The theory of limiting diffusion-migration currents in partially dissociated electrolytes

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Abstract

The theory of limiting diffusion–migration currents is presented for partially dissociated electrolytes without the assumption that the dissociation reaction is in equilibrium and is based on the Nernst diffusion layer model.

INTRODUCTION

The processes of diffusion-migration transport of ions in solutions of completely dissociated electrolytes have been well studied [1]. Of interest is analyzing the peculiarities of these processes proceeding under conditions where the electrolyte is only partially dissociated according to the reaction equation

$$v_1 \; A^{z_1+} + v_2 \; B^{|z_2|-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_{v_1} B_{v_2} \tag{1}$$

Here A^{z_1+} and $B^{|z_2|-}$ are cation and anion, z_1 and z_2 are charge numbers, $A_{v_1}B_{v_2}$, is a neutral molecule, v_1 and v_2 are stoichiometric coefficients, and k_1 and k_2 are association and dissociation rate constants. The stoichiometric coefficients v_1 and v_2 coincide with $|z_2|$ and z_1 in the case when $|z_2|$ and z_1 are mutually simple numbers (do not have any common divisors).

The diffusion transport of ions in systems with chemical equilibria in the absence of electromigration was analyzed in refs. 2–4.

The dependence of a limiting diffusion-migration current of cation discharge on the equilibrium constant of a partially dissociated electrolyte was studied in ref. 5 under the assumption that dissociation and recombination rate constants are rather

high, so that in the whole diffusion layer the concentrations of cations C_1, anions C_2 and non-dissociated neutral molecules C_3 are related by the equilibrium condition

$$\beta C_1^{v_1} C_2^{v_2} = C_3 \tag{2}$$

where $\beta = k_1/k_2$ is the equilibrium constant. One of the most interesting results of ref. 5 is the fact that for sufficiently high values of the non-dissociated substance diffusion coefficient the limiting current can be several times higher than the diffusion-migration current in fully dissociated electrolytes.

This paper presents the calculation of a limiting current of cation discharge in partially dissociated electrolyte in a more rigorous formulation without the assumption of equilibrium condition *(2)*. The analysis presented is based on the Nernst diffusion layer model [1],which is widely used in electrochemical macrokinetics and accounts in implicit form for the convective transfer of ions. The theory developed here can also be applied to systems with membrane covered electrodes.

STATEMENT OF THE PROBLEM AND THE GENERAL SOLUTION

Let us consider discharge of cations A^{z_1+} reducing under steady state conditions to a neutral species which does not interact with any other substance in the solution. We shall also suppose that anions $B^{|z_2|-}$ are electrochemically inert and that direct discharge of molecules $A_{v_1}B_{v_2}$ is impossible in the whole potential region.

The system of electrodiffusion equations describing the distribution of component concentrations C_1, C_2, C_3 and electric potential ϕ in the diffusion layer close to the electrode can be written as

$$D_1 \frac{dC_1}{d\xi} + v_1 D_3 \frac{dC_3}{d\xi} + z_1 D_1 C_1 \frac{d\Psi}{d\xi} = \frac{i}{z_1 F} \tag{3}$$

$$D_2 \frac{dC_2}{d\xi} + v_2 D_3 \frac{dC_3}{d\xi} + z_2 D_2 C_2 \frac{d\Psi}{d\xi} = 0 \tag{4}$$

$$D_3 \frac{d^2 C_1}{d\xi^2} = k_2 (C_3 - \beta C_1^{v_1} C_2^{v_2}) \tag{5}$$

$$z_1 C_1 = |z_2| C_2 \tag{6}$$

Here D_1, D_2, D_3 are diffusion coefficients of the corresponding components, $\Psi = F\phi/RT$ is the dimensionless potential, i is the cation discharge current density, ξ is a coordinate, and the remaining designations are generally accepted.

The first and the third terms in eqns. (3) and (4) describe diffusion and migration fluxes of cations and anions. The second terms in these equations correspond to the transfer of substances A^{z_1+} and $B^{|z_2|-}$ due to diffusion of $A_{v_1}B_{v_2}$. Equation (5) describes diffusion transport of $A_{v_1}B_{v_2}$ molecules taking account of reaction (1). Finally eqn. (6) presents the condition of local electroneutrality in the diffusion layer.

