KINETIC CURRENTS IN POLAROGRAPHY PART-II SPHERICAL DIFFUSION TO THE DME FOR PSEUDO - FIRST ORDER CATALYZED PROCESSES AND MODIFICATION OF ILKOVIC EQUATION

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Introducing Ilkovic's limitation regarding the range of diffusion distance from the electrode surface into three dimentional spherical diffusion equation and combining it with the functional relationship , as also employed by Kambara and Tachi, the following differential equation for spherical diffusion to a growing elecctrode is formulated.

$$\frac{\partial \Theta}{\partial t} = D \frac{\partial^2 \Theta}{\partial x^2} + \frac{2}{3} \frac{x}{t} \frac{\partial \Theta}{\partial x}$$

Where $\Theta = rC$ and $x = r - r_1$, with r_1 as the radius of the mercury drop. The following differential equations for spherical diffusion process to a growing mercury electrode for the cases involving chemical reactions occuring parallel to the electrode process have been formulated.

$$\frac{\partial \Theta_A}{\partial t} = D \frac{\partial^2 \Theta_A}{\partial x^2} + \frac{2}{3} \frac{x}{t} \frac{\partial \Theta_A}{\partial x} + kC_B \qquad \text{and}$$

$$\frac{\partial \Theta_B}{\partial t} = D \frac{\partial^2 \Theta_B}{\partial x^2} + \frac{2}{3} \frac{x}{t} \frac{\partial \Theta_B}{\partial x} - kC_B$$

Noting that C_B could be replaced by $({}^*\Theta_A - \Theta_A)/ r_1$ and introducing two new variables $s = xt^{2/3}(2\sqrt{3D/7})$ and $T = (1/4)\, t^{1/3}$ the first of the above two differrential equations takes the form

$$\partial\Theta_A/\partial T = \partial_A^2 \Theta / \partial s^2 + k/r_1 \, ({}^*\Theta_A - \Theta_A)$$

The initial and the boundary conditions are given and the differential equation is solved by the Laplace transform method. Expressions for C_A (r,t) and C_B (r,t) and for (i_t) total / $(i_d)_t$ are given. It is shown that when $k = 0$, the equations transform to those obtained for the case of spherical diffusion to a growing electrode. A discussion of the modification of Ilkovic equation is also given.

In Part I of this series<1> expression for catalytic current in the case of pseudo - first order reaction was obtained treating the problem as one of linear diffusion to a growing electrode. In this paper the above problem is treated as one of spherical diffusion to a growing electrode. The flux for the case of spherical diffusion to the growing electrode comes out as a special case when the rate constant for the parallel chemical reaction is put as zero. It may be pointed out that no treatment involving solution of spherical diffusion to a growing electrode for cases involving chemical reactions occuring parallel to the electrode process has been published. Koutecky solved the differential equation for linear diffusion to a growing electrode by the method of dimensionless parameters for catalytic currents <3> and then Koutecky and Cizek <2> have given correction for sphericity of the mercury drop.

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NOTATIONS

C_A (r, t): Concentration of the substance A at a distance r from the centre of the electrode at time t.

C_A (r_1, t): Concentration of the substance A at the electrode surface at time t ($^{\circ}C_A$, but in the present case 0)

$^{*}C_A$: Bulk concentration of A

C_B (r,t) : Concentration of the substance B formed by the reduction of A at a distance r from the centre of the electrode

C_B (r,0): Initial concentration of the substance B ($^{*}C_B$ but in the present case 0)

C_X : Concentration of X which is regarded constant. All C s in mole cm^{-3}

Θ : New dependent variable = rC

D_A and D_B : Diffusion coefficients of A and B in $cm^2 sec^{-1}$

D : Common diffusion coefficient since D_A and D_B are not very different

A : Area of the mercury drop considered as a sphere at any time 't' and given by $bt^{2/3}$ where $b = 4\pi (3m/4\pi d)^{2/3}$

r_1 : Radius of the mercury drop considered as a sphere at any time t and is equal to $at^{1/3}$ where $a = (3m/4\pi D)^{1/3}$

m : rate of flow of mercury in g/sec

d : specifivc gravity of mercury

$s = \dfrac{xt^{2/3}}{2\sqrt{3D/7}}$: new independent variable

T : $1/4\ t^{2/3}$: new independent variable (t in seconds)

x : distance from the electrode surface to the interior of the solution and is equal to $r - r_1$. This is equivalent to the coordinate system being changed from the centre of the drop to the surface.

p : variable in Laplace transformation

$L\Theta(s,T)$: Laplace transform of $\Theta(s,T) = u(s,p)$

L^{-1} u : inverse transform of u

k_1 and k_2 : rate constants of the forward and the backward processes of the parallel chemical reaction between B and X to generate A. k's in $mole^{-1}\ cm^3\ sec^{-1}$

THEORETICAL

Formulation Of The Differential Equation

Mac Gillavry and Rideal <4> treated the problem of diffusion to the dropping mercury electrode as three dimensional spherical diffusion and formulated the following differential equation.

