INFLUENCE OF OH- AND H$^+$ ION RECOMBINATION WITHIN THE DIFFUSION LAYER ON ELECTRODE REACTIONS OCCURRING IN PARALLEL

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The paper provides a theoretical analysis of the electrodiffusion problem arising when cations and anions are reduced in parallel at an electrode in acidic solutions and OH$^-$ and H$^+$ ions subsequently recombine in the Nernst diffusion layer in a homogeneous reaction. The conditions are estimated under which a limiting current of anion reduction will be realized in the system and under which hydrogen ions start to be directly involved in the electrode process.

1. INTRODUCTION

When two or more electrochemical reactions occur in parallel at an electrode and the solution contains no base electrolyte, they generally will influence each other owing to interaction of the reactant and product transport by diffusion and migration. This interaction of the electrode reactions can be unilateral [1, 2] or mutual [3], and the current of one of the processes can increase or decrease when that of the other increases. Some examples illustrating the complexities in the interaction of two kinetically independent processes have been reported in [4, 5].

In [4—7] different schemes of the parallel reduction of metal and nitrate ions in acidic solutions had been investigated. This was done under the assumption that hydrogen ions are involved in anion reduction at the electrode. It was seen from a mechanistic analysis of the parallel reduction of cations and oxygen in acidic solutions performed in [8] that under certain conditions the interaction of the ionic transport processes produces a changeover from a mechanism where the hydrogen ions are directly involved in the reduction of oxygen at the electrode, to another mechanism where hydroxyl ions are formed at the electrode which then are neutralized by hydrogen ions in the diffusion layer.

In the present work we examine the parallel reduction of anions and metal cations in acidic solutions under conditions where the hydroxyl ions produced in anion reduction undergo homogeneous recombination with hydrogen ions in the diffusion layer.

2. FORMULATION OF THE PROBLEM

Consider two electrode reactions occurring in parallel; copper is electrodeposited at the electrode:

$$Cu^{2+}+2e\rightarrow Cu^0\downarrow \tag{1}$$

while NO_3^- ions are reduced according to the scheme of

$$NO_3^-+H_2O+2e\rightarrow NO_2^-+2OH^-. \tag{2}$$
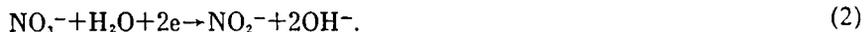
The NO_2^- and OH^- ions-produced in reaction (2) are transported by diffusion and migration from the electrode into the solution, and the OH ions undergo recombination with the opposing flow of H$^+$ ions in the diffusion layer:

$$OH^-+H^+\rightarrow H_2O. \tag{3}$$

The scheme considered here, which involves the homogeneous reaction (**3**) following the electrode reaction (2), differs from the scheme (4) analyzed in detail in [5], where it was assumed that the H$^+$ ions are directly involved in NO_3^- reduction:

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O. \tag{4}$$

A generalization of scheme (1) to (3) for ions of arbitrary charge is the system of two electrode reactions

$$A_1^{\tilde{z}_1+} + \tilde{z}_1 e \rightarrow A_1^0 \downarrow, \tag{5}$$

$$A_3^{\tilde{z}_3-} + B_1^0 + (n\tilde{z}_5) e \rightarrow A_4^{\tilde{z}_3-} + nA_5^{\tilde{z}_5-}, \tag{6}$$

which is supplemented by the consecutive homogeneous reaction of recombination of the $A_5^{\tilde{z}_5-}$ ions in the diffusion layer:

$$\tilde{z}_2 A_5^{\tilde{z}_5-} + \tilde{z}_5 A_2^{\tilde{z}_2+} \rightarrow B_2^0. \tag{7}$$

Here suffixes 1 to 5 refer to the cations of the metal being deposited, to the cations involved in the homogeneous recombination reaction, to the anions being reduced, and to the products of electrode reaction (6); $A_i^{\tilde{z}_i}$ is the symbol of the corresponding component, B_1^0 and B_2^0 are the neutral substances, n is the stoichiometric coefficient, and $\tilde{z}_i$ is the charge number of the corresponding ion ($\tilde{z}_2$ and $\tilde{z}_5$ are assumed to be relatively prime numbers). In Eq. (6) the simplifying assumption was made that one original anion $A_3^{\tilde{z}_3-}$ yields one anion $A_4^{\tilde{z}_3-}$ having the same charge as $A_3^{z_3-}$, i.e., that $\tilde{z}_3 = \tilde{z}_4$, as in reaction (4). It will be assumed in the following, moreover, that the diffusion coefficients of these ions are also approximately the same.

