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Theory of the effect of migration current exaltation taking into account dissociation-recombination reactions

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Abstract

The influence of the recombination process of OH^- and H^+ ions on the migration current exaltation effect, which has been observed during the parallel reduction of cations and the neutral substance [1,2], is considered here. It is shown that qualitatively different types of behavior of the system studied are possible depending on the ratio of concentrations of discharging cations and H^+ ions in the solution. It is found that under certain conditions in acid solutions an unusual limiting diffusion-migration current of cation discharge may be observed due to the falling off to zero of the cation concentration within the diffusion layer. For neutral solutions, approximate analytical solutions and numerical solutions of the corresponding system of electrodiffusion equations are obtained. It is shown that for real values of the water dissociation-recombination equilibrium constant, due account of the recombination process leads to a relatively small correction in the theory of the migration current exaltation effect developed in refs. 3-6.

(1) INTRODUCTION

The increase of the limiting current of the cation reduction reaction during the simultaneous reduction of the neutral substance was first discovered experimentally in 1936 by Kemula and Michalski [1] and was called the effect of migration current exaltation. Quantitative study of the migration current exaltation effect was conducted by Heyrovsky and Bures [2]. The irreversible reduction of Na^+ ions from dilute NaCl solutions was studied. First, the polarographic wave corresponding to the discharge of Na^+ ions was recorded, then the solution was saturated with oxygen from the air, and a new polarographic wave was recorded. The limiting current in the second case was higher than the sum of the oxygen reduction current and the limiting current of Na^+ reduction in the absence of oxygen.

In refs. 3–6 a theory of the exaltation effect was put forward which takes account of the fact that as a consequence of the reaction of the neutral substance reduction (of O_2 , for instance) which proceeds in parallel with the reaction



of A^{z_1+} cation discharge, there may appear negatively charged products (OH^- , for instance) in the diffusion layer:



These substances may be absent in the bulk solution, but nevertheless the system of electrodiffusion equations describing parallel processes must include the equation for the aforementioned anions. The dependence of the density of the limiting current of Na^+ cation reduction, i_1' , upon the density of the neutral substance reduction current i_2 equals [4]

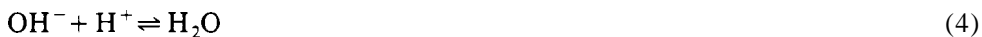
$$i_1' = \frac{z_1 + z_2}{z_2} \frac{FD_1c^0}{L} + \frac{D_1z_1}{D_3z_3} i_2 \quad (3)$$

where D_1 , z_1 and D_3 , z_3 are the diffusion coefficients and the absolute values of the charges of the cations and of the products of reduction of the neutral substance respectively, z_2 is the absolute value of the anion's charge, c^0 is the concentration of cations in the bulk electrolyte, L stands for the thickness of the Nernst diffusion layer, and F is the Faraday constant.

It follows from eqn. (3) that the limiting current of the cation discharge rises linearly with the increase of the neutral substance reduction current.

Equation (3) was first derived in refs. 3 and 4 within the frame of the model of stationary processes of cation reduction and parallel reduction of neutral substances and using the approximation of the Nernst diffusion layer model. These approximations are well justified for the case of the rotating disk electrode. In ref. 5 the effect of migration current exaltation was analyzed numerically for the case of a growing mercury drop electrode. This analysis took into account explicitly convective transport of ions as well as transport by diffusion and migration and also the non-stationary nature of the process due to the growth of the drop. The results of ref. 5 were found to be in good agreement with the theory developed in refs. 3 and 4, thus demonstrating the possibility of using the Nernst diffusion layer model for describing the migration current exaltation effect in classical polarography.

In constructing the theory of the migration current exaltation effect, it was assumed that there are no neutral substance reduction products (in the case at issue, OH^-) in the bulk solution. Besides, the existence of H^+ cations was also ignored which may emerge as a result of the water dissociation–recombination homogeneous reaction



The present paper presents a theoretical analysis of the parallel processes of reduction of cations and of the oxygen dissolved in water for arbitrary values of pH of the solution. OH^- anions, generated during the reduction of O_2 , enter into the

diffusion layer where they undergo a recombination reaction with H^+ cations. If the concentration of H^+ cations in the solution is not high, then we may expect that the resultant process will be fairly similar to the process which takes place in the migration current exaltation effect. In the reverse limiting case, when the concentration of H^+ ions in the solution is high, one may expect that practically all OH^- ions will react with H^+ in the immediate vicinity of the electrode's surface, so that the resultant reaction of oxygen reduction becomes



Here we have the parallel reduction of cations of the solution and of H^+ cations, which is described by the theory of the effect of migration current correlation exaltation [7].

For intermediate concentrations of H^+ cations in the solution, a transition is expected from the situation described by the migration current exaltation effect to the situation corresponding to the effect of migration current correlation exaltation.

(2) GENERAL FORMULATION OF THE PROBLEM

For simplicity, we will suppose that all ions in the system are singly charged. The results obtained below may easily be generalized to any system of ions having equal absolute charges.

The system of electrodiffusion equations describing parallel reduction of A^+ cations according to eqn. (1) and reduction of oxygen in eqn. (2) with the subsequent recombination (eqn. 4) within the Nernst diffusion layer, is given by

$$\frac{dc_1}{dx} + c_1 \frac{d\Psi}{dx} = \frac{i_1 L}{FD_1 c^0} = j_1 \quad (6)$$

$$\frac{dc_2}{dx} - c_2 \frac{d\Psi}{dx} = 0 \quad (7)$$

$$\frac{d^2 c_3}{dx^2} - \frac{d}{dx} \left(c_3 \frac{d\Psi}{dx} \right) = \frac{L^2 c^0}{D_3} \left(k_2 c_3 c_4 - k_1 / (c^0)^2 \right) \quad (8)$$

$$\frac{d^2 c_4}{dx^2} + \frac{d}{dx} \left(c_4 \frac{d\Psi}{dx} \right) = \frac{L^2 c^0}{D_4} \left(k_2 c_3 c_4 - k_1 / (c^0)^2 \right) \quad (9)$$

$$c_2 + c_3 = c_1 + c_4 \quad (10)$$

Here, c_1 , c_2 , c_3 and c_4 are the concentrations of cations, anions, OH^- ions and H^+ ions, respectively, divided by c^0 , being the concentration of A^+ cations in the bulk solution; $\Psi = F\phi/RT$ is the dimensionless electric potential; x is a dimensionless coordinate ($0 < x < 1$); i_1 stands for the cation discharge current density; k_2 is the rate constant of H^+ and OH^- recombination; k_1 is the water dissociation reaction rate constant; all other notations are standard. Equation (10) expresses the condition of local electroneutrality.

