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Evaluation of the Current Function in Linear Sweep Voltammetry by Pade Approximation and Epsilon Convergence*

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Abstract—Two procedures, viz., the epsilon convergence algorithm and Pade approximation scheme, are used to evaluate the current function values, graphical representation of the output, and verification of the model using existing data are carried out. For theoretical simulations of voltammograms, closed form of rational expressions using Pade approximant for the response of various reactions schemes involving soluble reactant and product, as well as coupled chemical process to an imposed linear scans were derived. Similarly, it was demonstrated epsilon convergence as an alternative procedure is much easier and elegant to use by an electroanalytical chemist with extreme ease.

Key words: Pade approximant, epsilon convergence, linear sweep voltammetry, current function, infinite series

1. INTRODUCTION

Voltammetry techniques have grown rapidly in popularity not only as means of obtaining a quick electrochemical spectrum of charge transfer systems but also as method for detailed examination of reaction mechanisms. For simple electron transfer processes, without coupled chemical reactions, direct solutions were obtained very early by Randles [1] and Sevick [2]. For electron transfer processes coupled with preceding, parallel or succeeding chemical reactions, analytical solutions are much more difficult to arrive at. In these cases, numerical integration approach was adopted [3–5].

Digital simulation has become one of the most powerful methods for the study of electrochemical problems. A fast quasi-explicit finite-difference method for the simulation of cyclic voltammetry of electrochemical systems comprising heterogeneous and homogeneous kinetics was developed [6–8]. Explicit finite-difference methods are being widely used, and detailed descriptions are also available in the literature [9–12]. Further refinements in the explicit finite-difference approach [13–15] are also being reported from time to time. Explicit and implicit finite-difference method [16–19] has been introduced. Rudolph and his coworkers have introduced a fast implicit finite-difference method algorithm [20] and CV Simulator software based on this approach [21]. Reinmuth has described a method [22] for writing series solutions for the numerical integral equations of the types as described in [4]. Nicholson and Shain have found difficulty in summing up these highly divergent series solutions. Subsequent efforts for finding analytical expressions for the current function are confined to charge transfer process without coupled chemical reactions, i.e., reversible and irreversible charge transfer reactions. These efforts include modification of Reinmuth power series approach [23, 24], orthogonal collocation procedure [25, 26], and Gaussian quadrature method [27]. Basha and Sankarnarayanan have evaluated the current function values for the first two cases, namely reversible charge transfer and irreversible charge transfer [28]. Recently, Mocak [29] reports in calculating the mechanisms reported in [4] with excellent accuracy and over a much wider potential range. However, these calculations were laborious and rather slow in the problematic potential region beyond the peak, even when using a relatively powerful computer. Further, it was also demonstrated by Mocak and Bond [30] using MATHEMATICA software the analytical solutions to be achieved for the current–potential response in linear sweep voltammetry using exponential infinite series for the cases of simple reversible charge transfer as well as catalytic reactions with reversible charge transfer. In these cases, the problems with divergence or slow convergence of the respective series can be overcome and a considerable gain both in accuracy of computation as well as augmenting the potential range can be achieved when using polylogarithm or Lerch functions.

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Continuous search for obtaining analytical solutions for the current potential relations are being made. The diagnostic criteria for distinguishing several types of electron transfer scheme are essentially based upon the compilation of the current function values dealt with eight common cases at various electrochemical process by Nicholson and Shain [4].

In the present work, two equivalent procedures, viz. (*i*) the epsilon convergence algorithm [31] for the acceleration of convergence of the original series and (*ii*) Pade approximation [31], using only the first few terms of the given series are found to be a very efficient mathematical apparatus for summing up highly divergent or slowly converging series solutions. The aim of this work is to demonstrate the efficient and straightforward use of the series solution presented by Nicholson and Shain [4] in the epsilon convergence algorithm and Pade approximation to compute the results of all the eight common cases independently and present them in the tables along with the data of Nicholson and Shain [4] for comparison.

Epsilon algorithm and Pade approximation procedures are briefly explained in Sections 2 and 3, respectively. For stationary electrode polarography, various solutions with coupled chemical reactions are described briefly in Section 4. Finally, discussion and conclusion are made in Section 5.

2. EPSILON ALGORITHM

The results of the analysis of theoretical models or experimental fits of several problems of physical interest may be expressed as an infinite power series of the form

$$F(x) = \sum_{n=0}^{\infty} a_n x^n. \quad (1)$$

This series may or may not be rapidly convergent and is frequently divergent for some finite value of x. When equation (1) is divergent, the "sum" termed the antilimit by Shanks [8], and is generally depends upon the value of the function most naturally associated with the series. When one resorts to the summation of a slowly convergent (or an alternating or a divergent) series, another difficulty encountered in this process is in getting information about the values of successive coefficients, and excessive computer time may be needed even to obtain these estimates. To circumvent this, one normally resorts to efficient extrapolation techniques, that is, with the knowledge of the partial sums of the series, the "total sum" can be approximately derived. The mth partial sum of equation (1) is defined as

$$S_m(x) = \sum_{i=0}^{m} a_i x^i \quad (m = 0, 1, 2, 3\ldots). \quad (2)$$

For a reasonably smooth, regular types of (convergent or divergent) series, such as those arising from physical problems, an excellent analytical or numerical approximation to $F(x)$ may be obtained from its first (or any sequential) $2n + 1$ partial sums by applying the epsilon algorithm to them. This nonlinear sequence-to-sequence transformation is given by

$$\varepsilon_{s+1}^m = \varepsilon_{s-1}^{m+1} + [\varepsilon_s^{m+1} - \varepsilon_s^m]^{-1}, \quad (3)$$

with $\varepsilon_{-1}^m = 0$ and $\varepsilon_0^m = S_m(x)$. The quantities ε_{s+1}^m are generated from the $2n + 1$ partial sum. S may conveniently be arranged in a lozenge diagram (for $n = 5$, the lozenge diagram is given below in (4)). The subscripts s of ε_s^m denote the column, and the superscripts m denote the progression down the column. The first column ε_{-1}^m is defined to be zero, and the second column ε_0^m is the given sequence (partial sum).

$$\begin{array}{ccccccc}
\varepsilon_{-1}^1 & & \varepsilon_0^1 & & & & \\
& & & \varepsilon_1^1 & & & \\
\varepsilon_{-1}^2 & & \varepsilon_0^2 & & \varepsilon_2^1 & & \\
& & & \varepsilon_1^2 & & \varepsilon_3^1 & \\
\varepsilon_{-1}^3 & & \varepsilon_0^3 & & \varepsilon_2^2 & & \varepsilon_4^1 \\
& & & \varepsilon_1^3 & & \varepsilon_3^2 & \\
\varepsilon_{-1}^4 & & \varepsilon_0^4 & & \varepsilon_2^3 & & \\
& & & \varepsilon_1^4 & & & \\
\varepsilon_{-1}^5 & & \varepsilon_0^5 & & & &
\end{array} \quad (4)$$

The even column of ε-diagram above show the converging sequence gradually, and the entry in the furthermost even column denotes the required final limit. Then, the quantities ε_0^m, ε_2^m, $\ldots\varepsilon_{2m}^m$ are successively better and better approximations to $F(x)$. We see Appendix 1, by example, that the ε-algorithm used to sum divergent series. The computation of sequence-to-sequence transformation by ε-algorithm to the series solution of current function of various schemes discussed [4] in their work is carried and presented in Section 4. The next section is devoted to understand the power series representation of function, by the description of Pade approximant technique.

