

The paper examines the influence of recombination of the OH^- and H^+ ions on the effect of migration-current exaltation observed when cations and a neutral substance are reduced in parallel [1, 2]. Approximate analytical solutions and numerical computer solutions were obtained for the corresponding system of electrodiffusion equations. It was shown that for realistic values of the equilibrium constant of water dissociation and recombination, the inclusion of recombination leads to a relatively small correction to the theory of migration-current exaltation developed in [3-5].

INTRODUCTION

The phenomenon that the limiting current of cation reduction increases when a neutral substance is reduced at the same time was detected experimentally in 1936 [1], and was called the effect of migration-current exaltation. A quantitative discussion of migration-current exaltation was given in [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 air oxygen and a new polarographic wave was recorded. In the second case the limiting current was found to be higher than the sum of the oxygen reduction current and of the limiting current of Na^+ reduction in the absence of oxygen.

In [3-5] a theory of the exaltation effect was proposed which allows for the fact that as a result of reduction of a neutral substance (eg, O_2), negatively charged products appear in the diffusion layer (eg, OH^-). These products may be absent from the bulk solution, but the system of electrodiffusion equations describing the parallel processes should include an equation for said anions. In cases where all ions in the system are monovalent the limiting current density, j_1 , of cation reduction depends on the current density, j_0 , of reduction of the neutral substance as follows:

$$j_1 = 2FD_1c_0/L + j_0D_1/D_3, \quad (1)$$

where D_1 and D_3 are the diffusion coefficients of the cations and of the reduction products of the neutral substance, respectively, c_0 is the cation concentration in the bulk electrolyte, L is the Nernst diffusion-layer thickness, and F is the Faraday constant. Introducing the corresponding dimensionless fluxes I_0 and I_1 :

$$I_0 = \frac{L}{FD_3c_0} j_0; \quad I_1 = \frac{L}{FD_1c_0} j_1, \quad (2)$$

one can rewrite Eq. (1) more simply as

$$I_1 = 2 + I_0. \quad (3)$$

Thus, the current of cation discharge increases linearly with the reduction current of the neutral substance.

It had not been taken into account when deducing Eq. (1) that the OH^- ions appearing at the electrode upon reduction of the neutral substance could recombine with the H^+ ions present in water. These reactions are known to be relatively fast, so that one can assume sufficiently correctly that the equilibrium

$$c_{\text{H}^+} \cdot c_{\text{OH}^-} = K$$

is established in the diffusion layer; here K is the equilibrium constant, which has a value of 10^{-14} (mole/liter)².

It was the aim of the present work to investigate the influence of dissociation and recombination of the OH^- and H^+ ions on the phenomenon of migration-current exaltation.

A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Elektrokhimiya*, Vol. 24, No. 12, pp. 1657-1663, December, 1988. Original article submitted February 1, 1988.

FORMULATION OF THE PROBLEM

Allowing for water dissociation and recombination, one can describe the effect of migration-current exaltation arising in the parallel reduction of cations and a neutral substance (oxygen), in terms of the Nernst diffusion-layer model by the system of electrodiffusion equations (all ions are regarded as monovalent, for the sake of simplicity):

$$\frac{dc_1}{dx} + c_1 \frac{d\Psi}{dx} = \frac{j_1 L}{FD_1 c_0} = I_1, \quad (4)$$

$$\frac{dc_2}{dx} - c_2 \frac{d\Psi}{dx} = 0, \quad (5)$$

$$D_3 \left(\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} \right) = -\frac{j_0 L}{Fc_0} + \Delta I \quad (6)$$

$$D_4 \left(\frac{dc_4}{dx} + c_4 \frac{d\Psi}{dx} \right) = \Delta I. \quad (7)$$

Here c_1, c_2, c_3, c_4 are the concentrations of the cations (Na^+), anions (Cl^-), reduction products of the neutral substance (OH^-), and conjugate products of water dissociation (H^+), respectively, D_l ($l = 1-4$) are the corresponding diffusion coefficients, $\Psi = F\varphi/RT$ is the dimensionless potential, x ($0 < x < 1$) is the dimensionless coordinate (made dimensionless through the Nernst diffusion-layer thickness L), $\Delta I = \Delta I(x)$ is the change in flux of the H^+ and OH^- ions on account of water dissociation and recombination, j_1 is the current density of cation discharge, c_0 is the salt concentration in the bulk solution, and j_0 is the current density of reduction of the neutral substance.