The boundary conditions at $\mathbf{x} = 1$ (the boundary between the diffusion layer and bulk solution) are as follows:

$$c_1(1) = 1, \quad c_2(1) = 1 + k - m, \quad c_3(1) = m, \quad c_4(1) = k, \quad \Psi(1) = 0 \quad (11)$$

Combining eqns. (8) and (9), one can obtain

$$D_3 \left(\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} \right) - D_4 \left(\frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} \right) = - \frac{i_2 L}{F c^0} = - D_3 j_2 \quad (12)$$

where i_2 is the oxygen reduction current density, and j_2 is the corresponding dimensionless flux.

The current of the neutral substance reduction (in this case, of O_2) does not depend on the rate of reduction of other substances and is specified only by the concentration of O_2 in the stirred part of the solution. Therefore, the value of the current density i_2 in the problem in question may be considered as a given external parameter.

The values of the constants k_1 and k_2 under normal conditions are [8] $k_1 = 2.5 \times 10^{-5} \text{ s}^{-1}$ and $k_2 = 1.4 \times 10^{11} \text{ l}^2 \text{ mol}^{-1} \text{ s}^{-1}$. Therefore, provided that reaction (4) proceeds mainly in the direction of H^+ and OH^- ion recombination, this reaction may be considered fast compared with the diffusion-migration transport of ions. Thus, we can assume that equilibrium is maintained within the diffusion layer:

$$c_3 c_4 = k_1 / k_2 (c^0)^2 \equiv \epsilon^2 \quad (13)$$

where ϵ^2 stands for the equilibrium constant of reaction (4) reduced to the dimensionless form by dividing it by the square of the concentration of discharging cations in the bulk solution. For a typical value for c^0 of 0.1 M and the values of k_1 and k_2 given above, $\epsilon^2 \approx 1.3 \times 10^{-14} \ll 1$.

Therefore, the initial system of electrodiffusion equations is reduced to the system of three equations (eqns. 6, 7 and 12), two algebraic relations (eqns. 10 and 13), and the boundary conditions (eqn. 11). This system, generally, does not have an analytical solution, and so, to solve it, additional simplifications are needed. Thus, in section 3 below it is supposed that $\epsilon = 0$. In sections 4–6 ϵ is assumed to be small, $\epsilon \ll 1$, but non-zero. The results of section 4 are valid for the case of small currents, $j_i \ll 1$, and those of section 6 pertain to the case of strong currents, $j_i > 2$. In section 5, the general solution of the initial system (eqns. 6, 7, 10–13) is presented for the case of neutral solution, and in section 7 the results of numerical integration of the system of equations are described.

(3) THE MIGRATION CURRENT EXALTATION EFFECT IN ACID SOLUTIONS

As stated in section 2, the value of the equilibrium constant is $\epsilon^2 \ll 1$ and thus we can put $\epsilon^2 \equiv 0$ with high accuracy. This enables us to use the approximate equality $c_3 c_4 \approx 0$ instead of eqn. (13), which means that at any point within the diffusion layer, in the zero-order approximation, there exist either OH^- ions or H^+ ions but not both kinds of ion together. Since we are studying an acid medium, we

have to set the value of m , corresponding to the concentration of OH^- ions in the bulk solution, equal to zero in the boundary conditions (eqn. 11).

Thus, the diffusion layer is divided by the point $x = \theta$ of H^+ and OH^- ion recombination into two regions: $0 \leq x \leq \theta$ and $\theta \leq x \leq l$. In the region to the right of $x = \theta$ we can assume $c_4 > 0$ and $c_3 \approx 0$, and in the region to the left of $x = \theta$ we may put $c_3 > 0$ and $c_4 \approx 0$. These approximations make it possible to go from eqns. (12) and (13) to the following two equations:

$$\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} = -\frac{i_2 L}{FD_3 c^0} = -j_2 \quad 0 < x < \theta \quad (14)$$

$$\frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} = \frac{i_2 L}{FD_4 c^0} = j_2 \nu \quad \theta < x < l \quad (15)$$

where $\nu = D_3/D_4$. Note that the dimensionless fluxes j_1 and j_2 , introduced in eqns. (6) and (14), are positive.

This way the initial electrodiffusion system of eqns. (6)–(9) is split into two simpler systems of first order equations. In the region $0 \leq x \leq \theta$, the system is given by eqns. (6), (7), (14) and (10) and coincides with the system of equations used for the description of the migration current exaltation effect. In the region $\theta \leq x \leq l$, the system is given by eqns. (6), (7), (15) and (10) and coincides with the system of equations used for the description of the migration current correlation exaltation effect.

At the point $x = \theta$ all concentrations c_i must be continuous. The point θ itself must be found simultaneously with the solution of the system of electrodiffusion equations. In accordance with the aforesaid, its position should depend on the values of the currents i_1 and i_2 as well as on the parameters ν and k , i.e. on the value of the concentration of H^+ ions in the solution. It is reasonable to expect that with the increase of the latter the point $x = \theta$ will come nearer to the electrode, and for sufficiently high concentrations of H^+ , when reaction (1) is replaced by reaction (2), θ falls off to zero.

We begin our investigation with the case when the point $x = \theta$ lies within the interval $(0, l)$.

Let us find the concentration distributions $c_1(x)$, $c_2(x)$, $c_3(x)$, and $c_4(x)$ in each of the regions $0 \leq x \leq \theta$ and $\theta \leq x \leq l$.

The concentration $c_2(x)$ in the region $\theta \leq x \leq l$ may be obtained easily by addition and subsequent integration of eqns. (6), (7) and (10) with due account of the boundary conditions (eqn. 11):

$$c_2 = (j_1 + \nu j_2)(x - l)/2 + 1 + k \quad (16)$$

Owing to (eqn. 16), from eqn. (7) we find

$$\frac{d\psi}{dx} = -\frac{j_1 + \nu j_2}{2(1 + k) + (j_1 + \nu j_2)(x - l)} \quad (17)$$

Substituting eqn. (17) into eqn. (6) and then integrating the linear equation thus obtained, with eqn. (11) in view, we find the distribution of cations $c_1(x)$ in the region $\theta \leq x \leq 1$:

$$c_1 = \frac{1 - j_1(1+k)/(j_1 + \nu j_2)}{(x-1)(j_1 + \nu j_2)/2(1+k) + 1} + \frac{j_1(1+k)}{j_1 + \nu j_2} \left[(x-1) \frac{j_1 + \nu j_2}{2(1+k)} + 1 \right] \quad (18)$$

The concentration $c_4(x)$ in this region follows from the electroneutrality condition (eqn. 10) and the condition $c_3(x > \theta) = 0$.

