THE DIFFUSION FLOW TO A ROTATING LINE ELECTRODE

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A mathematical model for convective diffusion to the so-called line electrode was solved by combination of the analytical and numerical approaches. All terms of the diffusion equation were respected. A semiempirical formula was derived, extending appreciably its applicability with respect to the decisive physical and geometric parameters.

An electrode having the shape of a narrow segment of an annulus of a rotational cylinder, the so-called line electrode, was developed in 1967 as a means for various physicochemical measurements[1]. Analytical mathematical methods were applied, after a considerable simplification, to solve the boundary problem for convective diffusion, and the solution was used to derive an approximate formula for the diffusion flow to the electrode. The validity of the formula was tested across a range of standard values of the decisive physical parameters, and a relatively good agreement was found. It was a shortcoming of the work (due to the absence of appropriate computer techniques) that the range of validity of the diffusion flow formula was not specified precisely enough and that no more precise formula for a wider range of the parameters was derived. Therefore we returned now to the problem of the line electrode and, by combining suitable analytical and numerical procedures, we solved a mathematical model describing the convective diffusion process in the environment of the line electrode. In contrast to the paper[1] we retained all terms in the partial differential equation for the steady-state convective diffusion, and approximated more closely the exact boundary conditions. The outcome was formula (*22*), whose range of validity covers less standard values of some physical or geometrical parameters as well and also confirms a good applicability of the formula[1] to the values then used.

Analytical Solution of the Mathematical Model

The steady-state convective diffusion process in the environment of the line electrode is described, in the polar coordinates r, φ, by the partial differential equation[1]

$$r^{-1} v_\varphi \, \partial c/\partial\varphi \;=\; D\,(\partial^2 c/\partial r^2 \;+\; r^{-1}\partial c/\partial r \;+\; r^{-2}\partial^2 c/\partial\varphi^2)\,, \qquad (1)$$

where (ref.[2])

$$v_\varphi \;=\; \omega\, r\,(1 - a^2 r^{-2})/(1 - a^2 b^{-2}) \qquad (2)$$

with the boundary conditions

$$c(a,\varphi) \;=\; 0 \quad \text{for} \quad \varphi \in \langle 0,\frac{m}{a}\rangle \qquad (3a)$$

$$\partial c/\partial r(a,\varphi) \;=\; 0 \quad \text{for} \quad \varphi \in \langle \frac{m}{a},2\pi\rangle \qquad (3b)$$

$$\partial c/\partial r(b,\varphi) \;=\; 0 \quad \text{for} \quad \varphi \in \langle 0,2\pi\rangle\,. \qquad (4)$$

In the equations, c is the solution concentration, D is the solute diffusion coefficient, v_φ is the tangential velocity of flow of the solution, ω is the angular velocity, a and b are the radii of the inner and outer cylinders, respectively, and m is the line electrode width.

The boundary problem so formulated has a single solution, $c(r,\varphi) = 0$, for $r \in \langle a,b\rangle$, $\varphi \in \langle 0,2\pi\rangle$. Physical explanation of this consists in the fact that we assumed an infinitely long line electrode. In reality, the electrode has a finite length. In this case it can be proved that the solution of the boundary problem for the limiting case of $b \to \infty$ is non-zero. For reasons which are physically acceptable we change the boundary condition (*4*) to

$$\lim_{b\to\infty} c(b,\varphi) \;=\; c_0 \;\neq\; 0\,. \qquad (5)$$

Introducing the dimensionless variables

$$y \;=\; \frac{r - a}{a}\,, \quad x \;=\; \frac{a}{m}\,\varphi\,, \quad C \;=\; \frac{c}{c_0} \qquad (6)$$

we obtain Eq. (*1*) in the form

$$B\,(1 - (1+y)^{-2})\,\partial C/\partial x = \partial^2 C/\partial y^2 + (1+y)^{-1}\,\partial C/\partial y + $$
$$+ A\,(1+y)^{-2}\,\partial^2 C/\partial x^2\,, \qquad (7)$$

where

$$A = \frac{a^2}{m^2}\,, \quad B = \frac{a}{m}\,\omega\, a^2\, D^{-1}(1 - \frac{a^2}{b^2})^{-1}\,. \qquad (8)$$