The system of equations *(3)–(5)* should be supplemented by the boundary condition

$$\frac{dC_3}{d\xi}\bigg|_{\xi=0} = 0 \tag{7}$$

corresponding to the electrochemical inertness of molecules $A_{v_1}B_{v_2}$, and the condition

$$C_1(0) = 0 \tag{8}$$

corresponding to the limiting current of cation discharge. At the diffusion layer boundary $\xi = L$ concentrations C_1, C_2, C_3 are equal to their equilibrium values:

$$C_i(L) = C_i^0(\beta) \qquad i = 1, 2, 3 \tag{9}$$

The values of equilibrium concentrations C_1^0, C_2^0 and C_3^0 can be related to the total concentration C^0 of substance $A_{v_1}B_{v_2}$ in a solution and with the equilibrium constant β by equations

$$\beta(C_1^0)^{v_1}(C_2^0)^{v_2} = C_3^0 \tag{10}$$

$$z_1 C_1^0 = |z_2| C_2^0 \tag{11}$$

$$C_1^0 + v_1 C_3^0 = v_1 C^0 \tag{12}$$

Combining eqns. (10)-(12), one obtains the equation that determines the $C_1^0(\beta)$ dependence

$$C_1^0 + v_1 \beta (C_1^0)^m (z_1/|z_2|)^{v_2} = v_1 C^0 \tag{13}$$

where $m = v_1 + v_2$ is, the formal order of the recombination reaction. Substituting the solution of eqn. *(13)* into eqns. *(11)* and (10), one determines the equilibrium concentrations appearing in eqn. *(9)*.

The calculations in ref. 5, based on the solution of a system of eqns. (2)–(4) and *(6)* with boundary conditions (7)-(9), correspond to the limiting case, when the dimensionless parameter $\delta = D_3/k_2 L^2$ tends to zero, so that eqn. *(5)* should be replaced by eqn. *(2)* for any $0 < \xi < L$.

It follows from the local electroneutrality condition *(6)* and from eqns. *(3)* and (4) that

$$\frac{dC_1}{d\xi}\left(1 + \frac{z_1}{|z_2|}\right) + \left(\frac{D_3 v_1}{D_1} + \frac{D_3 v_2}{D_2}\right)\frac{dC_3}{d\xi} = \frac{i}{z_1 F D_1} \tag{14}$$

After passing to dimensionless variables:

$$x = \xi/L \qquad c_i = C_i/C^0 \tag{15}$$

eqns. (5), *(14)* and boundary conditions (7)–(9) are written in the form

$$\gamma \frac{dc_1}{dx} + \frac{dc_3}{dx} = j \tag{16}$$

$$\delta \frac{d^2 c_3}{dx^2} = c_3 - \bar{\beta} c_1^m \tag{17}$$

$$c_1(1) = C_1^0/C^0 = k \qquad c_3(1) = C_3^0/C^0 = l \tag{18}$$

$$c_1(0) = 0 \qquad \left.\frac{dc_3}{dx}\right|_{x=0} = 0 \tag{19}$$

where the following designations for combinations of parameters are introduced:

$$\gamma = \left(1 + \frac{z_1}{|z_2|}\right)\Bigg/\left(\frac{D_3v_1}{D_1} + \frac{D_3v_2}{D_2}\right)$$

$$j = \frac{iL}{z_1FD_1C^0}\Bigg/\left(\frac{D_3v_1}{D_1} + \frac{D_3v_2}{D_2}\right)$$

$$\bar{\beta} = \beta(C^0)^{m-1}(z_1/|z_2|)^{v_2}$$

Integrating (16), one obtains

$$\gamma c_1 + c_3 = jx + b. \tag{20}$$

Using conditions (19), one concludes that $c_3(0) = b$, and using conditions (18), one has

$$j + b = j^0 \tag{21}$$

where

$$j^0 = \gamma k + l$$

Quantity j^0 is the expression for a dimensionless current in the case $\delta = 0$, i.e. under the conditions of equilibrium of the dissociation–recombination reaction. Indeed, letting $\delta = 0$ in *(17)* and (19), one obtains $j = j^0$. Quantity b can be treated in two ways simultaneously: as a dimensionless concentration of non-dissociated substance near the electrode and as a correction to dimensionless current j^0 for small 6. As was shown above, $b \to 0$ at $\delta \to 0$.