The system of electrodiffusion equations describing the scheme (5) to (7) is as follows:

$$\frac{dc_1}{dx} + \tilde{z}_1 c_1 \frac{d\tilde{\Psi}}{dx} = \frac{1}{\tilde{z}_1} \frac{i_1 L}{FD_1 c^0} = j_1, \tag{8}$$

$$\frac{d^2 c_2}{dx^2} + \frac{d}{dx}\left(\tilde{z}_2 c_2 \frac{d\tilde{\Psi}}{dx}\right) = Kc_2^{\tilde{z}_5} c_5^{\tilde{z}_2}, \tag{9}$$

$$\tag{10}$$

$$\frac{dc_3}{dx} - \tilde{z}_3 c_3 \frac{d\tilde{\Psi}}{dx} = \frac{1}{n\tilde{z}_5} \frac{i_2 L}{FD_3 c^0} = j_2, \tag{10}$$

$$\frac{dc_4}{dx} - \tilde{z}_3 c_4 \frac{d\tilde{\Psi}}{dx} = -\frac{1}{n\tilde{z}_5} \frac{i_2 L}{FD_3 c^0} = -j_2, \tag{11}$$

$$\frac{d^2 c_5}{dx^2} - \frac{d}{dx}\left(\tilde{z}_5 c_5 \frac{d\tilde{\Psi}}{dx}\right) = Kc_2^{\tilde{z}_5} c_5^{\tilde{z}_2}, \tag{12}$$

$$\tilde{z}_1 c_1 + \tilde{z}_2 c_2 = \tilde{z}_3 (c_3 + c_4) + \tilde{z}_5 c_5. \tag{13}$$

Here c_i are the corresponding concentrations made dimensionless through c^0, which is the metal ion concentration in the bulk solution, D_i are the corresponding diffusion coefficients, $\Psi = FE/RT$ is the dimensionless potential, x is the dimensionless coordinate ($0 \leq x \leq 1$), L is the thickness of the Nernst diffusion layer, i_1 and i_2 are the current densities of reactions (5) and (6), $j_1 > 0$ and $j_2 > 0$ are dimensionless fluxes, and K is the rate constant of the recombination reaction (7). Equation (13) is a statement of the condition of local electroneutrality. The values of potential and component concentrations will be regarded as given at the diffusion-layer boundary of $x = 1$:

$$c_1(1) = 1, \ c_2(1) = k, \ c_3(1) = (\tilde{z}_1 + k\tilde{z}_2)/\tilde{z}_3,$$

$$c_4(1) = c_5(1) = 0, \ \tilde{\Psi}(1) = 0. \tag{14}$$

The system of differential equations (8) to (12) contains two second-order equations, hence two additional boundary conditions must be specified to solve it; in this capacity one can use the condition that ions $A_2^{\tilde{z}_2+}$ are not present at the electrode: $c_2(0) = 0$, and that the fluxes of ions $A_5^{\tilde{z}_5-}$ and $A_4^{\tilde{z}_3-}$ away from the electrode are determined by the stoichiometry of reaction (6).

System (8) to (14) is quite complicated, and has no analytical solution in its general form. We shall consider that the recombination process (7), just as reaction (3), is relatively fast and hence is restricted to a narrow region rather
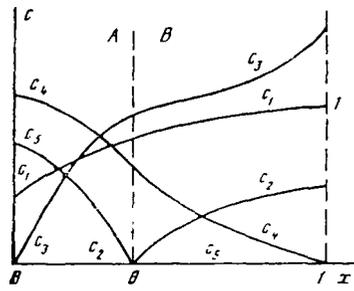
Fig. 1. Schematic of the component concentration distributions in the diffusion layer; θ is the region where the recombination reaction (7) is localized.

smaller in thickness than the diffusion layer [9]. It can assumed in this case that the recombination reaction (7) occurs at some point θ within the diffusion layer: $0 < \theta < I$, and hence one of the Eqs. (9) and (12) can be replaced by the condition*

$$c_2 c_3 \approx 0. \tag{15}$$

This condition implies that the diffusion layer can be split up into two regions: a region B to the right of point θ, where ions $A_5{}^{\bar{z}5-}$ are absent, i.e., $c_5(x) = 0$ for $\theta < x < 1$; and a region A adjacent to the electrode (to the left of point θ), where ions $A_2{}^{\bar{z}2+}$ are absent, i.e., $c_2(x) = 0$ for $0 < x < \theta$ (Fig. I). It is obvious that then the fluxes of ions $A_2{}^{\bar{z}2+}$ and $A_5{}^{\bar{z}5-}$ are constant within the corresponding intervals, and can be stated in terms of flux j_2 and the stoichiometric relations with the aid of the reaction Eqs. (6) and (7). Then it will be sufficient to use boundary conditions (14) as well as the boundary conditions $c_2(0) = 0$ and $c_2'(0) = 0$.