It has been demonstrated[1] that it is convenient to introduce a new variable, u, as

$$u = y\, f(x)\,, \qquad (9)$$

where $f(x)$ is an approximation of the gradient of concentration C at the active surface. Thereby the function $(y,x) \rightarrow C(y,x)$ transforms to

$$(u,x) \rightarrow C\left(\frac{u}{f(x)},x\right) = \tilde{C}(u,x)$$

and Eq. (*7*) transforms to

$$B\left(1 - \left(1 + \frac{u}{f(x)}\right)^{-2}\right)\left(u\,\frac{f'(x)}{f(x)}\,\partial\tilde{C}/\partial u + \partial\tilde{C}/\partial x\right) = f^2(x)\,\partial^2\tilde{C}/\partial u^2 +$$

$$+ f(x)\left(1 + \frac{u}{f(x)}\right)^{-1}\partial\tilde{C}/\partial u + A\left(1 + \frac{u}{f(x)}\right)^{-2}\left[\left(u\,\frac{f'(x)}{f(x)}\right)^2\partial^2\tilde{C}/\partial u^2 +\right.$$

$$+ u\,f^{-2}(x)\,(f(x)\,f''(x) - (f'(x))^2)\,\partial\tilde{C}/\partial u +$$

$$\left. + 2u\,\frac{f'(x)}{f(x)}\,\partial^2\tilde{C}/\partial u\partial x + \partial^2\tilde{C}/\partial x^2\right]. \qquad (10)$$

The boundary conditions (*3a*), (*3b*), (*5*) now are in the form

$$\tilde{C}(0,x) = 0 \quad \text{for} \quad x \in \langle 0,1 \rangle \tag{11a}$$

$$\partial\tilde{C}/\partial u(0,x) = 0 \quad \text{for} \quad x \in \langle 1, 2\pi \frac{a}{m} \rangle \tag{11b}$$

$$\lim_{u \to \infty} \tilde{C}(u,x) = 1 \quad \text{for} \quad x \in \langle 0, 2\pi \frac{a}{m} \rangle . \tag{12}$$

The boundary problem (*10*) – (*12*) was solved for the asymptotic case of $B \to \infty$ by the iterative approach. The first iteration $\tilde{C}_1(u,x)$ was taken from ref.[1]

$$\tilde{C}_1(u,x) = E_0^{-1} \int_0^{\beta t} \exp(-s^3)\mathrm{d}s , \tag{13}$$

where

$$E_0 = \int_0^{\infty} \exp(-s^3)\mathrm{d}s , \quad t = u f^{-1}(x)\,(1 + u f^{-1}(x))^{-1} = u\,(f(x) + u)^{-1} ,$$

$$f(x) = k\,x^{-1/3} , \quad \beta = -\left(\frac{2}{3} B \frac{f'(x)}{f(x)}\right)^{1/3} = \left(\frac{2}{9}\frac{B}{x}\right)^{1/3} . \tag{14}$$

Further iterations were defined by the equation

$$f^2(x)\,\partial^2\tilde{C}_n/\partial u^2 + \left(f(x)\left(1 + \frac{u}{f(x)}\right)^{-1} + B\,u\,\frac{f'(x)}{f(x)}\left(\left(1 + \frac{u}{f(x)}\right)^{-2} - 1\right)\right)\partial\tilde{C}_n/\partial u =$$

$$= B\left(1 - \left(1 + \frac{u}{f(x)}\right)^{-2}\right)\partial\tilde{C}_{n-1}/\partial x - A\left(1 + \frac{u}{f(x)}\right)^{-2} .$$

$$.\left[\left(u\,\frac{f'(x)}{f(x)}\right)^2 \partial^2\tilde{C}_{n-1}/\partial u^2 + u\,f^{-2}(x)\,(f(x)\,f''(x) - (f'(x))^2)\ .\right.$$

$$\left. .\ \partial\tilde{C}_{n-1}/\partial u + 2\,u\,\frac{f'(x)}{f(x)}\,\partial^2\tilde{C}_{n-1}/\partial u\,\partial x + \partial^2\tilde{C}_{n-1}/\partial x^2\right], \quad n \geq 2 . \tag{15}$$

