

# Generalization of the Ilkovič equation corrected with respect to concentration dependence of the diffusion coefficient

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In this paper the theory of polarographic method is generalized for the case that the diffusion coefficient is a linear function of concentration of the depolarizer. Besides, the spherical diffusion is also taken into account. The case of reversible reactions in the presence of indifferent electrolyte is solved. The solution results in the generalized corrected Ilkovič equation and in the relation between "apparent" diffusion coefficient and heterodiffusion coefficient.

В работе была обобщена теория полярографического метода в случае, когда коэффициент диффузии является линейной функцией концентрации деполаризатора и одновременно учитывается сферическая диффузия. Был решен случай обратимых реакций в присутствии постороннего электролита. Решение приводит к обобщенному, исправленному уравнению Ильковича и к соотношению между «кажущимся» коэффициентом диффузии и коэффициентом гетеродиффузии.

The theory of polarographic method was developed on the assumption that the diffusion coefficient is independent of concentration of electroactive particles, *i.e.*  $D = \text{const}$ . The result of this theory is the Ilkovič equation [1] which presumes a plane diffusion layer. The real curvature of diffusion layer was taken into consideration by Koutecký [2], who corrected the Ilkovič equation and exactly solved the equation of convective diffusion in spherical coordinates by means of infinite series. In a later paper [3] published by Levich, another approximative method of solution is proposed. This solution leads to an inhomogeneous equation of convective diffusion which is easier to be solved and the result is in agreement with the correction according to Koutecký.

The aim of this study is to generalize the theory of polarographic method on the assumption that a linear relationship between diffusion coefficient and concentration of the depolarizer exists. Reversible reactions and the presence of indifferent electrolyte which enables us to neglect the migration currents due to electric field in the solution with respect to the diffusion current will be taken into consideration.

**Theoretical**

Let us consider the equation of convective diffusion

$$\frac{\partial c}{\partial t} + \mathbf{v} \operatorname{grad} c = \operatorname{div} [D(c) \operatorname{grad} c] \quad (1)$$

which is written in spherical coordinates for the case of central symmetry

$$\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = D(c) \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) + \frac{\partial D(c)}{\partial r} \frac{\partial c}{\partial r} \quad (2)$$

If we insert the expression

$$D(c) = D_h(1 + \alpha c) \quad (3)$$

where  $D_h$ ,  $\alpha$ , and  $c$  are the heterodiffusion coefficient for  $c \rightarrow 0$ , the coefficient characterizing the linear concentration dependence of the diffusion coefficient, and the concentration of the depolarizer, respectively, we obtain

$$\begin{aligned} \frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = & D_h \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) + \\ & + \alpha D_h \left[ c \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) + \left( \frac{\partial c}{\partial r} \right)^2 \right] \end{aligned} \quad (4)$$

For polarography, the initial and boundary conditions of the equation of diffusion (4) are

$$\begin{aligned} c(r, t = 0) &= c_0 \\ c(r = a, t) &= c(\varphi) \quad c(r \rightarrow \infty, t) = c_0 \end{aligned} \quad (5)$$

where  $a$ ,  $c_0$ , and  $\varphi$  are the radius of drop, the concentration of depolarizer inside solution, and the potential of mercury dropping electrode, respectively. According to [3], it holds

$$c(\varphi) = c_0 A e^{-\frac{nF}{RT}\varphi} \quad (6)$$

where  $A$  is a constant proportional to the activity coefficient of ions.

The solution of polarographic method necessitates further treatment of eqn (4) which is described in original papers, e.g. [1] and [3] and we shall, therefore, present only the results.

The diffusion takes place in a thin layer the thickness of which is very small in comparison with the drop radius  $a(t)$  that increases with time. We may substitute the following expression for the coordinate  $r$

$$r \approx a(t) + y; \quad y \ll a(t) \quad (7)$$

Then it holds [1, 4]

$$\left(\frac{\partial c}{\partial t}\right)_r = \left(\frac{\partial c}{\partial t}\right)_y - \frac{\gamma}{3 t^{2/3}} \frac{\partial c}{\partial y} \quad (8)$$

where

$$\gamma = \left(\frac{3d^2 U_0}{16}\right)^{1/3} = \left(\frac{3}{4\pi} \frac{m}{\rho}\right)^{1/3} \quad (9)$$

