

# LINEAR SWEEP VOLTAMMETRY OF IRREVERSIBLE CHARGE TRANSFER COUPLED WITH IRREVERSIBLE CATALYTIC REACTION UNDER DIFFUSION-CONVECTION CONTROL : AN INTEGRAL EQUATION APPROACH

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The theory of linear sweep voltammetry at tubular electrodes, under hydrodynamical conditions, has been developed for the processes controlled by convective diffusion and by the rate of catalytic reaction which regenerate the reactant at the surface of electrode. The mathematical model developed under appropriate initial and boundary conditions is converted to an integral equation which is solved numerically to show the effects of experimentally measurable parameters on current potential voltammograms. A simple procedure to predict the kinetic reaction rate for unknown system is suggested.

**Key Words :** Linear Sweep Voltammetry; Irreversible Charge Transfer; Diffusion Convection Control; Kinetic Reaction Rate

## NOMENCLATURE

The values of various constants and parameters used for numerical calculations are given as:

$a$  radius of the electrode (0.1 cm)

$l$  length of the electrode (1.0 cm)

$C_0^0$  Initial bulk molar concentration ( $10^{-7}$  mol ml $^{-1}$ )

$D$  Diffusion coefficient ( $0.567 \times 10^{-5}$  cm sec $^{-1}$ )

$R$  Gas constant (8.31 joules, mol $^{-1}$  K $^{-1}$ )

$T$  Absolute temperature (298 K)

$F$  Faraday's constant (96487 cal mol $^{-1}$ )

$E^0$  Standard electrode potential ( $-0.063$ V vs SCE)

$u$  Parameter ( $= \ln \theta$ ) representing the difference of initial potential  $E_i$  and syandard electrode potential  $E^0$  (8)

$v$  Potential scan rate (0.0083, 0.0167, 0.0501 V sec<sup>-1</sup>.)

$v_a$  Axial flow velocity (0.5305, 1.0161, 1.6977 cm sec<sup>-1</sup>.)

$\alpha$  transfer coefficient (0.66)

$n$  Number of electrons involved in charge transfer reaction (2)

$k_0$  charge transfer rate constant ( $4.0 \cdot 10^{-5}$  cm sec<sup>-1</sup>.)

$k_f$  chemical reaction rate (44.9 sec<sup>-1</sup>.)

$\delta = (k_f)/(nFv/RT)$ , a non-dimensional kinetic parameter

$\lambda_n$  Magnitude of  $n^{\text{th}}$  zero of  $Ai'(\eta)$

(value of first seventy zeros of  $Ai'(\eta)$  are used for calculations?)

## 1. INTRODUCTION

Nicholson and Shain<sup>1</sup> presented the theory of linear sweep voltammetry for different types of electrode processes coupled with first order chemical reaction under quiescent conditions. Since no consideration was given to natural convection developed in the solution due to density variations in the above investigation, attempts were made to develop the theory of linear sweep voltammetry under well defined forced convective field conditions.<sup>2-8</sup> Galus and Adams<sup>9</sup> made theoretical studies of an irreversible first order chemical reaction succeeding a reversible charge transfer occurring at the rotating disc electrode. These results were experimentally validated by Tong *et al.*<sup>10</sup> and Philip<sup>11</sup>. The theory of coupled electrode charge transfer reaction followed by chemical reaction known as EC reaction occurring at tubular and channel electrodes under steady state conditions was developed by Compton and clones and Takuda *et al.*<sup>12</sup>.