We shall introduce the relative charge numbers z_i and the potential Ψ as defined by the relations

$$z_1 = \tilde{z}_1/\tilde{z}_3, \quad z_2 = \tilde{z}_2/\tilde{z}_3, \quad z_5 = \tilde{z}_5/\tilde{z}_3, \tag{16}$$

$$Y = \tilde{z}_3 \widetilde{\Psi}$$

in order to simplify subsequent formulation of the equations. Using (15) and (16) we can rewrite the system of Eqs. (8) to (13) in region A $(0 < x < \theta)$ as:

$$\frac{dc_1}{dx} + z_1 c_1 \frac{d\Psi}{dx} = j_1, \tag{17}$$

$$\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} = j_2, \tag{18}$$

$$\frac{dc_4}{dx} - c_4 \frac{d\Psi}{dx} = -j_2, \tag{19}$$

$$\frac{dc_5}{dx} - z_5 c_5 \frac{d\Psi}{dx} = -\eta j_2, \tag{20}$$

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*Strictly speaking, instead of condition (15) we should have written

$$c_2^{\tilde{z}_4} c_6^{\tilde{z}_2} = K',$$

where K' is the equilibrium constant of the dissociation—recombination reaction. Considering that usually the recombination constant is much larger than the dissociation constant, and hence equilibrium constant K' extremely small, condition (15) will be sufficiently exact.
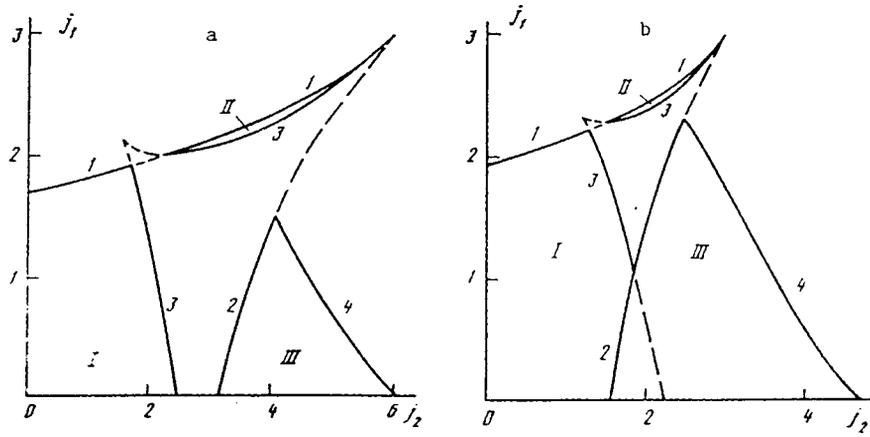
Fig. 2. Relative positions of the regions of a steady state with respect to the parallel processes following the scheme of (1) to (3) (region III) or the scheme of (1) and (4) (regions I and II) in the plane of j_1 and j_2, at k–values of: a) 0.6 (regions I and III do not touch), b) 0.3 (regions I and III have a common boundary). Explanations in the text.

$$z_1 c_1 = z_5 c_5 + c_3 + c_4, \quad c_2 \equiv 0, \tag{21}$$

where the parameter $\eta = nD_3/D_5$. In region B ($\theta < x < 1$), Eqs. (17) to (19) enter the system of electrodiffusion equations without any changes, but the Eqs. (20) and (21) must be replaced by the equations

$$\frac{dc_2}{dx} + z_2 c_2 \frac{d\Psi}{dx} = \nu j_2, \tag{22}$$

$$z_1 c_1 + z_2 c_2 = c_3 + c_4, \tag{23}$$

where $\nu = nD_3 z_5 / D_2 z_2$. At point θ, the conditions of continuity must be fulfilled for the potential and all concentrations. The value of θ itself will be found while solving the problem.

3. MATHEMATICAL ANALYSIS OF THE PROBLEM

We start our discussion with region A in Fig. 1, which corresponds to $0 < x < \theta$. To find the distributions of Ψ and c_i in this region one must solve the system of Eqs. (17) to (21) with the boundary conditions ,

$$c_1(\theta) = G, \quad c_3(\theta) = Gz_1(1-r), \quad c_4(\theta) = Gz_1 r,$$
$$c_5(\theta) = 0, \quad \Psi(\theta) = \Psi_\theta, \tag{24}$$

where G, r, and Ψ_θ are constants specifying the values of the concentrations and of potential at the right–hand boundary of interval $(0, \theta)$; they will be found later from the continuity conditions for c_i and Ψ at $x = 0$.