For $x = \theta$, the concentrations c_1 and c_2 , given by eqns. (16) and (18), take equal values, according to the above-mentioned condition $c_3(\theta) = c_4(\theta) = 0$,

$$c_1(\theta) = G, \quad c_2(\theta) = G \quad (19)$$

When finding the concentration distributions $c_i(x)$ in the region $0 \leq x \leq \theta$, we will use the continuity relations

$$c_1(\theta - 0) = c_1(\theta + 0) = G, \quad c_2(\theta - 0) = c_2(\theta + 0) = G \quad (20)$$

as the boundary conditions at $x = \theta$. The two eqns. (19) make up a system of equations from which we can determine the unknown θ and G :

$$G = \sqrt{(1+k)(1 - j_1 k / \nu j_2)} \quad (21)$$

$$\theta = 1 - 2(1+k) \left[1 - \sqrt{(1 - j_1 k / \nu j_2) / (1+k)} \right] / (j_1 + \nu j_2) \quad (22)$$

The solution of the system of eqns. (6), (7), (10) and (14) in the region $0 \leq x \leq \theta$ with the boundary conditions (eqn. 10) may be found in a similar way to that used in ref. 3, and is given by the following expressions:

$$c_1 = (j_1 - j_2)(x - \theta) / 2 + \quad (23)$$

$$\frac{d\Psi}{dx} = \frac{j_1 + j_2}{(j_1 - j_2)(x - \theta) + 2G} \quad (24)$$

$$c_2 = G \left[(j_1 - j_2)(x - \theta) / 2G + 1 \right]^{(j_1 + j_2) / (j_1 - j_2)} \quad (25)$$

The concentration distributions for all components and for the potential in the whole region $0 \leq x \leq 1$ is given by eqns. (16)-(18), (20)-(25) and (10), provided that the conditions

$$\nu j_2 > k j_1 \quad 0 \leq \theta \leq 1 \quad (26)$$

$$c_1(x) \geq 0 \quad \text{for } 0 \leq x \leq 1 \quad (27)$$

are fulfilled.

Note that the fulfillment of condition (26) is necessary for the existence of G (see eqn. 21) as well as of θ (see eqn. 22). One can readily make sure that the condition $\theta \leq 1$ does not impose any additional restrictions on the parameters ν , k , j_1 and j_2 . Given by eqn. (22), the value of θ generally decreases with the increase of j_1 for fixed j_2 . The condition $\theta = 0$ leads to the following relation between j_1 and j_2 :

$$j_1 = \nu j_2 \left(1 - (1+k)(2k/\nu j_2 - 1)^2 \right) / k \quad (28)$$

Proper account of inequality (26) leads to the fact that j_1 in eqn. (28) may vary in the range $0 \leq j_1 \leq 2$. Meanwhile, the value of νj_2 in eqn. (28) may vary from $\nu j_2 = 2\sqrt{1+k}(\sqrt{1+ik}-1)$ for $j_1 = 0$ to $\nu j_2 = 2k$ for $j_1 = 2$. On the plane (j_2, j_1) , region I (Fig. 1) corresponds to the condition $0 < \theta \leq 1$, and lies to the right of the curve $j_1(j_2)$ specified by eqn. (28) and below the straight line $j_1 = \nu j_2/k$ (see eqn. 26) which conforms with the condition $G = 0$.

Let us now consider more closely the situation when the oxygen reduction reaction proceeds according to eqn. (5), and the diffusion layer does not contain OH^- anions. There, in the whole region $0 \leq x \leq 1$, the distributions c_1, c_2, c_4 and Ψ are described by eqns. (6), (7), (15) and (10) and the boundary conditions (eqn. 11), the solutions of which are given by eqns. (16), (18) and (10). The values of surface concentrations $c_1(0)$ and $c_4(0)$ both depend on the parameters ν and k , and the values of the currents j_1 and j_2 . In accord with the generally accepted definition of limiting current, we shall assume that the condition $c_1(0) = 0$ corresponds to the cation reduction limiting current j_1^c . This current depends on the current j_2 of the parallel oxygen reduction reaction. The dependence of j_1^c on j_2 follows from eqn. (18) and the condition $c_1(0) = 0$, and is given [4] by the expression

$$j_1^c = \frac{2(1+k)}{1+\nu j_2/j_1^c} \left(1 - \sqrt{\frac{k-\nu j_2/j_1^c}{1+k}} \right) \quad (29)$$

and is presented in Fig. 1. The curve $j_1^c(j_2)$ emerges at $j_2 = 0$ from the point

$$j_1^c = 2(1+k) \left(1 - \sqrt{1-1/(1+k)} \right)$$

corresponding to Eucken's formula [9], and when $\nu j_2/k = 2$ it passes through the point Q, where $j_1^c = 2$, where it joins the curve (eqn. 28), and becomes the straight line $j_1 = \nu j_2/k$. For $j_1 < j_1^c$ and $c_4(0) > 0$ the system's behavior corresponds to region II on the plane (j_1, j_2) (Fig. 1). When the flux j_1 is constant and the flux j_2 increases the concentration $c_4(0)$ diminishes (see Fig. 2, curves 1 and 2). When the condition $c_4(0) = 0$ is satisfied, which, as one can readily verify, coincides with the condition $\theta = 0$ (see Fig. 2, curve 3), we come to the right-hand boundary of region II specified by eqn. (28). We lay emphasis on the fact that turning $c_4(0)$ to zero does not imply the appearance of the limiting current of the oxygen reduction reaction, but corresponds to the switch of the electrode reaction mechanism from eqn. (5) to eqns. (2) and (4). On further rise of j_2 in region I the point $x = \theta$, given by eqn. (22), is shifted to the right (curves 4 and 5 in Fig. 2), and in the region $0 < x < \theta$ OH^- ions generated on the electrode are spread.