The system of eqns. *(16)* and *(17)* with boundary conditions *(18)* and *(19)* is nonlinear *(c,* enters eqn. *(17)* in powers of $m \geqslant 2$) and, hence, it does not have any general analytical solution. Below, analytical solutions will be given for the limiting cases of recombination reaction $\delta = 0$, as well as for high and low dissociation-recombination reaction rates *($\delta \ll 1$ and $\delta \gg 1$)*. The results of numerical solution of a system will be given for the intermediate region of δ values of the order of unity.

THE CASE OF THE RECOMBINATION–DISSOCIATION REACTION EQUILIBRIUM

As mentioned above, quantity j^0 is the expression for dimensionless limiting current in the case of the dissociation–recombination reaction equilibrium $\delta = 0$, that was analyzed in ref. 5. The corresponding limiting current in dimensionless units can be written as

$$i = \frac{z_1FD_1}{L}\left[\left(1 + \frac{z_1}{|z_2|}\right)C_1^0 + \left(\frac{D_3v_1}{D_1} + \frac{D_3v_2}{D_2}\right)\left(C^0 - \frac{C_1^0}{v_1}\right)\right] \tag{22}$$

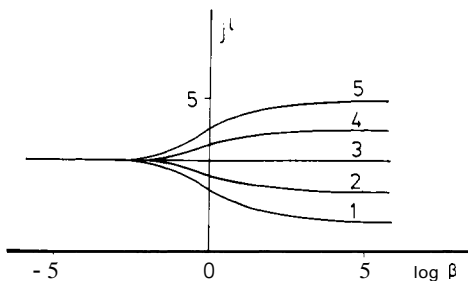In eqn. *(22)* the current i depends on $\bar{\beta}$ via the $C_1^0(\bar{\beta})$ dependence only.

Fig. 1. The $i(\bar{\beta})$ dependence for $z_1 = 2$, $|z_2| = 1$ and for the following values of the parameter $D_3 z_1 / D_2 + D_3 |z_2| / D_1$: (1) 1; (2) 2; (3) 3; (4) 4; (5) 5.
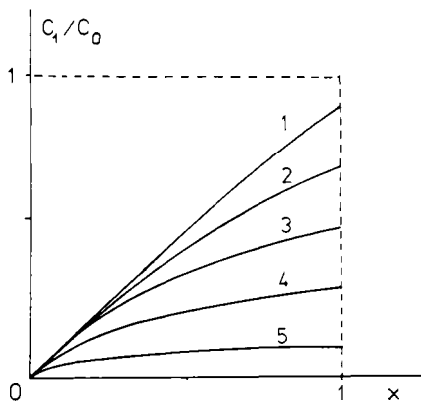
Fig. 2. The $c_1(x)$ dependence for $z_1 = 2$, $|z_2| = 1$ and $D_1 = D_2 = D_3$ and for values of $\bar{\beta}$: (1) 0.0343; (2) 0.2187; (3) 1; (4) 6.481; (5) 225.

The $i(\bar{\beta})$ dependence, determined by eqns. (13) and (22), is shown in Fig. 1. For a high dissociation degree, when $\bar{\beta} \ll 1$, the dimensionless concentration of cations is $c_1^0 \approx |z_2|$, and the current tends to the value

$$i = (z_1 + |z_2|) z_1 F D_1 C^0 / L$$

which coincides with the value of i in a binary solution of fully dissociated electrolyte. For a low dissociation degree, when $\bar{\beta} \gg 1$, the dimensionless concentration of electroactive ions is $c_1^0 \ll 1$, and the limiting current tends to the value

$$i = \frac{z_1 F D_1 D_3 C^0}{L} \left(\frac{v_1}{D_1} + \frac{v_2}{D_2} \right)$$

We should mention an important fact. Although the concentration of discharging cations in a solution decreases with lowering of the degree of dissociation, the limiting current tends to the asymptotic constant value which depends on the ratio of diffusion coefficients D_1, D_2, D_3 of components and parameters v_1 and v_2. In this case the value of i for $\bar{\beta} \to \infty$ can be either higher, or lower than its value for $\bar{\beta} \to 0$.

In the simplest case, when all diffusion coefficients are equal ($D_1 = D_2 = D_3$), the dimensionless limiting current is equal to 1 and does not depend on $\bar{\beta}$.

