Mass transport to tubular electrodes

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The mathematical treatment of mass transport in tubular electrodes has been examined for the EC process when a reversible electrode charge transfer is followed by a reversible chemical reaction. The transition from fast chemical reaction to slow chemical reaction is investigated. The system of convective-diffusion equations, representing the physical phenomena, are solved using properties of the integral transform and numerical computation of the integral equation. The effects of the chemical equilibrium parameter, the axial velocity of the flow and the potential scan rate on theoretical current-potential curves are elucidated and a simple procedure to determine the chemical reaction rate constant is presented.

1. Introduction

Recently, tubular and channel electrodes have been used in hydrodynamic voltammetry both for electroanalytical and mechanistic investigations of electrode processes [1,3–5,9,10,14–18,20,21]. Electrochemical techniques in which tubular electrodes have been used include linear and cyclic voltammetry, chronopotentiometry [2], chronoamperometry [6] and AC voltammetry [7]. In our earlier reported work, we have developed mathematical treatment of mass transport involved in LSV and CV for simple as well as complex electrode processes [10–13,18,19].

In this paper, the theory of linear sweep voltammetry for the process in which reversible charge transfer is followed by reversible chemical reaction, is developed. The governing initial boundary value problem in the form of coupled and time dependent convective-diffusion equations with interactive boundary conditions is transformed to a set of integral equations which are solved numerically using Wagner's method [22].

The theoretical current-potential curves are obtained and the effects of chemical

equilibrium constant $K(=k_f/k_b)$ and other parameters, viz. the potential scan rate and the axial flow velocity of solution through the tubular electrode are investigated and are shown in figures (1–5).

2. Formulation of the problem

The reaction process in which a reversible electrode charge transfer is followed by a reversible chemical reaction is generalized as

$$O + ne^- \rightleftharpoons R, \tag{2.1}$$

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Z, \tag{2.2}$$
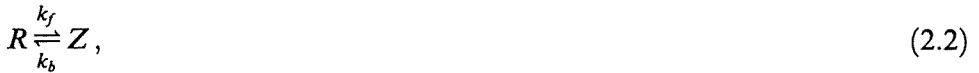
where k_f and k_b are forward and backward chemical reaction rate constants and n is the number of electrons involved in charge transfer reactions.

The mathematical model representing the above process in which the reactants are flowing through a tabular electrode, laminarly, is

$$\frac{\partial C_O}{\partial t} + v_a\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C_O}{\partial z} = D_O\left[\frac{\partial^2 C_O}{\partial r^2} + \frac{1}{r}\frac{\partial C_O}{\partial r}\right], \tag{2.3}$$

$$\frac{\partial C_R}{\partial t} + v_a\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C_R}{\partial Z} = D_R\left[\frac{\partial^2 C_R}{\partial r^2} + \frac{1}{r}\frac{\partial C_R}{\partial r}\right] - k_f C_R + k_b C_Z, \tag{2.4}$$

$$\frac{\partial C_Z}{\partial t} + v_a\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C_Z}{\partial Z} = D_Z\left[\frac{\partial^2 C_Z}{\partial r^2} + \frac{1}{r}\frac{\partial C_Z}{\partial r}\right] + k_f C_R - k_b C_Z, \tag{2.5}$$

subject to

$$t = 0, 0 < r < a, 0 < z < l; \quad C_O = C_O^*, \quad C_R = C_R^*(\approx 0), \quad C_Z = KC_R^*(\approx 0),$$

$$K = \frac{k_f}{k_b};$$

$$t > 0, 0 < r < a, z = 0; \quad C_O = C_O^*, \quad C_R = C_R^*(\approx 0), \quad C_Z = KC_R^*(\approx 0);$$

$$t > 0, r = 0, 0 < z < l; \quad C_O = C_O^*, \quad C_R = C_R^*(\approx 0), \quad C_Z = KC_R^*(\approx 0);$$

$$t > 0, r = a, 0 < z < l; \quad D_O\frac{\partial C_O}{\partial r} = -D_R\frac{\partial C_R}{\partial r} = -\frac{i(t)}{nFA}, \quad D_Z\frac{\partial C_Z}{\partial r} = 0;$$

$$t > 0, r = a, 0 < z < l; \quad \frac{C_O}{C_R} = \exp\left[\frac{nF}{RT}(E - E^0)\right], \tag{2.6}$$

where

$$E = E_i - vt, \text{ and}$$

$E_i = $ initial electrode potential.

