

# **Theory of the rotating disc method in binary electrolytes at concentration dependent coefficients of diffusion and concentration dependent viscosity**

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A generalized RDE theory is presented based on the assumption that the dependence of diffusion coefficients and viscosity on concentration is linear. On the basis of the general transport equations of ions, the boundary conditions of these equations have been determined and simplified transport equations have been derived. By integrating the equations, the distribution of the concentration of ions has been calculated, which makes possible to estimate the values of limiting currents. From the electric field distribution and ion concentration, the potential and voltametric characteristics of the method may be derived. In this paper, the limiting current densities of binary electrolytes are compared with the limiting currents in the solutions containing indifferent electrolyte. Furthermore, some possible applications of the theory to the determination of concentration dependence of the diffusion coefficients of cations and anions from the ratio of current densities at different concentrations, the change in ohmic resistance of electrolyte, and the change in limiting currents due to varying concentration are presented. The theory is illustrated by numerical calculations.

В работе предложена обобщенная теория РДЭ в предположении линейной зависимости коэффициентов диффузии и вязкости от концентрации. Исходится из общих уравнений транспорта ионов, определяются граничные условия этих уравнений и выводятся упрощенные транспортные уравнения. Интегрированием уравнений вычисляется распределение концентраций ионов и отсюда определяется значение предельных токов. Из распределения электрического поля и концентраций ионов получится потенциал и вольтамметрические характеристики метода. В работе проводится сравнение предельных плотностей тока в случае двойных электролитов с предельными токами и растворов, содержащих индифферентный электролит. Далее приводятся возможные применения теории при определении концентрационных зависимостей коэффициентов диффузии катионов и анионов из отношения плотностей тока при разных концентрациях, изменения омического сопротивления электролита и предельных токов при изменении концентрации. Теория иллюстрируется цифровыми расчетами.

The theory of the rotating disc method for dissolving disc electrode and electrochemical variants of the method in solutions with indifferent electrolyte and in binary electrolytes was developed by *Levich* [1]. A full survey of the applications of this method in electrochemistry has been given in [2]. The Levich theory is based on the assumption that the diffusion coefficient is independent of concentration. In [3], this theory is generalized for ionic melts and solutions with indifferent electrolyte supposing that the diffusion coefficient and viscosity depend on concentration linearly and the Einstein—Stokes relationship between diffusion coefficient and viscosity is taken into account. The presence of indifferent electrolyte allowed to neglect the magnitude of migration current with respect to diffusion current.

In this paper, a generalized theory of the rotating disc method (RDE) is presented for the fundamental case, *i.e.* binary electrolytes. A linear dependence of the diffusion coefficients of cations and anions and of viscosity on the concentration of ions is assumed again. Since, in this case, the migration flow due to the electric field in electrolyte must not be neglected with respect to the diffusion and convection flow, the solution of this problem is much more complicated.

#### *Flow in a binary electrolyte and derivation of the transport equations for $D = D(c)$*

Let us consider the ions of both kinds (positive and negative) in a binary electrolyte. The transport of ions will take place owing to convection, diffusion of the ions to electrode, and migration in the electric field. Hence, it holds for the total flow  $\mathbf{j}_i$  of the ions of the  $i$ -th kind [1]

$$\mathbf{j}_i = c_i \mathbf{v} - D_i \text{grad } c_i + \frac{D_i z_i \mathbf{E} F}{RT} c_i \quad (1)$$

where  $c_i$ ,  $z_i$ ,  $D_i$ ,  $\mathbf{E}$ ,  $F$ ,  $R$ ,  $T$ , and  $\mathbf{v}$  are concentration of the ions of the  $i$ -th kind, valence of these ions, diffusion coefficient, intensity of electric field, Faraday charge, universal gas constant, temperature, and velocity of the motion of electrolyte, respectively. If we consider the law of mass conservation, the time change of the concentration will be described by the equation

$$\frac{\partial c_i}{\partial t} = -\text{div } \mathbf{j}_i \quad (2)$$

Supposing the electroneutrality of solution, the following relation will be fulfilled in a binary electrolyte

$$z_1 c_1 - z_2 c_2 = 0 \quad (3)$$

Instead of the concentrations  $c_1$  and  $c_2$ , the normal concentration  $c$  may be introduced

$$c = \frac{c_1}{z_2} = \frac{c_2}{z_1} \quad (4)$$

By inserting from eqns (4) and (1) into eqn (2), we obtain the initial system of equations

$$\frac{\partial c}{\partial t} + \mathbf{v} \text{ grad } c = \text{div} (D_1 \text{ grad } c) + \frac{z_1 F}{RT} \text{div} (c D_1 \mathbf{E}) \quad (5)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \text{ grad } c = \text{div} (D_2 \text{ grad } c) - \frac{z_2 F}{RT} \text{div} (c D_2 \mathbf{E}) \quad (6)$$

where the signs in front of the last terms on the right side of eqns (5) and (6) have been chosen in such a way that  $F$  represents the absolute value of the charge.

First of all, we subtract eqn (6) from eqn (5)

$$\text{div} (D_1 \text{ grad } c) - \text{div} (D_2 \text{ grad } c) + \frac{F}{RT} [z_1 \text{div} (c D_1 \mathbf{E}) + z_2 \text{div} (c D_2 \mathbf{E})] = 0 \quad (7)$$

and subsequently we shall integrate eqn (7). On integration, it may be written

$$(D_1 - D_2) \text{ grad } c + \frac{F}{RT} (z_1 D_1 + z_2 D_2) c \mathbf{E} = \mathbf{P} \quad (8)$$

where  $\mathbf{P}$  is a vector which should be determined by further calculations and for which it holds  $\text{div} \mathbf{P} = 0$ .

Now, we are going to pay attention to the calculation of the electric current density  $i_i$  which is evidently given by the expression

$$i_i = F z_i j_i \quad (9)$$

where the value of  $j_i$  may be calculated from eqn (1). Thus, it holds

$$i_1 = D_1 F z_1 \text{ grad } c_1 + \frac{D_1 F^2 z_1^2}{RT} c_1 \mathbf{E} + F z_1 c_1 \mathbf{v} \quad (10)$$

$$i_2 = -D_2 F z_2 \text{ grad } c_2 + \frac{D_2 F^2 z_2^2}{RT} c_2 \mathbf{E} - F z_2 c_2 \mathbf{v} \quad (11)$$

The choice of signs is determined by defining the positive orientation of the current vector from the negative electrode and by respecting the signs of charges [1]. The vector of the total current density  $i$  is given by the sum of the current densities of positive and negative ions and will be expressed by the equation

$$i = i_1 + i_2 = \left[ (D_1 - D_2) \text{ grad } c + \frac{F}{RT} (z_1 D_1 + z_2 D_2) c \mathbf{E} \right] F z_1 z_2 \quad (12)$$

For the solution of eqn (12) we used eqns (10), (11), and (4). If we compare eqn (12) to eqn (8), we obtain for the vector  $\mathbf{P}$

$$\mathbf{P} = \frac{\mathbf{i}}{F z_1 z_2} \quad (13)$$

By using eqns (8) and (13), the distribution of the electric field intensity in solution may be determined

$$\mathbf{E} = \frac{RT}{F^2(z_1 D_1 + z_2 D_2) z_1 z_2 c} \mathbf{i} - \frac{(D_1 - D_2) RT}{F(z_1 D_1 + z_2 D_2) c} \text{grad } c \quad (14)$$

If we substitute in eqn (14)

$$A = \frac{RT}{F^2(z_1 D_1 + z_2 D_2) z_1 z_2}; \quad G = \frac{(D_1 - D_2) RT}{F(z_1 D_1 + z_2 D_2)} \quad (15)$$

it may be written

$$\mathbf{E} = A \frac{\mathbf{i}}{c} - G \frac{\text{grad } c}{c} \quad (16)$$

For the solution of eqns (5) and (6), the value of  $\text{div}(c D_i \mathbf{E})$  is to be determined. The divergence of the product of scalar  $f$  and vector  $\mathbf{b}$  obeys the following expression

$$\text{div}(f \mathbf{b}) = f \text{div } \mathbf{b} + \mathbf{b} \text{ grad } f \quad (17)$$

By the use of eqns (17) and (16), we obtain

$$\text{div}(c D_i \mathbf{E}) = \mathbf{i} \text{ grad}(A D_i) - G D_i \Delta c - \text{grad } c \text{ grad}(G D_i) \quad (18)$$

When deriving eqn (18), we must realize that  $\text{div } \mathbf{i} = 0$  (see eqn (13) and the text following eqn (8)).

If we insert from expression (18) into eqns (5) and (6), we obtain

$$\begin{aligned} \frac{\partial c}{\partial t} + \mathbf{v} \text{ grad } c = D_1 \Delta c + \text{grad } D_1 \text{ grad } c + \frac{z_1 F}{RT} [\mathbf{i} \text{ grad}(A D_1) + \\ - G D_1 \Delta c - \text{grad } c \text{ grad}(G D_1)] \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{\partial c}{\partial t} + \mathbf{v} \text{ grad } c = D_2 \Delta c + \text{grad } D_2 \text{ grad } c - \frac{z_2 F}{RT} [\mathbf{i} \text{ grad}(A D_2) + \\ - G D_2 \Delta c - \text{grad } c \text{ grad}(G D_2)] \end{aligned} \quad (20)$$

Eqns (19) and (20) are the starting transport equations which give the dependence of normal concentration on time and coordinates, and involve the diffusion of ions, the convection, and the migration of ions due to the electric field

in solution. The last component, as we shall see later, will be also respected in boundary conditions. It is obvious that eqns (19) and (20) enable us to study the concentration dependence of the coefficients of diffusion  $D_1 = D_1(c_1)$  and  $D_2 = D_2(c_2)$ . Moreover, we must take into consideration that the right sides of eqns (19) and (20) are equal and eqns (19) and (20) are, therefore, identical. The equality of the right sides is given by the condition (7) which yields expression (14) for the electric field intensity  $E$  in solution.