For catalytic reactions which regenerate the reactants at the surface of the electrode, theoretical developments were made under steady state conditions by Gerischer<sup>13</sup>, Klatt and Blaedel<sup>14</sup>, Aoki *et al.*<sup>15</sup> and Ng and Chen<sup>16</sup>. Fully time dependent mathematical models for catalytic as well as other kinetic cases of first order homogeneous chemical reaction following a reversible charge transfer at the electrode surface were developed by the authors.<sup>17-18</sup>

In the present investigation, a mathematical model for fully time dependent, convective-diffusion process was developed in which an irreversible charge transfer at the electrode surface is followed by an irreversible catalytic reaction which regenerates the reactant at the electrode surface and the solution containing electro-active species is flowing laminarly through the tubular electrode. Using the appropriate initial and boundary conditions, the model is converted to an integral equation that is solved, numerically, to depict the quantitative behaviour of electroactive species through current potential curves, commonly known as CV curves or current-potential voltammograms. The effects of experimentally controlled parameters, namely potential scan rate and axial flow rate on these curves are shown graphically. The effect of catalytic reaction rate is governed by a non-dimensional parameter  $\delta$ . For diagnostic investigations, a relationship between peak current and  $\delta$  is developed which suggests a simple procedure to predict catalytic reaction rates for unknown system. An earlier model developed by the authors<sup>7</sup> for irreversible charge transfer reaction only without the coupling of catalytic reaction is obtainable from the present general model for  $\delta = 0$ .

## 2. FORMULATION OF THE PROBLEM

The reaction process in which an irreversible redox reaction is followed by an irreversible catalytic reaction is represented as:



and



$R$  produced by electrode reduction process reacts chemically with  $Z$  to produce the initial substance  $O$ .

For these reactions occurring at the tubular electrode through which the solution containing electroactive species passes under laminar flow regime, the time-dependent convective diffusion boundary value problem may be written as:

$$\frac{\partial C_0}{\partial t} + v_a \left( 1 - \frac{r^2}{a^2} \right) \frac{\partial C_0}{\partial z} = D_0 \left[ \frac{\partial^2 C_0}{\partial r^2} + \frac{1}{r} \frac{\partial C_0}{\partial r} \right] + k_f C_R; \quad \dots (2.3)$$

and

$$\frac{\partial C_R}{\partial t} + v_a \left( 1 - \frac{r^2}{a^2} \right) \frac{\partial C_R}{\partial z} = D_R \left[ \frac{\partial^2 C_R}{\partial r^2} + \frac{1}{r} \frac{\partial C_R}{\partial r} \right] + k_f C_R; \quad \dots (2.4)$$

with initial and boundary conditions

$$t = 0, 0 \leq r \leq a, 0 \leq z \leq l; C_0 = C_0^0, C_R = C_R^0 (\approx 0), \quad \dots (2.5)$$

$$t > 0, 0 \leq r \leq a, z = 0; C_0 = C_0^0, C_R = C_R^0 (\approx 0), \quad \dots (2.5a)$$

and

$$t > 0, r = 0, 0 \leq z \leq l; C_0 = C_0^0, C_R = C_R^0 (\approx 0), \quad \dots (2.5b)$$

$$t > 0, r = a, 0 \leq z \leq l; D_0 \frac{\partial C_0}{\partial r} = -D_R \frac{\partial C_R}{\partial r} = -\frac{i(t)}{nFA} \quad \dots (2.5c)$$

$$t > 0, r = a, 0 \leq z \leq l; D_0 \frac{\partial C_0}{\partial r} = -k^l C_0, \quad \dots (2.5d)$$

where  $C_0$ ,  $C_R$  and  $D_0$ ,  $D_R$  are concentrations and diffusion coefficients of electroactive species  $O$  and  $R$  respectively;  $r$ ,  $z$  are the radial and axial space variables in cylindrical coordinates system;  $a$ ,  $l$  are the radius and length of the tubular electrode;  $C_0^0$  is the initial bulk molar concentration of  $O$ ;

$k'$  and  $k_f$  are redox reaction rate and catalytic reaction rate respectively and  $V_a$  is the axial flow rate. The term  $i(t)$  is the unknown current density function.