The significance of various variables and parameters is given in the nomenclature.

3. Solution

The mathematical expressions given in eqs. (2.1) to (2.6) are non-dimensionalized and transformed as

$$k = k_f + k_b = k_f \frac{(1+K)}{K},$$

$$\psi = C_R + C_Z,$$

$$\phi = \left(C_R - \frac{C_Z}{K} \right) \exp(kt),$$

$$D_O = D_R = D_Z = D,$$

$$P = \left[\frac{2v_a \sqrt{D}}{al} \right]^{1/3},$$

$$\Lambda = P/\sqrt{k},$$

$$\xi = \frac{\Lambda \sqrt{k}(a-r)}{\sqrt{D}},$$

$$t' = \Lambda^2 kt. \tag{3.1}$$

The transformed model is

$$\frac{\partial \overline{C_O^\Lambda}}{\partial t'} + \xi \overline{C_O^\Lambda} = \frac{\partial^2 \overline{C_O^\Lambda}}{\partial \xi^2}, \tag{3.2}$$

$$\frac{\partial \psi}{\partial t'} + \xi \psi = \frac{\partial^2 \psi}{\partial \xi^2}, \tag{3.3}$$

$$\frac{\partial \phi}{\partial t'} + \xi \phi = \frac{\partial^2 \phi}{\partial \xi^2}, \tag{3.4}$$

subject to

$$t' = 0, 0 < \xi < a\Lambda k^{1/2} D^{-1/2}; \quad \overline{C_O^\Lambda} = \psi = \phi = 0; \tag{3.5}$$

$$t' = 0, \xi = a\Lambda k^{1/2}D^{-1/2}; \quad \overline{C_O^\Lambda} = \psi = \phi = 0; \tag{3.6}$$

$$t' > 0, \xi = 0; \quad \frac{\partial \overline{C_O^\Lambda}}{\partial \xi} = \frac{i(t')}{nFA\Lambda k^{1/2}D^{1/2}} = f(t') \quad \text{(say)}; \tag{3.7}$$

$$\frac{\partial \psi}{\partial \xi} = -f(t'); \tag{3.8}$$

$$\frac{\partial \phi}{\partial \xi} = -f(t') \exp(\Lambda^{-2}t'); \tag{3.9}$$

$$t' > 0, \xi = 0; \quad \frac{\overline{C_O^\Lambda} + C_O^*}{C_R} = \frac{\overline{C_O^\Lambda} + C_O^*}{\frac{1}{1+K}(\psi + Ke^{-kt'}\phi)} = \theta e^{-\sigma t'} \tag{3.10}$$

with

$$\theta = \exp\left[\frac{nF}{RT}(E_i - E^0)\right],$$

$$\sigma = \frac{nFv}{RTP^2}.$$

The above transformations are based on following assumptions:

(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. $v_a a^2/lD \gg 1$.

(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 approximation is known as the Leveque approximation [9].

(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 approximation is referred to as Singh and Dutt approximation [8].

The use of the Laplace transformation of eqs. (3.2) to (3.4) with respect to t' reduces them to

$$\frac{d^2\overline{C_O}}{d\eta^2} = \eta\overline{C_O}, \tag{3.11}$$

$$\frac{d^2\bar{\psi}}{d\eta^2} = \eta\bar{\psi}, \tag{3.12}$$

$$\frac{d^2\bar{\phi}}{d\eta^2} = \eta\bar{\phi}. \tag{3.13}$$

With $\eta = s + \xi$ and s as the parameter of Laplace transformation, these equations are of the form of Airy's equation. Since the region of interest under investigation is near the electrode surface and not the whole flow regime, the condition at the axis of the tubular electrode can be safely taken as at infinity. Thus the bounded solutions of eqs. (3.11) to (3.13) are

$$\overline{C_O^A} = L^{-1}\left[F(s)\frac{Ai(\eta)}{Ai'(\eta_0)}\right], \tag{3.14}$$

$$\psi = -L^{-1}\left[F(s)\frac{Ai(\eta)}{Ai'(\eta_0)}\right], \tag{3.15}$$

$$\phi = -L^{-1}\left[F(s - \Lambda^{-2})\frac{Ai(\eta)}{Ai'(\eta_0)}\right], \tag{3.16}$$