3. PADE APPROXIMATION

The Pade approximant represents a function by the ratio of two polynomials. The coefficient of the power occurring in the polynomial is determined by the coefficients in Taylor series expansion of the function if the power series expansion is not given. Exploitation of this

simple idea and its extension has led to many insights. To define more explicitly, a Pade approximant is that rational function whose power series expansion agrees with a given power series to the highest possible order. If the rational function is,

$$[L/M] = \frac{(A_0 + A_1x + A_2x^2 + \ldots + A_Lx^L)}{(1 + B_1x + B_2x^2 + \ldots + B_Mx^M)}. \quad (5)$$

Then, [*L*/*M*] is said to be a Pade approximant to the infinite series of the form (1), i.e.,

$$F(x) = \sum_{k=0}^{\infty} a_k x^k. \quad (6)$$

The $L + M + 1$ coefficients (unknowns) $A_0, A_1, \ldots A_L$, B_1, B_2, $\ldots B_M$ are such that, in the Pade approximant [*L*/*M*] in powers of *x*, agree with the coefficients a_0, a_1, a_2, … of $F(x)$ up to order $L + M$. To calculate *A*'s and *B*'s, equate (5) and (6), multiply both by the denominator of equation (5), and equate all powers of *x* that have either *A*'s or *B*'s in their coefficients; then, we have

$$A_0 = a_0 \quad (7)$$

$$\sum_{m=1}^{N} B_m a_{N-m+k} = -a_{N+k} \quad (8)$$

$$\sum_{m=0}^{k} B_m a_{k-m} = A_k. \quad (9)$$

Consider the typical expression for the expression given in (6). Equating the series with a [5/6] Pade approximant in a rational polynomial as $F(x)$ = [5/6], we see that

$$a_0 + a_1x + a_2x^2 + \ldots + a_{11}x^{11} = \frac{(A_0 + A_1x + A_2x^2 + \ldots + A_5x^5)}{(1 + B_1x + B_2x^2 + \ldots + B_6x^6)} \quad (10)$$

or

$$(a_0 + a_1x + a_2x^2 + \ldots + a_{11}x^{11}) \times (1 + B_1x + B_2x^2 + \ldots + B_6x^6) = (A_0 + A_1x + A_2x^2 + \ldots + A_5x^5). \quad (11)$$

By matching the coefficient of x^6 to x^{11}, we get a set of linear equations for *B*'s in matrix form as

$$\begin{pmatrix} a_5 & a_4 & a_3 & a_2 & a_1 & a_0 \\ a_6 & a_5 & a_4 & a_3 & a_2 & a_1 \\ a_7 & a_6 & a_5 & a_4 & a_3 & a_2 \\ a_8 & a_7 & a_6 & a_5 & a_4 & a_3 \\ a_9 & a_8 & a_7 & a_6 & a_5 & a_4 \\ a_{10} & a_9 & a_8 & a_7 & a_6 & a_5 \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} -a_6 \\ -a_7 \\ -a_8 \\ -a_9 \\ -a_{10} \\ -a_{11} \end{pmatrix}. \quad (12)$$

We then solve for *B*'s as

$$\begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} a_5 & a_4 & a_3 & a_2 & a_1 & a_0 \\ a_6 & a_5 & a_4 & a_3 & a_2 & a_1 \\ a_7 & a_6 & a_5 & a_4 & a_3 & a_2 \\ a_8 & a_7 & a_6 & a_5 & a_4 & a_3 \\ a_9 & a_8 & a_7 & a_6 & a_5 & a_4 \\ a_{10} & a_9 & a_8 & a_7 & a_6 & a_5 \end{pmatrix}^{-1} \begin{pmatrix} -a_6 \\ -a_7 \\ -a_8 \\ -a_9 \\ -a_{10} \\ -a_{11} \end{pmatrix}. \quad (13)$$

The coefficients A_0, A_1, A_2, A_3, A_4, and A_5 are then obtained by equating the constant terms and the coefficients of x, x^2, x^3, x^4, and x^5 in (11) to give

$$\begin{aligned} A_0 &= a_0 \\ A_1 &= a_0B_1 + a_1 \\ A_2 &= a_0B_2 + a_1B_1 + a_2 \\ A_3 &= a_0B_3 + a_1B_2 + a_2B_1 + a_3 \\ A_4 &= a_0B_4 + a_1B_3 + a_2B_2 + a_3B_1 + a_4 \\ A_5 &= a_0B_5 + a_1B_4 + a_2B_3 + a_3B_2 + a_4B_1. \end{aligned} \quad (14)$$

In Appendix 2, we also illustrate the calculations explicitly through [5/6] Pade approximant for an infinite series for the case of catalytic reaction with irreversible charge transfer.

4. PROBLEMS AND ANALYSIS

The linear potential sweep technique has grown rapidly in popularity not only as a means of obtaining a quick electrochemical spectrum of a charge transfer system but also as a method of examination of reaction mechanisms. These analyses have been redescribed by number of authors including the very thorough account by Nicholson and Shain [4]. The essential features of their treatment are reproduced here in the following sections along with a rational expression for current function.

The values for current function vs. potential are tabulated which are numerically evaluated by epsilon algorithm and Pade approximant together with values of Nicholson and Shain [4] for comparison.

Table 1. Current function ($\sqrt{\pi}\chi(at)$) values with a [5/6] Pade approximation sequence and its coefficients for the reversible charge transfer scheme

Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0092	0.0092	0.009	10	0.3283	0.3283	0.328
100	0.0198	0.0198	0.02	0	0.3801	0.3801	0.38
80	0.0418	0.0418	0.042	–10	0.4188	0.4188	0.418
60	0.0850	0.0850	0.084	–20	0.4408	0.4408	0.441
50	0.1183	0.1183	0.117	–30	0.4447	0.4461	0.446
40	0.1610	0.1610	0.16	–40	0.4357	0.4376	0.438
30	0.2125	0.2125	0.211	–50	0.4099	0.4196	0.421
20	0.2701	0.2701	0.269	–60	0.3470	0.3952	0.399

Note: Reaction: O + $ne \rightleftharpoons$ R; series solution: $\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\sqrt{j}\exp\left[\frac{-jnF}{RT}(E-E_{1/2})\right]$, where $a = nFv/RT$; potential scale: $(E - E_{1/2})n$; in epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant: $\sqrt{\pi}\chi(at) = \frac{(1.7726 + 0.9557x + 0.1329x^2 - 0.0136x^3 - 0.0017x^4 + 0.0x^5)}{(1 + 3.1868x + 3.7306x^2 + 1.8889x^3 + 0.3337x^4 - 0.01684x^5 - 0.0055x^6)}$.

4.1. Reversible Charge Transfer (E_r-Scheme)

For the simple reversible electron transfer reaction

$$O + ne \Leftrightarrow R \tag{15}$$

taking place at a plane electrode, the diffusion equations are written as

$$\frac{\partial c_O}{\partial t} = D_O\frac{\partial^2 c_O}{\partial x^2} \tag{16}$$

$$\frac{\partial c_R}{\partial t} = D_R\frac{\partial^2 c_R}{\partial x^2} \tag{17}$$

and they are subject to the following initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_O = c_O^b : c_R = c_R^b \tag{18}$$

$$t \geq 0, \quad x \longrightarrow \infty : c_O \longrightarrow c_O^b : c_R \longrightarrow c_R^b \tag{19}$$

$$t \geq 0, \quad x = 0 : D_O\frac{\partial c_O}{\partial x} = -D_R\frac{\partial c_R}{\partial x} = \frac{i}{nFA} \tag{20}$$

$$\frac{c_O}{c_R} = \exp[(nF/RT)(E - E^0)] \tag{21}$$

for which the current response is evaluated by [32]:

$$i = nFAc_O^b\sqrt{\pi D_O a}\chi(at), \tag{22}$$

where $a = nFv/RT$ and $\chi(at)$ is the current function which refers to the dimensionless part of the current response in the voltammetric technique. The expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\sqrt{j}\exp\left[\frac{-jnF}{RT}(E-E_{1/2})\right]. \tag{23}$$

The current function represented by above equation (23) is converted to a useful rational function using the Pade approximation, in [5/6] approximant, and is expressed as

$$\sqrt{\pi}\chi(at) = \frac{(1.7726 + 0.9557x + 0.1329x^2 - 0.0136x^3 - 0.0017x^4 + 0.0x^5)}{(1 + 3.1868x + 3.7306x^2 + 1.8889x^3 + 0.3337x^4 - 0.01684x^5 - 0.0055x^6)} \tag{24}$$

where $x = \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]$. Once again, using the procedure adopted for epsilon algorithm with the value of N as 9, the current function is computed. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant

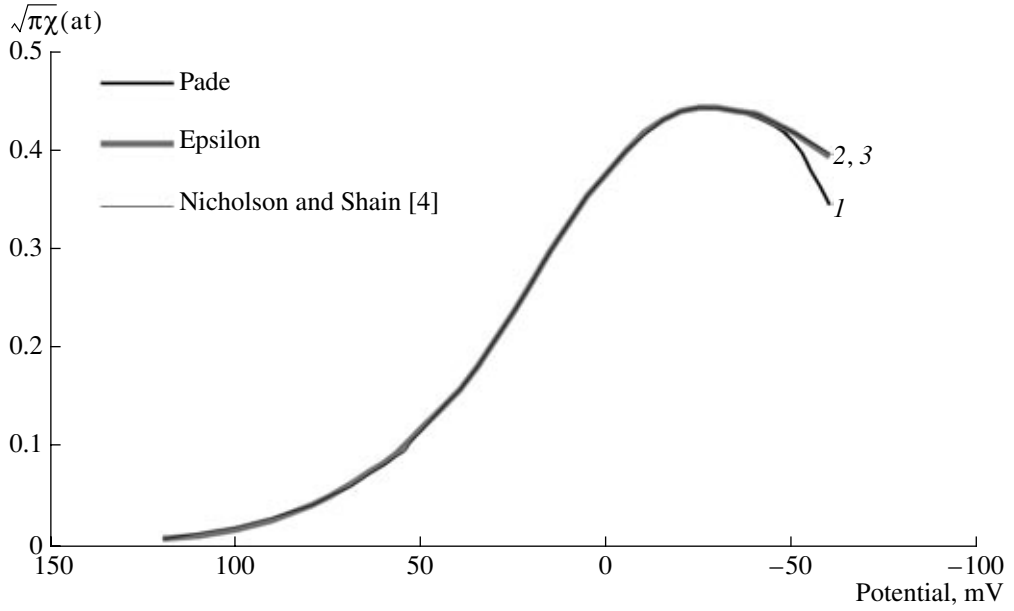

Fig. 1. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the simple reversible charge transfer scheme.

are tabulated in Table 1 with the Nicholson and Shain [4]. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 1.

