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Analytical Expression Of Current-Time Behavior In Rapid Flash Photolytic Processes At A Planar Electrode

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ABSTRACT

Analytical expression of current in rapid photolytic processes at a planar electrode is derived. The model is based on non stationary diffusion equation containing a non-linear term related to flash photolytic processes. The derivation is given for a planar electrode. An excellent agreement with the previous analytical results is noted.

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KEYWORDS

Non-linear diffusion equation;
Pade approximation;
Photolytic processes;
Planar electrodes.

INTRODUCTION

Non-linear reaction-diffusion models and their study arise in various contexts. Among them mention may be made of polymer modified ultramicroelectrodes^[1], homogeneous mediated enzyme catalyzed reaction^[2], electrodes modified with multi layered enzyme system^[3], electrodes modified with nanostructure porous film^[4], and rapid photolytic processes^[5-7] etc. Therefore these models have been the subject of intense theoretical, numerical and experimental study over the past decades. In the above all fields, the dimensionless non-linear reaction diffusion equation is

$$\frac{\partial C}{\partial T} = \nabla^2 C - \varphi(C) \quad (1)$$

where C represents the dimensionless concentration of the electro active species, T represents the dimensionless time and $\varphi(C)$ represents the homogeneous reaction term generally polynomial in the concentrations (which is non-linear in concentration). Most non-linear

differential equations are difficult to solve in closed form. It is very difficult to obtain the exact solution to most non-linear differential equation. Moreover, even when closed-form solution is known, it may be so complicated that its qualitative properties are obscured. Thus, for most non-linear differential equations it is necessary to have reliable techniques to determine the approximate behavior solutions.

In Michaelis-Menten kinetics, the non-linear term is

$$\varphi(C) = \frac{KC}{1 + \alpha C} \quad (2)$$

When $\alpha C < 1$, non-linear term in the above equations is approximately equal to KC. When $\alpha C > 1$, the non-linear term can be written as K/α . This model is completely discussed in^[18,19]. We have discussed^[8-10] some of the reaction diffusion equations when

$$\varphi(C) = \alpha_1 C \quad (3)$$

In photolytic process^[7], the non-linear reaction term is

$$\varphi(C) = \alpha_2 C^2 \quad (4)$$

In Birk - Perone system^[5] (rapid photolytic processes) the reactions are



Chronoamperometry has been employed as a method for monitoring intermediates generated by flash photolysis^[5,11,12] and has been applied successfully to the determinations of several photochemical mechanisms^[13,14]. The application of electro-chemical techniques for the study of transient photolytic reactions was prompted by the observation that most photochemical processes appear to involve free radical and other electroactive intermediates^[11]. Furthermore, it appeared that many photolytically-induced chemical processes were similar to electrolytic ally-induced chemical processes^[11]. Thus, not only could electrochemical techniques be applied to the study of photolytic intermediates, but their qualitative characterization could be simplified by purely electrochemical studies of the chemical processes in question. Furthermore, electrochemical measurements have several analytical advantages for photolysis studies: sensitivity is available for dilute concentrations of a wide range of compounds; nearly the same detection limit exists for all electroactive compounds, since response depends primarily on mass transfer; and time-resolution in the microsecond range is available^[11].

Most pertinent to the work reported here are the studies of Berg^[15] who has applied polarized electrode techniques to the study of flash photolytic processes in solution. Berg's approach has been primarily exploratory and has involved conventional polarographic instrumentation and technique. In addition, he has reported the observation of transient photo-product currents during the drop-life of individual drops at the dropping mercury electrode. Thus, his studies of rapid kinetics have involved analysis of current-time behavior at individual expanding mercury drops. This quantitative approach was admittedly inaccurate and insensitive, however, because of the general difficulty in developing theory for kinetic currents at the dropping electrode, and because of the additional complications of handling second-order kinetic processes.

Both Berg and Schweiss^[15] and Perone and Birk^[5]

have demonstrated the general applicability of electroanalytical techniques to the study of photolytic processes. Qualitative information has been obtained from current-potential plots with the polarographic technique using continuous irradiation^[11], and with the stationary-electrode potentiostatic technique using flash irradiation^[11]. Rate data have been obtained by a variety of techniques which have included time-delayed potentiostatic analysis^[11], classical kinetic analysis^[15], and theoretical electrochemical kinetic-diffusion studies^[3].

An analytical solution for this problem was first attempted by Birk and Perone^[5], who however oversimplified their assumption^[7]. But this result was incorrect and was later corrected by Britz and Kastening^[6]. Britz and Kastening^[6] presented a rigorous derivation of the solution to the problem for various electrode geometries in the form of infinite series. The purpose of this communication is to derive a closed form of analytical expression of current at planar electrode for the electrochemical monitoring of a second order decay of radicals generated by flash photolysis or pulse radiolysis.