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) - \frac{a^3}{3r^2}\frac{\partial C}{\partial r}$$

It is rather difficult to transform the above differential equation into an easily integrable form by introducing a new dependent variable $\Theta = rC$. Since Θ is also a function of the independent variables r and t and if the origin of the coordinate system is transferred from the center of the drop to the surface of the drop, one can write $\Theta = \Theta(r - r_1, t)$.

$$d\Theta = \frac{\partial \Theta}{\partial t}dt + \frac{\partial \Theta}{\partial (r-r_1)}d(r-r_1) \quad \text{or}$$

$$\frac{d\Theta}{dt} = \frac{\partial \Theta}{\partial t} + \frac{\partial \Theta}{\partial (r-r_1)}\frac{d(r-r_1)}{dt} \qquad \ldots\ldots\ldots (1)$$

Following Ilkovic<5>, Kambara and Tachi<6> identified $d\Theta/dt$ with pure diffusion term i.e $D.\partial^2\Theta/\partial(r-r_1)^2$. They have handled the term $d(r-r_1)/dt$ differently but they get the same final expression as in the present paper.

To appreciate the approximations involved the following procedure is followed. In consonance with Ilkovic <5>, let us assume that the range of $(r - r_1)$ i,e. distance from the electrode surface into the interior of the solution, be limited such that $A(r - r_1)$ is constant. Differentiating $A(r - r_1)$ with respect to t and noting that A, (the area of the mercury drop at any time t) is equal to $bt^{2/3}$, it can be written

$$A\ d/dt\ (r - r_1) + (r - r_1)\ dA/dt$$

$$= A\ d/dt\ (r - r_1) + (r - r_1)\ 2/3\ bt^{-1/3}$$

$$= A\ d/dt\ (r - r_1) + (r - r_1)\ 2/(3t)\ A = 0$$

or $d/dt\ (r - r_1) = -2\,(r - r_1)/(3t)$

Substituting in equation 1 one gets

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial (r-r_1)^2} + \frac{2}{3}\frac{(r - r_1)}{t}\frac{\partial \theta}{\partial (r-r_1)} \quad ..(2)$$

Putting $r - r_1 = x$, the above equation can be written thus:

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial \theta}{\partial x} \quad .....(3)$$

The above differential equation is of the same form as that of linear diffusion to a growing electrode. To formulate the differential equation for the case consisting of parallel chemical reaction to the electrode reaction, one has to add kinetic terms to the R.H.S. of the above differential equation. For the scheme

$A + ne \rightleftharpoons B$, $B + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A$: under conditions $k_2 << k_1 C_X$ constant, the following equations can be written

$$\frac{\partial \theta_A}{\partial t} = D_A \frac{\partial^2 \theta_A}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial \theta_A}{\partial x} + k_1 C_X C_B \quad ...(4)$$

$$\frac{\partial \theta_B}{\partial t} = D_B \frac{\partial^2 \theta_B}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial \theta_B}{\partial x} - k_1 C_X C_B \quad ...(5)$$

Putting $C_B = {}^*C_A - C_A$ and noting that $C_B = \theta_B/r = {}^*C_A - C_A$, $D_A \simeq D_B = D$ one can write

$$\frac{\partial \theta_A}{\partial t} = D \frac{\partial^2 \theta_A}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial \theta_A}{\partial x} + k_1 C_X \frac{({}^*\theta_A - \theta_A)}{r} \quad ...(6)$$

where $r = r_1 + x$. Since $x << r_1$, one can write $r \simeq r_1$ and also putting $k_1 C_X = k$, one can write equation 6 as follows:

$$\frac{\partial \theta_A}{\partial t} = D \frac{\partial^2 \theta_A}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial \theta_A}{\partial x} + \frac{k}{r_1}({}^*\theta_A - \theta_A) \quad .....(7)$$