4.2. Irreversible Charge Transfer (E_{ir}-Scheme)

For an irreversible electron transfer reaction

$$O + ne \xrightarrow{k_f} R \tag{25}$$

taking place at a plane electrode, the diffusion equation is written as

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} \tag{26}$$

and is subject to the following initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_O = c_O^b \tag{27}$$

$$t \geq 0, \quad x \longrightarrow \infty : c_O \longrightarrow c_O^b \tag{28}$$

$$t > 0, \quad x = 0 : D_O \frac{\partial c_O}{\partial x} = k_f c_O,$$
$$i = nFAk_f c_O \quad (x = 0), \tag{29}$$

where $k_f = k_f^0 e^{-bE}$. Using the above boundary conditions, the current is given by [32]:

$$i = nFAc_O^b \sqrt{\pi D_O b}\,\chi(bt), \tag{30}$$

where $b = \alpha n_a F v/RT$. The expression for the current function $\chi(at)$ as an infinite series for this irreversible charge transfer reaction is given by [4]:

$$\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}} \times \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi D_O b}}{k_s}\right)\right)\right]. \tag{31}$$

For numerical evaluation of the above series, current function is transformed to [5/6] Pade approximation. Then, the current function is expressed as

$$\sqrt{\pi}\chi(bt) = \frac{1.8096 + 1.1664x + 0.3904x^2 + 0.0786x^3 + 0.0056x^4 + 0.0000007x^5}{1 + 2.7935x + 3.3881x^2 + 2.2931x^3 + 0.9181x^4 + 0.2075x^5 + 0.0208x^6}, \tag{32}$$

where

$$x = \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi D_O b}}{k_s}\right)\right)\right].$$

Using the procedure adopted for epsilon algorithm, for the value of $N = 9$, once again the equation (31) is evaluated. The values of current obtained for various potential values obtained by epsilon algorithm and Pade

approximant are tabulated in Table 2 along with the Nicholson and Shain [4]. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 2.

4.3. Chemical Reaction Preceding a Reversible Charge Transfer (C_rE_r-Scheme)

The chemical/electrochemical mechanism where the reversible electron transfer process preceding a reversible chemical reaction is written as

$$\mathrm{X} \underset{k_b}{\overset{k_f}{\Leftrightarrow}} \mathrm{O}, \quad \mathrm{O} + n\mathrm{e} \Leftrightarrow \mathrm{R} \tag{33}$$

taking place at a plane electrode. The corresponding diffusion equations are

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} + k_f c_X - k_b c_O \tag{34}$$

$$\frac{\partial c_X}{\partial t} = D_X \frac{\partial^2 c_X}{\partial x^2} + k_b c_O - k_f c_X \tag{35}$$

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial x^2} \tag{36}$$

and are subject to the following initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_O/c_X = K : c_R = c_R^b; \quad c_O + c_X = c^b \tag{37}$$

$$t \geq 0, \quad x \longrightarrow \infty : c_O/c_X \longrightarrow K, \quad c_R \longrightarrow c_R^b(\sim 0), \quad c_O + c_X \longrightarrow c^b \tag{38}$$

$$t > 0, \quad x = 0 : D_O \frac{\partial c_O}{\partial x} = -D_R \frac{\partial c_R}{\partial x} = \frac{i}{nFA}, \quad D_X \frac{\partial c_X}{\partial x} = 0. \tag{39}$$

From the boundary conditions, current is evaluated and given by

$$i = nFAc_O^b \sqrt{\pi D_O a}\, \chi(at). \tag{40}$$

The explicit expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty} (-1)^{j+1} \left[\sqrt{j} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{i}}{K\sqrt{(1/a)+i}} \right) \right] \times \exp\left[\frac{-jnF}{RT} \left(E - E_{1/2} - \frac{RT}{nF} \ln\left(\frac{K}{K+1} \right) \right) \right]. \tag{41}$$

For numerical evaluation of the current function, the above expression is changed to the [5/6] Pade approximant and which is written as

$$\sqrt{\pi}\chi(at) = \frac{1.7726 + 0.9557x + 0.1328x^2 - 0.0136x^3 - 0.0018x^4 - 0.0000002x^5}{1 + 3.1868x + 3.7305x^2 + 1.8889x^3 + 0.3337x^4 - 0.0168x^5 - 0.0055x^6}, \tag{42}$$

where $x = \exp\left[\frac{-jnF}{RT} \left(E - E_{1/2} - \frac{RT}{nF} \ln\left(\frac{K}{K+1} \right) \right) \right]$. For evaluation of current function, the value of $N = 9$ is adopted in the procedure of epsilon algorithm. The values of current are obtained for various potential values obtained by epsilon algorithm and Pade approximant together with the Nicholson and Shain [4] are tabulated in Table 3. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 3.

4.4. Chemical Reaction Preceding an Irreversible Charge Transfer (C_rE_{ir}-Scheme)

The CE mechanism where the electron transfer process preceding the reversible chemical reaction is considered to be irreversible is written as

$$\mathrm{X} \underset{k_b}{\overset{k_f}{\Leftrightarrow}} \mathrm{O}, \quad \mathrm{O} + n\mathrm{e} \Leftrightarrow \mathrm{R} \tag{43}$$

takes place at a plane electrode, the diffusion equations are

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} + k_f c_X - k_b c_O \tag{44}$$

$$\frac{\partial c_X}{\partial t} = D_X \frac{\partial^2 c_X}{\partial x^2} + k_b c_O - k_f c_X \tag{45}$$

the appropriate initial and boundary conditions for this scheme are as follows:

$$t = 0, \quad x \geq 0 : c_O/c_X = K : c_X = c_X^b, \quad c_O = c_O^b \tag{46}$$

$$t \geq 0, \quad x \longrightarrow \infty : c_O/c_X \longrightarrow K, \quad c_X \longrightarrow c_X^b, \quad c_O \longrightarrow c_O^b \tag{47}$$

$$t > 0, \quad x = 0 : c_O = 0, \quad D_X \frac{\partial c_X}{\partial x} = 0, \quad D \frac{\partial c_O}{\partial x} = \frac{i}{nFA} = kc_O = k_i c_O e^{bt}. \tag{48}$$

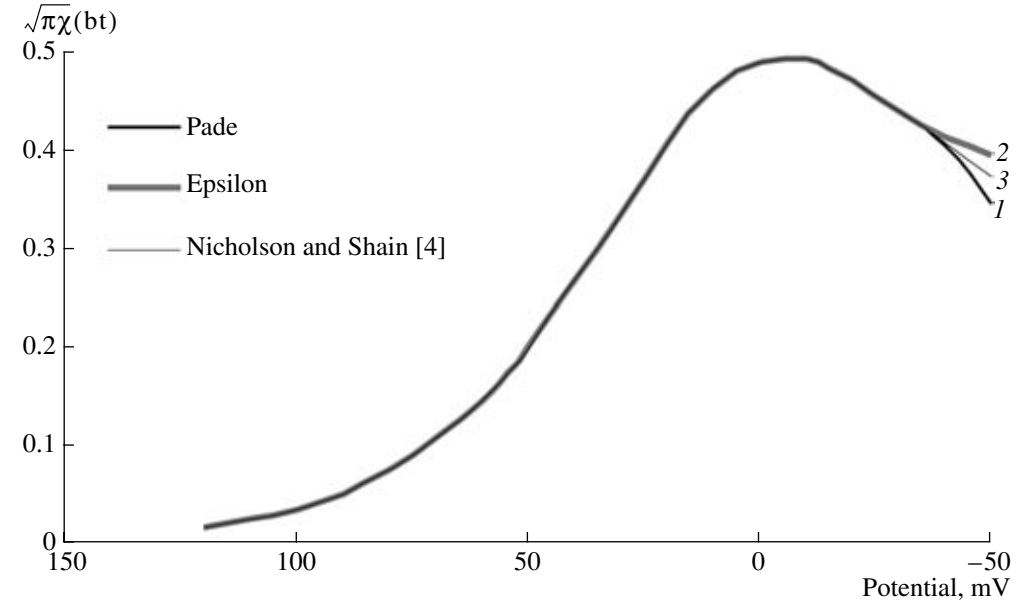

Fig. 2. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the simple irreversible charge transfer scheme.