Turning back to the investigation of region I in Fig. 1, let us analyze the trend of the change of the cations concentration $c_1(x)$ when the current j_1 of the reduction reaction changes and the flux j_2 is fixed.

For $j_1 = 0$ the concentration $c_1(x)$ decreases linearly with the increase of x in the region $0 \leq x \leq \theta$ and keeps falling in the region $\theta \leq x \leq 1$. Upon increase of the flux j_1 , the concentration $c_1(x)$ in the region $0 \leq x \leq \theta$ still changes linearly, and $c_1(0)$ and $c_1(\theta) = G$ diminish with rising j_1 . For sufficiently high values of $j_1 > \nu j_2/(1+k)$

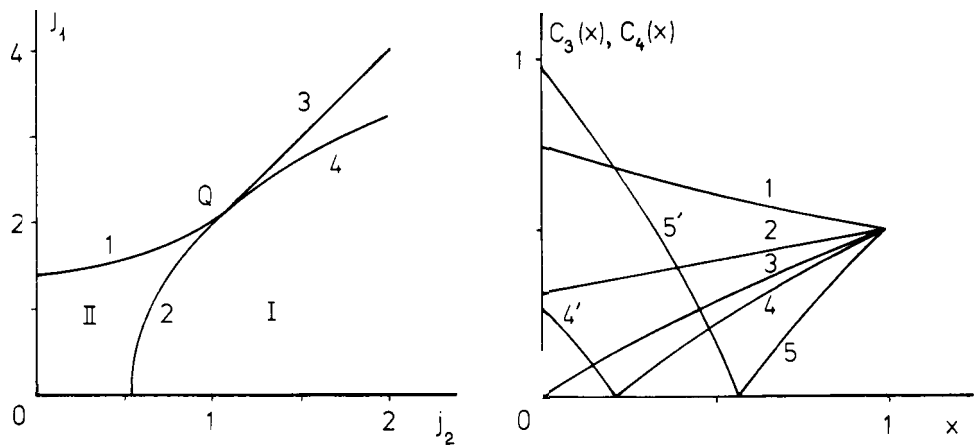


Fig. 1. Lay-out of regions of different behavior of the system on the plane j_1, j_2 for $k < \nu$. (1) curve $j_1^e(j_2)$ described by eqn. (29), (2) curve $\theta = 0$ described by eqn. (28), (3) curve $G = 0$ described by eqn. (21). (4) curve $j_1^{e0}(j_2)$ described by eqn. (31).

Fig. 2. Distribution of the concentrations $c_4(x)$ (curves 1-5) and $c_3(x)$ (curves 4', 5'). Curves 1 and 2 correspond to region II, curves 4, 4', 5, 5' correspond to region I, curve 3 corresponds to the condition $\theta = 0$.

$2k$), there appears a minimum for $x = \theta^*$ on the curve of $c_1(x)$ dependence in the region $\theta \leq x \leq 1$ (see Fig. 3a), which is determined by the expression

$$\theta^* = 1 - 2(1+k) \left[1 - \sqrt{(\nu j_2 - j_1 k) / (j_1(1+k))} \right] / (j_1 + \nu j_2)$$

Upon further increase of j_1 a situation may arise (for $j_1 > j_2$) where $c_1(0)$ becomes less than G (see Fig. 3b). The condition $c_1(0) = 0$, where c_1 is given by eqn. (23), conforms with the conventional definition of the limiting current j_1^{e0} of cation discharge and leads to the following relation:

$$j_1^{e0} = 2 \left[1 + k + J(\nu + 1) \sqrt{(1 - k/(\nu J))(1+k)} / (1 - J) \right] / (1 + \nu J) \quad (30)$$

where the value of $J = j_2/j_1^{e0}$ is bounded by the inequality $J < 1$ which, together with condition (25), is realized in the case $k < \nu$. The dependence $j_1^{e0}(j_2)$, described by eqn. (30) for $k < \nu$, is shown in Fig. 1. We stress that the curve $j_1^{e0}(j_2)$ for $k < \nu$ lies beneath the straight line $j_2 = k j_1 / \nu$, that corresponds to the condition $G = 0$, and, therefore, that the curve $j_1^{e0}(j_2)$ serves as the upper boundary of region I in which there exists a solution with $0 \leq \theta \leq 1$. It begins at the point Q in Fig. 1 and for $j_2 \gg 1$ approaches the straight line $j_1^{e0} = j_2 + 2\sqrt{(1+k)(1-k\nu)}$ asymptotically. The concentration distributions for all components, corresponding to the condition $c_1(0) = 0$ and eqn. (30), are presented in Fig. 3c.

For $k > \nu$, the concentration $c_1(0)$ does not vanish for any values of j_1 and j_2 . The increase of j_1 when j_2 is fixed leads to the advanced decrease of $c_1(\theta) = G$ in