The system of four differential equations (4) to (7) must be supplemented by the electroneutrality condition:

$$c_1 + c_4 = c_2 + c_3, \quad (8)$$

and by the condition of equilibrium in the water dissociation reaction:

$$c_3 c_4 = \varepsilon^2, \quad (9)$$

where $\varepsilon^2 = K/c_0^2$ is the dimensionless equilibrium constant, which in the following will always be assumed to be a small quantity: $\varepsilon \ll 1$. We shall assume that in the bulk solution H^+ and OH^- are present in equal concentrations (neutral solution): $c_3(1) = c_4(1)$. From this condition and from relations (8) and (9) the boundary conditions for all $c_l(x)$ ($l = 1-4$) are obtained thus:

$$c_1(1) = c_2(1) = 1, \quad c_3(1) = c_4(1) = \varepsilon, \quad \Psi(1) = 0. \quad (10)$$

In the case of interest to us, ie, the limiting current of the cations being reduced, the relation

$$c_1(0) = 0. \quad (11)$$

should hold.

We notice that by virtue of condition (9), the concentrations of all other components cannot simultaneously become zero at the electrode under limiting-current conditions. As a result, the potential gradient and the potential itself also remain finite, according to (5). Thus, in the system being discussed where dissociation is taken into account, the logarithmic divergence of potential usually encountered in electrodiffusion problems when calculating the limiting current is missing.

Subtracting (7) from (6) and transforming the resulting equation as well as the condition (8) while allowing for (9) one can eliminate concentration c_4 from the system of equations:

$$c_3' - c_3 \Psi' = -\frac{I_0}{1 + \frac{\varepsilon^2}{c_3^2}}, \quad (12)$$

$$c_1 + \frac{\varepsilon^2}{c_3} = c_2 + c_3, \quad (13)$$

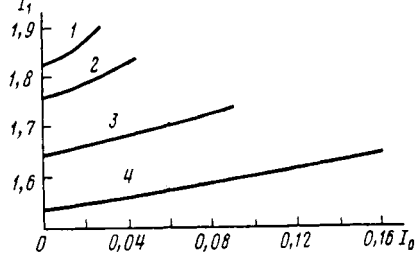


Fig. 1

Fig. 1. Plots of I_1 against I_0 for $I_0 \ll 1$ and ϵ -values of: 1) 0.01, 2) 0.02, 3) 0.05, and 4) 0.1.

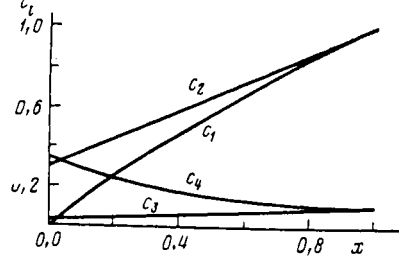


Fig 2

Fig. 2. Component concentration distributions obtained from relations (9), (13), (17), and (18) for $I_0 = 0$ and $\epsilon = 0.1$.

where $\nu = D_4/D_3 \sim 2$ is the ratio of diffusion coefficients of H^+ and OH^- . For $\epsilon \rightarrow 0$ the system of Eqs. (4), (5), (12), (13) changes into the equations of [3] where water dissociation is disregarded, and which when solved yield expression (3) for the limiting currents.

The right-hand side of Eq. (12) is a nonlinear function of c_3 , and hence the system of Eqs. (4), (5), (12), (13) cannot be reduced to a linear system by changing to the new independent variable Ψ as done in [4]. Thus, the problem formulated here requires the development of new methods for integrating the system of nonlinear differential equations.

THE SOLUTION IN THE CASE OF $I_0 \ll 1$

At low $I_0 \ll 1$ one can assume when allowing for the fact that the OH^- ions are generated owing to currents I_0 , and in view of equilibrium condition (9), that concentration c_3 is small as compared with c_4 , practically everywhere in the diffusion layer, to the exclusion of a very narrow region near $x = 1$. We therefore neglect c_3 relative to c_4 for $I_0 \ll 1$, and instead of (12) obtain the simplified equation

$$dc_i/dx + c_i d\Psi/dx = I_0 \nu. \quad (14)$$

The resulting system of Eqs. (4), (5), (13), (14) was solved in [6]. The corresponding relation for the limiting current I_1 as a function of I_0 is given by

$$I_1 = 2(1+\epsilon) - I_0/2\nu - \sqrt{4(1+\epsilon)(\epsilon - I_0/2\nu) + (I_0/2\nu)^2}. \quad (15)$$

For $I_0 = 0$ the limiting current I_1 is given by the relation

$$I_1 = 2(1+\epsilon) (1 - |\epsilon/(1+\epsilon)|) \quad (16)$$

The plots of I_1 against I_0 for $I_0 \ll 1$ which correspond to relation (15) are reported for a number of values of parameter ϵ in Fig. 1.