A physical explanation for such behavior of $i(\bar{\beta})$ is the fact that electroactive cations are transferred in a diffusion layer both via their diffusion and migration (the distribution of concentrations $c_1(x)$ for some values of $\bar{\beta}$ is shown in Fig. 2) and via diffusion transfer to the electrode with subsequent dissociation of neutral molecules $A_{v_1} B_{v_2}$. (The distribution of concentration $c_3(x)$ is shown in Fig. 3.) The rate of the latter mechanism is proportional to the diffusion coefficient D_3 of
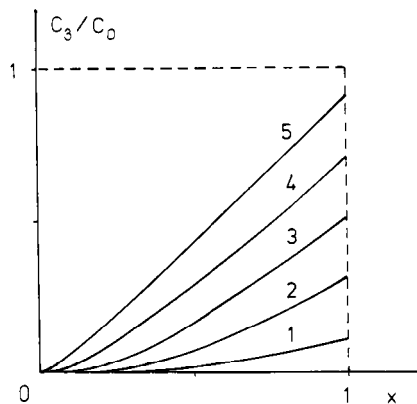
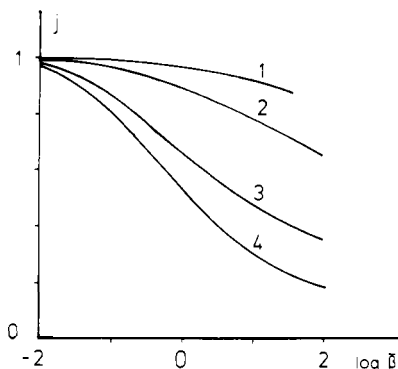Fig. 3. The $c_3(x)$ dependence for the same parameters as in Fig. 2

Fig. 4. The dependence of cation flux to the electrode on log $\bar{\beta}$ for different values of δ: (1) 0.02; (2) 0.1; (3) 1; (4) 10.

neutral molecules, and the corresponding contribution to the limiting current is given by the second term in eqn. *(22)*.

In case of $D_1 = D_2 = D_3$ the decrease of the contribution of diffusion–migration transfer of A^{z_1+} cations, caused by decreasing C_1^0 with growing $\bar{\beta}$, is fully compensated by diffusive supply of dissociating neutral $A_{v_1} B_{v_2}$ molecules to the electrode, which just provides the independence of the limiting current of $\bar{\beta}$.

ANALYTICAL SOLUTION FOR THE CASE OF HIGH REACTION RATES $\delta \ll 1$

Since eqn. *(17)* contains a small parameter at a higher order derivative and is non-linear, we shall replace the dependent and independent variables in this equation in such a manner, that all terms of eqn. *(17)* should be of the same order of magnitude [6-8]. Let $y = x/\sqrt{\delta}$. As follows from eqn. (20), for $x = \sqrt{\delta}$ the sum of concentrations $\gamma c_1 + c_3$ is also of the order of $\sqrt{\delta}$. We shall seek the solution of eqn. *(17)* in the form of

$$c_3 = \delta^{m/2} W(y) \quad c_1 = \delta^{1/2} U(y) \tag{23}$$

where $W(y)$ and $U(y)$ are functions of the order of unity. It follows from eqns. *(19)* and (20), that $b \sim \delta^{m/2}$. Neglecting the terms of the order of $\delta^{m/2}$ in eqn. (20), one obtains the approximate expression for function U:

$$U(Y) = jy/\gamma \tag{24}$$

Substituting eqns. *(23)* and *(24)* into eqn. (17), one obtains the equation for function W:

$$\frac{d^2 W}{d y^2} = W - \bar{\beta} \left(\frac{jy}{\gamma} \right)^m \tag{25}$$

with boundary conditions

$$\left.\frac{dW}{dy}\right|_{y=0} = 0 \qquad W(0) = b\delta^{-m/2} \tag{26}$$

The general solution $W(y)$ of homogeneous eqn. (25) is

$$W = s_1 \exp(-y) + s_2 \exp(y) \tag{27}$$

The particular solution W of a non-homogeneous equation can be found by the method of constants variation. Summing up the general solution of a homogeneous equation with the particular solution of a non-homogeneous equation, one obtains the general solution of a non-homogeneous equation, that satisfies the $W'(0) = 0$ condition, in the form

$$W(y) = (\bar{\beta}/2)(j/\gamma)^m \left[e^y \int_y^\infty dt\, e^{-t} t^m + e^{-y} \int_0^y dt\, e^t t^m + m! \right] \tag{28}$$

where $m!$ is the factorial function. Using eqn. (28) and the second condition in eqn. (26), one finds the value $b = \bar{\beta}(j\sqrt{\delta}/\gamma)^m m!$. Substituting the latter one into eqn. (21), one obtains the equation for j:

$$j = j^0 - \delta^{m/2}\bar{\beta}(j/\gamma)^m m! \tag{29}$$

One may ignore the small difference between j and j^0 in the right-hand side of eqn. (28) and write down the approximate expression for dimensionless current in the form

$$j = j^0 - \delta^{m/2}\bar{\beta}(j^0/\gamma)^m m! \tag{30}$$

Thus, for low values of parameter $\sqrt{\delta}$, i.e. for hlgh dissociation rates, the limiting diffusion-migration current decreases proportionally to $\delta^{(v_1+v_2)/2}$.

