GENERALIZATION OF THE SAND EQUATION TAKING INTO ACCOUNT THE CONCENTRATION DEPENDENCE OF DIFFUSION COEFFICIENT

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The theory of the chronopotentiometric method was generalized under the assumption of a linear dependence of the diffusion coefficient on the concentration of electroactive substance. The resulting simple final equations enable to determine from experimental data the heterodiffusion coefficient D_h and a coefficient, α, which characterizes the linear dependence of the diffusion coefficient on the concentration of the electroactive substance.

The theory of the chronopotentiometric method, which is one of the most often used electrochemical methods, has been elaborated under the assumption that the diffusion coefficient is independent of the concentration of electroactive diffusing particles, *i.e.* $D = \text{const}$. It is the aim of the present work to remove this restriction and to find analytical final expressions suitable for practical purposes.

THEORETICAL

We shall assume linear diffusion in the presence of an indifferent electrolyte where the reactants and products are soluble. The diffusion problem will be formulated as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D(C)\,\frac{\partial C}{\partial x} \right] \tag{1}$$

with the initial and boundary conditions

$$t = 0, \quad x > 0: \quad C(x, 0) = C_0, \tag{2}$$

$$x = 0, \quad t > 0: \quad D[C(0, t)]\,(\partial C/\partial x)_{x=0} = i/nF = \text{const.}, \tag{3}$$

$$x \to \infty: \qquad C(\infty, t) = C_0, \tag{4}$$

where $C(x, t)$ denotes concentration of diffusing particles as a function of the coordinate and time, C_0 starting concentration of the ions in the electrolyte, D dif-

fusion coefficient, i current density on the electrode, n number of transferred electrons, and F Faraday's constant. The chronopotentiometric method as a method of constant imposed current is characterized by the condition (3).

To solve the present problem, we shall make certain simplifying assumptions. In common practical cases characterized by the values of C_0 it is sufficient to assume, as a first approximation, a linear dependence of the diffusion coefficient on the concentration of the diffusing electroactive substance, *i.e.*

$$D[C(x, t)] = D_h[1 + \alpha\, C(x, t)] ,\tag{5}$$

where D_h denotes heterodiffusion coefficient for $C \to 0$, α the corresponding coefficient characterizing the linear concentration dependence.

Eqs $(1) - (5)$ can be solved approximately; we shall seek the solution in the form

$$C(x, t) = C_1(x, t) + \alpha\, C_2(x, t) .\tag{6}$$

We shall further assume that the following inequality holds:

$$|\alpha|\, C_0 \ll 1 .\tag{7}$$

It is apparent from what follows that the function $C_1(x, t)$ is of a basic importance for the solution, whereas $C_2(x, t)$ represents a correction function whose influence is dependent on α. We shall proceed in several steps.

We assume that the function $C_1(x, t)$ fulfills the equation

$$\partial C_1(x, t)/\partial t = D_h\, \partial^2 C_1(x, t)/\partial x^2 \tag{8}$$

with the initial and boundary conditions

$$C_1(x, 0) = 0 , \quad x > 0 \tag{9}$$

$$(\partial C_1(x, t)/\partial x)_{x=0} = v(t) , \quad t > 0 \tag{10}$$

$$x = \infty : \quad C_1(x, t) \to 0 . \tag{11}$$

We shall choose the function $v(t)$ so that it will fulfill the boundary condition (3) to Eq. (1) with an accuracy sufficient from the experimental point of view.

We now introduce the function $C(x, t)$ from (6) and $D[C(x, t)]$ from (5) into Eq. (1) and use Eq. (8). Thus, we obtain for $C_2(x, t)$ the equation

$$\partial C_2(x, t)/\partial t - D_h\, \partial^2 C_2(x, t)/\partial x^2 = F(x, t, \alpha) \tag{12}$$

with initial and boundary conditions

$$C_2(x, 0) = 0, \quad x > 0 \tag{13}$$

$$(\partial C_2(x, t)/\partial x)_{x=0} = 0, \quad C_2(\infty, t) \to 0, \quad t > 0, \tag{14}$$

where the function $F(x, t, \alpha)$ fulfills the equation

$$F(x, t, \alpha) = D_h \left[\frac{\partial C}{\partial x} \frac{\partial C_1}{\partial x} + C \frac{\partial^2 C_1}{\partial x^2} + \right.$$
$$\left. + \alpha \left(\frac{\partial C}{\partial x} \frac{\partial C_2}{\partial x} + C \frac{\partial^2 C_2}{\partial x^2} \right) \right] \tag{15}$$