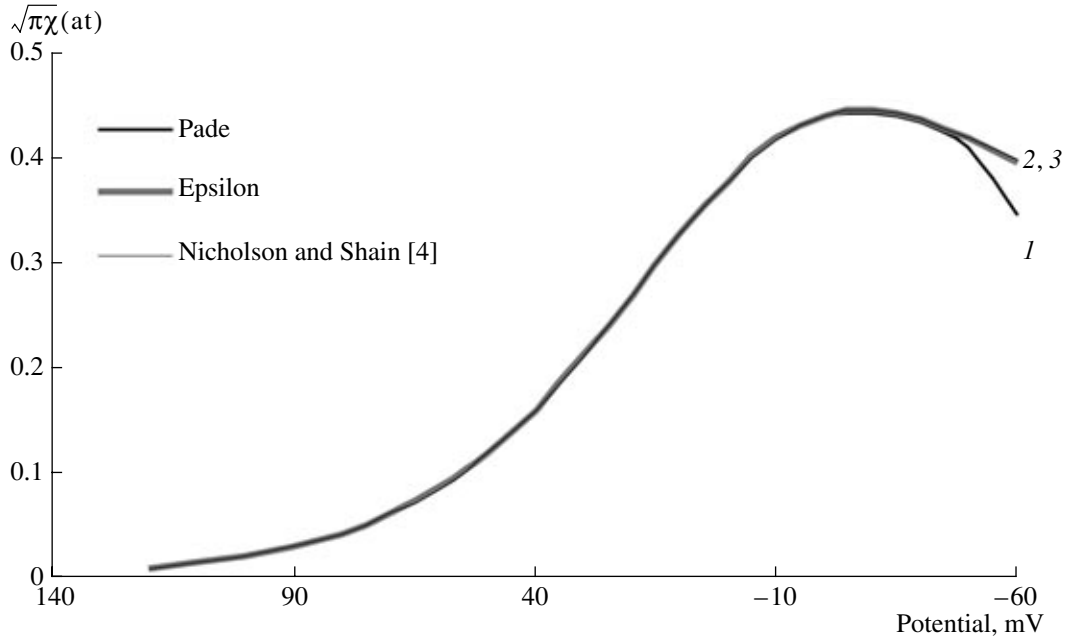

Fig. 3. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of chemical reaction preceding a reversible charge transfer.

From the above boundary conditions, current is evaluated and given by

$$i = nFAc_{\mathrm{O}}^{\mathrm{b}}\sqrt{\pi D_{\mathrm{O}}a}\,\chi(bt). \tag{49}$$

The explicit expression for the current function $\chi(bt)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{(\sqrt{\pi})^{j}}{\sqrt{(j-1)!}}\prod_{i=1}^{j-1}\left(1+\frac{\sqrt{i}}{K\sqrt{(1/b)+i}}\right)\right] \times \exp\left[\frac{-j\alpha n_{\mathrm{a}}F}{RT}(E-E^{0}+V)\right], \tag{50}$$

Table 2. Current function ($\sqrt{\pi}\chi(bt)$) values with a [5/6] Pade approximation sequence and its coefficients for the irreversible charge transfer scheme

Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0163	0.0163	0.016	10	0.4620	0.4620	0.462
100	0.0349	0.0349	0.035	0	0.4918	0.4918	0.492
80	0.0729	0.0729	0.073	–10	0.4930	0.4930	0.493
60	0.1454	0.1454	0.145	–20	0.4722	0.4725	0.472
50	0.1991	0.1991	0.199	–30	0.4400	0.4419	0.441
40	0.2643	0.2643	0.264	–40	0.4032	0.4129	0.406
30	0.3365	0.3365	0.337	–50	0.3457	0.3961	0.374
20	0.4067	0.4067	0.406				

Note: Reaction: O + $ne \xrightarrow{k}$ R; series solution: $\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\frac{(\sqrt{\pi})^{j}}{\sqrt{(j-1)!}}\exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi D_0 b}}{k_s}\right)\right)\right]$; potential scale: $(E - E^0)\alpha n_a + (RT/F)\ln(\sqrt{\pi D_0 b}/k_s)$; in epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant: $\sqrt{\pi}\chi(bt) = \frac{1.8096 + 1.1664x + 0.3904x^2 + 0.0786x^3 + 0.0056x^4 + 0.0000007x^5}{1 + 2.7935x + 3.3881x^2 + 2.2931x^3 + 0.9181x^4 + 0.2075x^5 + 0.0208x^6}$.

Table 3. Current function ($\sqrt{\pi}\chi(at)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of chemical reaction preceding a reversible charge transfer

Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0092	0.0092	0.009	10	0.3283	0.3283	0.328
100	0.0198	0.0198	0.02	0	0.3801	0.3801	0.38
80	0.0418	0.0418	0.042	–10	0.4188	0.4188	0.418
60	0.0850	0.0850	0.084	–20	0.4408	0.4408	0.441
50	0.1183	0.1183	0.117	–30	0.4447	0.4461	0.446
40	0.1610	0.1610	0.16	–40	0.4357	0.4376	0.438
30	0.2125	0.2125	0.211	–50	0.4099	0.4196	0.421
20	0.2701	0.2701	0.269	–60	0.3470	0.3952	0.399

Note: Reaction: Z $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ O, O + $ne \rightleftharpoons$ R; series solution: $\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\sqrt{j}\prod_{i=1}^{j-1}\left(1 + \frac{\sqrt{i}}{K\sqrt{(1/a)+i}}\right)\right]$ $\times \exp\left[\frac{-jnF}{RT}\left(E - E_{1/2} - \frac{RT}{nF}\ln\left(\frac{K}{K+1}\right)\right)\right]$; potential scale: $(E - E_{1/2})n - (RT/F)\ln(K/K+1)$; in the case of epsilon convergence algorithm: $N = 9$, current expression using [5/6] Pade approximant:

$$\sqrt{\pi}\chi(at) = \frac{1.7726 + 0.9557x + 0.1328x^2 - 0.0136x^3 - 0.0018x^4 - 0.0000002x^5}{1 + 3.1868x + 3.7305x^2 + 1.8889x^3 + 0.3337x^4 - 0.0168x^5 - 0.0055x^6}.$$

Table 4. Current function ($\sqrt{\pi}\chi(bt)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of chemical reaction preceding an irreversible charge transfer

Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0163	0.0163	0.016	10	0.4620	0.4423	0.414
100	0.0349	0.0347	0.035	0	0.4918	0.4706	0.44
80	0.0729	0.0719	0.07	–10	0.4930	0.4739	0.443
60	0.1454	0.1414	0.14	–20	0.4722	0.4580	0.43
50	0.1991	0.1919	0.19	–30	0.4400	0.4319	0.407
40	0.2643	0.2521	0.248	–40	0.4032	0.4035	0.381
30	0.3365	0.3259	0.312	–50	0.3457	0.3784	0.355
20	0.4067	0.3912	0.37	–60	0.1383	0.3595	0.333

Note: Reaction: $Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$, $O + ne \rightleftharpoons R$; series solution: $\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}}\prod_{i=1}^{j-1}\left(1+\frac{\sqrt{i}}{K\sqrt{(1/b)+i}}\right)\right]$ $\times \exp\left[\frac{-j\alpha n_a F}{RT}(E-E^0+V)\right]$, where $V=\frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)-\frac{RT}{\alpha n_a F}\ln\left(\frac{K}{K+1}\right)$; potential scale: $-(E-E^0)\alpha n_a-(RT/F)\ln(\sqrt{\pi Db}/k_s)$ $+(RT/F)\ln(K/(K+1))$; in case of epsilon convergence algorithm: $N=9$; current expression using [5/6] Pade approximant: $\sqrt{\pi}\chi(bt)$ $= \frac{1.8096+1.1664x+0.3904x^2+0.0786x^3+0.0056x^4+0.0000007x^5}{1+2.7935x+3.3881x^2+2.2931x^3+0.9181x^4+0.2075x^5+0.0208x^6}$.

where $V=\frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)-\frac{RT}{\alpha n_a F}\ln\left(\frac{K}{K+1}\right)$ and $b=\alpha n_a F v/RT$. For numerical evaluation of the current function, the above expression is changed to the [5/6] Pade approximant and which is written as

$$\sqrt{\pi}\chi(bt) = \frac{1.8096+1.1664x+0.3904x^2+0.0786x^3+0.0056x^4+0.0000007x^5}{1+2.7935x+3.3881x^2+2.2931x^3+0.9181x^4+0.2075x^5+0.0208x^6}, \quad (51)$$

where $x=\exp\left[\frac{-j\alpha n_a F}{RT}(E-E^0+V)\right]$. For evaluation of current function, the value of $N=9$ is adopted in the procedure of epsilon algorithm. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant with the Nicholson and Shain [4] are tabulated in Table 4. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 4.