We stress that the limiting current I_1 decreases by an amount proportional to $\sqrt{\epsilon}$ when the recombination of OH^- and H^+ ions is taken into account. Moreover, for an I_0 -value which is strictly zero, the original system of Eqs. (4), (5), (12), (13) can be solved analytically without the assumption that $c_3 \ll c_4$. It follows immediately from (5) and (12) that

$$c_2 = e^\Psi, \quad c_3 = \epsilon e^\Psi. \quad (17)$$

Eliminating c_1 from (13) with the aid of c_2 and c_3 and substituting into (4) we obtain an equation for $d\Psi/dx$ which is readily integrated:

$$e^\Psi = 1 + \frac{I_1}{(1+\epsilon)}(x-1). \quad (18)$$

Using condition (11) we can find a value of the limiting current which coincides with (16). The distribution of component concentrations in the diffusion layer is shown for the case of $I_0 = 0$ in Fig. 2. One can see that the concentrations c_2 and c_3 decrease linearly as one comes closer to the electrode but do not become zero: $c_2(0) \approx c_4(0) \approx \sqrt{\epsilon}$ and $c_3(0) \sim \frac{3}{2}\sqrt{\epsilon}$. It must be pointed out, moreover, that practically everywhere in the diffusion layer the inequalities of $c_3 \ll c_4$ as well as $c_3, c_4 \ll c_1, c_2$ hold true.

GENERAL SOLUTION FOR $I_0 \neq 0$

It had already been pointed out above that in the case of $I_0 < 0$ the system (4), (5), (12), (13) cannot be integrated by the method described in [4]. This system can be solved in quadratures as follows.

Eliminating $d\Psi/dx$ from (4) and (12) with the aid of (5) we obtain

$$\frac{dW}{dx} = I_1 c_2, \quad (19)$$

$$\frac{dV}{dx} = \frac{I_0 c_1}{c_3^2 + \nu \epsilon^2}, \quad (20)$$

where we have introduced the dimensionless concentration combinations

$$W = c_1 c_2, \quad V = c_2 / c_3. \quad (21)$$

Eliminating c_1 and c_2 from (21) with the aid of c_3, W , and V and substituting into (13) one can state c_3 in terms of W and V :

$$c_3^2 = \frac{W/V + \epsilon^2}{1 + V}. \quad (22)$$

Thus, using (9), (21), and (22) one can state the concentrations of all solution components in terms of W and V , and system (10), (20) only contains the functions W and V , though in a rather complex way. The boundary conditions for W and V become

$$W|_{x=1} = 1, \quad V|_{x=1} = 1/\epsilon, \quad (23)$$

$$W|_{x=0} = 0. \quad (24)$$

Dividing (19) into (20) we can change to the new independent variable V :

$$\frac{dW}{dV} - \frac{\alpha}{(1+V)V} W = \alpha \epsilon^2 \left(\frac{1}{1+V} + \nu \right), \quad (25)$$

where $\alpha = I_1/I_0$ is the ratio of the currents. Relation (22) was used in deriving (25). Equation (25) is a first-order linear inhomogeneous equation. Its solution which for $x = 1$ satisfies boundary conditions (23) can be written as

$$W(V) = W_0(V) \left[1 + \int_{1/\epsilon}^V \alpha \epsilon^2 \left(\frac{1}{1+V'} + \nu \right) \frac{dV'}{W_0(V')} \right], \quad (26)$$

where $W_0(V)$ is the solution of the homogeneous Eq. (24) satisfying the boundary conditions (23):

$$W_0(V) = (1 + \epsilon)^{-\alpha} \left(\frac{V}{1+V} \right)^{\alpha}. \quad (27)$$

We thus find the function $W(V)$ which can be used, together with (21) and (22), to obtain the concentration distributions of all components as functions of the independent variable V under the condition that α is known. To find α one must use boundary condition (24). Integrating (24) we obtain

$$I_0 = I_1 \int_0^1 dx = \int_{1/\epsilon}^1 \frac{dV}{V} c_3 + \int_{1/\epsilon}^1 \frac{dV}{V} \frac{\nu \epsilon^2}{c_3} \quad (28)$$