To find the solutions for $C_1(x, t)$ and $C_2(x, t)$ it is necessary to express the function $v(t)$ from Eq. (10) and to replace the unknown function $C(x, t)$ from (15) by a known one. If we make use of the approximation $F(x, t, \alpha) \approx F(x, t, 0)$, this known function will be the solution of the diffusion equation $C_0(x, t)$ for the chronopotentiometric method under the assumption $D = \text{const}$. For $C_0(x, t)$ we have[1]

$$C_0(x, t) = C_0 - \frac{2i}{nF} \sqrt{(t/D_h)} \text{ ierfc} \frac{x}{2\sqrt{(D_h t)}}, \tag{16}$$

where

$$\text{ierfc} (z) \equiv (1/\sqrt{\pi}) e^{-z^2} - z \text{ erfc} (z). \tag{17}$$

We now shall use the function $C_0(0, t)$ following from Eq. (16) to express approximately the boundary condition (3) to Eq. (1) and to determine the function $v(t)$ in (10). We start from the approximate expression for the function $D[C(0, t)]$:

$$D[C(0, t)] = D_h[1 + \alpha C(0, t)] \approx D_h[1 + \alpha C_0(0, t)]. \tag{18}$$

By combining this with Eqs (3) and (16) we obtain

$$\left(\frac{\partial C}{\partial x} \right)_{x=0} D_h[1 + \alpha(C_0 - \beta \sqrt{(t/D_h)})] \approx i/nF, \tag{19}$$

which can be by using the Taylor series rearranged as

$$\left(\frac{\partial C}{\partial x} \right)_{x=0} \approx \frac{i}{nFD_h} [1 - \alpha(C_0 - \beta \sqrt{(t/D_h)})] = v(t) \tag{20}$$

provided that the inequality (7) applies. Now, the function $v(t)$ in (10) being known, we can solve Eq. (8) with the boundary conditions (9) and (10) and calculate the function $C_1(x, t)$. The solution can be written in the form[2,3]

$$C_1(x, t) = C_0 - 2D_h \int_0^t G_0(x, t, \tau)\, v(\tau)\, d\tau, \qquad (21)$$

where $G_0(x, t, \tau)$ is a source function on an infinite straight line. A continuously acting point source is located in the origin of coordinates $(x_0 = 0)$, *i.e.* in our case on the bounder of the diffusion region.

$$G_0(x, t, \tau) = \frac{1}{2\sqrt{[\pi D_h(t - \tau)]}}\, e^{-x^2/4D(t - \tau)}. \qquad (22)$$

The constant 2 before the integral in (21) is due to the use of the source function for an infinite straight line on a half-limited diffusion space, *i.e.* on an infinite half-line.

After introducing $G_0(x, t, \tau)$ and $v(\tau)$ from Eqs (22) and (20) into (21) we obtain

$$C_1(x, t) = C_0 - \frac{2i}{nFD_h}(1 - \alpha C_0)\sqrt{(D_h t)}\, \text{ierfc}\, \frac{x}{2\sqrt{(D_h t)}} +$$

$$- \frac{\alpha\beta^2}{2D_h}\int_0^t \sqrt{\frac{\tau}{t - \tau}}\, \exp\left(- \frac{x^2}{4D_h(t - \tau)}\right)\, d\tau. \qquad (23)$$

The following relation was used here:

$$\int_0^t u^{1/2}\, e^{-\varkappa/u}\, du = 2\sqrt{\pi}\sqrt{t}\, \text{ierfc}\sqrt{(\varkappa/t)}. \qquad (24)$$

We denote the integral in Eq. (23) as $J(x, t)$ and introduce the substitution $u = t - \tau$. To calculate it we shall differentiate it with respect to the parameter t. It can be shown that this integral fulfills the conditions for the differentiation and that (with $\varkappa = x^2/4D_h$)

$$\frac{\partial J(x, t)}{\partial t} = 0 + \frac{1}{2}\int_0^t (t - u)^{-1/2}\, u^{-1/2}\, e^{-\varkappa/u}\, du = \frac{1}{2}\pi\, \text{erfc}\sqrt{(\varkappa/t)} \qquad (25)$$

$$J(x, t) = \tfrac{1}{2}\pi \int_0^t \operatorname{erfc} \sqrt{(\varkappa/\tau)} \, d\tau =$$

$$= \tfrac{1}{2}\pi \left[\tau \operatorname{erfc} \sqrt{[\varkappa/\tau]} \Big|_0^t - \sqrt{(\alpha/\pi)} \int_0^t \tau^{-1/2} e^{-\varkappa/\tau} \, d\tau \right] =$$

$$= \tfrac{1}{2}\pi \left(t \cdot \operatorname{erfc} \frac{x}{2\sqrt{(D_h t)}} - \frac{x}{\sqrt{D_h}} \sqrt{t} \operatorname{ierfc} \frac{x}{2\sqrt{(D_h t)}} \right). \qquad (26)$$