### *Simplification of the transport equations*

A substantial simplification of the transport equations may be achieved for stationary conditions which come into consideration in voltametry with RDE, *i.e.* at  $\partial c/\partial t = 0$ . Furthermore, we shall assume a linear dependence of diffusion coefficients on concentration, which is an approximation satisfactory in a great number of experimental cases. The concentration involved in the coefficients of diffusion may be approximately expressed by means of a known convenient function  $c_1$ . Thus, with respect to eqn (4), it may be written

$$D_1(c_1) = D_{1h} (1 + \alpha_1 z_2 c) \approx D_{1h} (1 + \alpha_1 z_2 c_1) \quad (21)$$

$$D_2(c_2) = D_{2h} (1 + \alpha_2 z_1 c) \approx D_{2h} (1 + \alpha_2 z_1 c_1) \quad (22)$$

where  $D_{1h}$  and  $D_{2h}$  are the heterodiffusion coefficients of positive and negative ions,  $\alpha_1$  and  $\alpha_2$  are coefficients characterizing the concentration dependence of diffusion coefficients, and  $c_1$  is a function characterizing the distribution of ion concentration provided the diffusion coefficients are independent of concentration, *i.e.*  $D_1(c_1) = D_{1h}$  and  $D_2(c_2) = D_{2h}$ . It will appear later that the function  $c_1$  must satisfy eqn (36).

In relationships (21) and (22) the linear dependence of diffusion coefficients on concentration has been approximately expressed by means of the concentration  $c_1$ . Let us consider this approximation more minutely. The solution of eqns (19) and (20) may be expressed in the form of the following expansion

$$c \approx c_1 + (a_{11} \alpha_1 + a_{12} \alpha_2) c_{II} + (a_{21} \alpha_1^2 + a_{22} \alpha_1 \alpha_2 + a_{23} \alpha_2^2) c_{III} + \quad (23)$$

where  $a_{ij}$  are constants.

By substituting from eqn (23) into eqns (21) and (22), we can state that we have neglected the terms  $\alpha_i^n$ ,  $\alpha_i^m \alpha_j^p$  ( $n \geq 2$ ,  $m \geq 1$ ,  $p \geq 1$ ) in the approximate expression of diffusion coefficients, *i.e.* the terms of the littleness of the second and higher orders. In an approximate solution of this problem we are entitled to do that simplification provided it holds

$$|\alpha_i| c_0 \ll 1, \quad i = 1, 2 \quad (24)$$

where  $c_0$  is the concentration of electrolyte in such a distance from rotating electrode which is much larger than the thickness of diffusion layer.

By using eqns (21), (22), and (15), the functions  $A D_i$ ,  $G D_i$ ,  $D_i(1 - z_i F G / RT)$ ,  $i = 1, 2$ , in transport eqns (19) and (20) may be expressed as follows

$$\frac{z_1 F}{RT} A D_1 \approx \frac{1}{F z_2 (z_1 + z_2)} \frac{D_{\text{eff}}}{D_{2h}} \left[ 1 + \frac{D_{\text{eff}}}{D_{1h}} \frac{z_2}{z_1 + z_2} (\alpha_1 z_2 + \alpha_2 z_1) c_1 \right] = Q_{11} (1 + \alpha_1 q_{11} c_1) \quad (25)$$

$$\frac{z_2 F}{RT} A D_2 \approx \frac{1}{F z_1 (z_1 + z_2)} \frac{D_{\text{eff}}}{D_{1h}} \left[ 1 - \frac{D_{\text{eff}}}{D_{2h}} \frac{z_1}{z_1 + z_2} (\alpha_1 z_2 - \alpha_2 z_1) c_1 \right] = Q_{12} (1 - \alpha_2 q_{12} c_1) \quad (26)$$

$$\frac{z_1 F}{RT} G D_1 \approx \frac{z_1}{z_1 + z_2} \frac{D_{1h} - D_{2h}}{D_{2h}} D_{\text{eff}} \left\{ 1 + \left[ \frac{D_{\text{eff}}}{D_{1h} - D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) + \alpha_1 z_2 \right] c_1 \right\} = Q_{21} (1 + \alpha_1 q_{21} c_1) \quad (27)$$

$$\frac{z_2 F}{RT} G D_2 \approx \frac{z_2}{z_1 + z_2} \frac{D_{1h} - D_{2h}}{D_{1h}} D_{\text{eff}} \left\{ 1 + \left[ \frac{D_{\text{eff}}}{D_{1h} - D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) + \alpha_2 z_1 \right] c_1 \right\} = Q_{22} (1 + \alpha_2 q_{22} c_1) \quad (28)$$

$$D_1 \left( 1 - \frac{z_1 F}{RT} G \right) \approx D_{\text{eff}} \left\{ 1 + \left[ \alpha_1 z_2 - \frac{z_1}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) \right] c_1 \right\} = D_{\text{eff}} (1 + \alpha_1 q_{31} c_1) \quad (29)$$

$$D_2 \left( 1 + \frac{z_2 F}{RT} G \right) \approx D_{\text{eff}} \left\{ 1 + \left[ \alpha_2 z_1 + \frac{z_2}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{1h}} (\alpha_1 z_2 - \alpha_2 z_1) \right] c_1 \right\} = D_{\text{eff}} (1 + \alpha_2 q_{32} c_1) \quad (30)$$

$$D_{\text{eff}} = \frac{D_{1h} D_{2h} (z_1 + z_2)}{z_1 D_{1h} + z_2 D_{2h}} \quad (31)$$

In eqns (25—30) we omitted the terms of littleness of the second and higher orders again, in particular, we used the approximation

$$\frac{1}{1 + \text{const } \alpha_1 c_1} \approx 1 - \text{const } \alpha_1 c_1 \quad (32)$$

Let us insert from eqns (25—30) into eqns (19) and (20). However, we express the function  $\text{grad}(D_i A)$  by means of the concentration  $c$  and not by means of the first approximation  $c_1$  (see relationships (21) and (22)), which simplifies integration of the equations, as it will be demonstrated later

$$\begin{aligned} \mathbf{v} \text{ grad } c \approx & D_{\text{eff}} \Delta c + \alpha_1 \{q_{31} D_{\text{eff}} c_1 \Delta c + \text{grad } c [i q_{11} Q_{11} + \\ & + (z_2 D_{1h} - Q_{21} q_{21}) \text{grad } c_i]\} \end{aligned} \quad (33)$$

$$\begin{aligned} \mathbf{v} \text{ grad } c \approx & D_{\text{eff}} \Delta c + \alpha_2 \{q_{32} D_{\text{eff}} c_1 \Delta c + \text{grad } c [i q_{12} Q_{12} + \\ & + (z_1 D_{2h} + Q_{22} q_{22}) \text{grad } c_i]\} \end{aligned} \quad (34)$$

By direct substitution of the expressions  $\alpha_i$ ,  $Q_{ij}$ , and  $q_{ij}$  from eqns (25—31) into the right sides of eqns (33) and (34), it may be demonstrated that the right sides of these simplified transport equations are equal and thus transport eqns (33) and (34) are identical again. Hence, eqns (33) and (34) may be written in the form

$$\mathbf{v} \text{ grad } c \approx D_{\text{eff}} \Delta c + D_{\text{eff}} X_1 c_1 \Delta c + \text{grad } c (X_2 + X_3 \text{grad } c_i) \quad (35)$$

where the quantities  $X_1$ ,  $X_2$ , and  $X_3$  may be obtained by comparing eqn (35) with eqn (34) or (33). Therefore eqn (35) is a simplified transport equation which describes the stationary case of diffusion, convection, and migration of ions in a binary electrolyte provided the diffusion coefficients are linear functions of concentration. The terms of littleness of the second and higher orders have been omitted in the derivation. If the diffusion coefficients are independent of concentration, *i.e.*  $\alpha_1 = \alpha_2 = 0$ , eqn (35) turns into the known equation of convective diffusion for binary electrolytes [1]

$$\mathbf{v} \text{ grad } c_1 = D_{\text{eff}} \Delta c_1 \quad (36)$$

where  $D_{\text{eff}}$  is given again by eqn (31).

### *Derivation of generalized boundary conditions*

For the determination of boundary conditions, we shall assume that, for instance, the cathode is a rotating disc, whereas the anode possesses the form of a planar electrode and is in the distance  $l$  from the cathode. We shall introduce a coordinate axis  $y$  passing through the axis of the rotating disc with the origin on its surface and directed from the disc to the planar electrode (anode). The boundary conditions valid for RDE can be derived from the following reasoning: At the anode, *i.e.* for  $y = l$ , the normal concentration must be equal to

$$c(y = l) = c_0 \quad (37)$$

On the surface of the disc electrode (cathode) the ions of the first kind are discharged while the ions of the second kind are not discharged and, for this reason, the electric current density which is transferred by these ions must equal zero at the rotating electrode [1]

$$i_{zn}(y=0) = -D_2 F z_2 \left. \frac{\partial c_2}{\partial n} \right|_{y=0} + \frac{D_2 F^2 z_2^2}{RT} c_2(y=0) E_n(y=0) = 0 \quad (38)$$

Eqn (38) may be derived from eqn (11) if we realize that the normal component  $v_n$  of the motion of liquid equals zero at the surface of the disc electrode. The index "n" denotes the normal components in eqn (38).

