

**THE LIMITING DIFFUSION AND MIGRATION CURRENTS AS FUNCTIONS
OF THE RATE CONSTANTS OF ELECTROLYTE DISSOCIATION
AND RECOMBINATION**

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The paper is concerned with the problem of calculating the limiting diffusion and migration currents in partly dissociated electrolytes. The limiting currents were investigated as functions of the equilibrium and rate constant of dissociation. Approximate analytical calculations of the limiting currents and a numerical solution of the problem were achieved.

In [1] the dependence of limiting diffusion and migration currents on the equilibrium constant of a partly dissociated electrolyte was investigated. It was assumed that the rate constants of dissociation and recombination are very high so that throughout the diffusion layer the concentrations of the cations (c_1), anions (c_2), and undissociated molecules (c_3) were related by the equilibrium condition of

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$$c_3 = \beta c_1^{\nu_1} c_2^{\nu_2}, \quad (1)$$

where β is the dissociation equilibrium constant, ν_1 and ν_2 are the stoichiometric coefficients, which coincide with the charges, z_1 and z_2 , of the cations and anions when these are simply related (have no common divisors). Ionic transport in systems with chemical equilibria was studied in [2-9].

In the present communication we examine the problem of calculating the limiting currents in partly dissociated electrolytes in the more rigorous formulation where the assumption of equilibrium (1) is not used.

The system of electrodiffusion equations describing discharge of cations in solutions of a partly dissociated electrolyte $A_{\nu_1}B_{\nu_2}$ can be written in the form of

$$D_1 \frac{dc_1}{dx} + \nu_1 D_3 \frac{dc_3}{dx} + z_1 D_1 c_1 \frac{d\Psi}{dx} = \frac{i}{nF}, \quad (2)$$

$$D_2 \frac{dc_2}{dx} + \nu_2 D_3 \frac{dc_3}{dx} - z_2 D_2 c_2 \frac{d\Psi}{dx} = 0, \quad (3)$$

$$D_3 \frac{d^2 c_3}{dx^2} = K(c_3 - \beta c_1^{\nu_1} c_2^{\nu_2}), \quad (4)$$

$$z_1 c_1 = z_2 c_2. \quad (5)$$

Here D_1 , D_2 , and D_3 are the diffusion coefficients of the cations, anions, and neutral molecules, $\Psi = FE/RT$ is the dimensionless potential, i is the current density of cation discharge, F is the Faraday constant, n is the number of electrons transferred in the electrode reaction, R is the gas constant, T is the temperature, and K is the dissociation rate constant.

At the diffusion layer boundary of $x = \sigma$ the equilibrium concentrations are defined as

$$c_i(\delta) = c_i^0(\beta), \quad i=1, 2, 3. \quad (6)$$

The equilibrium concentrations c_1^0 and c_3^0 can be related to the total concentration of substance $A_{\nu_1}B_{\nu_2}$ in the solution and the equilibrium constant β through

$$c_3^0 = \beta (c_1^0)^{\nu_1} (c_2^0)^{\nu_2}, \quad (7)$$

$$z_1 c_1^0 = z_2 c_2^0, \quad (8)$$

$$c_1^0 + \nu_1 c_3^0 = \nu_1 c^0. \quad (9)$$

Combining (7), (8), and (9) we obtain an equation defining the function $c_1^0(\beta)$:

$$c_1^0 + \nu_1 \beta (c_1^0)^{\nu_1 + \nu_2} (z_1/z_2)^{\nu_2} = \nu_1 c^0. \quad (10)$$

Substituting the solution of Eq. (10) into (8) and (7) one can determine the equilibrium concentrations contained in (6). The system (2) to (5) must be supplemented by the condition of

$$\left. \frac{dc_3}{dx} \right|_{x=0} = 0, \quad (11)$$

while in calculating the limiting currents one must demand in addition that

$$c_i(0) = 0. \quad (12)$$

The calculations performed in [1] which were based on a solution of system (1) to (3) and (5) with the boundary conditions (6), (11), and (12) correspond to the limiting case when the dimensionless parameter $\epsilon = D_3/K\delta^2$ tends toward zero so that Eq. (4) at all $0 < x < \sigma$ can be replaced by (1).