The difference of this model from that developed in ref. [7] is only in eq. (2.1) where Nerstian diffusion process is replaced by irreversible redox process in which the proportionality of reaction rate to potential difference at the electrode surface is governed by Eyring equation<sup>1</sup> as:

$$k' = k_0 \exp [- \alpha n F / RT \{ E(t) - E^0 \}], \quad \dots (2.6)$$

where  $\alpha$  is the transfer coefficient,  $E^0$  is standard electrode potential and  $n$  is the number of electrons involved in redox reaction.  $E(t)$  is a known potential function depending on time.

For linear sweep voltammetry.

$$E(t) = E_i - vt, \quad \dots (2.7)$$

where  $E_i$  is the initial electrode potential and  $v$  is the potential scan rate.

For further analysis, the diffusion coefficients  $D_0$  and  $D_R$  are taken equal to  $D$  that leads to a well-known consequence that

$$C_0(r, z, t) + C_R(r, z, t) = C_0^0, \quad \dots (2.8)$$

Furthermore, following three assumptions are used to simplify the mathematical expressions. These are :-

(i) The time taken for the reactants to diffuse across the tubular electrode ( $\approx a^2/D$ ) is much greater than the time taken for axial convection along the length of electrode ( $\approx l/v_a$ ) i.e.,  $v_a a^2 / l D \gg 1$ .

(ii) The diffusion layer is much smaller than the boundary layer near the tubular electrode surface and the flow profile is assumed linear instead of parabolic in the diffusion layer. This is known as Leveque approximation<sup>19</sup>.

(iii) The smallness of the dimensions of tubular electrode leads to the assumption of uniform accessibility of the electrode surface. Thus the concentration gradients of  $O$ ,  $R$ ,  $Z$  components along the axial direction are approximated by their average values over the whole length of the electrode. This is referred to as Singh and Dutt approximation<sup>20</sup> and mathematically represented as:

$$\frac{\partial C_0}{\partial z} \approx \frac{C_0 - C_0^0}{l} = \frac{\hat{C}_0}{l},$$

and

$$\frac{\partial C_R}{\partial z} \approx \frac{C_R - C_R^0}{l} = \frac{\hat{C}_R}{l}.$$

Furthermore, by using the transformations :

$$P = \left[ \frac{2v_a \sqrt{D}}{al} \right]^{\frac{1}{3}}, \quad \dots (2.9)$$

$$\Lambda = \frac{P}{\sqrt{k_f}}, \quad \dots (2.9a)$$

$$\xi = \frac{\Lambda \sqrt{k_f} (a-r)}{\sqrt{D}}, \quad \dots (2.9b)$$

$$t' = \Lambda^2 k_f t, \quad \dots (2.9c)$$

$$\Psi = (C_0 + C_R) - C_0^0 \quad \dots (2.10)$$

and

$$\phi = C_R \exp(k_f f), \quad \dots (2.11)$$

eqs. (2.3) to (2.4) are decoupled as

$$\frac{\partial \Psi}{\partial t'} + \xi \Psi = \frac{\partial^2 \Psi}{\partial \xi^2} \quad \dots (2.12)$$

and

$$\frac{\partial \phi}{\partial t'} + \xi \phi = \frac{\partial^2 \phi}{\partial \xi^2}. \quad \dots (2.13)$$

subject to the conditions:

$$t' = 0, 0 \leq \xi \leq a \Lambda \frac{k_f^{1/2}}{2} D^{-\frac{1}{2}}; \phi = \Psi = 0, \quad \dots (2.14)$$

$$t' > 0, \xi \rightarrow a \Lambda \frac{k_f^{1/2}}{2} D^{-\frac{1}{2}}; \phi = \Psi = 0, \quad \dots (2.14a)$$

$$t' > 0 = \xi = 0; \frac{\partial \Psi}{\partial \xi} = 0, \quad \dots (2.14b)$$

$$t' > 0, \xi = 0; \frac{\partial \phi}{\partial \xi} = - \frac{i(t') \exp(\Lambda^{-2} t')}{nFA \Lambda \sqrt{k_f} D} \quad \dots (2.14c)$$