In this calculation we used again Eq. (24). With this result in mind, we can express the concentration $C_1(0, t)$ as follows:

$$C_1(0, t) = C_0 - (1 - \alpha C_0) \beta \sqrt{(t/D_h)} - \tfrac{1}{4}\pi\alpha\beta^2 t/D_h \qquad (27)$$

where we have set for simplicity $\beta = (2/\sqrt{\pi}) \, i/n\mathbf{F}$.

Eqs (23) and (26) define the function $C_1(x, t)$; we now can solve Eq. (12) for the function $C_2(x, t)$. To this purpose we must express the function $F(x, t, \alpha)$, Eq. (15), and we shall use, as mentioned above, the first approximation

$$F(x, t, \alpha) \approx F(x, t, 0). \qquad (28)$$

If we introduce the function $C_1(x, t)$ into $F(x, t, 0)$ and express the function $C(x, t)$ by Eq. (6), we obtain

$$F(x, t, 0) = D_h \left[\left(\frac{\partial C_0(x, t)}{\partial x} \right)^2 + C_0(x, t) \frac{\partial^2 C_0(x, t)}{\partial x^2} \right]. \qquad (29)$$

We shall discuss the approximation (28). If we introduce the functions $C(x, t)$ and and $D[C(x, t)]$ from Eqs (6) and (5) into (1) and consider $C_1(x, t)$ from (23), the approximation (28) will mean that we have neglected in Eq. (1) the terms containing α^n with $n \geq 2$, i.e.. the small terms of higher order than the first.

If we introduce the solution $C_0(x, t)$ from (16) into (29), we have

$$F(x, t, 0) = D_h K \big[K(\operatorname{erfc} z)^2 + (2K/\pi) e^{-2z^2} -$$

$$+ (KC_0/\sqrt{\pi}) (D_h t)^{-1/2} e^{-z^2} - (K/\pi \sqrt{(D_h t)}) z e^{-z^2} \operatorname{erfc} z , \qquad (30)$$

where

$$K = i/n\mathbf{F}D_h = \beta \sqrt{\pi/2D_h} , \quad z = x/2\sqrt{(D_h t)} . \qquad (31)$$

The solution $C_2(x, t)$ of the inhomogeneous diffusion equation (12) on an infinite half-line with the zero initial condition (13) and zero Neumann boundary condition

(14) can be expressed with the aid of the source (Green's) function. Continuously acting point sources at time τ are located in points of coordinate ξ. For the solution $C_2(x,t)$ we then have[3]

$$C_2(x, t) = \frac{1}{2\sqrt{\pi}} \int_0^t \int_0^\infty \frac{1}{\sqrt{(D_h(t - \tau))}} \left\{ \exp\left[-\frac{(x - \xi)^2}{4D(t - \tau)} \right] + \right.$$

$$\left. + \exp\left[-\frac{(x + \xi)^2}{4D(t - \tau)} \right] \right\} F(\xi, \tau, 0) \, d\xi \, d\tau . \tag{32}$$

If we introduce into this equation the function (30) and shall seek the solution $C_2(x, t)$ in the point $x = 0$, we obtain

$$C_2(0, t) = K \sqrt{(D_h/\pi)} \left[K \int_0^t \int_0^\infty \frac{1}{\sqrt{(t - \tau)}} \exp\left[-\frac{\xi^2}{4D(t - \tau)} \right] \cdot \right.$$

$$\cdot \left(\text{erfc} \frac{\xi}{2\sqrt{(D_h\tau)}} \right)^2 d\xi \, d\tau + \frac{2K}{\pi} \int_0^t \int_0^\infty \frac{1}{\sqrt{(t - \tau)}} \exp\left[-\frac{\xi^2}{4D(t - \tau)} \right] \cdot$$

$$\exp\left(-2\xi^2/4D_h\tau \right) d\xi \, d\tau - C_0(\pi D_h)^{-1/2} \int_0^t \int_0^\infty (t - \tau)^{-1/2} \exp\left[-\xi^2/4D_h(t - \tau) \right] \cdot$$