We shall examine the solution of the system (2) to (6), (11), (12) for small but finite values of parameter ϵ . It follows from the condition of local electroneutrality (5) and the Eqs. (2) and (3) that

$$\frac{dc_1}{dx} \left(1 + \frac{z_1}{z_2} \right) + \left(\frac{D_3 \nu_1}{D_1} + \frac{D_3 \nu_2}{D_2} \right) \frac{dc_3}{dx} = \frac{i}{nFD_1} \quad (13)$$

We shall change to the dimensionless variables

$$y = x/\delta, \quad \bar{c}_i = c_i/c^0. \quad (14)$$

Then Eqs. (4) and (13) and the boundary conditions (6), (11), and (12) can be written as

$$\alpha \frac{d\bar{c}_1}{dy} + \frac{d\bar{c}_3}{dy} = I, \quad (15)$$

$$\varepsilon \frac{d^2\bar{c}_3}{dy^2} = \bar{c}_3 - \beta c_1^m, \quad (16)$$

$$\bar{c}_1|_{y=-1} = c_1^0/c^0, \quad \bar{c}_3|_{y=-1} = c_3^0/c^0, \quad (17)$$

$$\bar{c}_1|_{y=0} = 0, \quad \left. \frac{d\bar{c}_3}{dy} \right|_{y=0} = 0, \quad (18)$$

where for combinations of the parameters the following symbols were introduced:

$$\begin{aligned} \alpha &= (1 + z_1/z_2) / (D_3 v_1 / D_1 + D_3 v_2 / D_2), \\ I &= (i\delta/c^0 n F D_1) / (D_3 v_1 / D_1 + D_3 v_2 / D_2), \\ \beta &= \beta (c^0)^{v_1 + v_2 - 1} (z_1/z_2)^{v_2}, \quad m = v_1 + v_2. \end{aligned}$$

Integrating (15) we obtain

$$\alpha \bar{c}_1 + \bar{c}_3 = Iy + b. \quad (19)$$

Using the conditions (18) one can conclude that $\bar{c}_3(0) = b$, and using conditions (17) we have

$$I + b = I_0, \quad (20)$$

where

$$I_0 = \alpha c_1^0/c^0 + c_3^0/c^0. \quad (21)$$

Quantity I_0 is the expression for the dimensionless current in the case where $\varepsilon = 0$. In fact, setting $\varepsilon = 0$ in (16) and using (18) we find that $I = I_0$. Quantity b can be used in two capacities at the same time, viz, as the dimensionless concentration of undissociated substance near the electrode and as the correction to the dimensionless current I_0 at small ε . As shown above one has $b \rightarrow 0$ when $\varepsilon \rightarrow 0$.

Our problem is that of calculating I for $\varepsilon \ll 1$. Since Eq. (16) is nonlinear and has the small parameter as factor in front of the highest derivative, we can interchange the dependent and independent variable so that all terms of Eq. (16) become terms of the same order of magnitude [10]. Suppose that $\zeta = y/\sqrt{\varepsilon}$. It follows from (19) that when y is of the order of $\sqrt{\varepsilon}$ the concentration sum $\alpha \bar{c}_1 + \bar{c}_3$ also is of the order of $\sqrt{\varepsilon}$.