where L^{-1} is the inverse Laplace transform operator, η_0 is the value of the variable η at the surface of the electrode and

$$F(s) = \int_0^\infty e^{-st'}f(t')\,dt' = L[f(t')], \tag{3.17}$$

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

The calculus of residuals technique is applied to get the inverse Laplace transform of $Ai(\eta)/Ai'(\eta_0)$ as

$$L^{-1}\left[\frac{A_i(\eta)}{A_i'(\eta_0)}\right] = -\sum_{n=1}^\infty \frac{A_i(-\lambda_n + \xi)}{\lambda_n A_i(-\lambda_n)}\exp(-\lambda_n t')$$

$$= -g(\xi, t') \quad (\text{say}), \tag{3.18}$$

where λ_n is the magnitude of the nth zero of $Ai'(\eta)$. The expressions for C_O, ψ and ϕ are obtained as

$$C_O = C_O^* - \int_0^{t'} f(\tau)g(\xi, t' - \tau)\,d\tau, \tag{3.19}$$

$$\psi = \int_0^{t'} f(\tau)g(\xi, t' - \tau)\,d\tau, \tag{3.20}$$

$$\phi = \int_0^{t'} f(\tau)e^{-A^2\tau}g(\xi, t' - \tau)\, d\tau. \tag{3.21}$$

The expression for concentrations C_O, C_R, C_Z are obtained using the transformation (3.1).

$$C_O = C_O^* - \int_0^{t'} f(\tau)g(\xi, t' - \tau)\, d\tau, \tag{3.22}$$

$$C_R = \frac{K}{1+K}\left[\int_0^{t'} f(\tau)g(\xi, t' - \tau)(K^{-1} + e^{-A^2(t'-\tau)})\right] d\tau, \tag{3.23}$$

$$C_Z = \frac{K}{1+K}\left[\int_0^{t'} f(\tau)g(\xi, t' - \tau)(1 - e^{-A^2(t'-\tau)})\right] d\tau. \tag{3.24}$$

Since we are interested to depict the variation of current given by $f(t')$ with change of potential function $E(t')$, the expression of C_O and C_R from eqs. (3.22)–(3.23) are substituted in the Nernst equation (2.6) to get an integral equation:

$$\frac{1}{1+K}\int_0^y K_1(y, z)\chi(z)\, dz + \frac{K}{1+K}\int_0^y K_2(y, z)\chi(z)\, dz$$

$$= e^{(y-u)} - e^{(y-u)}\int_0^y K_1(y, z)\chi(z)\, dz. \tag{3.25}$$

The integral equation (3.25) is solved numerically using Wagner's method in which the range of integration is subdivided in small subintervals and in each subinterval the unknown function is replaced by a linear polynomial satisfying at the nodal points.

4. Results and discussion

The relationship between current and potential can be established after calculating the behavior of $\chi(\sigma t')$ with respect to $\sigma t'$ from eq. (3.25). Since $\chi(\sigma t')$ and $\sigma t'$ are related to current and potential, respectively, as

$$i(t') = nFAP\sigma D^{1/2}C_O^*\chi(\sigma t'), \tag{4.1}$$

$$E(t') - E^0 = \frac{RT}{nF}(\ln\theta - \sigma t'), \tag{4.2}$$

the behavior of current potential curves known as voltammograms is investigated to study the effects of different parameters in the process.

Depending on the magnitude of kinetic parameters, two limiting cases can be distinguished.

(i) The first limiting case to be considered is that in which the chemical reaction is very slow, so that essentially no chemical reaction takes place during the experiment. Thus as $\delta \to 0$ the integral equation (3.25) reduces to

$$\int_0^y K_1(y, z)\chi(z)\,dz = (1 + \theta e^{-y})^{-1},\tag{4.3}$$

which is the same as reported in our earlier investigation [12]. This equation in [12] was solved by taking only one term of the series in the kernel $K_1(y, z)$. Recently, Compton and Unwin [8] reported that eq. (4.3) can be solved in closed form which gives better results. In the present investigation, this constraint of retaining only one term in $K_1(y, z)$ is removed and the integral equation (4.3) is solved numerically by increasing the number of terms in the series of $K_1(y, z)$ till the convergence is achieved. This convergence is achieved by retaining 70 terms in the series of $K_1(y, z)$ and no further significant improvement was observed by including more terms. Thus, results calculated for the summation of the series for 70 terms are comparable with [8]. The effect of the scan rate and axial velocity on the voltammograms is shown in figs. 1 and 2.