Here V^* is the value of V which corresponds to $x = 0$ where, according to (24), one has $W(V^*) = 0$. One can readily see from (27) that for positive V , $W(V)$ will not become zero; therefore, the condition that is used to find V^* is a zero value of the term in square brackets in (26):

$$\int_{v^*}^{1/\alpha} \left(\frac{1}{1+V'} + v \right) \frac{dV'}{W_0(V')} = \frac{1}{\alpha \varepsilon^2} \quad (29)$$

Thus, for (28) one can find the integration limits (from (29), (27)) and the function under the integral sign (from (22), (26), (27)). Integrating in the right-hand side of (28) we obtain some function of the current ratio α . From the resulting equation, finally, one can extract I_1 as a function of I_0 and obtain the generalization of relation (3) to the case of migration-current exaltation which includes the recombination of the H^+ and OH^- ions.

Thus, a solution of the problem formulated has been obtained in quadratures. To obtain I_1 as a function of I_0 one must analytically evaluate the integrals contained in (26), (28), and (29). This is possible for the integral of (26), only with certain special values of α . (The integral of (26), which is contained in (28), can be evaluated only for integer and semiinteger values of α , while the integral on the right-hand side of (28) cannot be evaluated in an analytical form.) Below we report an approximate solution of the problem which utilizes the fact that parameter ε is small.

APPROXIMATE SOLUTION FOR $1 < \alpha < 2$

For the purposes of finding an approximate analytical solution of the problem one can utilize the fact that parameter ε is small: $\varepsilon \ll 1$. It will be our aim to find a correction term for the right-hand side of expression (3) which is a function of both ε and I_0 . Regarding (3) as zeroth approximation one can see that the condition of $\alpha < 2$ corresponds to currents $I_0 > 2$. The region of $\alpha > 2$ (or $0 < I_0 < 2$) corresponds to the transition region between $I_0 = 0$ and $I_0 > 2$ where the correction terms have values intermediate between terms of the order of $\sqrt{\varepsilon}$ for $I_0 = 0$ and terms of the order of ε for $I_0 > 2$, as will be shown below. We point out that the condition of $\alpha > 1$ (or $I_1 > I_0$) is fulfilled up to very large values of $I_0 = 1/\varepsilon \geq 10^3$, ie, throughout the range of values of parameter I_0 of interest to us. For $V \gg V^*$ one can write

$$W(V) = (1 + \varepsilon \alpha (1 - v)) \left(\frac{V}{1+V} \right)^\alpha, \quad (30)$$

which holds to terms of the order of ε , but for $V > V^*$ one has

$$W(V) = (1 + \varepsilon \alpha (1 - v)) (1 - \alpha V) V (V^{\alpha-1} - (V^*)^{\alpha-1}), \quad (31)$$

where

$$(V^*)^{\alpha-1} = \frac{\alpha \varepsilon^2}{\alpha - 1} (v + 1) \quad (32)$$

is a small quantity. When changing, in (28), to an integration over $\ln V$ we can replace the limits of integration by $\ln(1/\varepsilon)$ and $\ln V^*$, which in contrast to the values of $1/\varepsilon$ and V^* themselves can be regarded as quantities of the order of unity. The region of integration thus has a size of the order of unity, which implies that we are justified in suppressing terms smaller than ε in order of magnitude in the function under the integral sign, since we only are interested in the first correction to (3) with respect to ε . Substituting (30) and (31) into the right-hand side of (28) and integrating we obtain an equation which implicitly defines the function $I_1(I_0 \varepsilon)$:

$$I_0 = \frac{2}{\alpha - 1} - \frac{\varepsilon}{\alpha - 1} f(\alpha), \quad (33)$$

where

$$f(\alpha) = \pi \sqrt{\frac{\alpha(v+1)}{\alpha-1}} + (v-1) - \frac{2v}{\sqrt{\frac{\alpha(v+1)}{\alpha-1} - 1}} \left\{ \frac{\pi}{2} - \operatorname{arctg} \frac{1}{\sqrt{\frac{\alpha(v+1)}{\alpha-1} - 1}} \right\} \quad (34)$$

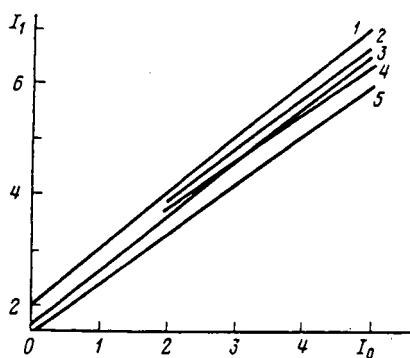


Fig. 3

Fig. 3. Comparison of the approximate analytical I_1 vs I_0 functions for $I_0 > 2$ with the functions obtained numerically; curve 1 is that defined by relation (3), curves (2) and (4) correspond to (36) for $\varepsilon = 0.05$ and $\varepsilon = 0.1$, curves 3 and 5 were computer-calculated for $\varepsilon = 0.05$ and $\varepsilon = 0.1$.