In order to calculate the boundary conditions for solving transport eqn (35) from condition (38) we must, first of all, express the electric field intensity  $\mathbf{E}$ . Therefore, we insert from eqns (21) and (22) into eqn (14) and obtain

$$\mathbf{E} = \frac{RT}{F^2 z_1 z_2 z_1 D_{1h} + z_2 D_{2h}} \left( \frac{i}{c} - W_2 i \right) - \frac{RT}{F} \frac{D_{1h} - D_{2h}}{z_1 D_{1h} + z_2 D_{2h}} \left[ \frac{\text{grad } c}{c} + (W_1 - W_2) \text{grad } c \right] \quad (39)$$

where

$$W_1 = \frac{\alpha_1 z_2 D_{1h} - \alpha_2 z_1 D_{2h}}{D_{1h} - D_{2h}}; \quad W_2 = \frac{z_1 z_2 (\alpha_1 D_{1h} + \alpha_2 D_{2h})}{z_1 D_{1h} + z_2 D_{2h}} \quad (40)$$

It ensues from the theory of rotating disc method developed by *Levich* [1] that the concentration  $c$  is dependent only on the distance  $y$  from the surface of rotating electrode. In this case, we may express the solution of transport eqn (35) in the form (see later)

$$c(y) = a_1(\alpha_i) J(y, \alpha_i) + a_2 \quad (41)$$

where  $a_1$  and  $a_2$  are constants,  $J(y, \alpha_i)$  is the investigated function, and the parameter  $\alpha_i$  reflects the dependence of the diffusion coefficients on concentration. If we substitute from eqns (39) and (41) into condition (38), we obtain

$$a_1(\alpha_i) \left. \frac{dJ(y, \alpha_i)}{dy} \right|_{y=0} = \frac{i}{F z_1 (z_1 + z_2) D_{1h}} [1 - \alpha_1 z_2 c(y=0)] \approx \frac{i}{F z_1 (z_1 + z_2) D_{1h}} [1 - \alpha_1 z_2 c_1(y=0)] \quad (42)$$

where  $c_1(y)$  is the known solution of equation of diffusion (36) valid for concentration independent diffusion coefficients. The approximation in eqn (42), i.e. the substitution of the known function value  $c_1(y=0)$  for  $c(y=0)$  represents neglecting the terms of littleness of the second and higher orders (23).

If it holds  $J(y \rightarrow l, \alpha_i) \rightarrow 0$  (see later), eqns (41) and (37) give



$$a_2 = c_0 \quad (43)$$

From boundary conditions (37) and (38) which are valid for the electrochemical problem solved, we obtain generalized boundary conditions (42) and (43) or (37) for transport eqn (35). The solution of this transport equation, as we shall demonstrate later, may be written in the form of eqn (41).

*Survey of the resulting relationships of RDE for concentration independent diffusion coefficients*

The solution of transport eqn (35) with boundary conditions (37) and (42) enables us to respect the linear dependence of diffusion coefficients on concentration. In order to carry out this solution, we must take into consideration and apply the results derived by *Levich* for concentration independent diffusion coefficients [1]. In this part, we give a survey of these relationships with respect to their application in our calculations. The concentration independence of diffusion coefficients in the mentioned relationships is denoted by the symbol  $\alpha_i = 0$ .

According to [1], the solution of the equation of diffusion (36) is as follows

$$c(y, \alpha_i = 0) = c_1(y) = a_1(\alpha_i = 0) \int_l^y \exp \left[ \frac{1}{D_{\text{eff}}} \int_0^{y'} v(y'') dy'' \right] dy' + a_2 \quad (44)$$

For the velocity of liquid flow  $v$  in the direction  $y$ , it holds

$$v(y) \approx -A_0 y^2; \quad A_0 = 0.51 \sqrt{\frac{\omega^3}{\nu_0}}; \quad y \leq \delta \ll \delta_0 \quad (45)$$

where  $\omega$  is the angular velocity of rotating disc,  $\nu_0$  is the kinematic viscosity of solution,  $\delta$  is the diffusion boundary layer, and  $\delta_0$  stands for the hydrodynamic boundary layer (the Prandtl layer) the magnitude of which is

$$\delta_0 = 3.6 \sqrt{\frac{\nu_0}{\omega}} \quad (46)$$

If we insert the velocity  $v(y)$  from eqn (45) into solution (44), we obtain

$$c_1(y) = c_0 \frac{a_1(\alpha_i = 0)}{B} [J_1(B y \rightarrow \infty) - J_1(B y)] \quad (47)$$

where

$$J_1(B y) = \int_0^{B y} e^{-u^3} du; \quad J_1(B y \rightarrow \infty) = 0.8934 \quad (48)$$

and

$$B = \frac{2}{\delta_0} \left( \frac{v_0}{D_{\text{eff}}} \right)^{1/3} = 0.555 \frac{\sqrt{\omega}}{D_{\text{eff}}^{1/3} v_0^{1/6}} \quad (49)$$

The value of  $D_{\text{eff}}$  is given by eqn (31) again. For the boundary diffusion layer  $\delta$  at concentration independent diffusion coefficients the following equation is valid

$$\delta(\alpha_i = 0) = \frac{J_1(B \ y \rightarrow \infty)}{B} = 1.61 \frac{D_{\text{eff}}^{1/3} v_0^{1/6}}{\sqrt{\omega}} \quad (50)$$

Then, the value of concentration at the surface of disc is

$$c_1(y = 0) = c_0 - a_1(\alpha_i = 0) \delta(\alpha_i = 0) \quad (51)$$

The coefficient  $a_1(\alpha_i = 0)$  is to be calculated from boundary condition (38) for  $\alpha_i = 0$

$$a_1(\alpha_i = 0) = \frac{i(\alpha_i = 0)}{z_1 F D_{1h}(z_1 + z_2)} \quad (52)$$

If we insert from eqns (50) and (51) into solution (47), we can write

$$c_1(y) = \frac{a_1(\alpha_i = 0)}{B} J_1(B \ y) + c_1(y = 0) \quad (53)$$

or

$$c_1(y) = [c_0 - c_1(y = 0)] \frac{J_1(B \ y)}{J_1(B \ y \rightarrow \infty)} + c_1(y = 0) \quad (54)$$

In further calculation, *Levich* [1] derived a relationship between the voltage  $V$  applied to electrodes and passing current density  $i(\alpha_i = 0)$ . He calculated the potential  $\varphi$  by integrating the distribution of the electric field intensity  $\mathbf{E}$  given by eqn (39) for  $\alpha_i = 0$ .

Then, the current density  $i(\alpha_i = 0)$  at concentration independent diffusion coefficients is described by the equation

$$\frac{i(\alpha_i = 0)}{i_L(\alpha_i = 0)} = \frac{a_1(\alpha_i = 0) \delta(\alpha_i = 0)}{c_0} = 1 - \frac{c_1(y = 0)}{c_0} \quad (55)$$

Furthermore, the subsequent relation between current density  $i(\alpha_i = 0)$  and the voltage  $V$  applied to the cathode has been derived

$$i(\alpha_i = 0) = i_L(\alpha_i = 0) \left[ 1 - e^{-\frac{F}{RT} \frac{z_1 z_2}{z_1 + z_2} (V - \Delta\varphi_{\text{ohm}}(\alpha_i = 0))} \right] \quad (56)$$

where  $i_L(\alpha_i = 0)$  is the limiting current density and  $\Delta\varphi_{\text{ohm}}(\alpha_i = 0)$  is the potential drop due to the ohmic resistance of solution. For our conditions, the rotating disc

was cathode. Therefore, we may write  $V < 0$ ,  $\Delta\varphi_{\text{ohm}} < 0$ . Thus, it holds for the limiting current density

$$i_L(\alpha_i = 0) = \frac{F z_1 (Z_1 + z_2) D_{11} c_0}{\delta(\alpha_i = 0)} = F z_1 D_{1h} \left(1 + \frac{z_1}{z_2}\right) \frac{c_1^{(0)} \sqrt{\omega}}{1.61 D_{\text{eff}}^{1/3} \nu_0^{1/6}} \quad (57)$$

$$c_1^{(0)} = z_2 c_0 \quad (\text{see eqn (4)}).$$

We shall use eqns (44—57) for the solution of our generalized problem.

*Integration of the transport equation at  $D = D(c)$  and  $v = v(c)$*

In the RDE method, the concentration  $c$  is solely a function of the coordinate  $y$ . In this sense, we may transcribe transport eqn (35)

$$v(y) \frac{dc(y)}{dy} = D_{\text{eff}} \frac{d^2c(y)}{dy^2} + D_{\text{eff}} X_1 c_1(y) \frac{d^2c(y)}{dy^2} + \left[ X_2 + X_3 \frac{dc_1(y)}{dy} \right] \frac{dc(y)}{dy} \quad (58)$$

where

$$\begin{aligned} X_1 &= \alpha_1 q_{31} = \alpha_2 q_{32}; & X_2 &= i \alpha_1 q_{11} & Q_{11} &= i \alpha_i q_{12} & Q_{12}; \\ X_3 &= \alpha_1 z_2 D_{1h} - \alpha_1 Q_{21} q_{21} = \alpha_2 z_1 D_{2h} + \alpha_2 Q_{22} q_{22} \end{aligned} \quad (59)$$

while the values of  $q_{ij}$  and  $Q_{ij}$  are given by eqns (25—30) and  $c_1(y)$  is defined by eqn (54). The equalities in relationships (59) may be tested by direct substitution.