(ii) The second limiting case is that of fast chemical reaction rates. In this situation, the system will be in equilibrium at all times and the only effect will be an anodic displacement of the wave along the potential axis. Thus for large value of δ (i.e. as $\delta \to \infty$), the integral equation (3.25) reduces to

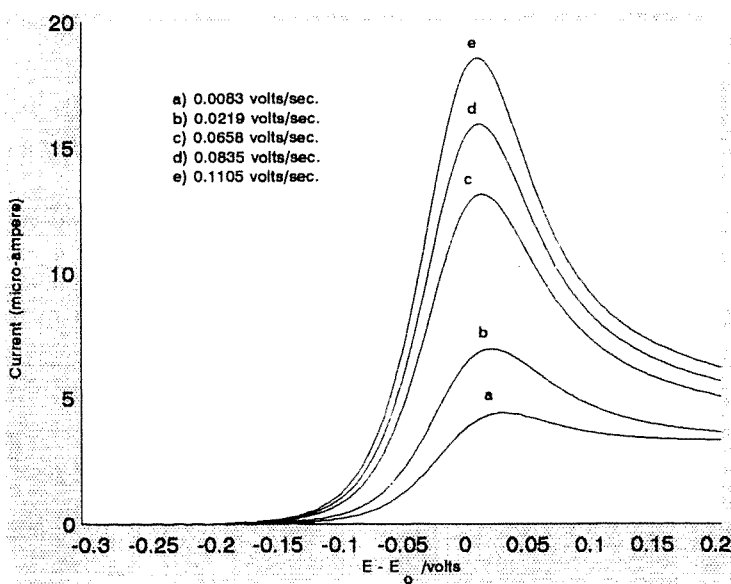$$\int_0^y K_1(y, z)\chi(z)\,dz = (1 + \theta' e^{-y})^{-1},\tag{4.4}$$

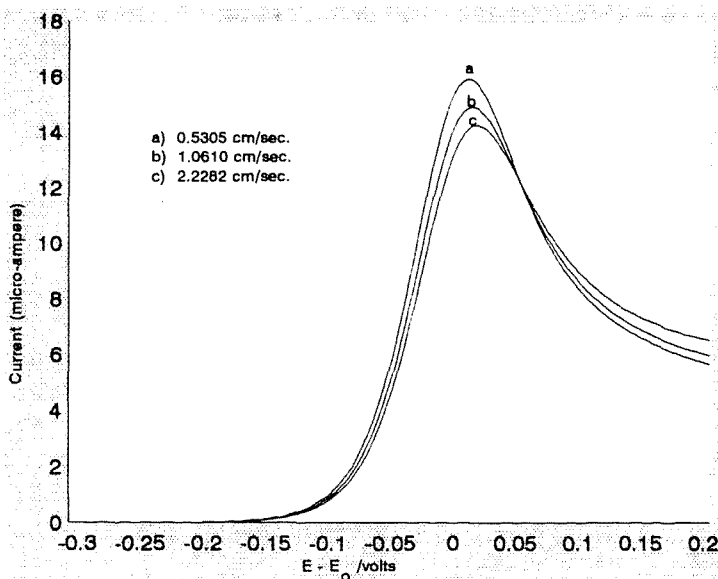Fig. 1. Current-potential curves ($K = 0$, $V_a = 0.5305$ cm/s). Variation of the scan rate.

Fig. 2. Current-potential curves ($K = 0$, $v = 0.0835$ V/s). Variation of the axial velocity.

where

$$\theta' = \exp(u - \ln(1 + K))$$

and the potential axis values are given by

$$(E - E^0) - \frac{RT}{nF}\ln(1 + K) = \frac{RT}{nF}(\ln \theta' - \sigma t') . \tag{4.5}$$

Another important case when δ is small but the chemical equilibrium K is large (i.e. $k_f \gg k_b$) can be considered as if the chemical reaction is treated as irreversible and results obtained are similar to those already reported [19].

The parameters, i.e. potential scan rate, v, and volume flow of the electrolyte through the tubular electrode (related to axial velocity, v_a), are represented by a non-dimensional parameter σ and chemical reaction rates are represented by two non-dimensional parameters δ and K. The variation of K from 1 to large positive values depicts the transition from perfectly reversible to quasi-reversible and then to irreversible chemical reactions. The numerical values used for different parameters and constants are given in the nomenclature. The calculations are carried out keeping 70 terms in the series of kernels K_1 and K_2. The effect of K on CV-curves is shown in fig. 3.