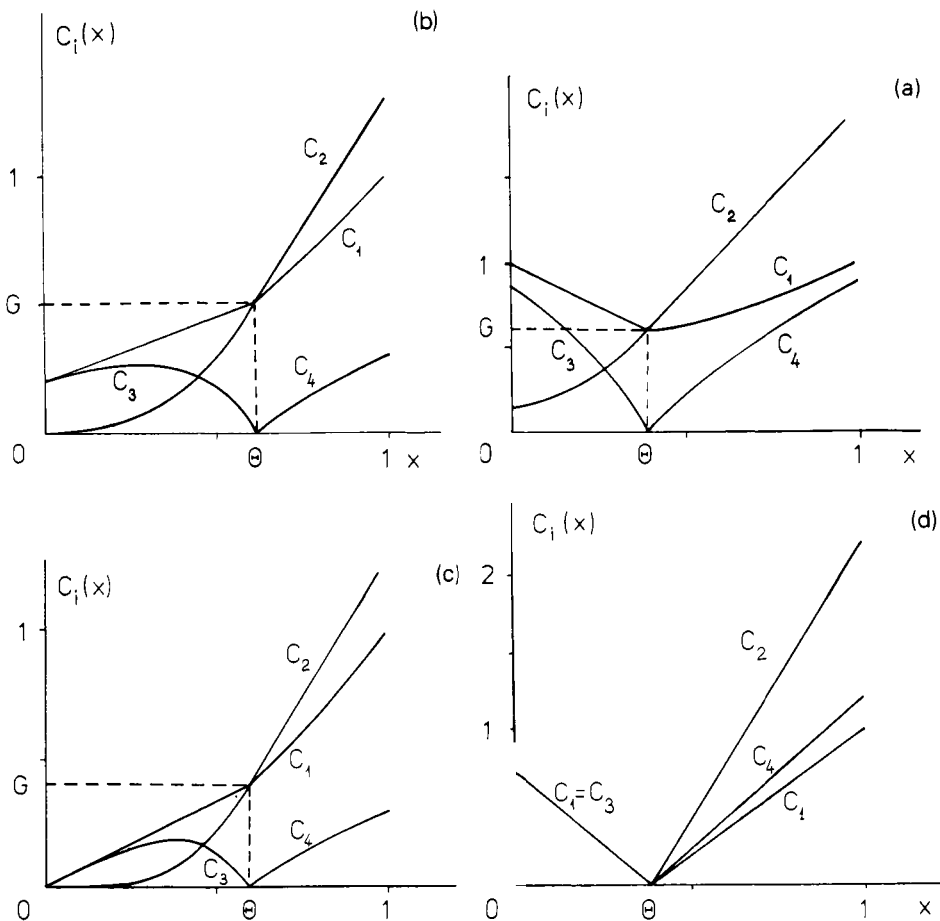


Fig. 3. Different types of distribution of the concentrations of ionic components, corresponding to region I in Figs. 1a and 1b. (a) the current j_1 is less than the limiting current and $c_1(0) > G$; (b) the current j_1 is less than the limiting current and $c_1(0) < G$; (c) the current j_1 is equal to the limiting current provided that $c_1(0) = 0$; (d) the current j_1 is equal to the limiting current provided that $c_1(\tilde{\theta}) = 0$.

comparison with $c_1(0)$. At the same time the value $x = \theta^*$, where $c_1(x)$ has a minimum, approaches to $x = \theta$ and for sufficiently high values of $j = j_1^{e\theta}$ the point θ^* merges with θ , and $c(\theta^*) = G$ becomes zero. This occurs for $j_1 =$ and $\theta \equiv \theta$:

$$j_1^{e\theta} = \nu j_2 / k \quad (31)$$

$$\tilde{\theta} = \theta^* = 1 - 2/j_1^{e\theta} = 1 - 2k/\nu j_2 \quad (32)$$

In this case region I is bounded by the conditions $G = 0$ and $\theta = 0$.

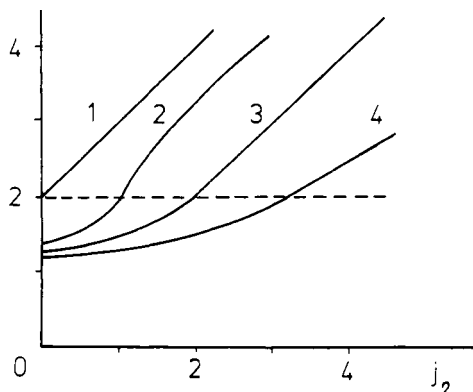


Fig. 4. The limiting current j_1^e of cation discharge as a function of the current j_2 : (1) $k = 0$; (2) $0 < k < \nu$; (3) $k = \nu$; (4) $k > \nu$.

The following formulas for the ion concentration distributions and electric field correspond to the situation when $c_1(\theta) = G = 0$:

$$c_1 = (x - \tilde{\theta}) / (1 - \tilde{\theta}), \quad c_2 = (1 + k)c_1, \quad c_3 = 0, \quad c_4 = kc_1, \quad (33)$$

$$d\Psi/dx = -1/(x - \tilde{\theta}) \quad \text{for } x > \tilde{\theta}$$

$$c_1 = c_3 = j_2(1 - \nu/k)(\tilde{\theta} - x)/2, \quad c_2 = c_4 = 0, \quad (34)$$

$$d\Psi/dx = -(k + \nu) / [(k - \nu)(\tilde{\theta} - x)] \quad \text{for } x < \tilde{\theta}$$

which follow from eqns. (16)-(18) and (23)-(25).

Note that there are no salt anions in the region $0 < x < \tilde{\theta}$ for $j_2 = j_1^{e0}$, i.e., the solution is a binary electrolyte that consists of discharging cations and OH^- anions generated on the electrode. Concentration distributions (33) and (34) are shown in Fig. 3d.

Dependences of the cation discharge limiting current on the oxygen reduction current for different values of k and ν are given in Fig. 4. For j_2 such that $j_1^e < 2$, the dependences $j_1^e(j_2)$ follow from the formulas of the theory of the migration current correlation exaltation. Further behavior of j_1^e is determined by the ratio of k and ν . For $k \geq \nu$ (curves 3 and 4) j_1^e depends linearly on j_2 , in accordance with eqn. (31). For $0 < k < \nu$ (curve 2) j_1^e is given by eqn. (30).

When the ratio k/ν goes to zero, the point Q in Figs. 1 and 4 tends to the vertical axis along the horizontal line $j_1 = 2$. The curve j_1^{e0} merges with the straight line $j_1^{e0} = j_2 + 2$ which corresponds to the theory of the migration current exaltation effect [3].

When the medium in the bulk solution is not acid but alkaline, k in the boundary condition must be set equal to zero: $k = 0, m > 0$. Concentration distribu-

tions throughout the diffusion layer are given by eqns. (6), (7), (10) and (14) and the boundary conditions (II). It can be shown easily that the limiting current j_1^c of cation discharge is given by the same relation as for a neutral medium ($k = 0$), $j_1^{c0} = j_2 + 2$, and it does not depend on the concentration of OH^- ions in the bulk solution.

Thus, in the system considered we have found an unusual behavior of the concentration of discharging cations within the diffusion layer. The concentration profile $c_1(x)$ under certain conditions has a minimum, and this makes it possible for c_1 to become zero for a certain value $x = \tilde{\theta}$ within the diffusion layer. Such behavior of c_1 is due to the great influence of two factors upon the process of cation feed to the electrode: first, the parallel process of oxygen reduction and, second, the homogeneous reaction of OH^- and H^+ ions recombination within the diffusion layer.

The generalized condition of the generation of limiting current in the system at issue is given by

$$c_1(x) = 0 \quad 0 \leq x < 1 \quad (35)$$

and, as the conducted investigation shows, may be realized both at the electrode surface $x = 0$ and, "breaking off" from the electrode and going into the diffusion layer, at the point $x = \tilde{\theta} < 1$.