We introduce the following common substitution into eqn (58)

$$f(y) = \frac{dc(y)}{dy}; \quad f'(y) = \frac{d^2c(y)}{dy^2} \quad (60)$$

On transcribing and rearranging, we obtain

$$\begin{aligned} \frac{f'(y)}{f(y)} &= \frac{v(y) - \left[ X_2 + X_3 \frac{dc_1(y)}{dy} \right]}{D_{\text{eff}} [1 + X_1 c_1(y)]} \approx \frac{1}{D_{\text{eff}}} \left\{ v(y) + \right. \\ &\quad \left. - \left[ X_2 + X_3 \frac{dc_1(y)}{dy} \right] \right\} [1 - X_1 c_1(y)] \end{aligned} \quad (61)$$

We substitute from expression (45) which involves the kinematic viscosity for the velocity  $v(y)$  into eqn (61). As the kinematic viscosity  $\nu$  is also a function of concentration, we may use the linear approximation again. Hence, it follows

$$v(c_i) = \nu_0(1 + \gamma c_i) = \nu_0(1 + \gamma z_2 c); \quad \gamma c_i \ll 1 \quad (62)$$

where  $\nu_0$  is the kinematic viscosity at  $c_0 \rightarrow 0$  and  $\gamma$  is a constant characterizing the linear dependence of kinematic viscosity on concentration. In eqn (62) we have used expression (4). Hence, eqn (45) gives the following relation for the velocity  $v(y)$

$$v(y) \approx -A_0 \left[ 1 - \frac{1}{2} \gamma z_2 c_1(y) \right] y^2 \quad (63)$$

Instead of the concentration  $c$ , we have inserted the function  $c_1$  into eqn (63) (see (54)), i.e. we neglected the terms of littleness of the second and higher orders. If we insert  $v(y)$  from eqn (63) into eqn (61), we obtain

$$\frac{f'(y)}{f(y)} = -\frac{1}{D_{\text{eff}}} \left[ A_0 y^2 - A_0 \left( X_1 + \frac{1}{2} \gamma z_2 \right) c_1(y) y^2 + X_2 + X_3 \frac{dc_1(y)}{dy} \right] \quad (64)$$

In rearranging eqn (64), we neglected the terms of littleness of the second and higher orders again. The integral of eqn (64) must be

$$\begin{aligned} f(y) &= \text{const}_1 \exp -\frac{1}{D_{\text{eff}}} \left\{ \frac{A_0}{3} y^3 - A_0 \left( X_1 + \frac{1}{2} \gamma z_2 \right) \cdot \right. \\ &\cdot \left. \int_0^y c_1(y') y'^2 dy' + X_2 y + X_3 [c_1(y) + c_1(y=0)] \right\} = \\ &= \text{const}_1 \exp -\left[ \frac{A_0}{3 D_{\text{eff}}} y^3 + \tilde{\varphi}(y) \right] \end{aligned} \quad (65)$$

where

$$\begin{aligned} \tilde{\varphi}(y) &= -\frac{A_0}{D_{\text{eff}}} \left( X_1 + \frac{1}{2} \gamma z_2 \right) \int_0^y c_1(y') y'^2 dy' + \frac{X_2}{D_{\text{eff}}} y + X_3 [c_1(y) + \\ &- c_1(y=0)] \end{aligned} \quad (66)$$

According to [2], we shall write the relationship for the integral in (66) by substituting from relation (54) for  $c_1(y)$

$$\begin{aligned} \int_0^y c_1(y') y'^2 dy' &= \frac{c_0 - c_1(y=0)}{J_1(B y \rightarrow \infty)} \int_0^y J_1(B y') y'^2 dy' + \\ &+ c_1(y=0) \frac{y^3}{3} = \frac{1}{3 B^3} \left\{ \frac{c_0 - c_1(y=0)}{J_1(B y \rightarrow \infty)} \cdot \right. \\ &\left. \left[ (B y)^3 J_1(B y) - \frac{1}{3} J_1(B y) + \frac{1}{3} (B y) e^{-(B y)^3} \right] + c_1(y=0) (B y)^3 \right\} \end{aligned} \quad (67)$$

where  $B$  is defined by expression (49). For further modifications, we must take into account that it holds (see eqns (49) and (45))

$$\frac{A_0}{3 D_{\text{eff}}} = B^3 \quad (68)$$

Respecting expressions (60), we shall integrate eqn (65). In the choice of the limits of integration, we shall respect the configuration described earlier and perform the integration analogously as in expression (44)

$$c(y) = \text{const}_1 \int_l^y \exp -[(B y')^3 + \tilde{\varphi}(y')] dy' + \text{const}_2 \quad (69)$$

The function  $\tilde{\varphi}(y)$ , when compared with  $(B y)^3$ , contains only the terms of littleness of the first order. In the function  $\tilde{\varphi}(y)$ , there are parameters  $\alpha_i$ ,  $D_i$ ,  $z_i$  and the constant  $\gamma$  relative to kinematic viscosity which may be found experimentally. For practice, it is of good use if the constants containing these parameters can be expressed explicitly and not only as coefficients in integrals. Therefore, we express the function under integral sign in eqn (69) by means of the first two terms of the Taylor series

$$c(y) \approx \text{const}_1 \left[ \int_l^y e^{-(B y')^3} dy' - \int_l^y e^{-(B y')^3} \tilde{\varphi}(y') dy' \right] + \text{const}_2 \quad (70)$$

Then we determine the values of  $\text{const}_1$  and  $\text{const}_2$  from boundary conditions (42) and (43). If we compare solution (69) or (70) with expression (41), we reveal the following relations

$$J(y=l, \alpha_i) = 0 \Rightarrow \text{const}_2 = c_0 \quad (71)$$

$$\left. \frac{dJ(y, \alpha_i)}{dy} \right|_{y=0} = 1 \Rightarrow \text{const}_1 = a_1(\alpha_i)$$

where the value of  $a_1(\alpha_i)$  is given by expression (42).

If we insert from expressions (71), (66), and (67) into eqn (70), we obtain the solution for  $c(y)$

$$\begin{aligned} c(y) \approx c_0 - a_1(\alpha_i) \frac{1}{B} \left\{ \int_{B y}^{B l} e^{-u^3} du - \left\{ \frac{X_2}{D_{\text{eff}} B} \int_{B y}^{B l} u e^{-u^3} du + \right. \right. \\ \left. \left. + \frac{X_3}{D_{\text{eff}}} \frac{c_0 - c_1(y=0)}{J_1(B y \rightarrow \infty)} \int_{B y}^{B l} J_1(u) e^{-u^3} du + \right. \right. \\ \left. \left. - \left( X_1 + \frac{1}{2} \gamma z_2 \right) \frac{c_0 - c_1(y=0)}{J_1(B y \rightarrow \infty)} \int_{B y}^{B l} \left[ u^3 J_1(u) - \frac{1}{3} J_1(u) + \right. \right. \\ \left. \left. + \frac{1}{3} u e^{-u^3} \right] e^{-u^3} du - \left( X_1 + \frac{1}{2} \gamma z_2 \right) c_1(y=0) \int_{B y}^{B l} u^3 e^{-u^3} du \right\} \quad (72) \end{aligned}$$

where  $u = B y$ ,  $J_1(B y \rightarrow \infty) = 0.8934$  (see eqn (48)) while  $c_1(y=0)$ ,  $a_1(\alpha_i)$ , and  $X_i$  ( $i = 1, 2, 3$ ) are given by expressions (51), (42), and (59), respectively.

Now, we shall calculate the concentration at the surface of rotating disc, *i.e.*  $c(y=0)$  which is of fundamental importance for the derivation of the final relationships provided by this method. As the thickness of the diffusion layer  $\delta$  is considerably smaller than the distance  $l$  between the surface of rotating disc and the planar electrode and the integrals in eqns (72) converge rapidly, we may write according to (50)  $B l = 0.893 l/\delta \rightarrow \infty$ . The values of integrals in solution (72) were found by means of a computer. Some of these integrals may be expressed by  $\Gamma$  function [1]

$$\begin{aligned} \int_0^{\infty} u e^{-u^3} du &= 0.4514; & \int_0^{\infty} J_1(u) e^{-u^3} du &= 0.3987; \\ \int_0^{\infty} u e^{-2u^3} du &= 0.2843; & \int_0^{\infty} u^3 J_1(u) e^{-u^3} du &= 0.2277; \\ \int_0^{\infty} u^3 e^{-u^3} du &= 0.2976; & J_1(\infty) = \int_0^{\infty} e^{-u^3} du &= 0.8934; \\ \int_0^{\infty} \left[ u^3 J_1(u) - \frac{1}{3} J_1(u) + \frac{1}{3} u e^{-u^3} \right] e^{-u^3} du &= 0.1896 \end{aligned} \quad (73)$$

On the basis of relations (72), (73), and (50), the concentration at the surface of rotating disc may be expressed by the equation

$$\begin{aligned} c(y=0, B l \rightarrow \infty) &\approx c_0 - a_1(\alpha_i) \delta(\alpha_i=0) \left\{ 1 - 0.5655 \frac{X_2 \delta(\alpha_i=0)}{D_{\text{eff}}} + \right. \\ &- \left[ 0.4995 \frac{X_3}{D_{\text{eff}}} - 0.2375 \left( X_1 + \frac{1}{2} \gamma z_2 \right) \right] [c_0 - c_1(y=0)] + \\ &\left. + 0.3331 \left( X_1 + \frac{1}{2} \gamma z_2 \right) c_1(y=0) \right\} \end{aligned} \quad (74)$$

where  $\delta(\alpha_i=0)$  is the thickness of diffusion layer for concentration independent diffusion coefficients (see (50)).

Hence, eqn (74) may be written in the form

$$c(y=0) = c_0 - a_1(\alpha_i) \delta(\alpha_i) \quad (75)$$

which is formally identical with eqn (51) valid for  $\alpha_i=0$ . According to eqns (74) and (75), the thickness of the diffusion layer  $\delta(\alpha_i)$  at concentration dependent diffusion coefficients obeys the following equation

$$\delta(\alpha_i) \approx \delta(\alpha_i=0) [1 - \xi(\alpha_i, z_i, D_{\text{th}}, \gamma)] \quad (76)$$

where the function  $(1 - \xi)$  is given by the expression in composite bracket on the right side of eqn (74).