Eq. (*15*) for function $\tilde{C}_n$ of variable u is actually an ordinary differential equation with parameter x. Solve it for the conditions

$$\tilde{C}_n(0) = 0\,, \quad \lim_{u \to \infty} \tilde{C}_n(u) = 1 \quad \text{and} \quad x \in (0,1)\,. \tag{16}$$

By solving the problem (*15*), (*16*) for $n = 2$ we obtain the second iteration in the form

$$\tilde{C}_2(u) = K \int_0^t \exp\left(\int_0^v M(w)\mathrm{d}w \right) \mathrm{d}v \, - $$

$$- \int_0^t \left[\left(\int_0^v N(w) \exp\left(-\int_0^w M(z)\mathrm{d}z \right) \mathrm{d}w \right) \exp\left(\int_0^v M(w)\mathrm{d}w \right) \right] \mathrm{d}v\,, \tag{17}$$

where quantity t has been introduced by formulas (*14*) and

$$M(t) = (1-t)^{-2} \left(1 - t + \frac{B}{3x} ((1-t)^2 - 1) \; t\,(1-t)^{-1} \right) \tag{18a}$$

$$N(t) = 1/(3E_0) \; \exp\left(-\frac{2}{9}\,\frac{B}{x}\,t^3 \right) \left(\frac{2}{9}\,\frac{B}{x^7} \right)^{1/3} (1-t)^{-4} \; .$$

$$. \left[B\,xt^2\,(1 - (1-t)^2) + A\,(1-t)^2 \left(t + \frac{t^2}{3} - \frac{2}{9}\,\frac{B}{x}\,t^4 \right) \right]. \tag{18b}$$

The first condition in Eq. (*16*) was respected here. By using the limiting condition in Eq. (*16*) we obtain a formula for the constant K,

$$K = \left\{ 1 + \int_0^1 \left[\left(\int_0^v N(w) \exp\left(-\int_0^w M(z)\mathrm{d}z \right) \mathrm{d}w \right) \exp\left(\int_0^v M(w)\mathrm{d}w \right) \right] \mathrm{d}v \right\} /$$

$$/ \int_0^1 \exp\left(\int_0^v M(w) \mathrm{d}w \right) \mathrm{d}v \, . \qquad (19)$$

It follows from formulas (*17*), (*14*) and (*9*) that

$$K = \partial C_2 / \partial y(0,x) \qquad (20)$$

which implies that K is an approximation of the gradient of the dimensionless concentration C at the active surface in dependence on variable x.

Detailed calculation (see Appendix) gives an approximation of the gradient of the dimensionless concentration C in the form

$$K \cong \beta / E_0 \left(1 + \frac{3}{4} E_1 / E_0 \, \beta^{-1} + 9/(32 \, E_0) \, \beta^{-2} + \right.$$

$$\left. + \frac{1}{8} (E_1 / E_0)^2 \, \beta^{-2} + A / (30 \, E_0 x^2) \, \beta^{-2} \right), \qquad (21)$$

where E_0 and β are as introduced in formulas (*14*) and

$$E_1 = \int_0^\infty s \exp(-s^3) \mathrm{d}s \, .$$

The mathematical model used has a singularity in point $x = 0$ and so one cannot expect convergence of the suggested iterative procedure in this point. Therefore, when calculating the total diffusion flow to the active surface,

$$Q = \int_0^1 K \, \mathrm{d}x \, ,$$

a theoretical formula following from Eq. (*21*) cannot be obtained. Equation (*21*), however, suggests that the semiempirical formula

$$Q = \left(\frac{3}{4} \right)^{1/3} E_0^{-1} B^{1/3} + \frac{3}{4} \, E_1 / E_0 + K_1 B^{-1/3} + K_2 A B^{-1/3} \qquad (22)$$

can conveniently be introduced.

The empirical constants K_1 and K_2 are calculated from the numerical results for various values of the parameters *A*, *B* as given later.