Note that for $\nu \neq 1$ (i.e. $D_3 \neq D_4$), in the region $x \approx \theta$ where the reaction of OH^- and H^+ ion recombination proceeds, an abrupt change of the values of the electric field E and of dE/dx takes place. In this region, as predicted by the Poisson equation, anomalies in the spread of space charge must be observed. In particular, when $G = c_1(\theta)$ tends to zero, a sharp peak of space charge is formed within the diffusion layer. The possibility of forming a space charge peak upon the electric current flow was predicted for systems which, apart from mobile charges, also have fixed charges [10-11].

(4) CORRECTIONS TO THE DIFFUSION-MIGRATION CURRENT j_1 OF CATION REDUCTION IN THE CASE OF SMALL CURRENTS j_2

The investigation carried out in the previous section essentially used the condition that the rate of H^+ and OH^- in recombination is rather high and, hence, that the reaction zone lies near the point $x = \theta$. Besides, the approximation of small dissociation constant, $\epsilon^2 \approx 0$, was used. This has led to the fact that at the point θ the concentrations c_3 and c_4 tend to zero, and other concentrations have a kink. In a stricter statement of the problem which uses relation (13), the concentrations fall down not to zero but to rather small values of the order of ϵ , and the profiles of all the concentrations retain their smoothness. Although all the salient features of the distributions of ionic components revealed remain valid, to make a comprehensive picture of the process, it is desirable to determine the concentration distributions for small but finite values of $\epsilon \ll 1$.

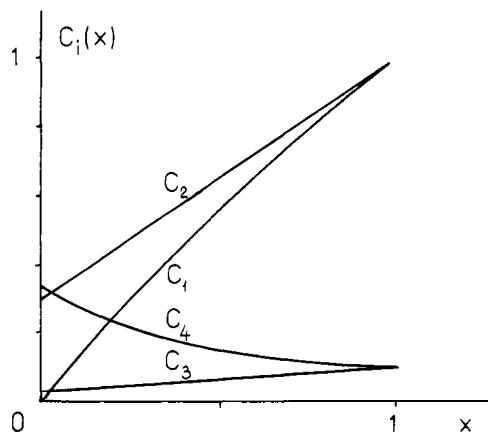


Fig. 5. Distribution of the component concentrations given by eqns. (10), (41) and (42) for $j_2 = 0$ and $\epsilon = 0.1$.

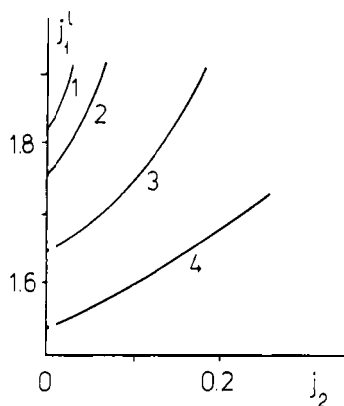


Fig. 6. The limiting current j_1^e as a function of j_2 for $j_2 \ll 1$ and for (1) $\epsilon = 0.01$; (2) $\epsilon = 0.02$; (3) $\epsilon = 0.05$; (4) $\epsilon = 0.1$.

In this section and sections to follow, we will confine ourselves to the case of neutral solutions, $c_3(1) = c_4(1)$, wherefrom, through the use of relation (13), we can write the boundary conditions (11) as

$$c_1(1) = c_2(1) = 1, \quad c_3(1) = c_4(1) = \epsilon, \quad \Psi(1) = 0 \quad (37)$$

Apart from that, we will concern ourselves with the case of the cation limiting current:

$$c_1(0) = 0 \quad (38)$$

First, let us find the solution corresponding to $j_2 = 0$. Substituting eqn. (13) into eqn. (12) and making some simple transformations, we find that in this case there occurs neither the H^+ cation transfer nor the transfer of OH^- :

$$\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} = 0 \quad (39)$$

$$\frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} = 0 \quad (40)$$

Adding together eqns. (7) and (39) and introducing the overall concentration of anions, we come to Eucken's problem [9]. The concentration distributions are shown in Fig. 5. The potential Ψ is a logarithmic function of the distance x :

$$e^\Psi = 1 + j_1(x-1)/(1+\epsilon) \quad (41)$$

and the concentrations c_2 and c_3 decrease linearly on approaching the electrode:

$$c_2 = e^\Psi \quad c_3 = \epsilon e^\Psi \quad (42)$$

but they do not take zero values at the electrode: $c_2(0) \approx \sqrt{\epsilon}$, $c_3(0) \approx \epsilon^{3/2}$. Note that

for the system in question this is a general rule: the concentrations of all components, except c_1 , cannot simultaneously become zero at the electrode in the limiting current regime owing to condition (11). This leads us to the fact that the gradient of the potential and the potential itself are also finite, as follows from eqn. (7). Thus, in the system under consideration, with due account of dissociation, there is no logarithmic divergence of the potential which is typical for calculations of the limiting current in electrodiffusion problems.

Since it follows from eqns. (13) and (42) that $c_4 = \epsilon e^{-\Psi}$, the inequalities

$$c_3 \ll c_4 \quad (43)$$

$$c_3, c_4 \ll c_1, c_2 \quad (44)$$

hold true practically throughout the whole diffusion layer. The value of the limiting current is given by Eucken's formula in the form

$$j_1 = 2(1 + \epsilon) \left(1 - \sqrt{\epsilon / (1 + \epsilon)} \right) \quad (45)$$

Let us now find the solution for small but non-zero values of j_2 such that inequalities (43) and (44) still hold. Neglecting c_3 in eqn. (12) in comparison with c_4 , we may recast eqn. (12) as

$$\frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} = \nu j_2 \quad (46)$$

By introducing the overall concentration of anions we reduce this problem to the problem of the discharge of two kinds of cation c_1 and c_4 against the motionless background of anions, that is to the problem of the migration current correlation exaltation resolved in refs. 4 and 7. The corresponding dependence of the limiting current j_1 upon j_2 is

$$j_1 = 2(1 + \epsilon) - \nu j_2 / 2 - \sqrt{4(1 + \epsilon)(\epsilon - \nu j_2 / 2) + (\nu j_2 / 2)^2} \quad (47)$$

The curves $j_1(j_2)$ described by eqn. (47) for $j_2 \ll 1$ and a number of different values of ϵ are presented in Fig. 6. When $j_2 = 0$, eqn. (47) changes into eqn. (45). We stress that, according to eqns. (45) and (47), the limiting current j_1 is reduced by a factor proportional to $\epsilon^{1/2}$ when recombination of OH^- and H^+ ions is taken into consideration.