THE CASE OF LOW REACTION RATES $\delta \gg 1$

In this case the solution can be sought in the form of expansion in powers of small parameter δ^{-1}:

$$c_1 = X + \delta^{-1}Y \tag{31}$$

where X, Y are functions of the order of unity. Substituting this expansion into eqn. (17), taking into account eqn. (16) and equating the terms at δ, one gets

$$\frac{d^2X}{dx^2} = 0 \tag{32}$$

After satisfying the boundary conditions (18) and (19) one obtains from the last equation the major part of the solution for c_1:

$$X = kx \tag{33}$$

To find Y, we equate the terms not containing δ and, substituting eqn. (33), we obtain

$$\gamma \frac{d^2 Y}{dx^2} = \bar{\beta}(kx)^m - (jx + k + l - j - \gamma kx) \tag{34}$$

Equations (20) and (21) were also taken into account in deriving eqn. (34). Function Y satisfies homogeneous boundary conditions:

$$Y(0) = 0 \qquad Y(l) = 0. \tag{35}$$

Integrating eqn. (34) using eqn. (35), one obtains

$$Y = \frac{1}{\gamma} \left[\frac{\bar{\beta} k^m (x^{m+2} - x)}{(m+2)(m+1)} + \frac{(\gamma k - j)(x^3 - x)}{6} + \frac{(j - k - l)(x^2 - x)}{2} \right] \tag{36}$$

This expression and the $j = dc_1/dx \,|_{x=0}$ condition give rise to the expression for a flux in case of low dissociation rates ($\delta \gg 1$):

$$j = k + \frac{1}{\delta \gamma} \left[\left(\frac{1}{2} - \frac{\gamma}{6} \right) k - \frac{l}{2} + \frac{\bar{\beta} k^m}{(m+2)(m+1)} \right] \tag{37}$$

The $j(\bar{\beta})$ dependence, given by eqn. (37), is determined mainly by the first term and represents a monotonically decreasing function.

THE NUMERICAL SOLUTION

The system of eqns. (16)–(19) has also been solved numerically for some intermediate δ values by using the Runge–Kutta method and the optimization procedure of searching for the j value satisfying the boundary conditions.

Fig. 4 shows the $j(\log \bar{\beta})$ dependences, calculated by numerical solution of the problem for some values of parameter δ. As follows from numerical calculations and from the results of an approximate analytical solution of the problem, the limiting current of reduction of cations decreases as parameter δ grows.

CONCLUSION

The above investigation shows that the limiting current in a partially dissociated binary electrolyte depends, first, on the electrolyte dissociation rate constant and, second, on the equilibrium constant. Analytical eqns. (30) and (37) for limiting current, obtained for the cases of high and low ($\delta \ll 1, \delta \gg 1$) electrolyte dissociation rate constants, allow the determination of the equilibrium constant β from experimental values of i and k_2. For intermediate δ values constant β can be determined by using the family of curves $j(\log \bar{\beta})$ obtained by numerical solution of the problem. In the $\delta \to 0$ limit the calculated $j(\beta)$ dependence transforms into the formula for j obtained in ref. 5. For low values of the dissociation rate constant ($\delta \gg 1$) the value of limiting diffusion-migration current is determined mainly by the value of equilibrium concentration of electroactive cations in the solution.

Note, in conclusion, that by changing the concentration C^0 in the solution, one can vary the value of parameter $\bar{\beta}$, which is proportional to $(C^0)^{m-1}$, whereas the value of parameter δ does not depend on C^0. This allows, in principle, for the dissociation rate constant k_1 and the reverse recombination reaction rate constant k_2 to be found from comparison of the experimental dependence of the limiting current on concentration C^0 and calculated $\mathbf{j}(\ln \bar{\beta})$ curves for different values of δ.

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