Now, let us calculate the coefficients  $X_1$ ,  $X_2$ , and  $X_3$  in eqn (74). We shall use expressions (59) and (25—31) for this calculation. We obtain

$$X_1 = \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_1 + z_2} (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) \quad (77)$$

$$X_2 = \frac{i}{F} D_{1h} D_{2h} \frac{\alpha_1 z_2 - \alpha_2 z_1}{(z_1 D_{1h} + z_2 D_{2h})^2} \quad (78)$$

$$\frac{X_3}{D_{\text{eff}}} = \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{z_1 z_2}{z_1 + z_2} (\alpha_1 D_{1h} + \alpha_2 D_{2h}) \quad (79)$$

We substitute the current  $i(\alpha_i = 0)$  from expressions (56) and (57) into  $X_2$ . If the rotating electrode is a cathode, we obtain

$$\begin{aligned} \frac{X_2 \delta(\alpha_i = 0)}{D_{\text{eff}}} &= \frac{z_1}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) c_0 \\ &\left[ 1 - e^{-\frac{F}{RT} \frac{z_1 z_2}{z_1 + z_2} (V - \varphi_{\text{ohm}}(\alpha_i = 0))} \right] = \\ &= \frac{z_1}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) c_0 L(\alpha_i = 0) \end{aligned} \quad (80)$$

where  $L(\alpha_i = 0)$  stands for the expression in square bracket in eqn (80) and  $L(\alpha_i = 0) \rightarrow 1$  means that the passing current approaches the limiting current density  $i_L$ , i.e. the current remains practically constant with increasing voltage  $V$ . On the basis of expressions (74—80), the thickness of diffusion layer  $\delta(\alpha_i)$  at concentration dependent diffusion coefficients is expressed by the equation

$$\begin{aligned} \delta(\alpha_i) = \delta(\alpha_i = 0) &\left\{ \left\{ 1 - 0.5655 \frac{z_1}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) c_0 L(\alpha_i = 0) + \right. \right. \\ &- \left. \left\{ 0.4995 \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{z_1 z_2}{z_1 + z_2} (\alpha_1 D_{1h} + \alpha_2 D_{2h}) - \right. \right. \\ &- 0.2375 \left[ \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_1 + z_2} (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) + \frac{1}{2} \gamma z_2 \right] \left. \right\} [c_0 - c_1(y = 0)] + \\ &+ 0.3331 \left[ \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_1 + z_2} (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) + \frac{1}{2} \gamma z_2 \right] c_1(y = 0) \left. \right\} \end{aligned} \quad (81)$$

where  $\delta(\alpha_i = 0)$  is given by expression (50),  $L(\alpha_i = 0)$  may be determined by means of expression (80), and  $c_1(y = 0)$  is defined by expression (51).

*Calculation of the limiting current density for  $D = D(c)$  and  $\nu = \nu(c)$*

On the basis of the known thickness of the concentration dependent diffusion layer  $\delta(\alpha_i)$  given by expression (81) and the value of  $a_1(\alpha_i)$  given by expression (42) and by the use of expression (75), the limiting current density  $i_L$  may be immediately determined. For this purpose, the calculation of the potential in an arbitrary point of electrolyte is not inevitable, *i.e.* it is not necessary to carry out the integration of eqn (39) which defines the electric field intensity  $\mathbf{E}$  in solution at concentration dependent diffusion coefficients.

The value of limiting current density is proportional to the diffusion flow which corresponds to the maximum possible value of concentration slope. Thus, according to [1], the concentration of ions at the surface of rotating disc cathode equals zero for limiting current, *i.e.*  $c(y=0) = c_1(y=0) = 0$ . Hence, it ensues from eqn (75)

$$c_0 = a_1(\alpha_i, i_L) \delta[\alpha_i, c(y=0)=0] \quad (82)$$

If we insert from expression (42) into eqn (82), we may write for the limiting current  $i_L$

$$i_L = \frac{F z_1(z_1 + z_2) D_{1h} c_0}{\delta[\alpha_i, c(y=0)=0]} \quad (83)$$

or by substituting from expressions (81), (50), and  $L(\alpha_i=0) = 1$ , we obtain

$$\begin{aligned} i_L = F z_1 D_{1h} \left(1 + \frac{z_1}{z_2}\right) \frac{c_1^{(0)} \sqrt{\omega}}{1.61 D_{\text{eff}}^{1/3} \nu_0^{1/6}} \left\{ \left\{ 1 + \left\{ 0.5655 \frac{z_1}{z_2(z_1 + z_2)} \right. \right. \right. \\ \left. \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) + 0.4995 \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{z_1}{z_1 + z_2} (\alpha_1 D_{1h} + \alpha_2 D_{2h}) + \right. \\ \left. - 0.2375 \left[ \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_2(z_1 + z_2)} (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) + \right. \right. \\ \left. \left. + \frac{1}{2} \gamma \right] \right\} c_1^{(0)} \left. \right\} = i_L(\alpha_i=0) (1 + \varepsilon) \quad (84) \end{aligned}$$

$$c_1^{(0)} = z_2 c_0 \quad (\text{see eqn (4)}).$$

Thus, we derived the final relationship for the limiting current density  $i_L$  at concentration dependent diffusion coefficients, which is represented by the terms with the coefficients  $\alpha_1$  and  $\alpha_2$  while the concentration dependence of viscosity is represented by the coefficient  $\gamma$ . In the whole derivation, we used solely one approximation by omitting the terms of littleness of the second and higher orders, *i.e.*  $\alpha_i^2 c_0 \rightarrow 0$ ,  $\alpha_i \alpha_j c_0 \rightarrow 0$ ,  $\alpha_i \gamma c_0 \rightarrow 0$ , and the assumption of a linear dependence of diffusion coefficients and viscosity on concentration (see eqns (21), (22), and



(62)). The comparison with eqn (57) for  $i_L(\alpha_i = 0)$  derived by Levich shows that the effects of the above-mentioned concentration dependence are described by the terms in the composite bracket of eqn (84), *i.e.* by means of the function  $(1 + \varepsilon)$ . The results derived are valid, if the rotating disc is a cathode.

*Comparison of the limiting currents in binary electrolytes  
with the limiting currents in solutions containing indifferent electrolyte*

The migration current may be neglected with respect to the diffusion current for ionic melts and the solutions of electroactive substances with indifferent electrolyte [1]. For these cases, the influence of the linear concentration dependence of diffusion coefficient on the results obtained by the method of rotating disc was studied in [3]. In this study, the following relations have been derived for the limiting current density

$$i_L \approx F z D_h^{2/3} \frac{c_1^{(0)} \sqrt{\omega}}{1.61 \nu_0^{1/6}} (1 + 0.35 \alpha c_1^{(0)} + \dots) \quad \alpha > 0$$

$$i_L \approx F z D_h^{2/3} \frac{c_1^{(0)} \sqrt{\omega}}{1.61 \nu_0^{1/6}} (1 + 0.41 \alpha c_1^{(0)} + \dots) \quad \alpha < 0 \quad (85)$$

In [3], the Einstein—Stokes relationship between diffusion coefficient and viscosity was applied to the deduction of eqns (85)

$$D \approx \frac{\text{const}}{\nu} \quad \text{and} \quad D = D_h(1 + \alpha c_1)$$

from which it follows

$$\nu = \nu_0(1 - \alpha c_1) \quad (86)$$

If we compare expression (86) with expression (62), it must be  $\gamma = -\alpha$ .

Now, we shall pay attention to binary electrolytes and consider a special case when it holds

$$z_1 = z_2 = z; \quad D_{1h} = D_{2h} = D_h \Rightarrow D_{\text{eff}} = D_h;$$

$$\alpha_1 = \alpha_2 = \alpha; \quad c_1 = c_2 \quad (87)$$

We insert from expressions (87) as well as  $\gamma = -\alpha$  into eqn (84). On rearrangement, we may write for binary electrolytes

$$i_L = 2 F z D_h^{2/3} \frac{c_1^{(0)} \sqrt{\omega}}{1.61 \nu_0^{1/6}} (1 + 0.38 \alpha c_1^{(0)}) \quad (88)$$

If we compare the coefficients of the product  $\alpha c_1^{(0)}$  in expressions (88) and (85), we see that 0.38 is the arithmetic mean of the values 0.35 and 0.41. If we take into consideration the fact that the derivation of eqns (88) and (85) has been quite different, we must admit that these relationships are in a fairly good agreement. The coefficient 2 in eqn (88), therefore, characterizes the case of binary electrolytes for special conditions (87).

The comparison of eqns (88) and (85) leads to an important conclusion. The influence of the concentration dependence of diffusion coefficients on the value of limiting current density is equal for binary electrolytes and the solutions containing indifferent electrolyte provided the diffusion coefficients and charges of positive and negative ions of the binary electrolytes are equal, *i.e.* relationships (87) are valid.

#### *Dependence of current density on the voltage applied for $D = D(c)$ and $v = v(c)$*

Up to now, we have derived and discussed the generalized relationship for the limiting current density  $i_L$  in which the linear dependence of  $D_i$  and  $v$  on concentration is involved. However, the relationship between current density  $i$  and the voltage  $V$  applied to the cathode has not been analyzed thus far.

The potential  $\varphi$  in an arbitrary point of solution is to be obtained by integrating eqn (39),  $\mathbf{E} = -\text{grad } \varphi$ . If we integrate in the interval  $\langle l, 0 \rangle$ , we obtain — as we shall see later — the voltage drop  $\Delta\varphi$  due to the ohmic resistance of electrolyte. According to [1], it holds for the potential  $\varphi$  and the voltage  $V$  applied

$$-V = -\Delta\varphi + \eta; \quad \eta = \frac{RT}{F z_1} \ln \frac{c(y=0)}{c_0} \quad (89)$$

where  $\eta$  is the concentration overvoltage (polarization) at the electrode, *i.e.* electromotive force acting in the direction of increasing concentration. The minus signs in expression (89), *i.e.*  $-V$ ,  $-\Delta\varphi$ , mean that there is negative voltage on the cathode. If we integrate eqn (39) in which we insert the solution  $c(y)$  from eqn (41) and the expression  $a_2 = c_0$  (see eqn (43)) and subsequently use relations (89), we obtain

$$\begin{aligned} -V = & + \frac{RT i}{F^2 z_1 z_2 z_1 D_{1h} + z_2 D_{2h}} \left[ \int_l^0 \frac{dy'}{a_1(\alpha_i) J(y', \alpha_i) + c_0} + \right. \\ & \left. + W_2 l \right] - \frac{RT}{F} \frac{D_{1h} - D_{2h}}{z_1 D_{1h} + z_2 D_{2h}} \left\{ \ln \frac{c(y=0)}{c_0} + (W_1 - W_2)[c(y=0) - c_0] \right\} + \\ & + \frac{RT}{F z_1} \ln \frac{c(y=0)}{c_0} \quad (90) \end{aligned}$$

where  $W_1$  and  $W_2$  are given by expressions (40). The integral in eqn (90) can be determined by using the approximation proposed by *Levich* [1]. We may utilize the circumstance that the inside integral  $J(y, \alpha_i)$  rapidly converges in a distance from the surface of disc which is comparable with the thickness of the diffusion layer  $\delta$ . Thus, we integrate in two integration intervals

$$\begin{aligned} & \int_l^{\delta(\alpha_i)} \frac{dy'}{a_1(\alpha_i) J(y', \alpha_i) + c_0} \int_{\delta(\alpha_i)}^0 \frac{dy'}{a_1(\alpha_i) J(y', \alpha_i) + c_0} \approx \\ & \approx -\frac{l - \delta(\alpha_i)}{c_0} - \frac{\delta(\alpha_i)}{c_0 - a_1(\alpha_i) \delta(\alpha_i)} \approx -\frac{l}{c_0} + \\ & - \frac{\delta(\alpha_i)}{c_0 \left[ 1 - \frac{a_1(\alpha_i) \delta(\alpha_i)}{c_0} \right]} = -\frac{l}{c_0} - \frac{\delta(\alpha_i)}{c(y=0)} \end{aligned} \quad (91)$$

In the first integral, the value of  $J(y, \alpha_i)$  is practically equal to zero while the second integral signifies  $J(y \rightarrow 0, \alpha_i) \approx \delta(\alpha_i)$  (see relations (41), (74), and (75)).