This clearly depicts that the effect of chemical equilibrium constant K can be visualized only during transient current stages and the steady state is not affected by it. The current peak becomes sharp for the transition from perfectly reversible to quasi-reversible chemical reaction following the electrode charge transfer.
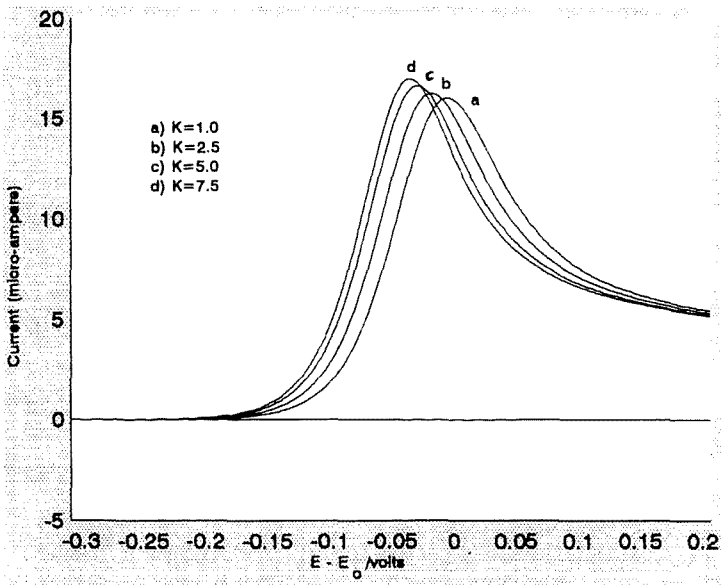
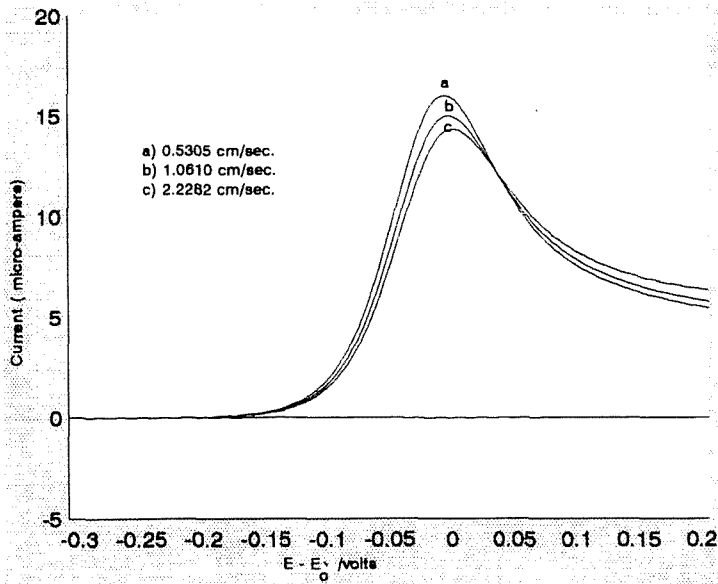Fig. 3. Current-potential curves ($V_a = 0.5305$ cm/s, $v = 0.0835$ V/s). Variation of reaction rates ratio.

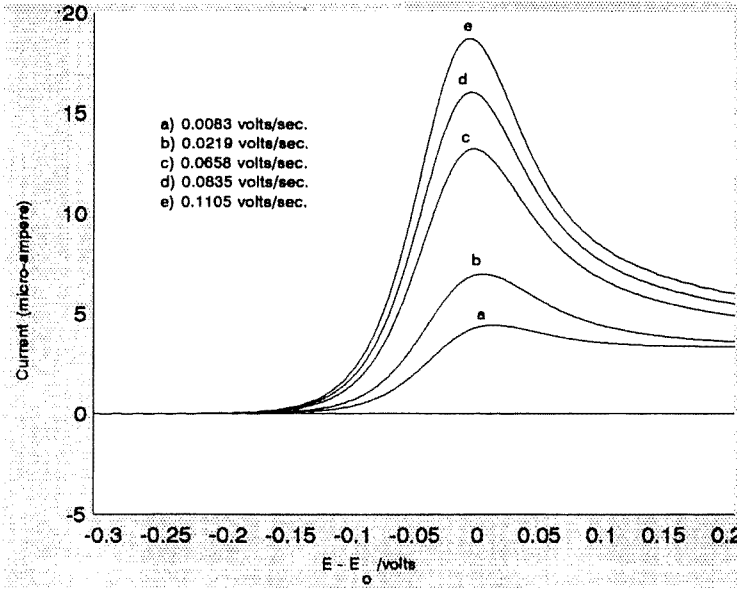Fig. 4. Current-potential curves ($K = 1, v = 0.0835$ V/s). Variation of the axial velocity.