Mathematical formulation of the problem

Mathematically, the situation involving kinetics and diffusion at a planar electrode can be described by Fick's laws^[6]

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} - 2kc^2(x,t) \quad (6)$$

Here x is the distance from the electrode, t is the time after A is initially produced around the electrode, which is being held at constant potential and k is the rate constant of the homogeneous chemical reaction and $c(x, t)$ is the concentration of A at x and t . Britz and Kastening^[6] presented a concise discussion of the mathematical formulation of this problem for planar electrode which is summarized briefly here for completeness. The initial and boundary conditions are

$$\begin{aligned} c(x,0) &= c^* & x &\geq 0 \\ c(0,t) &= 0 & t &> 0 \\ \lim_{x \rightarrow \infty} c(x,t) &= c^* / (1 + 2kct^*) \end{aligned} \quad (7)$$

The required expression of the current is^[6]

$$i_k = \eta FAD \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (8)$$

where η is the number of moles of electrodes involved in the

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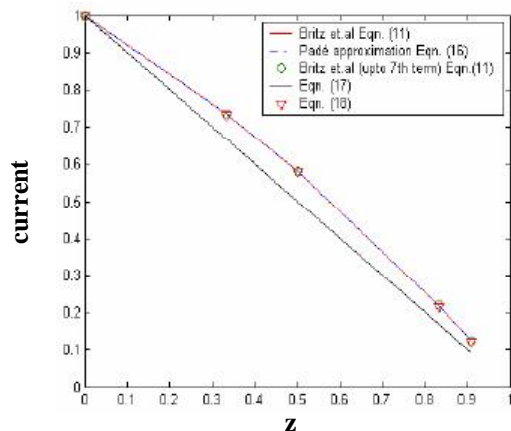


Figure 1 : Current at planar electrode for various values of z ($z=0$ to $z=0.9091$)

oxidation or reduction of one mole of the radical, F is the Faraday constant, A is the area of the electrode and D is the diffusion coefficient. Normalizing all the variables as usual, the non-linear diffusion eqn. (6) becomes

$$\frac{\partial C(X, T)}{\partial T} = \frac{\partial^2 C(X, T)}{\partial X^2} - KC^2(X, T) \quad (9)$$

where $K=2kc^*t$. Now the initial and boundary conditions are

$$\begin{aligned} C(X, 0) &= 1 \\ C(0, T) &= 0 \end{aligned} \quad (10)$$

$$\lim_{X \rightarrow \infty} C(X, T) = (1 + KT)^{-1}$$

Birk and Perone^[5] was found the solution of this problem first time and the more rigorous solutions (current only) was found to be^[6]

$$\frac{i_k}{i_{k=0}} = \sum_{n=0}^{\infty} \alpha_n z^n \quad (11)$$

$$i_{k=0} = nFADC_0 / \sqrt{\pi Dt} \quad (12)$$

$$\theta = 2kc^*t = KT \text{ and } z = \theta / (1 + \theta) \quad (13)$$

$$\begin{aligned} \alpha_0 &= 1, \alpha_1 = -0.72676, \alpha_2 = -0.18997, \alpha_3 = -0.05434, \\ \alpha_4 &= -0.01731, \alpha_5 = -0.00622, \alpha_6 = -0.00254, \\ \alpha_7 &= -0.00117, \alpha_8 = -0.00061, \alpha_9 = -0.00034, \\ \alpha_{10} &= -0.00021, \alpha_{11} = -0.00053 \end{aligned} \quad (14)$$

Using the first seven terms of the eqn. (11), the Pade approximant (see appendix A) can easily be constructed as

$$\frac{i_k}{i_{k=0}} = \left[\frac{p_0 + p_1 z + p_2 z^2 + p_3 z^3}{1 + q_1 z + q_2 z^2 + q_3 z^3} \right] \quad (15)$$

The numerical values of p_0 - p_3 and q_1 - q_3 are $p_0=1, p_1=-1.9767, p_2=1.1853, p_3=-0.2086, q_1=-1.2499, q_2=0.4669$ and $q_3=-0.0524$.

