x^3 + 1.52319x^4} \quad (32)$$

where $x = \tau^{-1/2}$.

Table 2 indicates the dimensionless chronoamperometric current for disk electrodes evaluated using eq 32 together with the simulation results of (i) Heinze,[17] calculated using the alternating direction method, (ii) Shoup and Szabo,[30] employing the hopscotch method, (iii) Amatore,[20] using a combination of conformal maps and the hopscotch algorithm method, (iv) Jin et al.,[19] using finite analytical and numerical (FAM) methods, and (v) Alden et al.,[16] using the strongly implicit procedure (SIP). The average relative difference between our [5/4] Padé approximant (eq 32) and Heinze's numerical results is ca. 0.006%. Shoup and Szabo's[30] de facto expression

$$i/i_0 = 0.7854 + 0.8862\tau^{-1/2} + 0.2146\exp(-0.7823\tau^{-1/2}) \quad (33)$$

yields results within 0.6% of Heinze's simulated data. Aoki and Osteryoung[5,6] derived analytical equations for the current for short and long time using the Wiener–Hopf factorization technique. The transient current i/i_0 in this case[5,6] is given by

$$\lim_{\tau\rightarrow\infty}\frac{i}{i_0} = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2} \quad (34)$$

$$\lim_{\tau\rightarrow 0}\frac{i}{i_0} = 0.88623\tau^{-1/2} + 0.7854 + 0.094\tau^{1/2} \quad (35)$$

Equation 31 derived by us is identical with eq 34 given above. The first two terms of (35) are also consistent with our eq 30, and the third term of eq 35 (derived by Aoki and Osteryoung at[5,6]) has been shown to be incorrect elsewhere by Phillips et al.[10]

Short-time diffusion-limited current for more planar geometries were determined by Oldham[7] and by Phillips and Jansons.[10] The short-time current can be written as

$$i = nFDC_0\left[\frac{A}{\sqrt{\pi DT}} + \frac{P}{2} + \frac{\sqrt{\pi DT}}{2} + ...\right] \quad (36)$$

where A is the area of the electrode, P is the perimeter, and T denotes time. From the above expression, it follows that the short-time response generally has the following components: (i) an evanescent term ($T^{-1/2}$) that decreases with increase in time; (ii) a time-independent prompt component; (iii) augmentative components whose magnitude increase with time, as $T^{1/2}$, T, $T^{3/2}$, etc. If appropriate values for A and P pertaining to disk geometry are substituted in eq 36, we obtain the first three terms of our short-time expression. For long time, Szabo's result[8] is expressed as

$$i/nFDC_0 = l_0 + l_0{}^2/(4\pi^3DT)^{1/2} \quad (37)$$

where l_0 is the steady-state limit of the electrode. Phillips[9] has reported the next term in eq 37 using the method of matched asymptotic expansions. The first three terms of our eq 31 are identical with eq 35 of ref 9.

Summary

The steady-state current in the case of first-order EC′ reaction is evaluated using scattering analogue techniques for ultramicro disk electrodes. A two-point Padé approximant is derived for

TABLE 2: Transient Chronoamperometric Current at Ultramicrodisc Electrodes i/i_0 with $\tau = 4Dt/a^2$ [a]