Transformation of The Differential Equation

Expressing the equation (7) in terms of the new independent variables s and t analogous to the work of the author on the Laplace Transform method for the solution of Ilkovic differential equation <7> and on the problem of catalytic kinetic currents from the standpoint of linear diffusion to a growing electrode <1> the following transformations can be written employing chain rule.

$$\frac{\partial \theta_A}{\partial t} = \frac{\partial \theta_A}{\partial s}\frac{1}{4}\frac{7}{3}t^{4/3} + \frac{\partial C_A}{\partial s}\frac{2}{3}\frac{s}{t} \quad .....(8)$$

$$D\frac{\partial^2 \theta_A}{\partial x^2} = D\frac{t^{4/3}}{\{(2\sqrt{3D/7})\}^2}\frac{\partial^2 \theta_A}{\partial s^2} \quad .....(9)$$

$$\frac{2}{3}\frac{x}{t}\frac{\partial \theta_A}{\partial x} = \frac{2}{3}\frac{s}{t}\frac{\partial \theta_A}{\partial s} \quad .....(10)$$

Substituting the above in differential equation (7) one gets

$$\frac{\partial \theta_A}{\partial T} = \frac{\partial^2 \theta_A}{\partial s^2} + \frac{k}{r_1}({}^*\theta_A - \theta_A) \quad .....(11)$$

Initial and the Boundary Conditions

The initial and the boundary conditions for various differential equations given above are summarized below.

(i) $C_A\ (r,t)$
$C_A\ (r_1, t) = 0$
$C_A\ (r, 0) = {}^*C_A$
$C_A\ (r, t) = {}^*C_A$ as $r \to \infty$

(ii) $C_A\ (x,t)$
$x = (r - r_1)$
$C_A\ (0, t) = 0$
$C_A\ (x, 0) = {}^*C_A$
$C_A\ (x. t) = {}^*C_A$ as $x \to \infty$

(iii) $C_A\ (s,T)$
$C_A\ (s, 0) = {}^*C_A$
$C_A\ (0, T) = 0$
$C_A\ (s, t) = {}^*C_A$ as $s \to \infty$

(iv) $\theta_A = (r,t)$
$\theta_A\ (r_1, t) = 0$
$\theta_A\ (r, 0) = {}^*\theta_A^{(r_1)} = r_1 {}^*C_A$ (at the electrode surface)

$${}^*\theta_A^{(r)} = r\,{}^*C_A$$

Interior of the solution

(v) $\theta_A\ (x,t)$
$x = r - r_1$

$\theta_A\ (0, t) = 0$
$\theta_A\ (x, 0) = {}^*\theta_A^{(r_1)}$ or ${}^*\theta_A^{(r)}$

(vi) $\theta_A\ (s,T)$
$\theta_A\ (s, 0) = {}^*\theta_A^{(r_1)}$ or ${}^*\theta_A^{(r)}$
$\theta_A\ (0, T) = 0$

(vii) $C_B\ (x,t)$
$C_B\ (x, 0) = 0$
$C_B = {}^*C_A - C_A$

(viii) $C_B = \theta_B/r = {}^*C_A - C_A$ .....(12)

Solutin of the Differential Equation (11)

The equation 11 is a partial differential equation with constant coefficients and the Laplace transform method has been used to solve this equation.

We define the Laplace transform of $\Theta_A(s,T)$ (abbreviated as $L\,\Theta_A(s,T)$, as

$$u(s,p) = \int_0^\infty \exp(-pT)\,\Theta_A(s,T)\,dT \quad \ldots\ldots(13)$$

Then $L\left(\frac{\partial \Theta_A}{\partial T}\right) = -\Theta_A(s,0) + p\,u(s,p)$ ..(14)

$$L\left(\frac{\partial^2 \Theta_A}{\partial s^2}\right) = \frac{d^2 u(s,p)}{ds^2} \quad \ldots\ldots(15)$$

$$L\,(k/r_i)\,{}^*\Theta_A = (k\,{}^*\Theta_A)/(r_i\,p) \quad \ldots\ldots(16)$$

The equation 11 is then transformed to

$$\frac{d^2u}{ds^2} - \left[p + (k/r_i)\right] u = -\left(\frac{p + (k/r_i)}{p}\right) {}^*\Theta_A \quad \ldots\ldots(17)$$

since ${}^*\Theta_A$ is the value of the function $\Theta_A(s,T)$ when $T = 0$. The solution of (17) is

$$u = u_c + u_p$$

$$= A_1 \exp\left(\sqrt{p+(k/r_i)}.\,s\right) + A_2 \exp\left(-\sqrt{p+(k/r_i)}.\,s\right) + \frac{-(1/p)\left[p+(k/r_i)\right]}{-\left[p+(k/r_i)\right]} {}^*\Theta_A^{(r)} \quad \ldots\ldots(18)$$