and

$$t' > 0, \xi = 0; \frac{\partial \phi}{\partial \xi} = - \frac{k_i \exp[(\beta + \Lambda^{-2}) t']}{\Lambda \sqrt{k_f} D} C_0. \quad \dots (2.14d)$$

where

$$k_i = k_0 \exp \left[ \frac{\alpha n F}{RT} (E^0 - E_i) \right] \quad \dots (2.15)$$

and

$$\beta = \frac{\alpha n F v}{RTP^2}. \quad \dots (2.16)$$

Using the properties from Laplace transformation, eqs. (2.12) to (2.13) reduce to Airy's equations whose solutions can be written as

$$\Psi = A_1 Ai(\eta) + B_1 Bi(\eta) \quad \dots (2.17)$$

and

$$\bar{\phi} = A_2 A_i(\eta) + B_2 B_i(\eta), \quad \dots (2.17a)$$

where  $A_1, A_2, B_1, B_2$  are arbitrary constants to be evaluated with the help of eqs. (2.14) to (2.14b).  $Ai(\eta)$  and  $Bi(\eta)$  are Airy functions. As the solution is being investigated within the diffusion layer which is very small as compared to the radius of the tube, the conditions on  $\Psi$  and  $\phi$  on the centre of the tube can be safely taken as  $\eta$  tends to infinity. Thus, to have finite and bounded solutions,  $B_1$  and  $B_2$  must be zero. Thus, we get

$$\phi = L^{-1} \left[ F(s) \frac{A_i(\eta)}{A_i'(\eta_0)} \right], \quad \dots (2.17b)$$

where  $L^{-1}$  is the inverse Laplace transform operator  $\eta = \xi + s$  ( $s$  being the parameter of Laplace transform) and  $\eta_0$  is the value of  $\eta$  at the surface of the electrode. Furthermore,

$$F(s) = \int_0^{\infty} e^{-st} f(t) dt = L[f(t)], \quad \dots (2.18)$$

where

$$f(t) = - \frac{i(t) \exp(\Lambda^{-2} t)}{nFA\Lambda\sqrt{k_f D}} \quad \dots (2.19)$$

or

$$f(t) = - \frac{k_i \exp(\beta + \Lambda^{-2})}{\Lambda\sqrt{k_f D}} C_0. \quad \dots (2.19a)$$

$Ai(\eta)$  and  $Ai'(\eta)$  are Airy function of first kind and its derivative respectively.

As calculus of residues helps to express inverse Laplace transform of  $Ai(\eta)/Ai'(\eta_0)$  in the form

$$L^{-1} \left[ \frac{Ai(\eta)}{Ai'(\eta_0)} \right] = - \sum_{n=1}^{\infty} \frac{Ai(-\lambda_n + \xi)}{\lambda_n Ai'(-\lambda_n)} \exp(-\lambda_n t') \\ = -g(\xi, t') \text{ (say),} \quad \dots (2.20)$$

where  $\lambda_n$  is the magnitude of  $n$ th zero of  $A_i'(\eta_0)$ , eq. (2.17b) can be written as

$$\phi = \int_0^{t'} f(T) g(\xi, t' - T) dT. \quad \dots (2.21)$$

Since at the surface of the electrode

$$g(\xi, t' - T) |_{\xi=0} = \sum_{n=1}^{\infty} \frac{1}{\lambda_n} \exp[-\lambda_n (t' - T)] \quad \dots (2.22)$$

so eq. (2.21) is

$$\phi = \int_0^{t'} \frac{k_i C_0 \exp(\beta + \Lambda^{-2}) T}{\Lambda \sqrt{k_f D}} \left[ \sum_{n=1}^{\infty} \frac{1}{\lambda_n} \exp(-\lambda_n (t' - T)) \right] dT. \quad \dots (2.23)$$