$$\cdot \tau^{-1/2} \exp\left(-\xi^2/4D_h \right) d\xi \, d\tau - (\pi D_h)^{-1/2} \int_0^t \int_0^\infty (t - \tau)^{-1/2} \exp\left(-\xi^2/4D_h(t - \tau) \right) \cdot$$

$$\cdot \tfrac{1}{2}\tau^{-1/2}\xi(D\tau)^{-1/2} \exp\left(-\xi^2/4D_h\tau \right) \text{erfc} \left[\xi/2\sqrt{(D\tau)} \right] d\xi \, d\tau \right] =$$

$$= \sqrt{(D_h/\pi)} K \left[K \int_0^t \int_0^\infty J_1(t, \tau, \xi) \, d\xi d\tau + (2K/\pi) \int_0^t \int_0^\infty J_2(t, \tau, \xi) \, d\xi \, d\tau + \right.$$

$$\left. - C_0(\pi D_h)^{-1/2} \int_0^t \int_0^\infty J_3(t, \tau, \xi) \, d\xi \, d\tau - (\pi D_h)^{-1/2} \int_0^t \int_0^\infty J_4(t, \tau, \xi) \, d\xi \, d\tau \right] . \tag{33}$$

Here we have introduced for the sake of simplicity the functions J_1 through J_4 the meaning of which is obvious. We shall calculate the double integrals in Eq. (33). The calculation of the first one will be approximate. To this purpose we express the function erfc z with the aid of a minorant function:

$$\text{erfc } z \approx e^{\lambda^2} e^{-(\lambda + z)^2} = e^{-(z^2 + 2\lambda z)} . \tag{34}$$

The constant λ will be determined from the condition that the slopes of the both functions in the origin of coordinates be equal:

$$\left(\frac{\mathrm{d}\,\mathrm{erfc}\,z}{\mathrm{d}z}\right)_{z=0} = \frac{\mathrm{d}}{\mathrm{d}z}\left(e^{\lambda^2}\,e^{-(\lambda+z)^2}\right)_{z=0} = -2/\sqrt{\pi}\,, \tag{35}$$

where $\lambda = 1/\sqrt{\pi}$. The course of erfc z and the minorant function $\exp\left(-z^2 - 2z/\sqrt{\pi}\right)$ is shown in Fig. 1. If we approximate the former function by the latter one we obtain the first integral in (33) in the form

$$\int_0^t \int_0^\infty J_1(t, \tau, \xi)\,\mathrm{d}\xi\,\mathrm{d}\tau \approx \int_0^t \int_0^\infty (t - \tau)^{-1/2}\exp\left[-\xi^2/4D_h(t - \tau)\right].$$

$$.\exp\left(-2/\pi - 2/\sqrt{\pi} - \xi^2/2D_h\right)\mathrm{d}\xi\,\mathrm{d}\tau =$$

$$= \sqrt{(\pi D_h)}\int_0^t \left(\frac{\tau}{2t - \tau}\right)^{1/2}\left[1 - \mathrm{erf}\left[\frac{2}{\sqrt{\pi}}\left(\frac{t - \tau}{2t - \tau}\right)^{1/2}\right]\right]\mathrm{d}\tau =$$

$$= \sqrt{(\pi D_h)}\,t\left[\int_0^1 \left(\frac{u}{2 - u}\right)^{1/2}\mathrm{d}u - \int_0^1 \left(\frac{u}{2 - u}\right)^{1/2}\mathrm{erf}\left[\frac{2}{\sqrt{\pi}}\left(\frac{1 - u}{2 - u}\right)^{1/2}\right]\mathrm{d}u\right] =$$

$$\sqrt{(\pi D_h)}\,t(\pi/2 - 1{\cdot}306)\,. \tag{36}$$

The value of the last integral was calculated by a computer.