The symbols  $d$ ,  $U_0$ ,  $\rho$ , and  $m$  in expression (9) stand for the diameter of the capillary from which mercury drops, the linear flow rate of mercury in the capillary, the specific weight of mercury, and the flow rate of mercury running off per second, respectively. The radial flow rate of liquid during the growth of drop  $v_r$  is given by the following expression [3]

$$v_r \approx \frac{\gamma}{3t^{2/3}} - \frac{2}{3} \frac{y}{t} + \frac{y^2}{\gamma t^{4/3}} \quad (10)$$

Now we must express the Laplace operator in spherical coordinates and substitute from eqn (7) and eqn (11) expressing the growing drop radius  $a(t)$  explicitly [4]

$$a(t) = \gamma t^{1/3} \quad (11)$$

Hence, we obtain

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \approx \frac{\partial^2 c}{\partial y^2} + \frac{2}{\gamma t^{1/3}} \frac{\partial c}{\partial y} \quad (12)$$

If we take into consideration eqns (12), (10), (8), and (7), the equation of convective diffusion (4) may be transformed into the form

$$\begin{aligned} \frac{\partial c}{\partial t} - \left(\frac{2}{3} \frac{y}{t} - \frac{y^2}{\gamma t^{4/3}}\right) \frac{\partial c}{\partial y} = D_h \frac{\partial^2 c}{\partial y^2} + \frac{2}{\gamma t^{1/3}} \frac{\partial c}{\partial y} + \\ + \alpha D_h \left[ c \left( \frac{\partial^2 c}{\partial y^2} + \frac{2}{\gamma t^{1/3}} \frac{\partial c}{\partial y} \right) + \left( \frac{\partial c}{\partial y} \right)^2 \right] \end{aligned} \quad (13)$$

If we suppose

$$|\alpha| c_0 < 1 \quad (14)$$

we can prove that the following inequality is fulfilled [3]

$$\frac{2}{r} \frac{\partial c}{\partial r} \approx \frac{2}{a(t)} \frac{\partial c}{\partial y} = \frac{2}{\gamma t^{1/3}} \frac{\partial c}{\partial y} \ll \frac{\partial^2 c}{\partial y^2} \quad (15)$$

On the basis of this reasoning, the terms of littleness of the second order in the composite bracket in eqn (13) may be omitted and it may be assumed

$$\alpha D_h c \frac{2}{\gamma t^{1/3}} \frac{\partial c}{\partial y} \rightarrow 0 \quad (16)$$

For illustration, we shall write eqn (13) with approximation (16) in the form

$$\frac{\partial c}{\partial t} - \frac{2y}{3t} \frac{\partial c}{\partial y} - D_h \frac{\partial^2 c}{\partial y^2} \approx \frac{2D_h}{\gamma t^{1/3}} \frac{\partial c}{\partial y} - \frac{y^2}{\gamma t^{4/3}} \frac{\partial c}{\partial y} + \alpha D_h \left[ c \frac{\partial^2 c}{\partial y^2} + \left( \frac{\partial c}{\partial y} \right)^2 \right] \quad (17)$$

Now let us consider eqn (17) the right side of which is supposed to equal zero. For initial and boundary conditions (5), the solution of this equation gives [1]

$$c_1(z, \tau) = \frac{2}{\sqrt{\pi}} [c_0 - c(\varphi)] \int_0^{z/(2\sqrt{\tau})} e^{-\xi^2} d\xi + c(\varphi) \quad (18)$$

where the new variables  $z$  and  $\tau$  are bound with the variables  $y$  and  $t$  by the subsequent relations

$$z = t^{2/3} y; \quad \tau = \frac{3}{7} D_h t^{7/3} \quad (19)$$

On the basis of the solution  $c_1$ , it is already easy to calculate the diffusion flow and the corresponding current density flowing through the mercury dropping electrode and thus to obtain the Ilkovič equation.

Now let us consider eqn (17) in which we substitute  $\alpha = 0$ . The solution is given in paper [3] by *Levich* and leads to a correction of the Ilkovič equation. As evident from eqn (17), the correction involves influence of the curvature of the diffusion layer and is identical with the correction derived earlier by *Koutecký* [2], more exactly with the first term of this correction.