From the transformations (2.10) and (2.11) and  $\Psi = 0$ , the relationship between  $\phi$  and  $C_0$  is

$$\phi = (C_0^0 - C_0) e^{\Lambda^{-2} t'}. \quad \dots (2.24)$$

Using eq. (2.19a) in (2.23), an integral equation is obtained as

$$\chi(y) = e^{(y-u)} - e^{(y-u)} \int_0^y K(y, z) \chi(z) dz, \quad \dots (2.25)$$

where

$$y = \beta t'; z = \beta T, \quad \dots (2.26)$$

$$u = \frac{\Lambda \beta \sqrt{k_f D}}{k_i}, \quad \dots (2.27)$$

$$\delta = \frac{\Lambda^{-2}}{\beta}, \quad \dots (2.28)$$

$$K(y, z) = \sum_{n=1}^{\infty} \frac{1}{\lambda_n} \exp \left[ - \left( \frac{\lambda_n}{\beta} + \delta \right) (y - z) \right] \quad \dots (2.29)$$

and

$$\chi(y) = \frac{i(y)}{nFA\sqrt{k_f D} \Lambda C_0^0 \beta} \quad \dots (2.30)$$

Equation (2.25) is a volterra integral equation of second kind. This reduces to the expression obtained by the authors in ref. [7] if  $\delta$  is taken as zero, i.e. when no catalytic reaction is following the electrochemical reduction from  $O$  to  $R$ . Thus model in ref. [7] is a sub model of the present general model.

### 3. SOLUTION

Since  $\chi(\beta t')$  and  $\beta t'$  can be represented by current function  $i(\beta t')$  and potential function  $E(\beta t')$  respectively, as given below.

$$i(\beta t') = nFA\sqrt{k_f D} \beta C_0^0 \chi(\beta t') \quad \dots (3.1)$$

and

$$\alpha n [E^0 - E(\beta t')] = \frac{DT}{F} \ln \left[ \frac{\Lambda \beta \sqrt{k_f D}}{k_i} \right] + \frac{RT}{F} (\beta t' - u). \quad \dots (3.2)$$

The relationship between current and potential can be established. Due to the presence of an infinite series in the kernel  $K(y, z)$  of the integral eq. (2.25), a numerical procedure as discussed by Wagner<sup>21</sup> is adopted to find the solution  $\chi(\beta t')$  in terms of  $\beta t'$ .

According to Nicholson and Shain<sup>1</sup>, the values of  $\chi(\beta t')$  are independent of  $u$ , which corresponds to selecting an initial potential positive to the foot of wave for a particular value of velocity and scan rate, provided its value is greater than 7. The entire wave shifts along the potential axis as a function of  $u$  with respect to initial potential. So in the present study, the value of  $u$  is fixed at 8. The numerical procedure given by Wagner<sup>21</sup> is applied to solve integral eq. (2.25) which gives the final expression for numerical computations as:

$$\chi(mh) = \frac{1 - \sum_{v=0}^{m-1} A(m, v) \chi(vh)}{e^{(u-mh)} + A(m, m)}, \quad \dots (3.3)$$

where  $A(m, v)$  are the weights of the numerical procedure. A brief outline of Wagner method is given in the Appendix. The current potential curves can be obtained from eqs. (3.1) and (3.2).

### 4. RESULTS AND DISCUSSION

The effects of experimentally measurable parameters viz. potential scan rate  $\nu$  or axial flow velocity  $v_a$  is investigated and shown in Figs. 1 and 2 respectively. The current peaks become predominant