Since the concentration of A does not increase indefinitely with increase in the value of s, we have to take $A_1 = 0$. Since $\Theta_A(0,T) = 0$, $u(0,p)$ is also zero. Hence

$$u = A_2 \exp\left(-\sqrt{p+(k/r_i)}.\,s\right) + {}^*\Theta_A^{(r)}/p \quad \text{or}$$

$$0 = A_2 + {}^*\Theta_A^{(r_i)}/p$$

As we are considering the electrode surface, we have to put ${}^*\Theta_A^{r_i}$ $A_2 = -({}^*\Theta_A^{r_i}/p)$ Therefore

$$u = -\left({}^*\Theta_A^{(r_i)}/p\right) \exp\left(-\sqrt{p+(k/r_i)}.s\right) + {}^*\Theta_A^{(r)}/p \quad ..(19)$$

$$\Theta_A(s,T) = L^{-1}\,u(s,p)$$

$$= L^{-1}\left[-\left({}^*\Theta_A^{(r_i)}/p.\right) \exp\left(-\sqrt{p+k/r_i}.\,s\right)\right] + L^{-1}\,{}^*\Theta_A^{r}/p \quad \ldots\ldots(20)$$

On the basis of Laplace transforms given in the Table of transforms <8,9> and using relevant theorem concerning transforms containing $(p + (k/r_i))$ the following can be written:

$$L^{-1}\left[-{}^*\Theta_A^{(r_i)}/\left[(p+(k/r_i)-(k/r_i)\right]\right] \exp\left(-\sqrt{p+(k/r_i)}\,s\right)$$

$$= -{}^*\Theta_A^{(r)} \exp\left(-(k/r_i).\,T\right)\left\{1/2 \exp\left[(k/r_i).\,T\right]\right.$$

$$\left[\exp\left(-\sqrt{k/r_i}.s\right) \operatorname{erfc}\left(s/2\sqrt{T} - \sqrt{kT}\right)\right.$$

$$\left.\left. + \exp\left(\sqrt{k/r_i}.s\right) \operatorname{erfc}\left(s/2\sqrt{T} + \sqrt{kT}\right)\right]\right\} \quad ..(21)$$

The Laplace transform of a constant is constant divided by p. Hence

$$L^{-1}\left({}^*\Theta_A^{r}/p\right) = {}^*\Theta_A^{r} \quad \ldots\ldots(22)$$

The following expression for $\Theta_A(s,T)$ can now be written

$$\Theta_A(s,T) = {}^*\Theta_A^{(r)} - {}^*\Theta_A^{(r_i)}$$

$$\left\{(1/2 \exp\left(-\sqrt{k/r_i}\,s\right)\left[1-\operatorname{erf}\left(s/2\sqrt{T} - \sqrt{k/r_i}.T\right)\right]\right.$$

$$\left. + 1/2 \exp\left(\sqrt{k/r_i}\,s\right)\left[1-\operatorname{erf}\left(s/2\sqrt{T} + \sqrt{k/r_i}\,T\right)\right]\right\} \quad .(23)$$

Replacing the independent variables s and T by x and t one gets

$$\Theta_A(x,t) = {}^*\Theta_A^{(r)} - {}^*\Theta_A^{(r_i)}\left\{1/2 \exp\left(-\sqrt{7kt^{7/3}/12r_i D}.x\right)\right.$$

$$\left[1 - \operatorname{erf}\left(x/2\sqrt{3Dt/7} - 1/2\sqrt{kt^{7/3}/r_i}\right)\right]$$

$$+ 1/2 \exp\sqrt{7kt^{7/3}/12 r_i D}\,x$$

$$\left.\left[1-\operatorname{erf}\left(x/2\sqrt{3Dt/7} + 1/2\sqrt{kt^{7/3}/r_i}\right)\right]\right\} \quad ...(24)$$