Let us solve eqn (17) for  $\alpha \neq 0$ , i.e. respecting linear concentration dependence of the diffusion coefficient (3). The solution may be performed by the method of successive approximations and expressed in the form

$$c = c_1 + c_k \quad |c_k| \ll c_1 \quad (20)$$

where  $c_k$  is a correction solution for the function  $c_1$  given by eqn (18). If we substitute from eqn (20) into eqn (17) the solution  $c_k$  must fulfil the following equation

$$\frac{\partial c_k}{\partial t} - \frac{2y}{3t} \frac{\partial c_k}{\partial y} - D_h \frac{\partial^2 c_k}{\partial y^2} \approx \frac{2D_h}{\gamma t^{1/3}} \frac{\partial c_1}{\partial y} - \frac{y^2}{\gamma t^{4/3}} \frac{\partial c_1}{\partial y} + \alpha D_h \left[ c_1 \frac{\partial^2 c_1}{\partial y^2} + \left( \frac{\partial c_1}{\partial y} \right)^2 \right] \quad (21)$$

for the following initial and boundary conditions

$$\begin{aligned} c_k(y, t = 0) &= 0 \\ c_k(y = 0, t) &= 0; \quad c(y \rightarrow \infty, t) = 0 \dots t > 0 \end{aligned} \quad (22)$$

The terms of littleness of the second and higher orders in eqn (21) have been neglected, *i.e.*

$$\frac{y^2}{\gamma t^{4/3}} \frac{\partial c_k}{\partial t} - \frac{2D_h}{\gamma t^{1/3}} \frac{\partial c_k}{\partial y} \rightarrow 0 \quad (23)$$

which is the approximation suggested by *Levich* [3]. Furthermore, we put

$$c \frac{\partial^2 c}{\partial y^2} + \left( \frac{\partial c}{\partial y} \right)^2 \approx c_1 \frac{\partial^2 c_1}{\partial y^2} + \left( \frac{\partial c_1}{\partial y} \right)^2 \quad (24)$$

(see eqns (20) and (17)).

Let us consider the function  $c_{k1}$  which is the solution of eqn (21) for  $\alpha = 0$  and initial and boundary conditions (22) where we write  $c_{k1}$  instead of the function  $c_k$ . This function was already presented in paper [3] by *Levich* and therefore we shall not analyze this problem in more detail.

Provided the function  $c_{k2}$  is the solution of the equation

$$\frac{\partial c_{k2}}{\partial t} - \frac{2y}{3t} \frac{\partial c_{k2}}{\partial y} - D_h \frac{\partial^2 c_{k2}}{\partial y^2} = \alpha D_h \left[ c_1 \frac{\partial^2 c_1}{\partial y^2} + \left( \frac{\partial c_1}{\partial y} \right)^2 \right] \quad (25)$$

at initial and boundary conditions (22) where we write  $c_{k2}$  instead of  $c_k$ , the solution of inhomogeneous eqn (21) for conditions (23) and  $\alpha \neq 0$  is the function

$$c_k = c_{k1} + c_{k2} \quad (26)$$

It is, therefore, obvious from these considerations that the generalized theory of the polarographic method respecting linear concentration dependence of the diffusion coefficient is reduced to the solution of eqn (25) at conditions (22). If we introduce substitution (19) in eqn (25), it may be written in the form

$$\begin{aligned} \frac{\partial c_{k2}}{\partial \tau} - \frac{\partial^2 c_{k2}}{\partial z^2} &= \alpha \left[ c_1(z, \tau) \frac{\partial^2 c_1(z, \tau)}{\partial z^2} + \left( \frac{\partial c_1(z, \tau)}{\partial z} \right)^2 \right] = \\ &= \alpha F(z, \tau) \end{aligned} \quad (27)$$

The particular solution of inhomogeneous eqn (27) at initial as well as boundary conditions corresponding to zero (22) on an infinite half line is given by the following expression [4]

$$\begin{aligned} c_{k2}(z, \tau) &= \frac{1}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{\sqrt{\tau - \kappa}} \left\{ e^{-\frac{(z-\xi)^2}{4(\tau-\kappa)}} + \right. \\ &\quad \left. - e^{-\frac{(z+\xi)^2}{4(\tau-\kappa)}} \right\} \alpha F(\xi, \kappa) d\xi d\kappa \end{aligned} \quad (28)$$