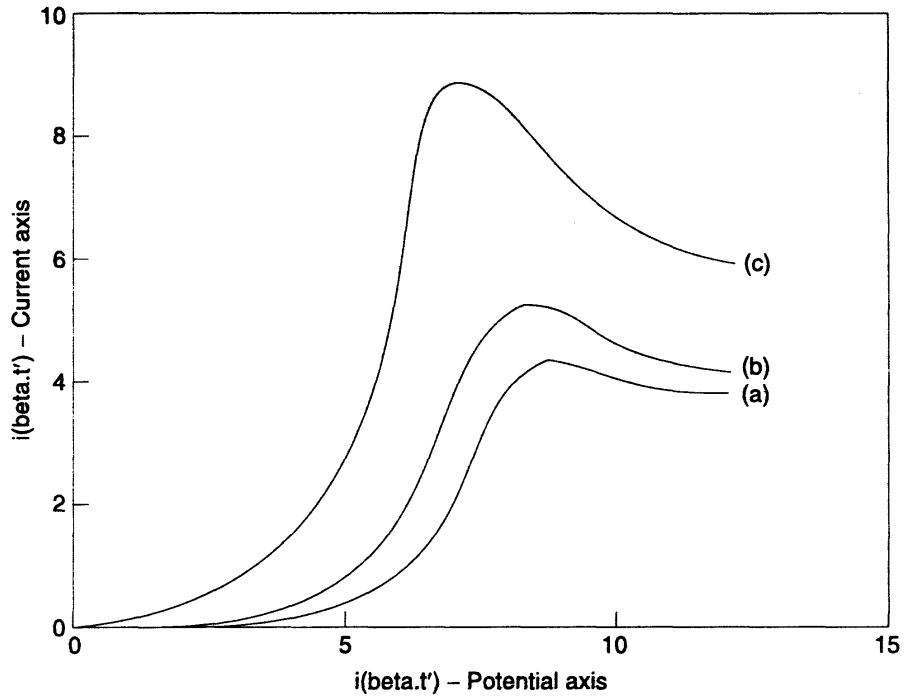


FIG. 1. Current Potential Curves ( $v = 0.5305$  cm/sec.  $\delta = 0.05$ ,  $n = 2$ ,  $u = 8$ ,  $\alpha = 0.66$ )  
 Values of scan rate (a) 0.0083, (b) 0.0617, (c) 0.0501 volts/sec.