If we insert the result from eqn (91) into eqn (90) and respect expression (75), we may write for  $W_1$  and  $W_2$  after rearranging and substituting from relations (40)

$$\begin{aligned} -V = & + \frac{D_{2h}(z_1 + z_2) RT}{F z_1(z_1 D_{1h} + z_2 D_{2h})} \left\{ \ln \frac{c(y=0)}{c_0} + \right. \\ & \left. + \frac{z_1}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) [c_0 - c(y=0)] \right\} + \\ & - \frac{RT l}{z_1 z_2 F^2 (z_1 D_{1h} + z_2 D_{2h}) c_0} (1 - W_2 c_0) i + \\ & - \frac{RT \delta(\alpha_i)}{z_1 z_2 F^2 (z_1 D_{1h} + z_2 D_{2h}) c(y=0)} i \end{aligned} \quad (92)$$

$$W_2 = \frac{z_1 z_2}{z_1 + z_2} \frac{D_{\text{eff}}}{D_{1h} D_{2h}} (\alpha_1 D_{1h} + \alpha_2 D_{2h}) \text{ — see expressions (40) and (31).}$$

The first term in eqn (92) stands for the voltage corresponding to concentration polarization, the second one corresponds to the voltage drop due to the ohmic resistance of electrolyte along the length  $l$  at constant concentration  $c_0$ , and the third one represents the voltage drop due to the ohmic resistance of electrolyte in the diffusion layer  $\delta$ , i.e. the voltage drop in solution for a concentration growing from the value  $c_0$  to the value  $c(y=0)$ .

Eqn (92) characterizes the dependence of the current density  $i$  flowing through solution on the voltage  $-V$  applied to the cathode and therefore, it is a general voltametric characteristic. Contrary to the relationship derived by *Levich* [1], eqn (92) respects the linear dependence of the diffusion coefficients of cations and

anions and of viscosity on concentration. Eqn (92) is too complicated for a common use because the current density  $i$  is also involved in the concentration  $c(y=0)$  (see eqns (75) and (42)) and it holds  $c(y=0)/c_0 = 1 - i/i_L$ .

We have already calculated the limiting current density  $i_L$ . On the basis of eqn (92), we shall calculate the relationship between  $i$  and  $V$  for low current densities  $i \ll i_L$ . First of all, we shall denote the voltage drop due to the ohmic resistance of electrolyte along the distance  $l$  by the symbol  $\Delta\varphi_{\text{ohm}}$  in eqn (92) (see the second term in eqn (92))

$$\Delta\varphi_{\text{ohm}}(\alpha_i) = w(\alpha_i) i = \frac{RT [1 - W_2 c_0] l}{F^2 z_1 z_2 (z_1 D_{1h} + z_2 D_{2h}) c_0} i \quad (93)$$

$$w(\alpha_i) = w(\alpha_i = 0)(1 - W_2 c_0)$$

where  $w(\alpha_i)$  is the concentration dependent ohmic resistance of electrolyte.

We shall perform further deduction on the assumption that

$$i \ll i_L \Rightarrow c(y=0) \approx c_0 \quad (94)$$

Thus, using eqn (75) we may write

$$\ln \frac{c(y=0)}{c_0} \approx - \frac{a_1(\alpha_i) \delta(\alpha_i)}{c_0} \Big|_{c(y=0) \approx c_0} \quad (95)$$

For the evaluation of the last term in eqn (92), we shall use eqns (42), (71), and (94)

$$\begin{aligned} \frac{1}{z_1 F} \frac{\delta(\alpha_i) i}{c(y=0)} &\approx \frac{1}{z_1 F} \frac{\delta(\alpha_i)}{c_0} = \\ &= \frac{z_1(z_1 + z_2) D_{1h}}{(1 - \alpha_1 z_2 c_0)} \frac{\delta(\alpha_i) a_1(\alpha_i)}{c_0} \Big|_{c(y=0 \approx c_0)} \approx \\ &\approx - \frac{z_1(z_1 + z_2) D_{1h}}{(1 - \alpha_1 z_2 c_0)} \ln \frac{c(y=0)}{c_0} \end{aligned} \quad (96)$$

If we insert from (96) into (92), we obtain after rearrangement

$$-V + w(\alpha_i) i \approx \frac{RT}{F} \frac{z_1 + z_2}{z_1 z_2} (1 + \kappa c_0) \ln \frac{c(y=0)}{c_0} \quad (97)$$

$$\kappa = \frac{z_1^2 z_2 D_{1h}}{(z_1 D_{1h} + z_2 D_{2h})^2} (\alpha_1 D_{1h} + \alpha_2 D_{2h}) \quad (98)$$

By inserting from (75) into (97), we may write

$$\frac{a_1(\alpha_i) \delta(\alpha_i)}{c_0} \Big|_{c(y=0) \approx c_0} \approx 1 - e^{+\frac{F}{RT} \frac{z_1 z_2}{z_1 + z_2} (1 - \alpha_1 c_0) [-V + w(\alpha_i) i]} \quad (99)$$

Moreover, it follows from expressions (81) and (42)

$$\delta[\alpha_i, c(y=0) \approx c_0] \approx \delta(\alpha_i = 0) \left\{ 1 + 0.3331 \left[ \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_1 + z_2} \cdot (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) + \frac{1}{2} \gamma z_2 \right] c_0 \right\} = \delta(\alpha_i = 0) (1 + \vartheta c_0) \quad (100)$$

$$a_1[\alpha_i, c(y=0) \approx c_0] \approx \frac{i}{F z_1 (z_1 + z_2) D_{1h}} (1 - \alpha_1 z_2 c_0) \quad (101)$$

For the derivation of eqn (100) from eqn (81), it holds evidently  $L(\alpha_i = 0) \approx 0$  assuming  $i \ll i_L$ .

By inserting from expressions (100) and (101) into the left side of eqn (99), we obtain

$$\frac{a_1(\alpha_i) \delta(\alpha_i)}{c_0} \Big|_{c(y=0) \approx c_0} = \frac{i}{i_0} \quad (102)$$

$$i_0 = i_L(\alpha_i = 0) [1 - (\vartheta - \alpha_1 z_2) c_0]$$

where  $i_L(\alpha_i = 0)$  is given by expression (57) and  $\vartheta$  by expression (100).

It is worth noticing that the current  $i_0$  is not equal to the limiting current density  $i_L$  given by expression (84). It differs in the terms of littleness of the first order, which is due to a different influence of the linear concentration dependences of  $D_1$ ,  $D_2$ , and  $v$  at small currents and at the limiting current density.

Assuming it holds

$$\frac{z_1 z_2}{z_1 + z_2} \frac{F}{RT} | -V + w i | \approx 40 \frac{z_1 z_2}{z_1 + z_2} | -V + w i | \ll 1 \quad (103)$$

the exponential function in expression (99) may be resolved in a series and after substituting from expression (102) and rearranging, we may write

$$i \approx \frac{\frac{z_1 z_2}{z_1 + z_2} \frac{F}{RT} i_L(\alpha_i = 0) V [1 - (\alpha_1 z_2 + \vartheta) c_0]}{1 + \frac{z_1 z_2}{z_1 + z_2} \frac{F}{RT} i_L(\alpha_i = 0) w(\alpha_i = 0) [1 - (\alpha_1 z_2 + \vartheta + W_2) c_0]} \approx \frac{V}{w(\alpha_i = 0) [1 - (\alpha_1 z_2 + \vartheta + W_2) c_0]} \approx \frac{V}{w(\alpha_i = 0) [1 - W_2 c_0]} \quad (104)$$

$$i < i_L; \quad i_L(\alpha_i = 0) w(\alpha_i = 0) \geq 0.5; \quad W_2 c_0 \leq 0.2 \div 0.3$$

where  $w(\alpha_i = 0)$  is defined by expression (93),  $\kappa$  and  $\vartheta$  by expressions (98) and (100), and  $W_2$  by expression (40) or (92).

The result involved in expression (104) may be also achieved directly from expression (92) if we realize that the ohmic resistance of a binary electrolyte, and thus the voltage drop in it, is much larger than the concentration polarization and voltage drop in the diffusion layer for  $i < 0.9 i_L$ . It means practically that the second term in eqn (92) is substantially larger than the sum of the first and third terms.

Thus, we can draw the conclusion that for  $i < i_L$  the flowing current density is practically given by the ohmic resistance of electrolyte  $w(\alpha_i = 0)$  (see expression (104)). It is evident that the value of voltage  $V$  is accounted from the decomposition voltage upwards. This conclusion is identical with the result ensuing from the analysis of the voltametric characteristic derived by *Levich* [1], *i.e.* from expression (92) for  $\alpha_1 = \alpha_2 = \gamma = 0$ . However, the major result consists in the fact that the correction factor  $(1 - W_2 c_0)$  could be derived from the generalized theory for concentration dependent quantities  $D_i(c)$  and  $v(c)$ . This factor accounts for the fact that the current densities  $i$ , even at low values of  $V$ , may be different more markedly at varying concentration  $c_0$  than the limiting current densities  $i_L$ . For evidence, it is sufficient to compare the quantities  $W_2$  and  $\varepsilon$  occurring in expressions (84) and (40) at equal values of  $\alpha_i$ .