Let us now proceed to the description of the general solution of the full system of equations without a prior assumption that ϵ is small.

(5) GENERAL SOLUTION OF THE PROBLEM FOR $j_2 \neq 0$

Our goal is to calculate the value of the limiting current j_1 , from the system of three differential equations (eqns. 6, 7 and 12), two algebraic equations (eqns. 10 and 13), and the boundary conditions (eqns. 38 and 39).

By substituting eqns. (10) and (12) into condition (13) we can eliminate the concentration c_4 :

$$\frac{dc_3}{dx} - c_3 \frac{d\psi}{dx} = -j_2 / \left(1 + \frac{\epsilon^2}{\nu c_3^2} \right) \quad (48)$$

$$c_1 + \epsilon^2/c_3 = c_2 + c_3 \quad (49)$$

When $r \rightarrow 0$, this system transforms into the system of equations from ref. 5 which takes no account of water dissociation and the solution of which leads to the expression for limiting currents (eqn. 3).

The right-hand side of eqn. (48) is a non-linear function of c_3 , and that is why the system of eqns. (6), (7), (48) and (49) cannot be reduced to a linear system by converting to a new independent variable Ψ , as was done in ref. 4. Therefore, the stated problem requires new methods of integration of the system of non-linear differential equations under consideration.

Eliminating $d\Psi/dx$ from eqns. (5) and (48) by means of eqn. (7), we obtain

$$\frac{dW}{dx} = j_1 c_2 \quad (50)$$

$$\frac{dV}{dx} = \frac{j_2 c_2}{c_3^2 + \epsilon^2/\nu} \quad (51)$$

where

$$W = c_1 c_2 \quad V = c_2 / c_3 \quad (52)$$

are dimensionless combinations of the concentrations. Expressing c_1 and c_2 in terms of c_3 , W and V from eqn. (52), and substituting them into eqn. (49), we can express c_3 in terms of W and V :

$$c_3^2 = \frac{W/V + \epsilon^2}{1 + V} \quad (53)$$

Thus, by means of eqns. (49), (52) and (53), the concentrations of all components of the solution are expressed in terms of W and V , and the system of eqns. (50) and (53) includes only the functions W and V in a fairly complicated way.

The boundary conditions for W and V take the form:

$$W|_{x=1} = 1, \quad V|_{x=1} = 1/\epsilon \quad (54)$$

$$W|_{x=0} = 0 \quad (55)$$

Dividing eqn. (50) by eqn. (51), we can convert to the independent variable V :

$$\frac{dW}{dV} - \frac{J}{(1+V)V} W = J\epsilon^2 \left(\frac{1}{1+V} + \frac{1}{\nu} \right) \quad (56)$$

where $J = j_1/j_2$. The derivation of eqn. (56) uses eqn. (53). Equation (56) is a first order linear non-homogeneous equation. Its solution satisfying the boundary conditions (54) for $x = 1$ may be written as

$$W(V) = W_0(V) \left[1 + \int_{1/\epsilon}^V J\epsilon^2 \left(\frac{1}{1+V'} + \frac{1}{\nu} \right) \frac{dV'}{W_0(V')} \right] \quad (57)$$

where $W_0(V)$ is the solution of the homogeneous equation satisfying the boundary conditions (54):

$$W_0(V) = \left[\frac{(1 + \epsilon)V}{1 + V} \right]^J \quad (58)$$

Thus we find $W(V)$, by means of which, through eqns. (52) and (53), we can obtain the concentration distributions for all components as functions of the independent variable V , provided that we already know J . To find J , it is necessary to use boundary condition (55). After the integration of eqn. (51) we have

$$j_2 = j_2 \int_0^1 dx = \int_{V^*}^{1/\epsilon} \frac{dV}{V} c_3 + \int_{V^*}^{1/\epsilon} \frac{dV}{V} \frac{\epsilon^2}{c_3 \nu} \quad (59)$$

Here, V^* is the value of V corresponding to $x = 0$, where, according to eqn. (55), $W(V^*) = 0$.

Since, as it is clear from (58), $W_0(V)$ does not vanish for positive V , the condition for finding V^* is that the expression between brackets in eqn. (57) is equal to zero:

$$\int_{V^*}^{1/\epsilon} \left(\frac{1}{1 + V'} + \frac{1}{\nu} \right) \frac{dV'}{W_0(V')} = \frac{1}{J\epsilon^2} \quad (60)$$

Thus we can determine the limits of integration (from eqns. 60 and 58) and the integrand (from eqns. 53, 57 and 58). Taking integrals in the right-hand side of eqn. (59) we get some function of the current ratio J in this right-hand side. Finally, from the equation obtained we can express j , as a function of j_2 and thus find the generalization of eqn. (3) for the case of migration current exaltation with proper account of recombination of H^+ and OH^- ions.

The procedure described makes it possible to find the solution of the stated problem by quadratures. In order to determine the relation between j_1 and j_2 , one has to take the integrals in eqns. (57), (59) and (60) analytically. For the integral in eqn. (57) this is possible only for some special values of J . (The integral in eqn. (57) may be taken only for integer and half-integer J , and the integral in the right-hand side of eqn. (59) cannot be taken analytically.) Below we give an approximate solution of the problem which uses the smallness of the parameter ϵ .

(6) APPROXIMATE SOLUTION FOR $1 < J < 2$

In order to find an approximate analytical solution of the problem we can make use of the smallness of the parameter ϵ : $\epsilon \ll 1$. Our goal is to find the correction term to the right-hand side of eqn. (3) as a function of both ϵ and j_2 . Viewing eqn. (3) as the zero-order approximation, we can say that the condition $J < 2$ corresponds to the currents $j_2 > 2$. The region $J > 2$ or $0 < j_2 < 2$ corresponds to the transition region from $j_2 = 0$ to $j_2 > 2$, where the correction terms have the intermediate values between the terms of the order of $\sqrt{\epsilon}$ for $j_2 = 0$ and the terms of the order of ϵ for $j_2 > 2$, as will be shown below. Note that the condition $J > 1$ or $j_1 > j_2$ is satisfied up to very large values of $j_2 = 1/\epsilon \geq 10^3$, i.e. in the whole range of

the parameter j_2 of interest to us. For $V \gg V^*$, up to the terms of the order of ϵ , we can write