4.5. Reversible Chemical Reaction Succeeding a Reversible Charge Transfer (E_rC_r)

The electrochemical/chemical mechanism where the electron transfer process preceding a reversible chemical reaction is considered to be reversible and is written as

$$O + ne \Leftrightarrow R, \quad R \underset{k_b}{\overset{k_f}{\Leftrightarrow}} Y. \quad (52)$$

The diffusion equations for a plane electrode are

$$\frac{\partial c_O}{\partial t} = D_O\frac{\partial^2 c_O}{\partial x^2} \quad (53)$$

$$\frac{\partial c_R}{\partial t} = D_R\frac{\partial^2 c_R}{\partial x^2} + k_b c_Y - k_f c_R \quad (54)$$

$$\frac{\partial c_Y}{\partial t} = D_Y\frac{\partial^2 c_Y}{\partial x^2} + k_b c_Y + k_f c_R \quad (55)$$

and are subject to the following initial and boundary conditions:

$$t=0, \quad x\geq 0 : c_Y/c_R^b = K : c_R = c_R^b, \quad c_O = c_O^b \quad (56)$$

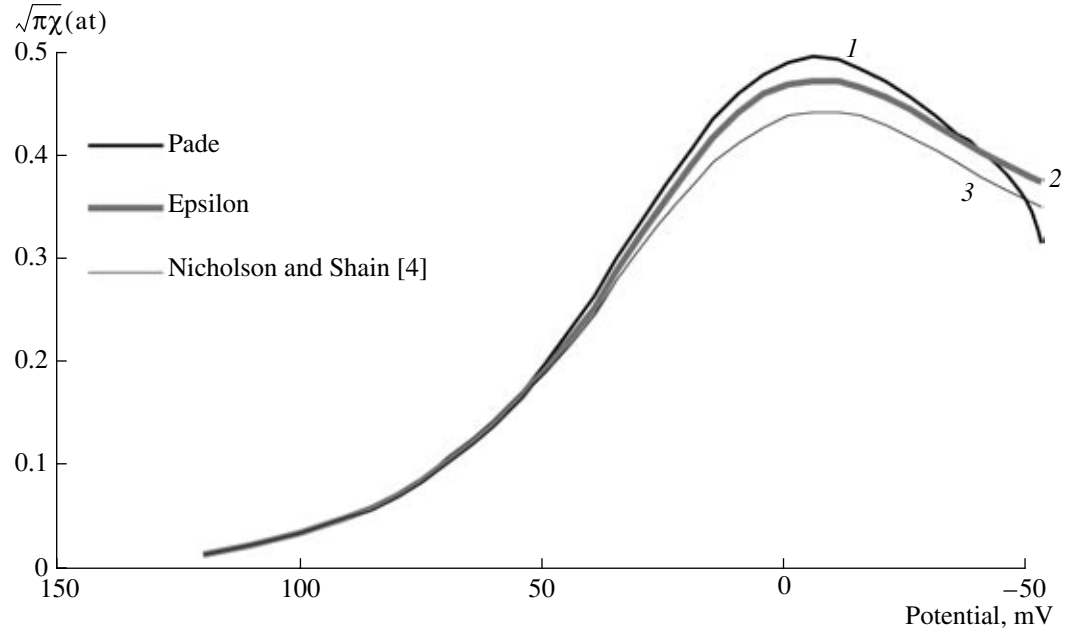

Fig. 4. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of chemical reaction preceding an irreversible charge transfer.

$$t \geq 0, \quad x \longrightarrow \infty : c_Y \longrightarrow 0, \quad c_R \longrightarrow 0, \quad c_O \longrightarrow c_O^b \tag{57}$$

$$t > 0, \quad x = 0 : D_O \frac{\partial c_O}{\partial x} = -D_R \frac{\partial c_R}{\partial x} = \frac{i}{nFA}, \quad D_Y \frac{\partial c_Y}{\partial x} = 0. \tag{58}$$

From the boundary conditions, current is evaluated and given by

$$i = nFAc_O^b \sqrt{\pi D_O a}\,\chi(at). \tag{59}$$

The explicit expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty} (-1)^{j+1} \left[\sqrt{j} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{i}}{\sqrt{(1/a)+i}} \right) \right] \times \exp\left[\frac{-jnF}{RT} \left(E - E_{1/2} - \frac{RT}{nF} \ln(K+1) \right) \right]. \tag{60}$$

The current function represented by above equation (60) is converted to a useful rational function using the Pade approximation, in [5/6] approximant, and is expressed as

$$\sqrt{\pi}\chi(at) = \frac{12.9358 + 19.4225x + 9.713x^2 + 1.657x^3 + 0.0627x^4 - 0.0000004x^5}{1 + 14.35x + 37.9851x^2 + 40.5856x^3 + 19.7314x^4 + 4.005x^5 + 0.0226x^6}, \tag{61}$$

where $x = \exp\left[\frac{-jnF}{RT} \left(E - E_{1/2} - \frac{RT}{nF} \ln(K+1) \right) \right]$. For evaluation of current function, the value of $N = 9$ is adopted in the procedure of epsilon algorithm. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant with the Nicholson and Shain [4] are tabulated in Table 5. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 5.

4.6. Irreversible Chemical Reaction Succeeding a Reversible Charge Transfer (E_rC_{ir}-Scheme)

The EC mechanism where the reversible electron transfer process preceding an irreversible chemical reaction is written as

$$O + ne \Leftrightarrow R, \quad R \xrightarrow{k_f} Y. \tag{62}$$

takes place at a plane electrode, the diffusion equations are

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} \tag{63}$$

Table 5. Current function ($\sqrt{\pi}\chi(at)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of charge transfer succeeding a reversible chemical reaction

Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0092	0.0092	0.008	10	0.3282	0.3283	0.316
100	0.0198	0.0198	0.018	0	0.3800	0.3801	0.372
80	0.0418	0.0418	0.037	–10	0.4186	0.4188	0.414
60	0.0850	0.0850	0.079	–20	0.4402	0.4408	0.44
50	0.1183	0.1183	0.108	–30	0.4450	0.4461	0.449
40	0.1610	0.1610	0.149	–40	0.4351	0.4376	0.443
30	0.2125	0.2125	0.2	–50	0.4102	0.4196	0.426
20	0.2701	0.2701	0.256	–60	0.3528	0.3952	0.405

Note: Reaction: $R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} N$, $O + ne \rightleftharpoons R$; series solution: $\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\sqrt{j}/\prod_{i=1}^{j-1}\left(1+\frac{K\sqrt{i}}{\sqrt{(1/a)+i}}\right)\right] \times \exp\left[\frac{-jnF}{RT}\left(E - E_{1/2} - \frac{RT}{nF}\ln(K+1)\right)\right]$; potential scale: $-(E - E_{1/2})n - (RT/F)\ln(1 + K)$; in case of epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant:

$$\sqrt{\pi}\chi(at) = \frac{12.9358 + 19.4225x + 9.713x^2 + 1.657x^3 + 0.0627x^4 - 0.0000004x^5}{1 + 14.35x + 37.9851x^2 + 40.5856x^3 + 19.7314x^4 + 4.005x^5 + 0.0226x^6}.$$

Table 6. Current function ($\sqrt{\pi}\chi(at)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of charge transfer succeeding an irreversible chemical reaction

Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(at)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0093	0.0093	0.009	10	0.3642	0.3988	0.333
100	0.0200	0.0200	0.02	0	0.4023	0.4915	0.384
80	0.0425	0.0425	0.042	–10	0.3702	0.5829	0.423
60	0.0880	0.0880	0.086	–20	0.1947	0.6659	0.444
50	0.1243	0.1246	0.12	–30	–0.2419	0.7354	0.448
40	0.1722	0.1733	0.163	–40	–1.1259	0.7889	0.439
30	0.2317	0.2357	0.216	–50	–2.7517	0.8259	0.421
20	0.2994	0.3117	0.273	–60	–5.5927	0.8469	0.399

Note: Reaction: $R \underset{}{\overset{k_f}{\rightleftharpoons}} Z$, $O + ne \rightleftharpoons R$; series solution: $\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{1}{\sqrt{(j-1)!}}\prod_{i=1}^{j}\sqrt{(k_f/a)+i}\right] \times \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]$; potential scale: $(E - E_{1/2})n$; in case of epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant:

$$\sqrt{\pi}\chi(at) = \frac{1.9707 + 1.3269x - 0.09x^2 - 0.1655x^3 - 0.0237x^4 + 0.0000001x^5}{1 + 2.9707x + 3.2788x^2 + 1.6352x^3 + 0.3503x^4 + 0.0225x^5 - 0.0002x^6}.$$