If we insert the solution  $c_1$  given by eqn (18) into eqn (27) and express the function  $F(\xi, \kappa)$  by means of eqn (28) or eqn (27), we obtain

$$\alpha F(\xi, \kappa) = \alpha \left[ K_1 \frac{\xi}{\kappa^{3/2}} e^{-\frac{\xi^2}{4\kappa}} \operatorname{erf} \frac{\xi}{2\sqrt{\kappa}} + K_2 \frac{\xi}{\kappa^{3/2}} e^{-\frac{\xi^2}{4\kappa}} + K_3 \frac{1}{\kappa} e^{-\frac{\xi^2}{4\kappa}} \right] \quad (29)$$

where

$$\begin{aligned} K_1 &= -\frac{1}{2\sqrt{\pi}} [c_0 - c(\varphi)]^2 \\ K_2 &= -\frac{1}{2\sqrt{\pi}} [c_0 - c(\varphi)] c(\varphi) \\ K_3 &= \frac{1}{\pi} [c_0 - c(\varphi)]^2 \end{aligned} \quad (30)$$

In polarography we are interested in the current density  $i$  flowing through the area of the mercury dropping electrode

$$i = nFD [c(\varphi)] \frac{\partial c}{\partial z} \Big|_{z=0} \frac{\partial z}{\partial y} \quad (31)$$

Therefore we shall differentiate the function  $c_{k2}$  expressed by eqn (28)

$$\frac{\partial c_{k2}(z, \tau)}{\partial z} \Big|_{z=0} = \frac{\alpha}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{(\tau - \kappa)^{3/2}} \xi e^{-\frac{\xi^2}{4(\tau - \kappa)}} F(\xi, \kappa) d\xi d\kappa \quad (32)$$

and insert the function  $F(\xi, \kappa)$  given by eqn (29). Then it holds

$$\frac{\partial c_{k2}}{\partial z} \Big|_{z=0} = \alpha [K_1 I_1 + K_2 I_2 + K_3 I_3] \quad (33)$$

where  $I_i$ ,  $i = 1, 2, 3$  are the following integrals

$$I_1 = \frac{1}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{(\tau - \kappa)^{3/2}} \frac{\xi^2}{\kappa^{3/2}} e^{-\frac{\xi^2}{4(\tau - \kappa)} - \frac{\xi^2}{4\kappa}} \operatorname{erf} \frac{\xi}{2\sqrt{\kappa}} d\xi d\kappa \quad (34)$$

$$I_2 = \frac{1}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{(\tau - \kappa)^{3/2}} \frac{\xi^2}{\kappa^{3/2}} e^{-\frac{\xi^2}{4(\tau - \kappa)} - \frac{\xi^2}{4\kappa}} d\xi d\kappa = \frac{1}{\sqrt{\tau}} \quad (35)$$

$$I_3 = \frac{1}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{(\tau - \kappa)^{3/2}} \frac{\xi}{\kappa} e^{-\frac{\xi^2}{4(\tau - \kappa)} - \frac{\xi^2}{4\kappa}} d\xi d\kappa = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{\tau}} \quad (36)$$

Now we are concerned with integral (34) the calculation of which we are going to carry out approximately. For this purpose, we express the functions  $\operatorname{erf} z$  by means of a majorant function [7]

$$\operatorname{erf} z \approx 1 - e^{-\frac{2}{\sqrt{\pi}}z} \quad (37)$$

If we insert from eqn (37) into eqn (34) and take into account integral (35), we may write

$$I_1 \approx I_2 - I_{11} \quad (38)$$

$$I_{11} = \frac{1}{2\sqrt{\pi}} \int_0^\tau \int_0^\infty \frac{1}{(\tau - \kappa)^{3/2}} \frac{\xi^2}{\kappa^{3/2}} e^{-\frac{\xi^2}{4(\tau - \kappa)} - \frac{\xi^2}{2\kappa} - \frac{1}{\sqrt{\pi}} \frac{\xi}{\sqrt{\kappa}}} d\xi d\kappa \quad (39)$$