The second integral in Eq. (33) is calculated as

$$\int_0^t \int_0^\infty J_2(t, \tau, \xi)\,\mathrm{d}\xi\,\mathrm{d}\tau = \sqrt{(\pi D_h)}\int_0^t (t - \tau)^{-1/2}\left(\frac{\tau(t - \tau)}{2t - \tau}\right)^{1/2}\mathrm{d}\tau =$$

$$= \sqrt{(\pi D_h)}\,t\int_0^1 \left(\frac{u}{2 - u}\right)^{1/2}\mathrm{d}u = \sqrt{(\pi D_h)}\,t(\pi/2 - 1)\,. \tag{37}$$
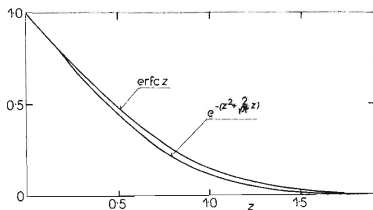

Fig. 1

Comparison of the Function erfc (z) with Minorant Function $\exp\left[-z^2 - 2z//\sqrt{\pi}\right]$

The third integral in Eq. (33) is given as

$$\int_0^t \int_0^\infty J_3(t, \tau, \xi) \, \mathrm{d}\xi \, \mathrm{d}\tau = \sqrt{(\pi D_\mathrm{h})} \, t^{-1/2} \int_0^t \mathrm{d}\tau = \sqrt{(\pi D_\mathrm{h} t)} \, . \qquad (38)$$

The fourth integral:

$$\int_0^t \int_0^\infty J_4(t, \tau, \xi) \, \mathrm{d}\xi \, \mathrm{d}\tau = 4 \sqrt{D_\mathrm{h}} \int_0^t (t - \tau)^{-1/2} \frac{t - \tau}{t} \, \cdot$$

$$\cdot \left[1 - \left(\frac{t - \tau}{2t - \tau} \right)^{1/2} \right] \mathrm{d}\tau = 4 \sqrt{(D_\mathrm{h} t)} \int_0^1 (1 - u)^{1/2} \left[1 - \left(\frac{1 - u}{2 - u} \right)^{1/2} \right] \mathrm{d}u = 0 \, . \qquad (39)$$

The integration with respect to ξ in the double integrals $(36)-(39)$ is carried out after simple substitutions by the *per partes* method. The obtained results are introduced into Eq. (33) to obtain

$$C_2(0, t) = -\tfrac{1}{2} C_0 \beta \sqrt{(t/D_\mathrm{h})} + 0{\cdot}49\beta^2 \, t/D_\mathrm{h} \, . \qquad (40)$$

If we introduce the particular solutions (27) and (40) into Eq. (6), we can write directly the approximate solution of Eq. (1) with the initial condition (2) and boundary conditions (3) and (4) in the point $x = 0$:

$$C(0, t) \approx C_0 - \left(1 - \tfrac{1}{2}\alpha C_0 \right) \beta \sqrt{(t/D_\mathrm{h})} - 0{\cdot}3\alpha\beta^2 \, t/D_\mathrm{h} \, , \qquad (41)$$

where $\beta = 2i/nF \sqrt{\pi}$. This is the time dependence of the concentration of the diffusing substance at the electrode surface in chronopotentiometry in the case where the diffusion coefficient is a linear function of the concentration of the electroactive substance. It should be stressed that D_h in this equation is the heterodiffusion coefficient, *i.e.* that

$$\lim_{C \to 0} D(C) = D_\mathrm{h} \, . \qquad (42)$$

The zero concentration at the electrode will be attained at a time $t = \tau$, *i.e.* $C(0, \tau) = = 0$, where τ is the transition time. From Eq. (41) and (39) follows the condition for the time τ.

$$C_0 = (1 - \alpha C_0) \beta' i \sqrt{(\tau/D_\mathrm{h})} + 0{\cdot}3\alpha(\beta' i)^2 \, \tau/D_\mathrm{h} \, . \qquad (43)$$

where $\beta' = 2/nF \sqrt{\pi}$. This is the generalized equation of the chronopotentiometric

method for the transition time τ; for $\alpha \rightarrow 0$ it apparently takes the form of the Sand's equation:

$$C_0 = \beta' i \sqrt{(\tau/D_h)} \Rightarrow i \sqrt{\tau} = 0.5 F C_0 \sqrt{(\pi D_h)}, \qquad (44)$$

where $D = \text{const.}$

Eq. (43) was derived under the following approximation: Eq. (18) or (20) and (28), expressing the linear dependence of the diffusion coefficient D on the concentration $C_0(x, t)$ (the uncorrected concentration, cf (16)) and the neglection of the terms with α^n, where $n \geqq 2$, in Eq. (1) (cf. note below Eq. (29)). Further we used the minorant (34) to simplify the calculation of the integral (36) which is a part of the solution for $C_2(0, t)$. This influences the accuracy in determining the constant 0.3 in Eq. (43) which, however, is negligible against experimental errors.