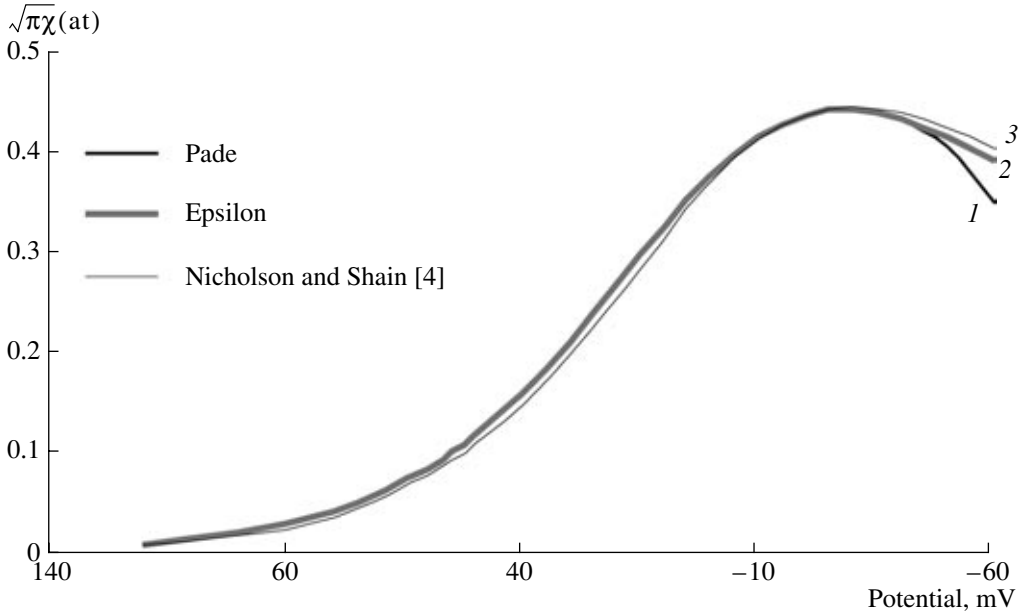

Fig. 5. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of reversible chemical reaction succeeding a reversible charge transfer.

$$\frac{\partial c_R}{\partial t} = D_R\frac{\partial^2 c_R}{\partial x^2} + k_f c_R. \quad (64)$$

and are subject to the following initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_R^b = 0, \quad c_O = c_O^b \quad (65)$$

$$t \geq 0, \quad x \longrightarrow \infty : c_R^b \longrightarrow 0, \quad c_O \longrightarrow c_O^b \quad (66)$$

$$0 < t < \tau, \quad x = 0 : c_O = 0,$$
$$D_O\frac{\partial c_O}{\partial x} + D_R\frac{\partial c_R}{\partial x} = 0 \quad (67)$$

$$t > \tau, \quad x = 0 : C_R = 0, \quad D_O\frac{\partial c_O}{\partial x} + D_R\frac{\partial c_R}{\partial x} = 0 \quad (68)$$

$$t > 0, \quad x = 0 : D_O\frac{\partial c_O}{\partial x} = \frac{i}{nFA}. \quad (69)$$

From the boundary conditions, current is evaluated and given by

$$i = nFAc_O^b\sqrt{\pi D_O a}\,\chi(at). \quad (70)$$

The explicit expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{1}{\sqrt{(j-1)!}}\prod_{i=1}^{j}\sqrt{(k_f/a)+i}\right] \times \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]. \quad (71)$$

For numerical evaluation of the current function, the above expression is changed to the [5/6] Pade approximant and which is written as

$$\sqrt{\pi}\chi(at) = \frac{1.9707 + 1.3269x - 0.09x^2 - 0.1655x^3 - 0.0237x^4 + 0.0000001x^5}{1 + 2.9707x + 3.2788x^2 + 1.6352x^3 + 0.3503x^4 + 0.0225x^5 - 0.0002x^6}, \quad (72)$$

where $x = \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]$. For evaluation of current function, the value of $N = 9$ is adopted in the procedure of epsilon algorithm. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant with the Nicholson and Shain [4] are tabulated in Table 6. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential val-

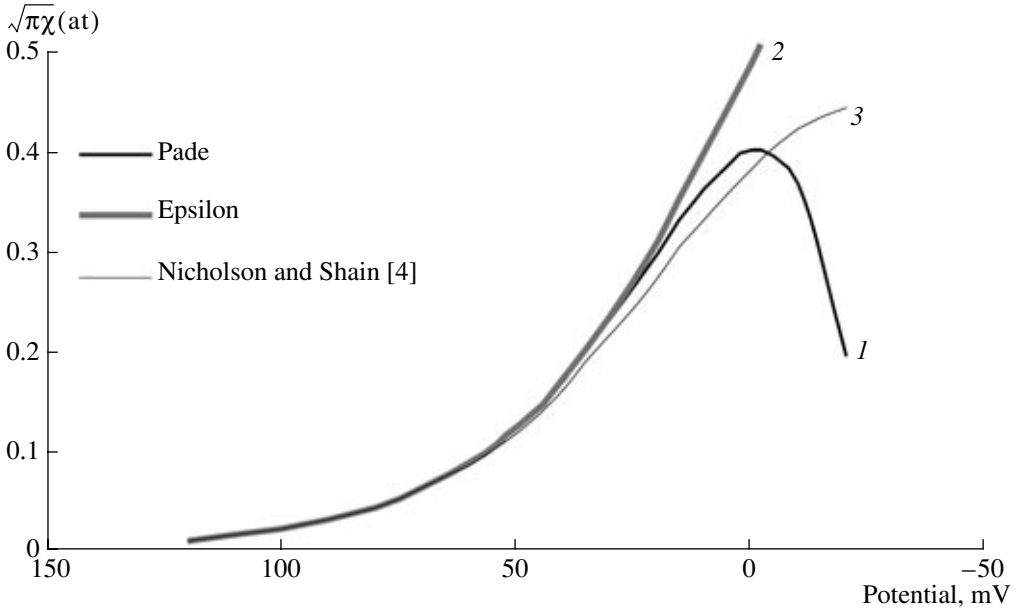

Fig. 6. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of irreversible chemical reaction succeeding a reversible charge transfer.

ues represented by Nicholson and Shain in his paper [4] in Fig. 6.

4.7. Catalytic Reaction with Reversible Charge Transfer (E_rC_{at}-Scheme)

In a catalytic mechanism with a simple electron transfer reversible reaction represented as

$$\mathrm{O} + n\mathrm{e} \rightleftharpoons \mathrm{R}, \quad \mathrm{R} + \mathrm{Z} \xrightarrow{k_\mathrm{f}} \mathrm{O}, \tag{73}$$

the diffusion equations for a plane electrode are

$$\frac{\partial c_\mathrm{O}}{\partial t} = D_\mathrm{O}\frac{\partial^2 c_\mathrm{O}}{\partial x^2} + k_\mathrm{f} c_\mathrm{O} \tag{74}$$

$$\frac{\partial c_\mathrm{R}}{\partial t} = D_\mathrm{R}\frac{\partial^2 c_\mathrm{R}}{\partial x^2} - k_\mathrm{f} c_\mathrm{R} \tag{75}$$

and are subject to the following initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_\mathrm{O} = c_\mathrm{O}^\mathrm{b}, \quad c_\mathrm{R} = c_\mathrm{R}^\mathrm{b}(\sim 0) \tag{76}$$

$$t \geq 0, \quad x \longrightarrow \infty : c_\mathrm{O} \longrightarrow c_\mathrm{O}^\mathrm{b}, \quad c_\mathrm{R} \longrightarrow 0 \tag{77}$$

$$t > 0, \quad x = 0 : D_\mathrm{O}\frac{\partial c_\mathrm{O}}{\partial x} = -D_\mathrm{R}\frac{\partial c_\mathrm{R}}{\partial x} = \frac{i}{nFA}. \tag{78}$$

From the boundary conditions, current is evaluated and given by

$$i = nFAc_\mathrm{O}^\mathrm{b}\sqrt{\pi D_\mathrm{O} a}\,\chi(at). \tag{79}$$

The explicit expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty}(-1)^{j+1}\sqrt{(k_\mathrm{f}/a) + j} \times \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]. \tag{80}$$

For numerical evaluation of the current function, the above expression is changed to the [5/6] Pade approximant and which is written as

$$\sqrt{\pi}\chi(at) = \frac{-2.5416 - 6.3525x - 3.7856x^2 - 0.7414x^3 - 0.0349x^4 - 0.0000004x^5}{1 - 1.091749x - 9.467979x^2 - 13.13504x^3 - 7.289048x^4 - 1.6335x^5 - 0.1041x^6}, \tag{81}$$

where $x = \exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]$. For evaluation of current function, the value of $N = 9$ is adopted in the procedure of epsilon algorithm. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant with the Nicholson and Shain [4] are tabulated in Table 7. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 7.