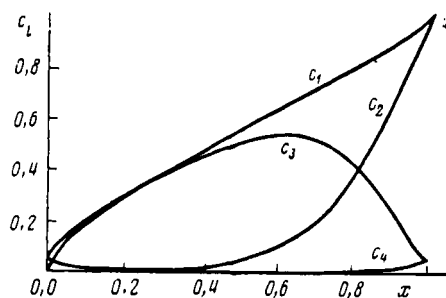


Fig. 4

Fig. 4. Component concentration distributions obtained by numerical solution of the system of Eqs. (19), (20) for $I_0 = 4$, $\varepsilon = 0.05$, and I_1 equal to the limiting current.

The first term on the right-hand side of (33) is the term corresponding to the zeroth approximation of (3), while the second term represents a small correction. Hence Eq. (33) can be solved for I_1 by the method of successive approximations; first we find α in the zeroth approximation:

$$\alpha_0 = \frac{I_0 + 2}{I_0}. \quad (35)$$

Multiplying (33) with $(\alpha - 1)$ and replacing α by α_0 in the right-hand part of the resulting expression we obtain

$$I_1 = 2 + I_0 - \varepsilon f(\alpha_0) \quad (36)$$

ie, the conclusive expression representing the generalization of the result (3) that had been obtained previously. The function $I_1(I_0)$ defined by expression (36) is shown in Fig. 3 together with function (3) and the results obtained by numerical solution of the problem.

NUMERICAL COMPUTER SOLUTION OF THE PROBLEM

The system of Eqs. (19), (20) with the boundary conditions (23), (24) was also solved by numerical integration with a computer. The algorithm for the solution was set up as follows. For fixed I_1 and I_0 , the system (19), (20) with boundary conditions (23) was integrated by the Runge—Kutta method. Two versions could be realized in the integration: either the values of W or V became negative in some step along coordinate x (a detailed analysis showed that this occurs simultaneously), or the relation of $W(x=0) > 0$ was fulfilled. For fixed I_0 , the variant to be realized was determined only by the value of I_1 . One thus can claim that some function of I_1 exists which has a root corresponding to $W(x=0) = 0$. To find the root of this function we used the method of divided differences. The results obtained when numerically calculating function $I_1(I_0)$ are shown in Fig. 3. One can see when comparing the approximate analytical functions $I_1(I_0)$ of (36) with the numerical calculations for different values of parameter ε that these are in fair agreement. Figure 4 shows the profiles of component concentrations c_i obtained by numerical solution of the problem.

CONCLUSION

Thus, the above analysis has shown that the effect of dissociation of ions OH^- and H^+ is most important for $I_0 \ll 1$, where the limiting current of cation reduction decreases by an amount of the order of $\sqrt{\varepsilon}$. At large currents, of $I_0 > 2$, the decrease in the limiting current of cation reduction is of the order of ε . It was seen from numerical calculations in the region of $\varepsilon < I_0 < 2$ that the limiting-current decrease is intermediate between $\sqrt{\varepsilon}$ and ε in order of magnitude, and is a smooth function of reduction current of the neutral substance.

We also point out that when the processes discussed occur in acidic solutions the recombination of OH⁻ and H⁺ ions will have more important effects, and at sufficiently high pH the resulting exaltation current should approach the value described by the theory of correlative migration-current exaltation [6].

LITERATURE CITED

1. W. Kemula and M. Michalski, *Rocz. Chem.*, **16**, 353 (1936).
2. J. Heyrovsky and M. Bures, *Collect. Czech. Chem. Commun.*, 8, 446 (1936).
3. Yu. I. Kharkats, *Elektrokhimiya*, **14**, 1040 (1978).
4. Yu. I. Kharkats, *J. Electroanal. Chem.*, **105**, 97 (1979).
5. V. V. Topolev and Yu. I. Kharkats, *Elektrokhimiya*, **19**, 515 (1983).
6. Yu. I. Kharkats, *Elektrokhimiya*, 14, 1716 (1978).