The distributions of concentrations c_i and of potential were obtained by changing the independent variable in system (17) to (21) from x to Ψ, in a way analogous to that used in [3]. Functions $c_1(\Psi)$, $c_2(\Psi)$, and $x(\Psi)$ are given by the relations

$$(x-\theta)j_1 = G[a(e^{\Psi-\Psi_\theta}-1) + b(e^{\lambda(\Psi-\Psi_\theta)}-1)], \tag{25}$$

$$c_1(\Psi) = \frac{G}{z_1 + z_5 J - z_1 z_5 (1-J)} [(1-z_5)z_1 e^{\Psi-\Psi_\theta} + z_5 J(1+z_1) e^{\lambda(\Psi-\Psi_\theta)}], \tag{26}$$

$$c_3(\Psi) = Ge^{\Psi-\Psi_\theta} \left\{ (1-r)z_1 + J\left[a(\Psi-\Psi_\theta) + b\frac{\lambda}{\lambda-1}(e^{(\lambda-1)(\Psi-\Psi_\theta)}-1) \right] \right\}, \tag{27}$$

where

$$\lambda = z_1 z_5 \frac{1-J\eta}{z_1 + z_5 J\eta}, \tag{28}$$

$$a = \frac{z_1(z_1+z_5)(1-z_5)}{z_1+z_5\eta J - z_1 z_5(1-J\eta)}, \tag{29}$$

$$b = \frac{(z_1+z_5)J\eta(1+z_1)}{(1-J\eta)(z_1+z_5J\eta-z_1z_5(1-J\eta))}, \tag{30}$$

and $J = j_2/j_1$ is the flux ratio.

Relations (25) to (30) describe in a parametric form the functions $c_i(x)$ which are schematically shown in Fig. 1.

Under conditions of a limiting current with respect to the anions being reduced, we have $c_3(0) = 0$ and from (27) and (25) we can obtain the relation between fluxes j_1 and j_2 in a parametric form:

$$j_1 = j_1(J) = \frac{G}{\theta}[a(1-e^{\Psi_0}) + b(1-e^{\lambda\Psi_0})], \tag{31}$$

$$j_2 = j_1 J. \tag{32}$$

Here $0 < J < \infty$ and $\Psi_0 = \Psi|_{x=0} - \Psi_\theta$ is the potential difference between the ends of segment $(0, \theta)$ which can be determined from the transcendental equation

$$(1-r)z_1/J + a\Psi_0 + b\lambda/(\lambda-1)(e^{(\lambda-1)\Psi_0}-1) = 0. \tag{33}$$

An immediate use of the analytical relations (28) to (33) is difficult since the transcendental Eq. (33) must be solved numerically. However, in the frequent case of $z_5 = 1$ ($z_3 = z_4 = z_5$) which in particular corresponds to the scheme (1) to (3), Eq. (33) is readily solved for Ψ_0. This is the case which we shall analyze in the following. Then instead of (31) we can obtain for j_1 the simple expression

$$j_1 = \frac{1}{\theta} P(J, G, r), \tag{34}$$

where

$$P(J,G,r) = \begin{cases} G\dfrac{z_1+1}{1-J\eta}\left\{1 + \left(1+\dfrac{1-r}{\eta}\right)^{\left[\frac{z_1(1-1/J\eta)}{1+z_1}\right]}\right\}, & \text{for } J\eta \neq 1 \\[3mm] Gz_1 \ln\left(1 - \dfrac{1-r}{\eta}J\right), & \text{for } J\eta = 1. \end{cases} \tag{35}$$

For a solution of the system of differential Eqs. (17) to (19), (22), (23) with boundary conditions (14) in the interval of $\theta < x < 1$, i.e., in region B of Fig. 1, we can use the solutions obtained for the same system of equations in [5] in the interval of $0 < x < 1$. The requirement that concentration c_2 be continuous at the matching point θ implies that the value of c_2 which is determined by solving the system of (17) to (19). (22), (23) should be zero at this point. The connection between currents j_1 and j_2 which follows from the condition of $c_2(0) = 0$ can be written parametrically, with the results of [5], in terms of the parameter J defined by relation (32):*

$$j_1 = \frac{1}{1-\theta} S(J), \tag{36}$$

where

$$S(J) = \frac{(z_1+1) + k(z_2+1)}{1+\nu J} - \frac{(z_1+kz_2)(1+z_1)}{z_2(1+\nu J)} \times \tag{37}$$
$$\left\{\frac{z_1[\nu J(z_1+1) - k(z_2+1)]}{\nu J(1+z_1)(z_1+kz_2)}\right\}^{\left[\frac{z_1+z_2\nu J}{z_1+z_2 J\nu+z_1z_2(1+J\nu)}\right]}.$$