Table 7. Current function ($\sqrt{\pi\chi}\,(at)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of catalytic reaction with reversible charge transfer

Potential, mV	Current functions $\sqrt{\pi\chi}\,(at)$ from			Potential, mV	Current functions $\sqrt{\pi\chi}\,(at)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0094	0.0094	0.009	10	0.3375	0.3375	0.336
100	0.0202	0.0202	0.02	0	0.3921	0.3920	0.391
80	0.0426	0.0426	0.042	–10	0.4339	0.4338	0.432
60	0.0867	0.0868	0.086	–20	0.4504	0.4590	0.459
50	0.1209	0.1209	0.12	–30	0.4671	0.4672	0.468
40	0.1646	0.1646	0.163	–40	0.4598	0.4609	0.463
30	0.2176	0.2176	0.216	–50	0.4336	0.4420	0.45
20	0.2770	0.2770	0.275				

Note: Reaction: $R \overset{k_f}{\rightleftharpoons} Z$, $O + ne \rightleftharpoons R$; series solution: $\sqrt{\pi\chi}\,(at) = \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{(k_f/a) + j}\exp\left[\frac{-jnF}{RT}(E - E_{1/2})\right]$; potential scale: $(E - E_{1/2})n$; in the case of epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant: $\sqrt{\pi\chi}\,(at) = \frac{-2.5416 - 6.3525x - 3.7856x^2 - 0.7414x^3 - 0.0349x^4 - 0.0000004x^5}{1 - 1.091749x - 9.467979x^2 - 13.13504x^3 - 7.289048x^4 - 1.6335x^5 - 0.1041x^6}$.

4.8. Catalytic Reaction with Irreversible Charge Transfer ($E_{ir}C_{at}$-Scheme)

The diffusion equation for the catalytic mechanism with an irreversible chemical reaction, i.e.,

$$O + ne \xrightarrow{k} R, \quad R + Z \xrightarrow{k_f} O, \tag{82}$$

which takes place at a plane electrode, has the diffusion equations

$$\frac{\partial c_O}{\partial t} = D_O\frac{\partial^2 c_O}{\partial x^2} + k_f c_R \tag{83}$$

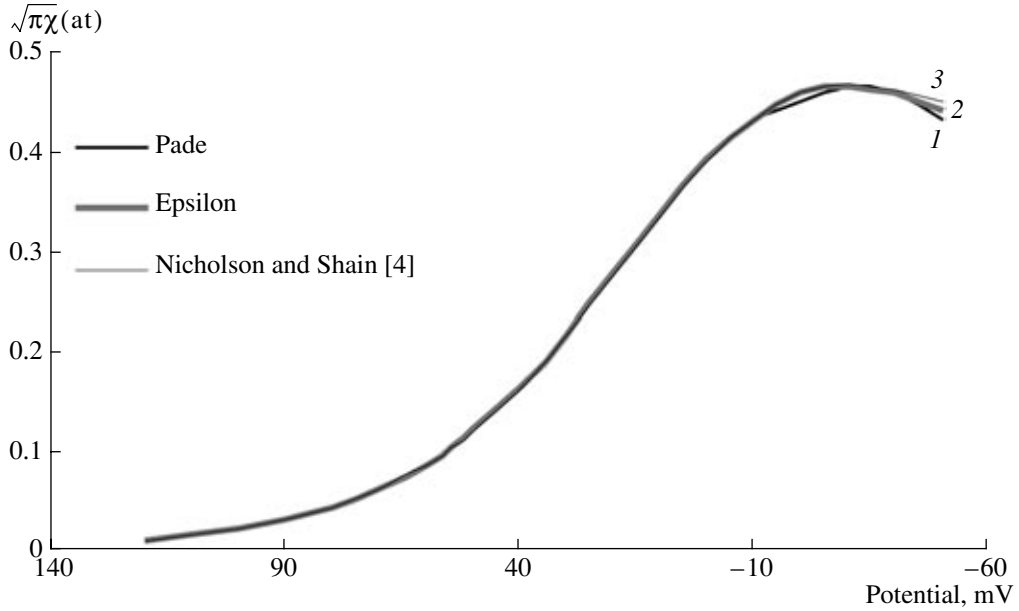

Fig. 7. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of catalytic reaction with reversible charge transfer.

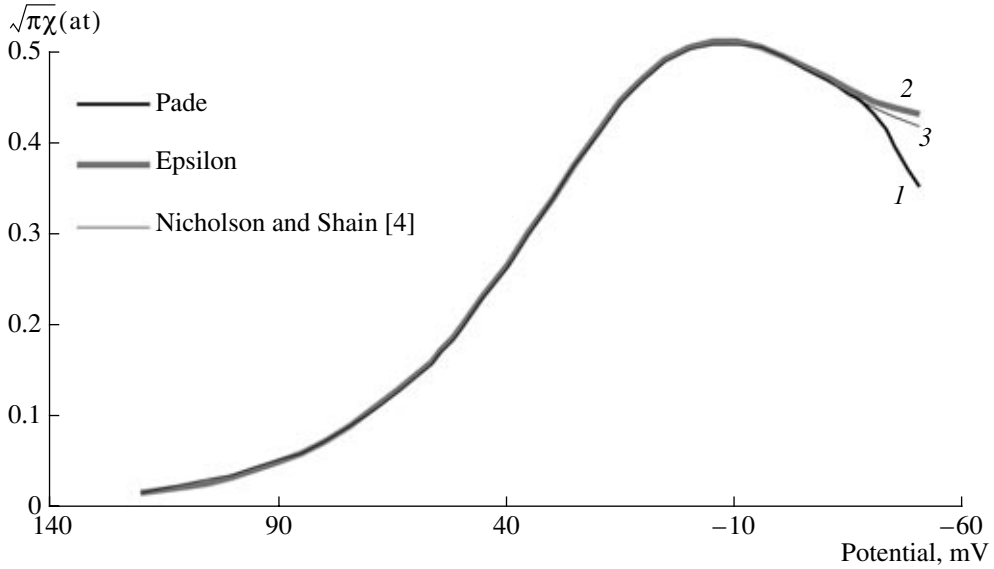

Fig. 8. Graph of current vs. potential using Pade approximation and epsilon algorithm procedures compared with values from Nicholson and Shain for the scheme of catalytic reaction with irreversible charge transfer.

$$\frac{\partial c_R}{\partial t} = D_R\frac{\partial^2 c_R}{\partial x^2} - k_f c_R. \quad (84)$$

The initial and boundary conditions are as follows:

$$t = 0, \quad x \geq 0 : c_O = c_O^b, \quad (85)$$

$$t \geq 0, \quad x \longrightarrow \infty : c_O \longrightarrow c_O^b, \quad (86)$$

$$t \geq 0, \quad x = 0 : D_O\frac{\partial c_O}{\partial x} = c_O k_i e^{bt} \quad (87)$$

$$D_O\frac{\partial c_O}{\partial x}(x = 0) = \frac{i}{nFA}. \quad (88)$$

From the boundary conditions, current is evaluated and given by

$$i = nFAc_O^b\sqrt{\pi D_O a}\,\chi(bt). \quad (89)$$

The explicit expression for the current function $\chi(at)$ as an infinite series for this scheme is given by [4]:

$$\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[(\sqrt{\pi})^j\prod_{i=1}^{j-1}\sqrt{(k_f/b)+i}\right] \times \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)\right)\right], \quad (90)$$

where $b = \alpha n_a F v/RT$. The current function represented by above equation (60) is converted to a useful rational function using the Pade approximation, in [5/6] approximant, and is expressed as

$$\sqrt{\pi}\chi(bt) = \frac{1.6344 + 1.0136x + 0.3063x^2 + 0.0573x^3 + 0.0035x^4 - 0.00000035x^5}{1 + 2.6603x + 3.0387x^2 + 1.9090x^3 + 0.6956x^4 + 0.1392x^5 + 0.0118x^6}, \quad (91)$$

where $x = \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)\right)\right]$.

For evaluation of current function, the value of $N = 9$ is adopted in the procedure of epsilon algorithm. The values of current obtained for various potential values obtained by epsilon algorithm and Pade approximant with the Nicholson and Shain [4] are tabulated in Table 8. And also the graph for the current vs. potential for the above two procedures are drawn with the current vs. potential values represented by Nicholson and Shain in his paper [4] in Fig. 8.