Numerical Solution

The standard network method was applied to numerically solve Eq. (*7*) for convective diffusion to the line electrode on the region (see Fig. 1)

$$(y,x) \in S = \langle 0,(b-a)/a \rangle \times \langle 0,1 \rangle$$

for the boundary conditions

$$C(0,x) = 0\,, \quad C((b-a)/a,x) = 1\,. \tag{23a}$$

The boundary conditions for $x = 0$ and $x = 1$ are determined by the convective diffusion process and are not known in advance. To obtain acceptable $C(y,0)$ and $C(y,1)$ values we applied the procedure as follows.

We divided the procedure into stages.

Stage I:

In this stage we solved Eq. (*7*) consecutively on the regions

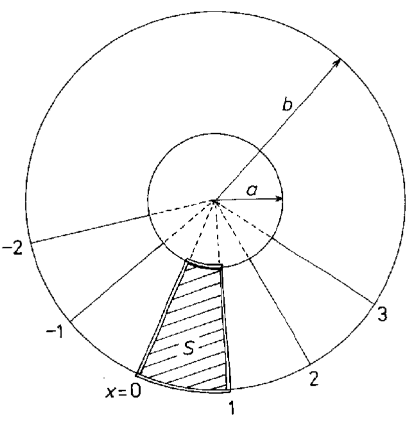

FIG. 1
Segmentation of the annulus for numerical treatment

$$(y,x) \in \langle 0,(b-a)/a\rangle \times \langle p-1,p+1\rangle\,, \qquad p = 1, 2, \ldots, P.$$

In the first step, $p = 1$, the conditions (*23a*) were extended for $x \in \langle 0,2\rangle$ and completed with the conditions

$$C(y,0) = 1\,, \quad C(y,2) = 1 \tag{23b}$$

$$\partial C/\partial y(0,x) = 0\,, \quad C((b-a)/a,x) = 1 \quad \text{for} \quad x \in (1,2\rangle\,. \tag{23c}$$

We denoted the solution of this problem C_1.

In the second step, $p = 2$, we solved Eq. (*7*) on the region

$$(y,x) \in \langle 0,(b-a)/a\rangle \times \langle 1,3\rangle$$

for the boundary conditions

$$C(0,1) = 0\,, \quad \partial C/\partial y(0,x) = 0 \quad \text{for} \quad x \in (1,3\rangle\,, \quad C((b-a)/a,x) = 1 \tag{24a}$$

$$C(y,1) = C_1(y,1)\,, \quad C(y,3) = 1\,. \tag{24b}$$

In the first condition (*24b*), the $C_1(y,1)$ value calculated in the first step ($p = 1$) was used for $x = 1$. The solution of problem (*7*), (*24a*), (*24b*) was denoted C_2.

The subsequent steps of Stage I were analogous. In the p-th step ($p > 2$), Eq. (*7*) was solved for the boundary conditions

$$\partial C/\partial y(0,x) = 0\,, \quad C((b-a)/a,x) = 1\,, \quad x \in \langle p-1,p+1\rangle \tag{25a}$$

$$C(y,p-1) = C_{p-1}(y,p-1)\,, \quad C(y,p+1) = 1\,, \quad y \in \langle 0,(b-a)/a\rangle\,, \tag{25b}$$

where C_{p-1} is the solution of the boundary problem in the $(p-1)$-st step.

Calculation in Stage I was terminated when the condition

$$|C_p(y,p) - 1| < 0.01\,, \quad y \in \langle 0,(b-a)/a \rangle \qquad (26)$$

was satisfied.

This step was denoted $\overline{P}$.

Stage II:

In this stage we solved Eq. (*7*) consecutively on the regions

$$\langle 0,(b-a)/a \rangle \times \langle p-2,p \rangle\,,\ p = 1, 2, \ldots, \overline{P}.$$

The boundary conditions were chosen as follows:

for $y = 0$: $C(0,x) = 0\ x \in \langle 0,1 \rangle$, elsewhere $\partial C / \partial y(0,x) = 0$

,

for $y = (b-a)/a$: $C((b-a)/a,x) = 1$ for any x.