We shall seek the solution of Eq. (16) in the form of

$$\bar{c}_3 = \varepsilon^{m/2} Z(\zeta), \quad \bar{c}_1 = \varepsilon^{1/2} U(\zeta), \quad (22)$$

where $Z(\zeta)$ and $U(\zeta)$ are functions of the order of unity. It follows from the conditions (18), (19) that b is of the order of $\varepsilon^{m/2}$. Neglecting terms of the order of $\varepsilon^{m/2}$ in relation (19) we obtain an approximate expression for function U :

$$U(\zeta) = I\zeta/\alpha. \quad (23)$$

Substituting (22) and (23) into (16) we obtain an equation for function Z :

$$\frac{d^2 Z}{d\zeta^2} = Z - \beta \left(\frac{I\zeta}{\alpha} \right)^m \quad (24)$$

with the boundary conditions

$$\left. \frac{dZ}{d\zeta} \right|_{\zeta=0} = 0, \quad Z(0) = \frac{b}{\varepsilon^{m/2}}. \quad (25)$$

The general solution $Z(\zeta)$ of the homogeneous Eq. (24) is

$$Z = A \exp(-\zeta) + B \exp(\zeta). \quad (26)$$

The partial solution Z of the inhomogeneous equation can be found by the method of variation of the constants. Adding the general solution of the homogeneous equation and the partial solution of the inhomogeneous equation we can obtain a general solution of the inhomogeneous equation that satisfies the condition of $Z'(0) = 0$ in the form of

$$Z = L \left[e^{\zeta} \int_0^{\infty} dt e^{-t^m} + e^{-\zeta} \int_0^{\zeta} dt e^{t^m} + \Gamma(m+1) \right], \quad (27)$$

where $L = 0.5\bar{\beta}(I/\alpha)^m$ and $\Gamma(m+1)$ is the gamma function. From (27) and the second condition in (25) we find the value of $b = \varepsilon^{m/2} 2L\Gamma(m+1)$ which, when it is substituted into (20), yields an equation for I :

$$I = I_0 - \varepsilon^{m/2} \bar{\beta} (I/\alpha)^m \Gamma(m+1). \quad (28)$$

On the right-hand side of (28) one can neglect the small difference between I and I_0 , and write an approximate expression for the dimensionless current in the form of

$$I = I_0 - \varepsilon^{m/2} \bar{\beta} (I_0/\alpha)^m \Gamma(m+1). \quad (29)$$

Thus, at small values of parameter $\sqrt{\varepsilon}$, i.e., high dissociation rates, the limiting diffusion and migration current is depressed in proportion to $\varepsilon^{(\nu_1 + \nu_2)/2}$.

We now turn to the opposite limiting case of $\varepsilon \gg 1$ (low dissociation rates). We shall seek the solution for \bar{c}_1 in the form of

$$\bar{c}_1 = u + \frac{1}{\varepsilon} v, \quad (30)$$

where u and v are functions of the order of unity. Substituting this expansion into (16), allowing for (15), and equating the terms in ε we obtain

$$d^2 u / dy^2 = 0. \quad (31)$$

Hence after satisfying the boundary conditions (17) and (18) we obtain the major part of the solution for \bar{c}_1 :

$$u = c_1^0 / c^0 y \quad (32)$$

For the purposes of finding v we equate the terms not containing ε , and substituting (32) we obtain

$$\alpha \frac{d^2 v}{dy^2} = \bar{\beta} (\bar{c}_1^0 y)^m - (I y + \bar{c}_1^0 + \bar{c}_s^0 - I - \alpha \bar{c}_1^0 y). \quad (33)$$

In deriving (33) we additionally allowed for relations (19) and (20). Function v satisfies the homogeneous boundary conditions of

$$v(0) = 0, \quad v(1) = 0. \quad (34)$$

Integrating (33) while allowing for (34) we obtain

$$v = \frac{1}{\alpha} \left[\frac{\bar{\beta} (\bar{c}_1^0)^m (y^{m+2} - y)}{(m+2)(m+1)} + \frac{(\alpha \bar{c}_1^0 - I)(y^3 - y)}{6} + \frac{(I - \bar{c}_1^0 - \bar{c}_s^0)(y^2 - y)}{2} \right]. \quad (35)$$

This expression, with the condition of $I = d\bar{c}_1/dy |_{y=0}$, yields an expression for the flux in the case of low dissociation