$$W(V) = [1 + \epsilon J(1 - 1/\nu)] [V/(1 + \nu)]^J \quad (61)$$

and for $V > V^*$

$$W(V) = [1 + \epsilon J(1 - 1/\nu)](1 - JV)V [V^{J-1} - (V^*)^{J-1}] \quad (62)$$

where

$$(V^*)^{J-1} = J\epsilon^2(1 + 1/\nu)/(J - 1) \quad (63)$$

is small. Integrating eqn. (59) over $\ln V$, we replace the limits of integration by $\ln(1/\epsilon)$ and $\ln(V^*)$ which, unlike $1/\epsilon$ and V^* , can be considered to be of the order of unity. Therefore, the range of integration is of the order of unity. This corroborates our decision to leave in the integrand quantities of the order not lower than that of ϵ , for we are interested only in the first correction term to eqn. (3) in terms of ϵ . Substituting eqns. (61) and (63) into the right-hand side of eqn. (59) and integrating, we obtain an equation which gives the $j_1(j_2, \epsilon)$ dependence implicitly

$$j_1 = \frac{2}{J-1} - \frac{\epsilon}{J-1} f(J) \quad (64)$$

where

$$f(J) = \pi \sqrt{\frac{J(1 + 1/\nu)}{J-1}} + 1/\nu - 1 - \frac{1}{\nu} \left(\pi - 2 \operatorname{arccctg} \sqrt{\frac{J(1 + 1/\nu)}{J-1} - 1} \right) \\ \left/ \sqrt{\frac{J(1 + 1/\nu)}{J-1} - 1} \right. \quad (65)$$

The first term in the right-hand side of eqn. (64) corresponds to the zero-order approximation (eqn. 3), and the second term is a small correction. Therefore, eqn. (64) may be solved for j_1 by the successive approximation method. First, we find J in the zero-order approximation:

$$J^0 = (j_2 + 2)/j_2. \quad (66)$$

Multiplying eqn. (64) by $J - 1$ and substituting J^0 for J in the right-hand side of the equation obtained, we get

$$j_1 = 2 + j_2 - \epsilon f(J^0) \quad (67)$$

a final expression, which is the generalization of the result (eqn. 3) obtained earlier. The dependence $j_1(j_2)$ described by eqn. (67) is presented in Fig. 7 together with the function (eqn. 3).

(7) NUMERICAL SOLUTION OF THE PROBLEM

The system of eqns. (50) and (51) with the boundary conditions (54) and (55) was also solved by numerical integration. The algorithm was as follows. For fixed j_1 and

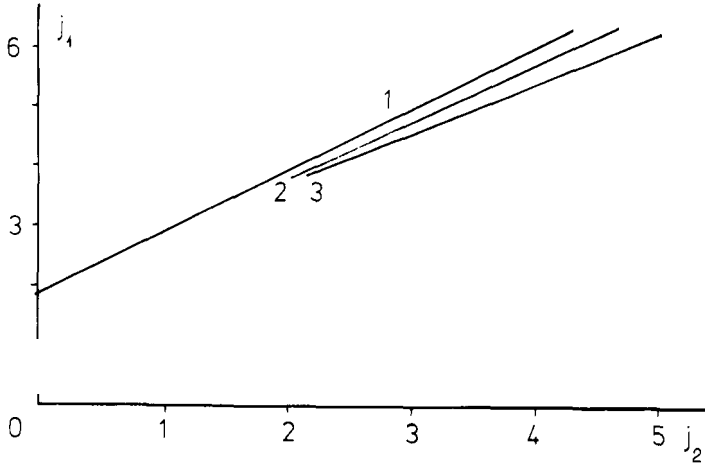


Fig. 7. The dependence of j_1 on j_2 : curve 1 is described by eqn. (3); curves 2 and 3 correspond to eqn. (67) for $\epsilon = 0.05$ and $\epsilon = 0.1$.

j_2 the system of eqns. (50),(51) with the boundary condition (54) was integrated by the Runge-Kutta method. There are two possibilities during integration: either the values of W or V become negative (a detailed analysis shows that it happens simultaneously) at a certain step for the coordinate x , or the relation $W(x=0) > 0$ holds true. For a fixed j_2 the realized possibility was determined only by the value of j_1 . Therefore, we may suppose that there is a certain function of j_1 , the root to

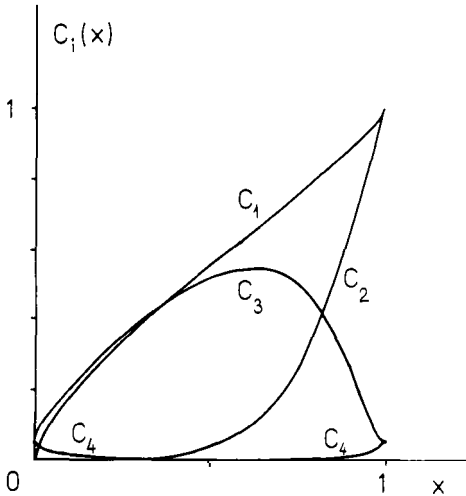


Fig. 8. Distribution of the component concentrations obtained by solution of the system of eqns. (50) and (51) for $j_2 = 4$, $\epsilon = 0.05$ and j_1 equal to the limiting current.

which $W(\mathbf{x}=0) = 0$ corresponds. To find the root of this function, the half-segment method was used. Comparison of the analytical dependences $j_1(j_2)$ by eqn. (67) with the results of computations for different values of ϵ shows their good concordance. Fig. 8 presents the concentration profiles c_i for different components obtained by numerical solution of the problem.

CONCLUSION

This analysis has shown that the effect of OH^- and H^+ ion dissociation in neutral solutions is more visible for $j_2 \ll 1$, when the limiting current of cation reduction decreases by a factor of the order of $\sqrt{\epsilon}$. For large currents $j_2 > 2$, this decrease is of the order of ϵ . Numerical calculations for the intermediate region $\epsilon < j_2 < 2$ have shown that the decrease of the limiting current of cation reduction has the order intermediate between $\sqrt{\epsilon}$ and ϵ and is a smooth function of the current of the neutral substance reduction.

In cases where the processes considered occur in acid solutions, the process of OH^- and H^+ ion recombination is more pronounced, and for sufficiently high pH the resulting exaltation current approaches the value described by the theory of the migration current correlation exaltation effect [4]. It was found that for sufficiently high concentrations of H^+ in the solution an unusual limiting diffusion-migration current of cation discharge may be observed which is due to the fact that their concentration falls to zero within the diffusion layer.

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