τ	[5/4] Pade eq 32	Rajendran et al.[27]	digital simulation of Heinze[17]	digital simulation of Szabo[30]	digital simulation of Amatore et al.[20]	digital simulation of Jin et al.[19]
0.01	9.659	9.659 (0.00)	9.660 (0.01)	9.632 (0.28)	9.688 (0.30)	9.673 (0.14)
0.04	5.238	5.240 (0.04)	5.237 (0.02)	5.226 (0.23)	5.243 (0.01)	5.242 (0.07)
0.09	3.771	3.775 (0.11)	3.772 (0.03)	3.768 (0.08)	3.772 (0.03)	3.771 (0.00)
0.25	2.609	2.615 (0.23)	2.609 (0.00)	2.601 (0.30)	2.607 (0.08)	2.606 (0.11)
0.64	1.969	1.977 (0.41)	1.969 (0.00)	1.969 (0.00)		1.965 (0.20)
1.21	1.688	1.696 (0.47)	1.688 (0.00)	1.680 (0.47)	1.686 (0.12)	1.684 (0.23)
2.25	1.495	1.500 (0.33)	1.495 (0.00)	1.491 (0.27)	1.493 (0.13)	1.490 (0.33)
4.00	1.367	1.370 (0.21)	1.367 (0.00)	1.366 (0.07)	1.365 (0.15)	1.363 (0.29)
6.76	1.280	1.282 (0.16)	1.280 (0.00)	1.279 (0.08)	1.279 (0.08)	1.276 (0.31)

[a] The number in parentheses denotes the magnitude of the percentage deviation from the values estimated by eq 32. i_0 is given by $4nFD_0C_0^ba$, where a is the radius of the disk electrode.

all values of reaction rate. By a proper transcription of variables,the methodology is extended to derive chronoamperometric current for diffusion-controlled processes, and excellent agreement with digital simulation data is noticed.

Appendix

The dimensionless diffusion eq 8a pertaining to the first-order Ec[1] reaction for the diffusion-limited regime, i.e K $\rightarrow \infty$ for the disk electrode can be represented as

$$\nabla^2 g = \alpha g \tag{A1}$$

with the following conditions:

$$g = 1 \text{ on } z = 0 \qquad |r| < 1 \tag{A2}$$

$$\frac{\partial g}{\partial z} = 0 \text{ on } z = 0 \qquad |r| > 1 \tag{A3}$$

$$g \rightarrow 0 \qquad |r| \rightarrow \infty \tag{A4}$$

The required expression for current is

$$i/nFc_O^bD_Oa = 2\pi\int_0^1 q(r)r\,\mathrm{d}r \tag{A5}$$

where $q(r) = [-\partial g/\partial z/]_{z=0}$. The general solution of eq A1 using the scattering analogue technique is given by[41]

$$g(\eta,\phi,x) = 2\sum_{n=0}^{\infty}\frac{i^n R_{on}^{(1)}(x, io)}{N_{on}R_{on}^{(3)}(x, io)}R_{on}^{(3)}(x, i\sinh\eta) \times S_{on}(x,1)S_{on}(x, \sin\phi) \tag{A6}$$

where (η,ϕ) are oblate spherical coordinates, S_{on} are angle functions, $R_{on}^{(1)}$ and $R_{on}^{(3)}$ are radial functions of the first and third kinds, and the factor N_{on} appropriately normalizes S_{on} relative to the Legendre polynominal P_n. Here $x = \alpha^{1/2} = a(k/D_R)^{1/2}$. The exact result for current is given by

$$\frac{i}{4nFc_O^bD_Oa} = -\frac{\pi}{x}\sum_{n=0}^{\infty}\frac{1}{N_{on}}\frac{R_{on}^{(1)}(x, io)}{R_{on}^{(3)}(x, io)}[S_{on}(x,1)]^2 \tag{A7}$$

Evaluation of the spheroidal wave function is complicated and laborious. Therefore the summation of the series becomes impractical. These forms, however, are not particularly useful; the exact solutions (A6) and (A7) are presented for the sake of completeness. The strategy is to express the solutions in expansions appropriate to small and large values of x, and these values are combined using the Padé approximant, which is simple and convenient. Fortunately, a number of relevant expansions are available in the scattering literature.[41] The asymptotic expansion of the current for small x is, in the present notation,

$$\frac{i}{4nFc_O^bD_Oa} = \sum_{n=0}^{6}a_nx^n \tag{A8}$$

Similarly for large x the expansion is

$$\frac{i}{4nFc_O^bD_Oa} = \sum_{n=0}^{4}b_nx^{1-n} \tag{A9}$$

where the constants a_0-a_6 and b_0-b_4 are as in eqs 14 and 17 of the text.

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