It is convenient to express the dependence of current density on concentration polarization and voltage drop in the diffusion layer, *i.e.* on the difference of potentials  $(V - \varphi_{\text{ohm}})$ . Then it follows from eqns (99–103)

$$i \approx \frac{z_1 z_2}{z_1 + z_2} \frac{F}{RT} i_L(\alpha_i = 0) [V - \varphi_{\text{ohm}}(\alpha_i)] [1 - (\kappa - \alpha_1 z_2 + \vartheta) c_0] \quad (105)$$

$$|\kappa - \alpha_1 z_2 + \vartheta| c_0 \leq 0.2 \div 0.3; \quad i \ll i_L.$$

The influence of the concentration dependence  $D_i(c)$  and  $v(c)$  on current density is expressed in relation (105) by the member  $[1 - (\kappa - \alpha_1 z_2 + \vartheta) c_0]$  where  $\kappa$  and  $\vartheta$  are defined by eqns (98) and (100).

### *Numerical illustration of the generalized theory*

In this part we shall illustrate the generalized theory numerically and graphically by calculating some voltametric characteristics and limiting current densities for a binary system with different normal concentrations  $c_0$ . For this purpose we introduce for simplification the transformed variables  $I$ ,  $\alpha'_i$ ,  $\alpha_0$

$$I = \frac{10^6 i}{F c_0}; \quad \alpha_i = \alpha'_i \alpha_0 \quad (106)$$

It is obvious from expressions (106) that the quantities  $\alpha'_i$  and  $(\alpha_0 c_0)$  are dimensionless whereas the dimension of  $I$  is  $\text{cm s}^{-1}$ .

Let us consider a binary electrolyte with the following parameters

$$\begin{aligned} D_{1h} &= 3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}; & z_1 &= 1; & \alpha'_1 &= -1; \\ D_{2h} &= 1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}; & z_2 &= 2; & \alpha'_2 &= -2; \\ c_0 &= 10^{-4} \text{ val cm}^{-3}; & \delta(\alpha_i = 0) &= 3 \times 10^{-3} \text{ cm}; \\ i_L(\alpha_i = 0) &\approx 3 \times 10^{-2} \text{ A cm}^{-2} \Rightarrow I_L(\alpha_i = 0) \approx 3 \times 10^3 \text{ cm s}^{-1}; \end{aligned} \quad (107)$$

$$\gamma = -\alpha_1 \quad \text{see eqn (86)}$$

where  $I_L$  is the limiting current density transformed according to expression (106).

For calculating the shape of voltametric curve on the basis of expressions (106) and (107) from general eqn (92), it is suited to express some auxiliary functions with substituted numerical values. The quantity  $a_1(\alpha_i)$  in eqn (42) may be expressed by means of the function

$$a_1(\alpha_i) = \frac{i}{F z_1(z_1 + z_2) D_{1h}} (1 + \Psi); \quad \Psi = -\alpha_1 z_2 c(y=0) \quad (108)$$

Expressions (76), (74), (81), and (107) give for the diffusion layer

$$\delta(\alpha_i) = 3 \times 10^{-3} (1 - \xi); \quad \xi = \left( 0.3331 - 1.0946 \frac{I}{I_L} \right) \alpha_0 c_0 \quad (109)$$

From eqns (108), (107), and (106) we obtain

$$\frac{a_1(\alpha_i)}{c_0} = \frac{I}{9} (1 + \Psi) \quad (110)$$

$$\Psi = +2 \left( 1 - \frac{I}{I_L} \right) \alpha_0 c_0 \quad (\text{see eqn (111)}).$$

On the basis of eqns (75), (109), and (110), it holds

$$\frac{c(y=0)}{c_0} = 1 - \frac{I}{3 \times 10^3} (1 - \xi) (1 + \Psi) = 1 - \frac{I}{I_L} \quad (111)$$

The limiting current density may be determined from eqns (82), (83), (84), (106), and (107) and on the assumption that  $\gamma = -\alpha_1$  (see the text following eqn (86)), we may write

$$I_L = 3 \times 10^3 (1 - 0.7615) \alpha_0 c_0 \quad (112)$$

We insert from expressions (106—112) into the general form of voltametric characteristic (92) and substitute  $RT/F = 2.6 \times 10^{-2}$ . Thus, we obtain

$$-V = 2.6 \times 10^{-2} \left\{ 0.6 \ln \left[ 1 - \frac{I}{3 \times 10^3} (1 - \xi) (1 + \Psi) \right] - \frac{l}{10} (1 + 2 \alpha_0 c_0) I - \frac{3 \times 10^{-4} (1 - \xi)}{1 - \frac{I}{3 \times 10^3} (1 - \xi) (1 + \Psi)} I \right\} \quad (113)$$

$$\Delta V = -V + \varphi_{\text{ohm}}(\alpha_i) = -V + 2.6 \times 10^{-2} \frac{l}{10} (1 + 2 \alpha_0 c_0) I \quad (114)$$

The relationships  $I = f(-V)$ ,  $I = f[V - \varphi_{\text{ohm}}(\alpha_i)]$  calculated from expressions (113) and (114) for  $\alpha_0 c_0 = 0, 0.1, 0.2, 0.3$  are represented in Figs. 1 and 2. In Fig. 2, the function  $I$  occurring in expression (114) is plotted in logarithmic coordinates. For the calculation, the distance between electrodes was chosen to be  $l = 1$  cm. The curves for  $\alpha_0 c_0 = 0$  in Figs. 1 and 2 correspond to the voltametric curve derived by Levich [1]. It is obvious that the slopes of voltametric curves decrease with increasing values of  $\alpha_0 c_0$  and the limiting current densities also decrease for the investigated case of a binary electrolyte characterized by parameters (107). On the basis of this real example, we can illustrate the accuracy and applicability of the approximate relationship (105) for  $i \ll i_L$ . If we insert from expressions (106) and (107) into expressions (105), (98), and (100), we obtain

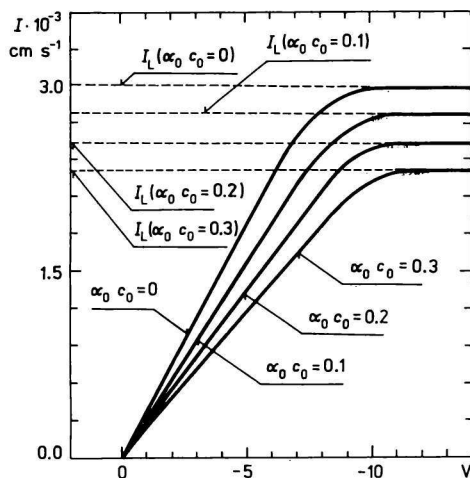


Fig. 1. Voltametric curves  $I = f(-V)$  and limiting current densities  $I_L$  for the electrolyte characterized by parameters (107) at  $\alpha_0 c_0 = 0, 0.1, 0.2, 0.3$ .

Transformed current density  $I$  is given by expression (106).

Case  $\alpha_0 c_0 = 0$  corresponds to the Levich theory.



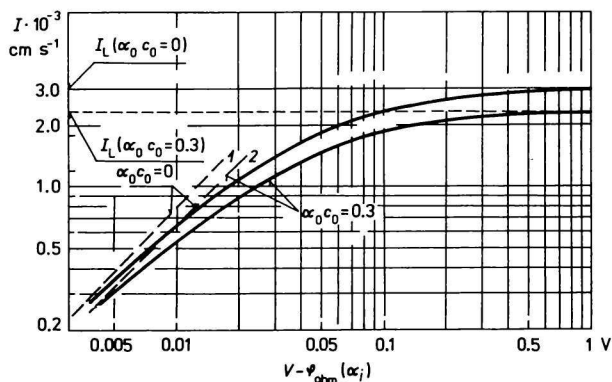


Fig. 2. Voltametric curves  $I = f[V - \varphi_{\text{ohm}}(\alpha_i)]$  and limiting current densities  $I_L$  in logarithmic coordinates for  $\alpha_0 c_0 = 0, 0.3$ .

Binary electrolyte is characterized by parameters (107).  $I$  is given by expression (106).

Plots 1 and 2 have been calculated according to approximate expression (115).

$$I \approx \frac{1}{2.6 \times 10^{-2}} \frac{z_1 z_2}{z_1 + z_2} I_L(\alpha_i = 0) [V - \varphi_{\text{ohm}}(\alpha_i)]$$

$$[1 - (\kappa - \alpha_1 z_2 + \vartheta) c_0] = 7.7 \times 10^4 (1 - 0.47 \alpha_0 c_0)$$

$$[V - \varphi_{\text{ohm}}(\alpha_i)] \quad I \ll I_L \quad (115)$$

The relationships  $I = I[V - \varphi_{\text{ohm}}(\alpha_i)]$  calculated according to approximate expression (115) are represented in Fig. 2 by curve 1 for  $\alpha_0 c_0 = 0$  and curve 2 for  $\alpha_0 c_0 = 0.3$ .

For application of the theory, the courses of the functions  $I(\alpha_0 c_0)/I(\alpha_0 c_0 = 0)$  calculated from accurate expression (114) or (92) must be, however, compared with the courses determined by means of approximate expression (115) or (105). This comparison is represented in Fig. 3 where the voltages  $V - \varphi_{\text{ohm}}(\alpha_i) \approx 0.005$ ,

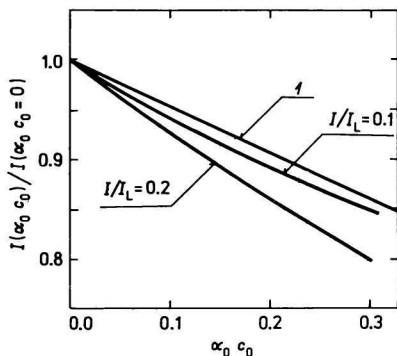


Fig. 3. Ratios of transformed current densities  $I(\alpha_0 c_0)/I(\alpha_0 c_0 = 0)$  for  $I/I_L = 0.1, 0.2$  calculated according to expression (114).