5. DISCUSSION AND CONCLUSIONS

Using the procedures described above, the current function was calculated for all the eight cases from the series solutions. By trial and error, it was found that [5/6] Pade and [10/11] Pade give highly reproducible current values in the negative potential region as well. And also $N = 9$ or $N = 11$ gives comparable values with those values presented by Nicholson and Shain [4]. In general, in these cases, Pade approximant was found to give quite accurate current function values. It was noted that, in the sixth scheme, for negative potentials, current

Table 8. Current function ($\sqrt{\pi}\chi(bt)$) values with a [5/6] Pade approximation sequence and its coefficients for the scheme of catalytic reaction with irreversible charge transfer

Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from			Potential, mV	Current functions $\sqrt{\pi}\chi(bt)$ from		
	Pade approximation	epsilon convergence	Nicholson and Shain [4]		Pade approximation	epsilon convergence	Nicholson and Shain [4]
120	0.0163	0.0163	0.016	10	0.4719	0.4719	0.469
100	0.0349	0.0349	0.035	0	0.5064	0.5064	0.504
80	0.0730	0.0730	0.072	–10	0.5130	0.5130	0.511
60	0.1459	0.1459	0.145	–20	0.4974	0.4977	0.497
50	0.2001	0.2001	0.198	–30	0.4694	0.4717	0.47
40	0.2661	0.2661	0.264	–40	0.4328	0.4463	0.44
30	0.3400	0.3400	0.339	–50	0.3529	0.4317	0.421
20	0.4127	0.4127	0.41				

Note: Reaction: $R \underset{}{\overset{k_f}{\rightleftharpoons}} Z$, $O + ne \longrightarrow R$; series solution: $\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[(\sqrt{\pi})^{j}\prod_{i=1}^{j-1}\sqrt{(k_f/b)+i}\right]$

$\times \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)\right)\right]$; potential scale: $(E-E^0)\alpha n_a - (RT/F)\ln\sqrt{\pi Db}/k_s$; in the case of epsilon convergence algorithm: $N = 9$; current expression using [5/6] Pade approximant:

$$\sqrt{\pi}\chi(bt) = \frac{1.6344 + 1.0136x + 0.3063x^2 + 0.0573x^3 + 0.0035x^4 - 0.00000035x^5}{1 + 2.6603x + 3.0387x^2 + 1.9090x^3 + 0.6956x^4 + 0.1392x^5 + 0.0118x^6}.$$

values are deeply divergent. Hence, a good rational function could not be represented by Pade approximation as well as by the epsilon algorithm. In such a case, that is, for the sixth scheme, we can consider the construction of a separate Pade function for current values of the negative potentials alone.

Typical current functions calculated for different potential values using the two procedures for all the eight cases are compared with those values presented by Nicholson and Shain [4] in Tables 1–8 together with the graphical representation. It is also to be noted that the orders of the Pade and epsilon convergence are not unique. For investigation of reaction mechanisms, only peak current and potential are normally used in the formulation of diagnostic criteria. A great deal of information contained in the rest of the wave is ignored. Now, the user of voltammetric technique can take the help of epsilon algorithm and Pade approximant procedures presented in this paper to exploit for investigation of the reaction mechanism not only the peak current in the formulation of the diagnostic criteria but also the information contained in the rest of the wave.

The series solution for the electron transfer processes involving coupled chemical reactions under linear sweep voltammetric conditions are indeed quite difficult to sum up. Some of the series are indeed highly divergent as shown by the coefficients of series solutions. In the Pade approximant [M/N], it was found that N should be greater than M or $N = M + 1$ to achieve optimal results over a wide potential range. In series solutions involving chemical reaction rate parameters, no simplifying approximation of the series was found to be necessary for finding out the solution. The availability of an algebraic expression is more preferable especially for simulating theoretically, the voltammograms for various values of system parameters. Finally, it is to be noted that the values of N or M are not the unique values. Only for illustration and to indicate the usefulness of the method, the values of $N = 9$ were used in epsilon algorithm and $M = 5$ and $N = 6$ were adopted. These values can be altered by the appropriately by the user his for analysis and implementation.

NOTATION

x—distance from the electrode
t—time
T—temperature, K
F—Faraday constant
R—gas constant
n—number of electrons
v—potential scan rate
k_i—rate constant at the initial potential
c_O—concentration of the substance O
c_R—concentration of the substance R
c_O^b—bulk concentration of the substance O
c_R^b—bulk concentration of the substance R
D_O, D_R, D_X—diffusion coefficient
E—potential of the electrode
E^0—formal electrode potential
$E_{1/2}$—polarographic half-wave potential
E_p—peak potential

APPENDIX 1

Consider the typical infinite series (90) in the scheme of catalytic reaction with irreversible charge transfer, which is divergent for negative potential. Now, we compute the value of the current function for the potential value –60 mV. A numerical approximation to current function is obtained from its first $2n + 1$ partial sums, and they are taken as ε_0^m with $\varepsilon_{-1}^m = 0$. The quantities ε_{s+1}^m are evaluated using (3) and tabulated as lozenge diagram in Table 9 for $N = 5$. Finally, ε_4^1 gives the current function value.

APPENDIX 2

Consider the typical infinite series (90) in the scheme of catalytic reaction with irreversible charge transfer given by [4]:

$$\sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty}(-1)^{j+1}\left[(\sqrt{\pi})^j\prod_{i=1}^{j-1}\sqrt{(k_f/b)+i}\right] \times \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)\right)\right]. \quad \text{(A2.1)}$$

The [5/6] Pade approximant is

$$[L/M] = (A_0 + A_1x + A_2x^2 + A_3x^3 + A_4x^4 + A_5x^5)/(1 + B_1x + B_2x^2 + B_3x^3 + B_4x^4 + B_5x^5 + B_6x^6), \quad \text{(A2.2)}$$

where

$$x = \exp\left[\frac{-j\alpha n_a F}{RT}\left(E - E^0 + \frac{RT}{\alpha n_a F}\ln\left(\frac{\sqrt{\pi Db}}{k_s}\right)\right)\right].$$

Equate the equations (A.1) and (A.2), and by matching the coefficient of x^6, x^7, x^8, x^9, x^{10}, x^{11}, we get a set of linear equations for B_i (i = 1 to 6) in matrix form as

$$\begin{pmatrix} -2.7089 & 1.954 & -1.3056 & 0.8163 & -0.4813 & 0.2692 \\ 3.4304 & -2.708 & 1.9540 & -1.3056 & 0.8163 & -0.4513 \\ -3.8893 & 3.430 & -2.7089 & 1.9540 & -1.3056 & 0.8163 \\ 3.8252 & -3.889 & 3.4304 & -2.7089 & 1.9540 & -1.3056 \\ -3.0818 & 3.825 & -3.8893 & 3.4304 & -2.7089 & 1.9540 \\ 1.7728 & -3.081 & 3.8252 & -3.8893 & 3.4304 & -2.7089 \end{pmatrix}\begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} 3.4304 \\ -3.8893 \\ 3.8252 \\ -3.0810 \\ 1.7728 \\ -3.0081 \end{pmatrix}. \quad \text{(A2.3)}$$

Solving above linear equations, we get the B values as

$$\begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} 2.6603 \\ 3.0387 \\ 1.9090 \\ 0.6956 \\ 0.1392 \\ 0.0118 \end{pmatrix}. \quad \text{(A2.4)}$$

Again, by equating the constant term and the coefficient of x, x^2, x^3, x^4, x^5, respectively, we have a set of linear equations as

$$\begin{aligned} A_0 &= 0.2692 \\ A_1 &= -0.4813 + (0.2692)B_1 \\ A_2 &= 8163 - (0.4813)B_1 + (0.2692)B_2 \\ A_3 &= -1.3056 + (8163069)B_1 - (0.4813)B_2 + (0.2692)B_3 \\ A_4 &= 1.9570 - (1.3056)B_1 + (8163069)B_2 - (0.4813)B_3 + (0.2692)B_4 \\ A_5 &= -2.7089 + (1.9540)B_1 - (1.3056)B_1 + (8163069)B_2 - (0.4813)B_3 + (0.2692)B_4. \end{aligned} \quad \text{(A2.5)}$$

Solution of the equations (A.5) gives the values of A as

$$\begin{pmatrix} A_0 \\ A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{pmatrix} = \begin{pmatrix} 1.6344 \\ 1.0136 \\ 0.3063 \\ 0.0573 \\ 0.0035 \\ 0.0000 \end{pmatrix}. \quad \text{(A2.6)}$$

By (A.2) and with the values of A's and B's, the Pade [5/6] approximant for the current function is expressed as

$$\sqrt{\pi}\chi(bt) = \frac{1.6344 + 1.0136x + 0.3063x^2 + 0.0573x^3 + 0.0035x^4 - 0.00000035x^5}{1 + 2.6603x + 3.0387x^2 + 1.9090x^3 + 0.6956x^4 + 0.1392x^5 + 0.0118x^6}. \quad \text{(A2.7)}$$

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