It is easy to integrate double integral (39) with respect to the variable  $\xi$  by using substitution

$$u = \frac{2\tau - \kappa}{2\sqrt{\kappa}\sqrt{\tau - \kappa}} \xi + \frac{1}{\sqrt{\pi}} \sqrt{\frac{\tau - \kappa}{2\tau - \kappa}} \quad (40)$$

and rearrange it into the form

$$I_{11} = \frac{4}{\sqrt{\pi}} \frac{1}{\sqrt{\tau}} \int_0^1 \frac{1}{(2 - \eta)^{3/2}} \left[ \frac{\sqrt{\pi}}{2} e^{-\frac{1-\eta}{2-\eta} \frac{1}{\pi}} \left( 1 - \operatorname{erf} \frac{1}{\sqrt{\pi}} \sqrt{\frac{1-\eta}{2-\eta}} \right) \times \right. \\ \left. \times \left( \frac{1}{2} + \frac{1}{\sqrt{\pi}} \frac{1-\eta}{2-\eta} \right) - \frac{1}{2\sqrt{\pi}} \sqrt{\frac{1-\eta}{2-\eta}} \right] d\eta = 0.256 \frac{1}{\sqrt{\tau}} \quad (41)$$

The value of  $I_{11}$  was determined by means of a computer.

If we insert from eqns (41), (38), (36), (35), and (30) into eqn (33), we obtain

$$\left. \frac{\partial c_{k2}}{\partial z} \right|_{z=0} \approx \frac{1}{2\sqrt{\pi}} \left[ c_0 - c(\varphi) \right] \frac{1}{\sqrt{\tau}} \{0.256[c_0 - c(\varphi)] - c(\varphi)\} \quad (42)$$

Now, it is already possible to calculate the current flowing through the mercury dropping electrode. If we take into account eqns (26) and (20), it will do to substitute the solution  $c_1$  expressed by eqn (18), the solution  $c_{k1}$  explicitly presented in [3], and eqn (42) into eqn (31). The current  $I$  flowing through a drop is related with the current density  $i$  also by the following expression [1]

$$I = 4\pi a^2(t) i \quad (43)$$

where the drop radius  $a(t)$  is given by eqn (11). Provided we replace the variables  $\tau$  and  $z$  by the variables  $y$  and  $t$  according to eqn (19) and take into account eqns (9) and (3), we may write for the instantaneous current

$$I \approx 0.732 n F D_h^{1/2} m^{2/3} t^{1/6} [c_0 - c(\varphi)] \left\{ \left\{ 1 + 3.9 \frac{D^{1/2} t^{1/6}}{m^{1/3}} [1 + \alpha c(\varphi)] + \right. \right. \\ \left. \left. + \alpha \left\{ 0.182 [c_0 - c(\varphi)] + \frac{1}{2} c(\varphi) \right\} \right\} \right\} \quad (44)$$

$$|\alpha| c_0 \leq 0.3$$

Eqn (44) is the generalized Ilkovič equation which respects linear dependence of the diffusion coefficient on concentration of the depolarizer (the third term in double parenthesis and the correction  $\alpha c(\varphi)$  in the second term) and the spherical diffusion as well (the second term in this parenthesis). By integrating with respect to the variable  $t$ , we obtain the mean current  $\bar{I}$  from eqn (44)

$$\bar{I} = 0.627 n F D_h^{1/2} m^{2/3} t_1^{1/6} [c_0 - c(\varphi)] \left\{ \left\{ 1 + 3.4 \frac{D^{1/2} t_1^{1/6}}{m^{1/3}} [1 + \alpha c(\varphi)] + \right. \right. \\ \left. \left. + \alpha \left\{ 0.182 [c_0 - c(\varphi)] + \frac{1}{2} c(\varphi) \right\} \right\} \right\} \quad (45)$$

$$|\alpha| c_0 \leq 0.3$$

where  $t_1$  is the drop time.

We shall summarize the approximations used for the deduction of the generalized Ilkovič equation. Approximation (23) corresponding to the correction for spherical diffusion has been discussed in [3] and we shall, therefore, dismiss it. From the view-point of the correction respecting the concentration dependence  $D(c)$  we have used approximation (16) which means that this correction does not take into account the influence of the curvature of diffusion layer which itself is a correction of littleness of the first order as well as approximation (24) which is justifiable solely on the assumption that  $|c_k| \ll c_1$ . Finally, we have approximated the function  $\text{erf } z$  by means of eqn (37). This approximation manifests itself in the value of integral  $I_1$  (see (34)) which is changed by 15%. The calculations were performed by computing integral (32) on a computer for particular values of  $\tau$ . Hence, it holds  $I_1 = 0.636 \tau^{-1}$  instead of  $I_1(\text{approx}) = 0.744 \tau^{-1}$ . This refinement was taken into consideration already in the value of the constant 0.182 in eqns (44) and (45).