Expressing Q's in terms of rC's, replacing the coordinates from the surface to the center of the drop, dividing both sides by r, expressing r_i under sq. roots by $at^{1/3}$, the following equation can be written:

$$C_A(r,t) = {}^*C_A - (r_i/r)\,{}^*C_A$$

$$\left\{1/2 \exp\left(-\sqrt{7kt/12aD}\,(r - r_i)\right)\right.$$

$$\left[1 - \operatorname{erf}\left(r-r_i\right)/2\sqrt{3Dt/7} - 1/2\sqrt{\frac{kt^2}{a}}\right]$$

$$+ 1/2 \exp\sqrt{7kt/12aD}\,(r - r_i)$$

$$\left.\left[1-\operatorname{erf}\left((r-r_i)/2\sqrt{3Dt/7} + 1/2\sqrt{\frac{kt^2}{a}}\right)\right]\right\} \quad ..(25)$$

The above equation gives C_A as a function of r and t. The instantaneous current at any time is given by the expression $i_t = nFAD\,(\partial C_A/\partial r)_{r=r_i}$. The value of $(\partial C_A/\partial r)_{r=r_i}$ be obtained by differentiating equation (25) with respect to r and putting $r = r_i$ in the resulting expression. It may be pointed out that in the course of differentiation one comes across differentiation

of error integral which involves differentiation under integral sign and is given below:

$$\frac{\partial}{\partial r}\left(\frac{2}{\sqrt{\pi}}\int_0^{\frac{r-r_1}{2\sqrt{\frac{1}{7}Dt}}-\frac{1}{2}\sqrt{\frac{k}{a}}t^2} e^{-u^2}\,du\right) = \frac{2}{\sqrt{\pi}}\,e^{-\left(\frac{r-r_1}{2\sqrt{\frac{1}{7}Dt}}-\frac{1}{2}\sqrt{\frac{k}{a}}t^2\right)^2}\cdot\frac{1}{2\sqrt{\frac{1}{7}Dt}} \quad \ldots\ldots\ldots (26)$$

The rest of the operations are normal.

$$\left(\frac{\partial C_A}{\partial r}\right)_{r-r_1} = {}^*C_A\left\{\left(\frac{1}{r_1}+\frac{1}{\sqrt{3\pi Dt/7}}\right)\exp\left(-kt^2/4a\right) + \sqrt{7kt/12aD}\ \operatorname{erf}\left(\sqrt{kt^2/4a}\right)\right\} \quad \ldots\ldots (27)$$

Modification of Ilkovic Equation

It may be pointed out that by putting k=0 we get the gradient at the electrode surface in the case of pure diffusion process.

$$\left(\frac{\partial C_A}{\partial r}\right)_{r-r_1} = {}^*C_A\left(\frac{1}{r_1}+\frac{1}{\sqrt{3\pi Dt/7}}\right) \quad \ldots\ldots (28)$$

The current at any time t is given by $nFAD(\partial C/\partial r)_{r=r_1}$ Expressing current in microamperes, A and r in terms of the amount of mercury flowing out in mg./second, integrating $(i_d)_t$ between 0 to t_{max} and dividing by t_{max} to obtain the mean current one gets.

$$i_d = 607nD^{1/2}\ {}^*C_A\ m^{2/3}\ t^{1/6}\ (1 + KD^{1/2}\ m^{-1/3}\ t^{1/6})$$

where K = 39 $\ldots\ldots\ldots (29)$

The above equation is a modification of the Ilkovic Equation <10>. Different authors used slightly different techniques and got the value of K as 17,39 or 45.1. Koutecky <11> has derived an equation in the following form.

$$i_d = 607nD^{1/2}\ {}^*C_A\ m^{2/3}\ t^{1/6}\ (1 + KD^{1/2}\ m^{-1/3}\ t^{1/6} + LDm^{-2/3}\ t^{1/3} + \ldots\ldots (30)$$

the value of K being 34. It has to be pointed out that there are two modes of approach to the solution of the problem. The first approach is to start with the flux in the case of stationary electrode

$$D\ (\partial C_A/\partial r)_{r=r_1} = D\ {}^*C_A\ (1/r_1 + 1/\sqrt{\pi Dt}) \quad (31)$$

and formulate an integral equation to take into effect of the moving surface. It may be pointed out that Kambara, Suzuki and Tachi <6> used the integral equation method of Stackelberg <6>, but in the subsequent mathematical operations the integration of $1/r_1$ is masked. In the integral equation treatment of this author <12> the effect of the growing drop on the thickness of the diffusion layer is separately evaluated on each of the terms in the expression for the flux and hence a value of 45.1 is obtained. In the differential equation method, the differential equation is formulated and solved under the boundary conditions of the problem. In this method both during formulation and solution of the differential equation, some approximations have to be made to obtain the solution in a suitable form. Although the formulation of the differential in Mac Gillavry and Rideal <4> treatment is rigorous, the subsequent approximations took away the effect of sphericity and the usual Ilkovic is obtained. Strehlow and Stackelberg <13> obtained a value of 17 for K. In the present work a value of 39 is obtained and it may be pointed out that in the very nature of solving the diferential equation the effect the growing drop might have on r_1 is masked as in the case of treatment of Kambara and Tachi <6>.