RESULTS AND DISCUSSION

The general equation (43) enables to determine the values of D_h and α from the results of at least two measurements from which we determine the values of $(i \sqrt{\tau})_k$ and $(i \sqrt{\tau})_j$ for two concentrations C_{0k}, C_{0j}. The form of this equation is, however, somewhat complicated for its practical use and therefore we shall derive its simpler form. By solving the quadratic equation (43) and using the Taylor series we obtain

$$\beta' i \sqrt{(\tau/D_h)} \approx C_0 (1 + 0.2\alpha C_0 - 0.11\alpha^2 C_0^2 + \ldots) \qquad (45)$$

provided that

$$1 \,.\, 2\alpha C_0 / (1 - 0.5\alpha C_0)^2 \ll 1 \,. \qquad (46)$$

We compare this result with the Sand equation (44). Since the latter does not take into account the dependence $D(C)$, the chronopotentiometric method gives "effective" diffusion coefficients $\tilde{D}$ which approach the heterodiffusion coefficients D_h if $\alpha C_0 \rightarrow 0$. If we write in Eq. (44) $\tilde{D}$ instead of D, we obtain by comparing Eq. (44) with (45)

$$\tilde{D} \approx (1 + 0.2\alpha C_0 - 0.11\alpha^2 C_0^2 + \ldots)^2 D_h \approx$$
$$\approx (1 + 0.4\alpha C_0 - 0.18\alpha^2 C_0^2 + \ldots) D_h \,. \qquad (47)$$

This is the relation between the "effective coefficient" $\tilde{D}$ and heterodiffusion coefficient D_h by means of which it is possible to determine the values of D_h and α from experimentally determined values of $\tilde{D}$ in solutions of different concentration C_0.

A more accurate expression for $\tilde{D}$ can be obtained from Eqs (44) and (45). Fig. 2 shows a comparison of the dependence of $\tilde{D}/D_h$ on αC_0 calculated from the approximate Eq. (47) and more accurate Eq. (43). It is seen that the results from the latter equation are practically identical with those calculated — for $\alpha C_0 \leqq 0.5$ — from the equation

$$\tilde{D} = (1 + 0.40\alpha C_0) D_h .\tag{48}$$

We shall now compare the conclusions obtained from the generalized theory of the chronopotentiometric method with those from the generalized chronoamperometric method, *i.e.* the generalized Cotrell's equation[4]. The following equation was derived for the "effective" coefficient $\tilde{D}$ in the chronoamperometric method[4] on the assumption of a linear dependence of the diffusion coefficient on the concentration:

$$\tilde{D} = (1 + 0.18\alpha C_0)^2 D_h \approx (1 + 0.36\alpha C_0) D_h .\tag{49}$$

It follows from the magnitude of the constants 0.4 and 0.36 in the latter two equations that the "effective coefficient" $\tilde{D}$ obtained in chronopotentiometry is somewhat more influenced by the concentration dependence of the diffusion coefficient. This is due to the fact that in chronopotentiometry the diffusion proceeds near the electrode at higher concentrations than in chronoamperometry. Besides that, it should be kept in mind that from the original equation of Cotrell and Sand it is possible to obtain on the basis of experimental data only the dependence of the "effective coefficient"
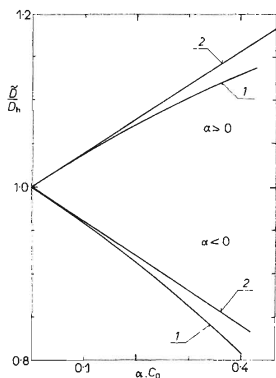

Fig. 2

Dependences of $\tilde{D}/D_h$ on αC_0 Calculated from Approximate Eq. (47) (1) and Exact Solution of Eq. (43) (2)

Curves 2 are practically identical with the function $\tilde{D}/D_h = 1 + 0.4\alpha C_0$.

$\tilde{D}$ on C_0 (*i.e.* the maximum depolarizer concentration, $C(\infty, t) \to C_0$) but not the function $D(C)$, *i.e.* the α value in Eq. (*5*).

The generalized theory of the chronopotentiometric method was derived in the first approximation, *i.e.* for $|\alpha| C_0 \ll 1$ — see text below Eq. (*43*). It was not shown for what maximum values of $|\alpha| C_0$ this first approximation applies with regard to the experimental accuracy. This question represents a special problem which could be analysed by computer techniques. On the basis of the results of the generalization of the Cotrell's equation[4] and the experience with the solution of analogous non-linear equations it can be assumed that our approximation will be satisfactory if $|\alpha| C_0$ does not exceed about 0·3.

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