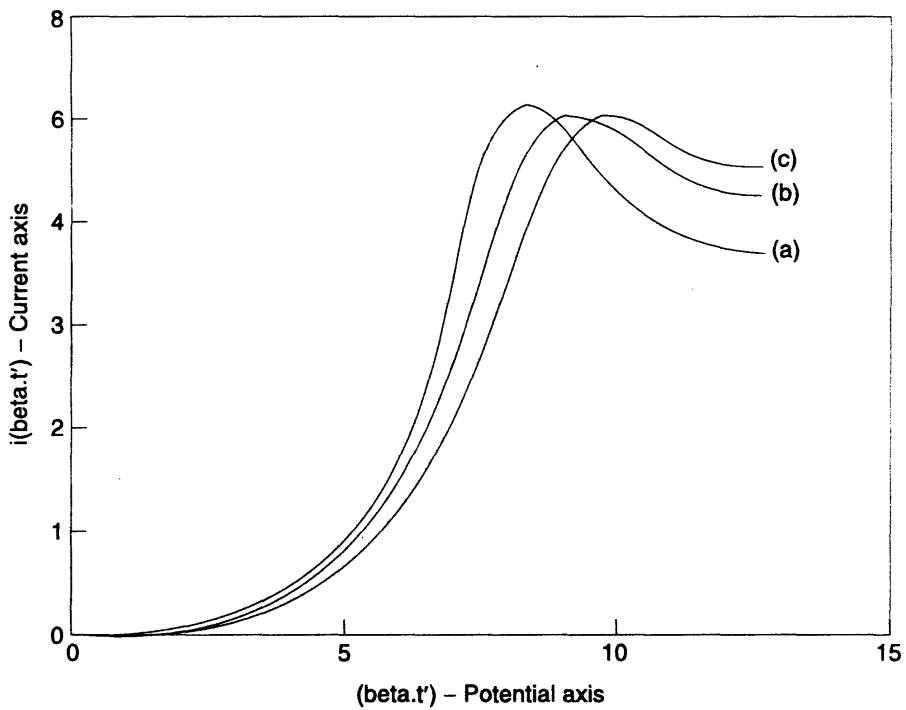


FIG. 2. Current Potential Curves ( $v = 0.0167$  volts/sec.  $\delta = 0.05$ ,  $n = 2$ ,  $u = 8$ ,  $\alpha = 0.66$ )  
 Values of axial velocity (a) 0.5305, (b) 1.0610, (c) 1.6977 cms/sec.

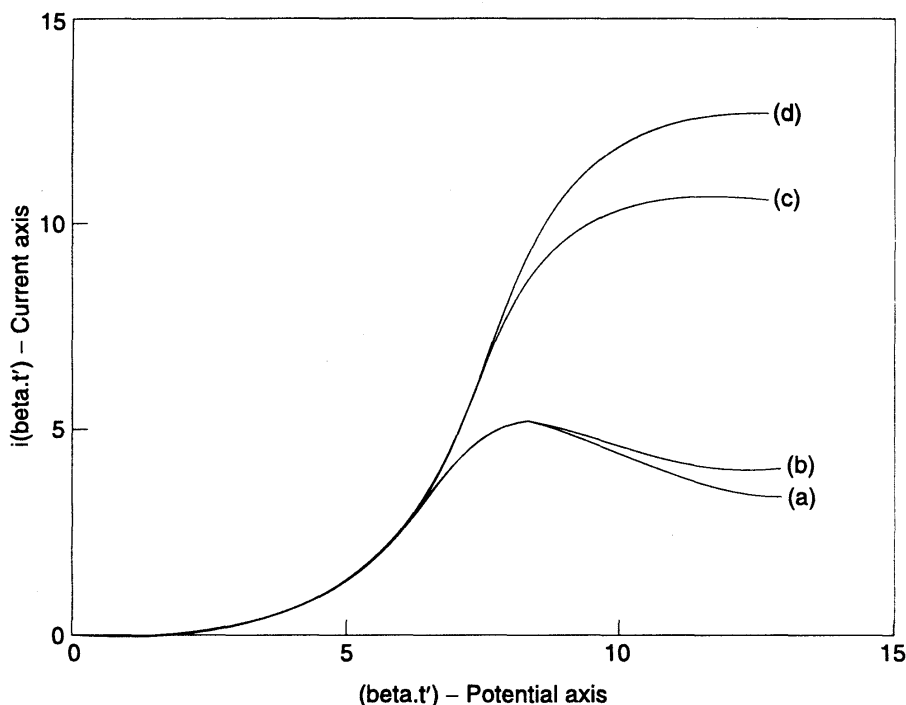


FIG. 3. Current Potential Curves ( $\nu = 0.5305$  cm/sec.,  $n = 2$ ,  $u = 8$ ,  $\alpha = 0.66$ )  
 Values of  $\delta$ : (a) 0.0005, (b) 0.05, (c) 1.0, (d) 1.5

as potential scan rate increases. These variations prove similar earlier finding in other electrochemical processes<sup>6,7,8,17,18</sup>.

These current-potential curves are affected by the catalytic reaction following the charge transfer reaction at the surface of the electrode. The effect of non-dimensional parameter  $\delta$  representing catalytic reaction rate, on current-potential curves is shown in Fig. 3. It depicts that peak current that is the essence of transient stage of linear sweep voltammetry, is prominent for slow catalytic reaction while fast catalytic reactions show only steady state current.