Fig. 5. Current-potential curves ($K = 1$, $V_a = 0.5305$ cm/s). Variation of the scan rate.

The effect of variation of potential scan rate and axial flow velocity on current-potential curves is shown in figs. 4 and 5, respectively, for $K = 1$. The behavior confirms the already reported results for the electrochemical process in which irreversi-
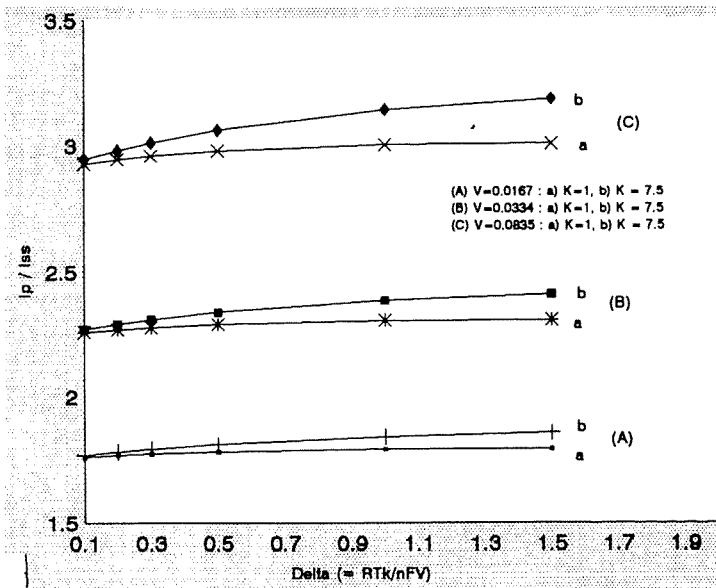

Fig. 6. Variation of δ with I_p/I_{ss}.

ble chemical reaction follows the reversible charge transfer [19]. A plot of the ratio of kinetic peak current (i_p) and steady state current i_{ss} versus the non-dimensional kinetic parameter δ at various values of σ is shown in fig. 6. At each value of σ, with the increase in δ, the ratio $(i_p)/i_{ss}$ increases. These curves are normally referred to as working curves and from these curves it is possible to calculate the reaction rate constants k_f and k_b if i_p/i_{ss} is recorded experimentally and the value of chemical equilibrium K is known.

Thus the present investigation clearly points out that the study of the effect of reversible chemical reaction following the electrode charge transfer reaction is feasible only in the transient stages of linear sweep voltammetry, whereas its steady state analysis does not reveal this effect. Furthermore, the present investigation suggests a procedure in the form of working curves to find out the chemical reaction rate constants of the reversible chemical reaction following the electrode charge transfer provided the chemical equilibrium constant is known.

5. Nomenclature

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

a radius of the electrode (0.1 cm),

l length of the electrode (1.0 cm),

C_O^* initial bulk molar concentration (10^{-1} mol ml^{-1}),

D diffusion coefficient (0.567×10^{-5} cm s^{-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 standard electrode potential E^0 (12),

v potential scan rate (0.5, 1, 2, 3 V min^{-1}),

v_a axial flow velocity (0.5305, 1.0161, 2.2822 cm s^{-1}),

σ nFv/RTP^2, non-dimensional parameter,

n no. of electrons involved in charge transfer reaction (1),

k_f, k_b forward and backward chemical reaction rates ($k_f = 44.9$ s^{-1}),

δ $(k_f + k_b)/(nFv/RT)$, a non- dimensional kinetic parameter,

K non-dimensional chemical equilibrium parameter $(= k_f/k_b)$ $(1, 2, 5, 7.5)$,

λ_n magnitude of the nth zero of $Ai'(\eta)$ (values of first seventy zeros of $Ai'(\eta)$ are used for calculations).

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