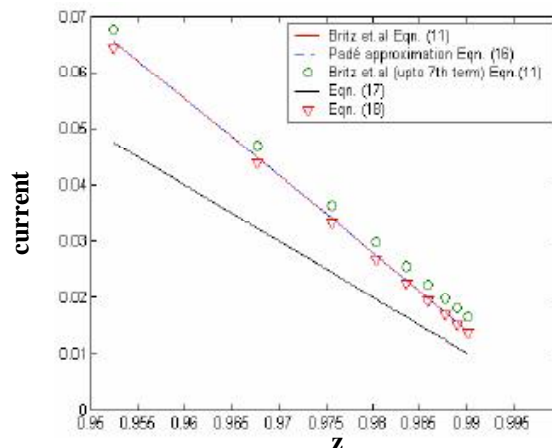


Figure 2 : Current at planar electrode for various values of z ($z=0.9524$ to $z=0.9901$)

Consequently

$$\frac{i_k}{i_{k=0}} = \left[\frac{1 - 1.9767z + 1.1853z^2 - 0.2086z^3}{1 - 1.2499z + 0.4669z^2 - 0.0524z^3} \right] \quad (16)$$

This is a simple closed form of analytical expression of the current for photolytic reaction at a planar electrode. The accuracy of the Pade approximation eqn. (16) was tested by comparison with rigorous eqn.(11) and other analytical results (Refer figure 1 and figure 2), which was computed for a wide range of z values.

RESULT AND DISCUSSION

Much work has been carried out on the electrochemical observation of a second order decay of radicals generated by flash photolysis or pulse radiolysis. Birk and Perone^[5] derived an approximate expression of current (Eqn (17)) at a planar electrode

$$\begin{aligned} \frac{i_k}{i_{k=0}} &= \frac{1}{1 + 2kc_0 t} = \frac{1}{1 + kt} = \frac{1}{1 + \theta} \\ &= 1 - z \end{aligned} \quad (17)$$

Eqn. (17) involves the assumption that the current at the electrode is smaller than the current in the absence of decay by the same factor as that by which the bulk concentration has decreased in the solution^[6]. Britz and Kastening^[6] obtained the rigorous derivation of the current (Eqn. (11)) in form of infinite series. Britz and Kastening^[6] also reported the approximate expression (Eqn. (18)) for current at a planar electrode.

$$\frac{i_k}{i_{k=0}} = \frac{1}{1 + 0.7268\theta} = \frac{1 - z}{1 - 0.2732z} \quad (18)$$

TABLE 1 : Current at planar electrode for different values of z

θ	z	Britz et al. ^[6] eqn.(11)	Pade appro. eqn.(16)	Britz et al. ^[6] (upto 7 th term)eqn.(11)	Eqn.(17)	Eqn.(18)
0	0	1.00000	1.0000	1.00000	1.0000	1.0000
0.5	0.3333	0.734412	0.734391	0.734413	0.6667	0.7335
1.0	0.5	0.581006	0.580968	0.581019	0.5000	0.5791
5.0	0.8333	0.218699	0.218634	0.219339	0.1667	0.2158
10.0	0.9091	0.123056	0.12301	0.124352	0.0909	0.1209
20.0	0.9524	0.06566	0.065635	0.067563	0.0476	0.0644
30.0	0.9677	0.044859	0.044842	0.047032	0.0323	0.0439
40.0	0.9756	0.034008	0.033995	0.036333	0.0244	0.0333
50.0	0.9804	0.027377	0.027367	0.029800	0.0196	0.0268
60.0	0.9836	0.022941	0.022932	0.025430	0.0164	0.0224
70.0	0.9859	0.019744	0.019737	0.022283	0.0141	0.0193
80.0	0.9877	0.017238	0.017231	0.019815	0.0123	0.0169
90.0	0.9890	0.015425	0.015419	0.018031	0.011	0.0151
100.0	0.9901	0.013889	0.013884	0.01652	0.0099	0.0136

The average relative error between the Britz and Kastening's infinite series expansion and the eqn.(18) (Birk and Perone^[5]) is 1.61% where as the relative error between the eqn.(11) and eqn.(17) is 21.76%. Among the above three approximations eqn.(16), eqn.(17), eqn.(18), our Pade approximation is a good approximation to the rigorous infinite series eqn.(11).

CONCLUSION

Pade approximants are typically used when there are some unknown coefficients in the function $f(z)$ eqn. (11). Britz and Kastening^[6] have computed the coefficients of current function eqn.(11) by laborious mathematical technique. Pade approximation can be constructed using the first few coefficients in the power series expansion, but they are not necessarily getting small, and we have no idea where(or whether) the power series is convergent. Here the Pade approximant coefficients (p_0 - p_3 , q_1 - q_3 (up to 7 terms)) are easily calculated from the seven coefficients(a_0 - a_6) of power series expansion (see appendix A).