The current potential curves also help to calculate the charge transfer reaction rate  $k'$  and transfer coefficient  $\alpha$ , for an unknown system. The procedure is as follows :

On combining equations (2.5d), (2.30) and (3.2) the relationship between peak concentration and experimental parameters can be written as:

$$\begin{aligned} \frac{(C_0)_p}{C_0} &= [\chi(\beta t')_p] \exp \left[ \frac{\alpha n F}{RT} \left\langle \frac{RT}{\alpha n F} \ln \frac{\Lambda \sqrt{kD} \beta}{k_0} - (E^0 - E_p) \right\rangle \right] \\ &= [\chi(\beta t')_p] \exp [u - (\beta t')_p] \end{aligned} \quad \dots (4.1)$$

Using this equation the relationship between peak potential and peak current can be expressed as

$$i_p = nFA(C_0)_p k_0 \exp \left[ \frac{\alpha n F}{RT} (E^0 - E_p) \right] \quad \dots (4.2)$$

From the current potential curve given by  $\chi(\beta t')$  vs.  $\beta t'$  the values of  $\chi(\beta t')$  the values of  $\chi(\beta t')$  and  $(\beta t')$  at the peak of the graph are substituted in eq. (4.1) to obtain the values of  $(c_0)_p/c_0^0$  which, in turn, is substituted in eq. (4.2). This equation enables to find a relationship between  $i_p$  and  $E_p$ . This eq. (4.2) clearly shows that the plot of  $\ln(i_p)$  vs.  $(E^0 - E_p)$  would be a straight line with intercept  $\ln[nFA \{(c_0)_p\}k_0]$  and slope  $\alpha nF/RT$ . Thus a set of points for peak currents and corresponding peak potentials are obtained from current potential curves by varying axial flow rate or potential scan rate and a straight line is fitted for  $\ln(i_p)$  and  $(E^0 - E_p)$ . The  $\ln(i_p)$ -intercept and slope of the fitted straight line gives  $k_0$  and  $\alpha$  respectively which when substituted in eq. (2.6) gives irreversible charge transfer reaction rate  $k'$ . The model developed can be applied to the reaction scheme studied by Saveant and Vianello.<sup>22</sup> They studied the catalytic currents arising from the chemical re-oxidation in the electrode region of an electrolytically reduced specie in the condition of linear potential sweep chronoamprometry. A theory was presented for the calculation of current/potential waves as a function of parameters of the electrode transfer and chemical processes. Experimental results have been presented for the reduction of  $T_i^{4+}$  in the presence of hydroxylamine. Our theoretical model developed in the present investigation will be tested for the same reaction scheme and the experimental results will be presented in the sequel of present paper.

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#### APPENDIX : BRIEF OUTLINE OF WAGNER'S METHOD

For the numerical solution of integral eq. (2.25) the interval of integration is divided into  $m$  equal parts with width  $h$  and integral is approximated by a summation, i.e.; where the weights are obtained on the assumption that in each subinterval, unknown function  $\chi(z)$  is approximated by a linear expression as -

$$\chi(z) = \chi(vh) + \frac{\zeta}{h} [\chi(vh + h) - \chi(vh)]; \quad vh \leq z \leq v + h,$$

$$\int_0^y K(y-z) \chi(z) dz \approx \sum_{v=0}^m A(m, v) \chi(vh)$$

and

$$\zeta = z - vh.$$

The weights are given by the expressions

$$A(m, 0) = i_0(m, 0) - i_1(m, 0),$$

$$A(m, v) = i_0(m, v) + i_1(m, v-1) - i_1(m, v) \quad \text{for } 1 \leq v \leq m-1$$

and

$$A(m, m) = i_1(m, m - 1),$$

where

$$i_0(m, v) = \int_0^h K(mh, vh + \zeta) d\zeta$$

and

$$i_1(m, v) = \frac{1}{h} \int_0^h \zeta K(mh, vh + \zeta) d\zeta.$$

The expression for numerical computation of  $\chi(mh)$  is

$$\chi(mh) = \frac{1 - \sum_{v=0}^{m-1} A(m, v) \chi(vh)}{e^{(u-mh)} + A(m, m)}$$

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