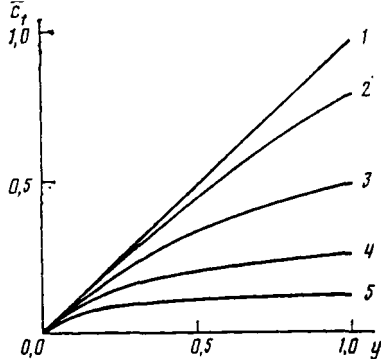


Fig. 1

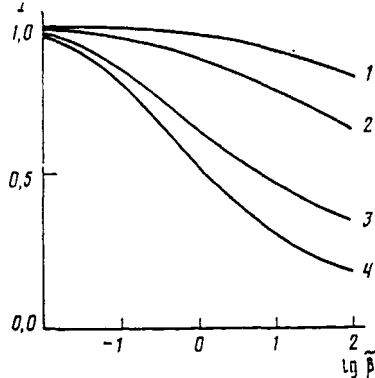


Fig. 2

Fig. 1. Plots of cation concentrations \bar{c}_1 against dimensionless distance y for $z_1 = 2, z_2 = 1, \epsilon = 0.1$, and different values of β : 1) 0.01, 2) 0.1, 3) 10, 4) 100, and 5) 1000.

Fig. 2. Plots of cation fluxes to the electrode as functions of $\log \beta$ for different values of ϵ : 1) 0.02, 2) 0.1, 3) 1, and 4) 10.

rates ($\epsilon \gg 1$):

$$I = \bar{c}_1^0 + \frac{1}{\epsilon \alpha} \left[\left(\frac{1}{2} - \frac{\alpha}{6} \right) \bar{c}_1^0 - \frac{\bar{c}_s^0}{2} + \frac{\beta (\bar{c}_1^0)^m}{(m+1)(m+2)} \right]. \quad (36)$$

Function $I(\beta)$ defined by (36) is a monotonically falling function.

For a number of intermediate values of ϵ the system of Eqs. (15) to (18) was also solved numerically by the Runge—Kutta method and by an optimized search procedure for values of I satisfying the boundary conditions. As an illustration of the numerical solution obtained for the problem, the concentration distributions \bar{c}_1 in the diffusion layer are shown in Fig. 1 for fixed values of parameter ϵ and widely varying values of the parameter β . Figure 2 shows functions $I(\log \beta)$ calculated by numerical solution of the problem for a number of values of parameter ϵ .

It follows from the numerical calculations and from the results of the approximate analytical solution of the problem that as parameter ϵ increases the limiting current of cation reduction decreases.

It thus can be seen from the above investigation that the limiting currents in partly dissociated binary electrolytes depend, (i) on the rate constant of electrolyte dissociation and (ii) on the dissociation equilibrium constant. The analytic relations (29) and (36) obtained for the limiting current in the cases of large and small ($\epsilon \gg 1$ and $\epsilon \ll 1$) rate constants of electrolyte dissociation allow the dissociation constant β to be determined from experimentally determined values of I and ϵ . In the case of intermediate ϵ -values the family of curves $I(\log \beta)$ obtained by numerical solution of the problem can be used for a determination of β . In the limit of $\epsilon \rightarrow 0$ the calculated function $I(\beta)$ changes to the relation obtained for I in [1]. At low values of the dissociation rate constant ($\epsilon \gg 1$) the limiting diffusion and migration currents are chiefly determined by the equilibrium concentration of electroactive cations in the solution.

We point out in conclusion that by varying the concentration c^0 in the solution one can vary the value of parameter β which is proportional to $(c^0)^{m-1}$, while parameter ϵ is independent of c^0 . In principle, therefore, one can find the dissociation rate constant K and the equilibrium constant β by comparing the experimental relations between limiting currents and concentrations c^0 with the calculated curves of $I(\log \beta)$ for different values of ϵ .

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