It is useful to outline a procedure useable for higher values  $|\alpha| c_0$  which enables us to appreciate the accuracy of the deduced first approximation as regards experimental errors for these values. In these cases, a numerical solution of eqn (27) would be performed on a computer for particular values of  $\alpha$ ,  $c_0$  and zero conditions (22). Then it should be put  $c_1 + c_{k2}$  instead of the solution  $c_1$  in eqn (27). Provided a more accurate analysis would be necessary, a numerical solution of eqn (13) involving substitutions (19) should be performed. After further calculations



the results of these solutions may be compared with the values calculated from eqn (44) or eqn (45).

### Discussion

In the generalized Ilkovič equation the heterodiffusion coefficient  $D_h$  appears. From the results of measurements obtained with different values  $c_0$ , this equation enables us also to determine the coefficient  $\alpha$  and thus the real coefficient of diffusion according to eqn (3).

The comparison of eqn (45) with the original corrected Ilkovič equation shows that it is the "apparent" coefficient of diffusion  $\bar{D}$  which results from this equation. For the limiting current it holds  $c(\varphi) = 0$  and the following relationship between apparent diffusion coefficient and heterodiffusion coefficient is valid

$$\bar{D}^{1/2} \left( 1 + 3.4 \frac{t_1^{1/6}}{m^{1/3}} \bar{D}^{1/2} \right) = D_h^{1/2} \left( 1 + 3.4 \frac{t_1^{1/6}}{m^{1/3}} D_h^{1/2} + 0.182 \alpha c_0 \right) \quad (46)$$

or

$$\bar{D} \left( 1 + 6.8 \frac{t_1^{1/6}}{m^{1/3}} \bar{D}^{1/2} \right) \approx D_h \left( 1 + 6.8 \frac{t_1^{1/6}}{m^{1/3}} D_h^{1/2} + 0.364 \alpha c_0 \right) \quad (47)$$

The magnitude of the term which in the generalized Ilkovič equation represents the influence of concentration dependence of the diffusion coefficient mainly depends on character of the depolarizer with respect to properties of the indifferent electrolyte, *i.e.* on the value of  $\alpha$  and concentration  $c_0$  used. It should be emphasized that the value of the heterodiffusion coefficient  $D_h$  as well as the value of  $\alpha$  is really dependent on concentration of the indifferent electrolyte  $c_{in}$ . Therefore the values of  $\alpha$  and  $D_h$  necessitate a statement for which concentration  $c_{in}$  they have been determined.

Provided the maximum value of  $|\alpha| c_0$  equals 0.35 in a concrete case, the value of limiting current changes according to eqn (45) by 6.4% while the value of the apparent coefficient of diffusion changes according to eqn (47) by about 13%. However, it ensues from eqn (3) that the real coefficient of diffusion at concentration  $c_0$ , *i.e.*  $D(c_0)$  must differ from the heterodiffusion coefficient already by 35% in this case. For higher values of  $|\alpha| c_0$  it is convenient to check the correction by numerical integration of eqn (27) as stated in the foregoing passage.

In case the correction for spherical diffusion may be neglected, the relationship between  $\bar{D}$  and  $\alpha$ ,  $D_h$  may be written in the form which is equal for other electrochemical methods and their generalized equations

$$\bar{D} \approx D_h (1 + \text{const } \alpha c_0) \quad (48)$$

The values of the constant in eqn (48) valid in the presence of indifferent electrolyte are given in Table 1.

Table 1

Values of the constant in generalized equations of electrochemical methods

Generalized equation	Constant	Ref.
Cottrell	0.36	[5]
Sand	0.40	[6]
Levich	0.53 $\alpha > 0$	[7]
	0.62 $\alpha < 0$	
Ilkovič	0.36	

Assuming the diffusion coefficients and valency of positive and negative ions are equal [8], the value  $\text{const} = 0.57$  results from the generalized Levich equation for binary electrolytes. This value is the mean of the values quoted in Table 1 for the Levich equation.

The consequences resulting from the generalized Ilkovič equation will be discussed from the view-point of experimental practice in the subsequent paper [9].

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