(vi) Equation For C_B (r,t)

The following equation can be written for C_B (r,t)

$$C_B(r,t) = {}^*C_A - C_A(r,t)$$

$$= {}^*C_A\ r_1/r\left\{1/2\ \exp\left(-\sqrt{7kt^{7/6}/12r_1D}\ \overline{r-r_1}\right)\left[1-\operatorname{erf}\left(\overline{r-r_1}/2\sqrt{3Dt/7}-1/2\sqrt{kt^{7/6}/r_1}\right)\right] + 1/2\ \exp\left(\sqrt{7kt^{7/6}/12r_1D}\ \overline{r-r_1}\right)\left[1-\operatorname{erf}\left(\overline{r-r_1}/2\sqrt{3Dt/7}+1/2\sqrt{kt^{7/6}/r_1}\right)\right]\right. \quad \ldots (32)$$

Expression for kinetic current with parallel Pseudo-first order chemical reaction

The instantaneous total current (with parallel chemical reaction) at any time t during droplife is given by

$$(i_t)_{total} = nFAD\ (\partial C_A/\partial r)_{r=r_1}$$

$$= nFAD\ {}^*C_A\left\{\left(1/r_1 + 1/\sqrt{3\pi Dt/7}\right)\exp(-kt^2/4a) + \sqrt{7\ kt/12aD}\ \operatorname{erf}\left(\sqrt{kt^2/4a}\right)\right. \quad \ldots\ldots (33)$$

The instantaneous difusion current (without parallel chemical reaction) at any time t during droplife is

$$(i_d)_t = nFAD\,(\partial C_A/\partial r)_{r=r_i}$$

$$= nFAD\,{}^{*}C_A\left\{1/r_i + 1\Big/\sqrt{3\pi Dt/7}\right\} \quad .....(34)$$

Hence

$$(i_t)_k = (i_t)_{total} - (i_d)_t$$

$$= nFAD\,{}^{*}C_A\left\{1/\sqrt{3\pi Dt/7}\left(\exp(-kt^2/4a)-1\right) + \sqrt{7kt/12a}\,D\ \operatorname{erf}\left(\sqrt{kt^2/4a}\right)\right\} \quad .....(35)$$

Where $(i_t)_k$ = Kinetic current at any time t
$(i_t)_{total}$ = Total current at any time t
$(i_d)_t$ = diffusion current at any time t

To put the expression into a neat form we make the slight approximation of identifying $nFAD\,{}^{*}C_A/\sqrt{3\pi Dt/7}$ with $(i_d)_t$. Not much error will be introduced into the treatment since this is our usual Ilkovic equation. We can therefore write

$$\frac{(i_t)_{total} - (i_d)_t}{(i_d)_t} = \exp\left(-\frac{kt^2}{4a}\right) - 1 + \sqrt{\frac{\pi}{4a}}\,kt^2 \operatorname{erf}\sqrt{\frac{kt^2}{4a}} \quad ..(36)$$

Rearranging the above expression and putting $\lambda = (kt^2)/4$ one gets

$$\frac{(i_t)_{total}}{(i_d)_t} = \lambda^{1/2}\left[\left(\frac{\pi}{a}\right)^{1/2} \operatorname{erf}\left(\frac{\lambda}{a}\right)^{1/2} + \frac{\exp(-\lambda/a)}{\lambda^{1/2}}\right] \quad (37)$$

This expression is of the same form as those obtained by Delahay<14> in the case of linear difusion to a stationary electrode and by Subrahmanya <1> in the case of linear diffusion to a growing electrode, which is given as equation 38.

$$\frac{(i_t)_{total}}{(i_d)_t} = \lambda^{1/2}\left[\pi^{1/2} \operatorname{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}}\right] \quad ...(38)$$

λ in Delahay is given by kt and of this author is given $kt^{7/3}/4$

In a later paper the implications of the equations obtained in the present paper will be discussed.

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