Conditions in the radial direction:

in the first step ($p = 1$), $C(y,-1) = 1$, $C(y,1) = C_1(y,1)$,

where $C_1(y,1)$ are values obtained in Stage I;

in the subsequent steps ($p > 1$), $C(y,p-2) = \overline{C}_{p-1}(y,p-2)$, $C(y,p) = C_p(y,p)$,

where C_p are values obtained in the p-th step of Stage I and $\overline{C}_{p-1}$ are values obtained in the ($p-1$)-st step of Stage II.

Calculation in Stage II was terminated when condition (*26*) for $\overline{C}_p$ ($p = \overline{P}$) was satisfied.

In all the subsequent stages we solved the problem on the regions

$$\langle 0,(b-a)/a \rangle \times \langle p-3,p-1 \rangle\,, \qquad p = 1, 2, \ldots, \tilde{P}$$

proceeding analogously. The last-calculated values in the current or preceding stage were used when determining the boundary conditions in the radial direction. In these stages we tested the values of concentration C for $x = 1$ in those nodal points of the network $(y_i,1)$ which occurred during the approximate calculation of grad C.

Denote Δ the difference between the concentrations in the current and preceding stages. The calculation was terminated if

$$\max_i |\Delta(y_i,1)| < 0.001 \ .$$

RESULTS AND DISCUSSION

The problem was solved numerically for all combinations of the following values of parameters A, B (Eq. (*8*)):

$$A = 100,\ 500,\ 1\ 000; \qquad B = 8\ 000,\ 15\ 625,\ 27\ 000.$$

The B values are the numbers 20, 25 and 30 cubed. This was chosen with regard to Eq. (*22*), where the overall diffusion flow Q is expressed in cube roots of B. The values of parameters A, B were chosen so as to obtain a formula with a range of validity wider than in ref.[1].

To obtain diffusion flow values Q as precise as possible, we solved the boundary problem, for each A, B pair, for three different steps in the radial direction and three different steps in the tangential direction. This enabled the results to be refined by applying the two-step Richardson extrapolation. The concentration gradients necessary to calculate the overall diffusion flow Q were approximated by a five-point differential formula. The diffusion flow Q was calculated by using Simpson's formula.

The Q values so obtained for the various A, B pairs are given in Table I.

TABLE I
Total diffusion flow Q

A	B		
	8 000	15 625	27 000
100	22.824	27.531	32.378
500	29.864	33.762	38.074
1 000	37.124	40.089	43.702

Using the Q values tabulated we determined the unknown coefficients K_1, K_2 in the semiempirical formula (*22*) by the least squares method. In this formula we have

$$E_0^{-1}\left(\frac{3}{4}\right)^{1/3} \cong 1.017\,, \qquad \frac{3}{4}E_1/E_0 \cong 0.425\,.$$

The least squares method was applied to the function

$$Q_1 = K_1 B^{-1/3} + K_2 A B^{-1/3}\,, \tag{27}$$

where

$$Q_1 = Q - E_0^{-1}\left(\frac{3}{4}\right)^{1/3} B^{1/3} - \frac{3}{4}E_1/E_0\,.$$

We obtained $K_1 \cong 13.604$, $K_2 \cong 0.339$.

The resulting semiempirical formula has the form

$$Q = 1.017\,B^{1/3} + 0.425 + 13.604\,B^{-1/3} + 0.339\,A\,B^{-1/3}\,. \tag{28}$$

Table II gives the Q values calculated from Eq. (*28*) and the percent deviations p of the values from those given in Table I.

Equation (*28*) demonstrates that the first term, $1.017\,B^{1/3}$, clearly dominates for appreciably high values of parameter B. This was confirmed by the experimental results in ref.[1] where the values approached $B = 10^6$, $A = 500$.

Inserting those values in Eq. (*28*) we obtain

$$Q \cong 101.745 + 0.425 + 0.136 + 1.694\,.$$

This result illustrates the effect of the individual terms in Eq. (*28*) for the parameters used and also confirms that the application of the formula

$$Q \cong 1.017\,B^{1/3}$$

is warranted within the region of physical parameters used in ref.[1].