In the TABLE 1 we have compared the Padé ap-

proximation and the seven terms $\left(\sum_{n=0}^6 \alpha_n z^n\right)$ of the equation(11) with complete power series expansion eqn. (11). The average relative error between our Pade approximant and Britz and Kastening's^[6] infinite series expansion eqn.(11) is 0.029% where as the average relative error between Britz and Kastening's^[6] infinite series

expansion(Eqn.(11)) and up to 7th term $\left(\sum_{n=0}^6 \alpha_n z^n\right)$ of the series is 7.09%. Note that both the values derived from the same seven original coefficient(a_0 - a_6) values. Hence the first seven terms, converted to a Pade approximant, gives a remarkable good representation of the whole current function for all values of z . Hence Pade approximation is a closed, an accurate and a powerful but in the end still mysterious mathematical technique. By a proper transcription of variables, the methodology will be extended to a stationary sphere, expanding plane and dropping mercury electrode^[6].

Appendix-A

A Pade approximant is a rational function approximation whose power series expansion agrees with the given infinite power series to the highest possible order^[17]. Let

$$f(z) = \sum_{i=0}^{\infty} \alpha_i z^i \quad (\text{A1})$$

be a formal given power series. Let m be a non-negative integer. The $[m/m]$ Pade approximant of $f(z)$ is the unique rational functions $R(z)$,

$$R(z) = \frac{p_0 + p_1 z + p_2 z^2 + \dots + p_m z^m}{1 + q_1 z + q_2 z^2 + \dots + q_m z^m} \quad (\text{A2})$$

Notice that in eqn. (A2), there are $m+1$ unknown numerator coefficients and m unknown denominator coefficients. In order to find the coefficients p_i and q_i we may write:

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$$R(z) \approx f(z),$$

$$p_0 + p_1z + p_2z^2 + \dots + p_mz^m = (1 + q_1z + q_2z^2 + \dots + q_mz^m) \quad (\text{A3})$$

$$(a_0 + a_1z + a_2z^2 + \dots)$$

Equating the coefficients of corresponding powers of z^i ($i=m+1$ to $2m$) we find

$$\begin{aligned} \alpha_1 q_m + \alpha_2 q_{m-1} + \alpha_3 q_{m-2} + \dots + \alpha_{m+1} &= 0 \\ \alpha_2 q_m + \alpha_3 q_{m-1} + \alpha_4 q_{m-2} + \dots + \alpha_{m+2} &= 0 \\ \vdots & \\ \vdots & \\ \alpha_m q_m + \alpha_{m+1} q_{m-1} + \alpha_{m+2} q_{m-2} + \dots + \alpha_{2m-1} q_1 + \alpha_{2m} &= 0 \end{aligned} \quad (\text{A4})$$

The above set of m equations (Eqn. (A5)) can be written as

$$\begin{bmatrix} \alpha_m & \alpha_m & \alpha_m & \dots & \alpha_m \\ \alpha_{m+1} & \alpha_{m+1} & \alpha_{m+1} & \dots & \alpha_{m+1} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \alpha_{2m-1} & \alpha_{2m-2} & \alpha_{2m-3} & \dots & \alpha_m \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_m \end{bmatrix} = \begin{bmatrix} \alpha_{m+1} \\ \alpha_{m+2} \\ \vdots \\ \alpha_{2m} \end{bmatrix} \quad (\text{A5})$$

$$\begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_m \end{bmatrix} = \begin{bmatrix} \alpha_m & \alpha_{m-1} & \alpha_{m-2} & \dots & \alpha_1 \\ \alpha_{m+1} & \alpha_m & \alpha_{m-1} & \dots & \alpha_2 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \alpha_{2m-1} & \alpha_{2m-2} & \alpha_{2m-3} & \dots & \alpha_m \end{bmatrix}^{-1} \begin{bmatrix} \alpha_{m+1} \\ \alpha_{m+2} \\ \vdots \\ \alpha_{2m} \end{bmatrix} \quad (\text{A6})$$

From which we can calculate the values of q_i 's ($i=1$ to m). The denominator coefficients p_0, p_1, \dots, p_m follow from eqn.(A3) by equating the coefficients of $1, z, z^2, \dots, z^m$:

$$\begin{aligned} p_0 &= \alpha_0 \\ p_1 &= \alpha_0 q_1 + \alpha_1 \\ p_2 &= \alpha_0 q_2 + \alpha_1 q_1 + \alpha_2 \\ p_3 &= \alpha_0 q_3 + \alpha_1 q_2 + \alpha_2 q_1 + \alpha_3 \\ \vdots & \\ \vdots & \\ p_m &= \alpha_0 q_m + \alpha_1 q_{m-1} + \alpha_2 q_{m-2} + \dots + \alpha_m \end{aligned} \quad (\text{A7})$$

Thus from eqns.(A6) and (A7) we determine the Pade numerator and denominator and these equations are called the Pade equations. We have obtained an $[m/m]$ Pade approximant which agrees with eqn.(A1) through order z^{m+m} .

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