1. Plot calculated according to approximate expression (115).

0.01 V corresponds to the ratios  $I/I_L=0.1$  and 0.2, respectively. The curves  $I(\alpha_0 c_0)/I(\alpha_0 c_0=0)$  corresponding to the above ratios  $I/I_L$  were calculated from expression (114) while curve 1 was calculated by means of approximate expression (115). It is obvious that the results are in a very good agreement for  $I/I_L \leq 0.1$ .

### *Application possibilities of the generalized theory*

The study of the concentration relationships of the diffusion coefficients of cations and anions in binary electrolytes by the method of rotating disc involves four unknown quantities  $D_{1h}$ ,  $\alpha_1$ ,  $D_{2h}$ , and  $\alpha_2$ , where index "1" denotes the diffusion of cations and index "2" the diffusion of anions. The knowledge of the concentration dependence of viscosity, *i.e.* of the coefficient  $\gamma$  in expression (58) is assumed. The first series of experiments is to be carried out at a very low concentration  $c_0(1) \rightarrow 0$  of binary electrolyte. According to the generalized theory (see expression (57)), when the rotating electrode is the cathode, the ratio  $D_{1h}/D_{\text{eff}}^{1/3}$  may be determined. In principle, two procedures may be used for the determination of the heterodiffusion coefficient  $D_{2h}$  of anions. For binary electrolytes with electrochemically active cations and anions, the rotating disc may be used as anode. The second possibility consists in the determination of the ohmic resistance of electrolyte  $w(\alpha_i=0)$  (see expression (93)).

Therefore, if the quantities  $D_{1h}/D_{\text{eff}}^{1/3}$  and  $D_{2h}/D_{\text{eff}}^{1/3}$  or  $D_{1h}/D_{\text{eff}}^{1/3}$  and  $w(\alpha_i=0)$  are known, the values of  $D_{1h}$  and  $D_{2h}$  may be determined by using the nongeneralized theory. Provided these values are known, we are able to approach the application of the generalized theory and determine the values of  $\alpha_1$  and  $\alpha_2$ .

For this purpose, the second series of experiments at a concentration  $c_0(2) \gg \gg c_0(1)$  is to be carried out and the limiting current densities should be determined experimentally. According to relation (84), the ratio of the limiting currents at both concentrations must obey the following equation

$$\frac{i_L[c_0(2)]}{i_L[c_0(1)]} \approx \frac{c_0(2)}{c_0(1)} \left\{ \left\{ 1 + \left\{ 0.5655 \frac{z_1}{z_1+z_2} \frac{D_{\text{eff}}}{D_{2h}} (\alpha_1 z_2 - \alpha_2 z_1) + 0.4995 W_2 + \right. \right. \right. \\ \left. \left. - 0.2375 \left[ \frac{D_{\text{eff}}}{D_{1h} D_{2h}} \frac{1}{z_1+z_2} (\alpha_1 z_2^2 D_{2h} + \alpha_2 z_1^2 D_{1h}) + \frac{1}{2} \gamma z_2 \right] \right\} c_0(2) \right\} \quad (116)$$

$$c_0(1) \ll c_0(2)$$

where  $c_0(1)$  and  $c_0(2)$  are normal concentrations and  $W_2$  is given by expression (40). In order to determine the values of  $\alpha_1$  and  $\alpha_2$  from the known values of  $D_{1h}$  and  $D_{2h}$ , we must get another linearly independent equation in addition to eqn (116). For this purpose, we may use, for instance, the dependence of the ohmic

resistance of electrolyte  $w(\alpha_i)$  on concentration (see (93)). If we experimentally determine the ratio of current densities at concentrations  $c_0(1)$  and  $c_0(2)$  assuming a constant voltage  $V$  applied, we obtain on the basis of eqns (104) and (40)

$$\frac{i[c_0(1)]}{i[c_0(2)]} \approx \frac{c_0(1)}{c_0(2)} [1 - W_2 c_0(2)] \quad (117)$$

$$V = \text{const}; \quad c_0(1) \ll c_0(2); \quad |W_2| c_0(2) \leq 0.3; \quad i < i_L.$$

From eqns (116) and (117), i.e. from the known limiting current densities and from the known ohmic resistance of electrolyte at two different concentrations, the quantities  $\alpha_1$  and  $\alpha_2$  may be already determined.

Let us consider eqn (105). If we determine the ratios of current densities at the concentrations  $c_0(1)$  and  $c_0(2)$  assuming a constant potential difference  $\Delta V = V - \varphi_{\text{ohm}}(\alpha_i)$ , we may obtain the following equation from expression (105)

$$\frac{i[c_0(2)]}{i[c_0(1)]} \approx \frac{c_0(2)}{c_0(1)} [1 - (\kappa - \alpha_1 z_2 + \vartheta) c_0(2)] \quad (118)$$

$$V - \varphi_{\text{ohm}}(\alpha_i) = \text{const}; \quad c_0(1) \ll c_0(2); \quad i \leq 0.1 i_L;$$

$$|\kappa - \alpha_1 z_2 + \vartheta| c_0(2) \leq 0.3$$

where  $\kappa$  and  $\vartheta$  are defined by relations (98) and (100).

It is evident that the values of  $\alpha_1$  and  $\alpha_2$  may be also obtained from eqns (116) and (118). A numerical illustration of this relationship for the electrolyte characterized by parameters (107) is given in Fig. 3.

## Conclusion

The generalized theory of the voltametry with RDE which respects the dependence of the diffusion coefficients of cations and anions as well as of viscosity on concentration is based on the generalized transport equations of ions in a binary electrolyte. These transport equations involve the diffusion, convection, and migration of ions. The very presence of the migration of ions due to the electric field in solution, which cannot be neglected in binary electrolytes, considerably complicates the solution of this problem.

This study is based on the premise that a linear dependence of the diffusion coefficients of cations and anions on concentration may be assumed in the first approximation for the investigated concentration region of binary electrolyte. This assumption leads to the simplification of the transport equations, the description of the electric field intensity for concentration dependent diffusion coefficients, and, last but not least, to the determination of the generalized boundary conditions for the transport equations.

In subsequent part of this paper where the transport equation is integrated, another generalization is introduced. It consists in respecting the dependence of viscosity on the concentration of binary electrolyte. A linear dependence is assumed again. From the mathematical view-point, only one approximation has been used in all calculations, *i.e.* the terms of littleness of the second and higher orders have been neglected. From this point of view, the validity of results is limited. The final relationships can be used if the magnitude of the terms of littleness of the first order (*i.e.* members with  $\alpha_i c_0$ ) is less than  $0.2 \div 0.3$ .

The integration of the transport equation leads to the determination of the concentration distribution and thus to the calculation of the concentration at RDE. In this way, it is possible to determine the generalized relationship for limiting current density which respects the concentration dependence of the diffusion coefficients and viscosity.

In order to estimate the current densities which are smaller than the limiting current density we should derive the generalized form of voltametric curve. For this aim, we must calculate the potential from the electric field intensity in electrolyte and the value of the applied voltage as a function of current density. In all components of this potential, the members respecting the concentration dependence of the diffusion coefficients appear, *i.e.* the generalized relationship for the ohmic resistance of electrolyte, *etc.* The generalized theory has been elaborated for the case when RDE is cathode and the valence of ions is equal to the number of the electrons exchanged. The relationships derived by Levich represent the limiting case in this theory and are valid for  $\alpha_i c_0 \rightarrow 0$ .

On the basis of theoretical analysis we have come to these principal conclusions :

The theory enables us to compare the limiting currents in binary electrolytes with the limiting currents in solutions with indifferent electrolyte. It appears that the influence of the concentration dependence of the diffusion coefficients on the value of the limiting current density is equal for binary electrolytes and the solutions of electroactive particles with indifferent electrolyte provided the diffusion coefficients and charges of positive and negative ions in binary electrolytes are equal.

If we use the experimental data obtained at very low concentrations for the evaluation of the heterodiffusion coefficients of cations and anions according to the relationships derived by Levich, the generalized theory also enables us to determine the coefficients  $\alpha_1$  and  $\alpha_2$  which characterize the linear dependence of the diffusion coefficients on concentration. For this purpose, the ratios of the limiting current densities and the ratios of the ohmic resistances of electrolyte must be experimentally ascertained for different concentrations. It is also possible to use the ratio of current densities which are substantially smaller than the limiting current density, *i.e.* to employ the beginning of voltametric curve.

Finally, the theory put forward enabled us, by both deductions and final relationships, to investigate deeper the processes occurring in a binary electrolyte

at rotating electrode from the view-point of their dependence on concentration.

In conclusion, the influence of corrections and boundary effects on the results presented must be taken into consideration. Gregory and Riddiford [4] took into account further members of the series expressing the velocity  $v(y)$  (see expression (45)) and came to a correction which increases the diffusion flow at the electrode by about 3—5%. On the contrary, other phenomena, e.g. the boundary effect (position of the disc in socket) reduce the diffusion flow and this correction is approximately equal to that one introduced by Riddiford. Therefore, the corrections compensate one another for a great part [1].

The mathematical relationships derived in this paper respect the linear concentration dependence of the diffusion coefficients and are valid if the relative magnitude of the expressions with  $\alpha_i c_0$  is smaller or equal to 20—30%. The values of  $\alpha_i$  are given merely by the character of ions in a binary electrolyte and, for certain electrolytes, the phenomena due to the concentration dependence of diffusion can several times exceed the above-mentioned corrections.

The region of validity of linear relations (21) and (22) for the diffusion coefficients may be experimentally verified for a given electrolyte by using eqn (84). The limiting current densities  $i_l$  ought to increase linearly with concentration (see eqn (84) or in a special case eqn (88)).

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