The importance of Eq. (*28*) is in the fact that it extends appreciably the range of validity with respect to the decisive physical parameters. Particularly significant is the last term, $0.339\, A\, B^{-1/3}$, which plays a major role for appreciable values of parameter *A*, i.e. for small widths of the line electrode. To suppress the effect of this term as much as possible it is convenient, when designing the line electrode, to choose a width as large as possible for a given length. On the other hand, however, the fact must be taken into account that the boundary effect, viz. the diffusion to the active surface in the vicinity of the two ends of the electrode, increases with increasing width of the electrode[1]. This effect fails to be accounted for in the mathematical model solved. To suppress the boundary effect the width of the line electrode must be chosen reasonably low, whereby the last term in Eq. (*28*) plays a role, particularly for low *B* values.

APPENDIX

This Appendix demonstrates how Eq. (*21*) is derived from Eq. (*19*). The following quantities in Eq. (*19*) are consecutively approximated by using Taylor series (functions *M* and *N* are defined in Eqs (*18a*), (*18b*)):

$$\int_0^v M(w)\mathrm{d}w = \int_0^v \left[(1-w)^{-1} + \frac{B\,w}{3\,x}\left((1-w)^{-1} - (1-w)^{-3}\right)\right]\mathrm{d}w \cong$$

$$\cong v + \frac{v^2}{2} + \frac{v^3}{3} - \frac{B}{3\,x}\left(\frac{2}{3}v^2 + \frac{5}{4}v^4 + \frac{9}{5}v^5\right). \qquad (A1)$$

TABLE II
Total diffusion flow *Q* calculated from Eq. (*28*)

A	*B*	*Q*	p^a
100	8 000	23.147	1.4
500	8 000	29.922	0.2
1 000	8 000	38.390	3.4
100	15 625	27.760	0.8
500	15 625	33.180	–1.7
1 000	15 625	39.954	–0.3
100	27 000	32.531	0.5
500	27 000	37.047	–2.7
1 000	27 000	42.692	–2.3

[a] Per cent deviation.

$$\int_0^1 \exp\left(\int_0^v M(w)\mathrm{d}w\right)\mathrm{d}v \cong \beta^{-1}(E_0 + E_1\beta^{-1} + \frac{1}{2}E_2\beta^{-2} - \frac{15}{8}E_4\beta^{-1} -$$

$$- \frac{27}{10}E_5\beta^{-2} + \frac{1}{2}E_2\beta^{-2} - \frac{15}{8}E_5\beta^{-2} + \frac{225}{128}E_8\beta^{-2}) , \qquad (A2)$$

where

$$E_n = \int_0^\infty s^n \exp(-s^3)\mathrm{d}s , \qquad n = 0, 1, 2, \ldots,$$

$$\beta = \left(\frac{2}{9}\frac{B}{x}\right)^{1/3}$$

(see Eq. (*14*)).

$$I = \int_0^v N(w)\exp\left(-\int_0^w M(z)\mathrm{d}z\right)\mathrm{d}w \cong$$

$$\cong \frac{3}{2}E_0^{-1}\left(\frac{1}{2}\beta^4 v^4 + \beta^4 v^5 + \frac{15}{32}\beta^7 v^8 + \frac{3}{2}\beta^4 v^6 + \frac{197}{120}\beta^7 v^9 + \frac{75}{256}\beta^{10} v^{12}\right) +$$

$$+ A/(3E_0 x^2)\left(\frac{1}{2}\beta v^2 + \frac{4}{9}\beta v^3 - \frac{1}{5}\beta^4 v^5 + \frac{7}{48}\beta^4 v^6 - \frac{5}{24}\beta^7 v^9\right). \qquad (A3)$$

$$\int_0^1 I \exp\left(\int_0^v M(w)\mathrm{d}w\right)\mathrm{d}v \cong$$

$$\cong 3/(2\beta E_0)\left(\frac{1}{3}E_1 + \frac{3}{16}\beta^{-1}\right) + A/(30E_0 x^2)\beta^{-2} . \qquad (A4)$$

Inserting all of the approximations in Eq. (*19*) we obtain formula (*21*).

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