Using the expressions found in [5] for concentrations $c_1(x)$ and $c_2(x)$ in region B we can write the parameters G and r introduced into (24) in terms of $c_1(\theta)$ and $c_4(\theta)$:

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*In [5], typographical errors are present in relations (29) and (30) which consist in an incorrect positioning of the exponents. The second square brackets in (29) and (30) are the exponents of the expressions in the first square brackets.

$$G = c_1(\theta) = \frac{z_1 + kz_2}{z_1} \times$$

$$\left\{ \frac{z_1[(z_1 + 1)\nu J - k(z_2 + 1)]}{\nu J (1 + z_1)(z_1 + kz_2)} \right\}^{\left[\frac{z_1 + z_2 \nu J}{z_1 + z_2 J \nu + z_1 z_2 (1 + \nu J)} \right]},$$

(38)

$$r = \frac{c_4(\theta)}{z_1 G} = \frac{J(z_1 + \nu J)}{z_1(z_1 + kz_2)[z_1(1 + z_2) + \nu J z_2(1 + z_1)]} \times$$

$$\left\{ \frac{(z_1 + kz_2)(1 + z_1)(1 + z_2)}{z_1(1 + z_2) + \nu J z_2(1 + z_1)} \ln \left\{ \frac{\nu z_2(1 + z_1) + z_1(1 + z_2)}{z_1[\nu J (z_1 + 1) - k(1 + z_2)]} \right\} - \right.$$

$$\left. \frac{z_2 k(z_1 - z_2)}{z_1 + z_2 \nu J} \right\}.$$

(39)

From relations (34) and (36) we can now determine the value of θ, which is the location of the recombination reaction (7):

$$\theta = P/(P+S).$$

(40)

Substituting the value of θ from (40) into (34) we can find the desired function $j_1(j_2)$ which corresponds to realization of the condition of $c_3(0) = 0$; in a parametric form, it is

$$j_1 = P(J, G, r) + S(J), \quad j_2 = j_1 \cdot J,$$

(41)

where functions P, S, G, and r depend on J and are determined by relations (35) and (37) to (39).

4. DISCUSSION OF THE RESULTS

As a result of the above analysis, condition (41) could be found which states how the limiting–current mode can be realized which comes about by slow transport of anions A to the electrode, in the situation where the parallel reduction of cations $A_1^{z_1+}$ and anions $A_3^{z_3-}$ is followed by the recombination reaction (7) occurring within the diffusion layer. The conditions required for this reaction mode are nonnegative concentrations of all components within the diffusion layer and validity of the inequality of $0 < \theta < 1$.

It is readily seen that for such a scheme of the full process, no other possibilities for attainment of the limiting–current mode exist, i.e., the concentrations $c_1(0)$, $c_4(0)$, and $c_5(0)$ are always positive.

We point out that the condition of $\theta < 1$ does not impose any limitations as to the possibilities of a stationary process. The position of the reaction zone at $x = \theta$ generally depends both on the partial currents and on the relative bulk solution concentration of cations $A_2^{z_2+}$. The value of θ decreases when this concentration increases, and when a value of $\theta = 0$ is reached the overall process will no longer be described by the scheme of (5) to (7). The condition of $\theta = 0$ coincides with that of $c_2(0) = 0$, i.e., with the condition under which a limiting current arises on account of slow supply of cations $A_2^{z_2+}$ in the case where there is no homogeneous recombination (7) and the two parallel reduction reactions of cations $A_1^{z_1+}$ (5) and anions $A_3^{z_3-}$ occur which involve cations $A_2^{z_2-}$:

$$A_3^{z_3-} + mA_2^{z_2+} + mz_2 e \rightarrow A_4^{z_4-} + B_3^0.$$

(42)

Transport of ions by diffusion and migration in a system described by reactions (5) and (42) was analyzed in detail in [5], where conditions were estimated, in particular, under which limiting currents with respect to components c_1, c_2, and c_3 will be realized (curves 1, 2, and 3 in Figs. 2a and 2b, respectively). The correlation obtained in [5] between j_1 and j_2 for the condition of $c_2(0) = 0$ coincides with the function $j_1(j_2)$ which follows from the condition of $\theta = 0$ mentioned above.

Thus, by combining the results of the present study with the results obtained in [5] in the instance of copper reduction in acidified nitrate solutions ($\bar{z}_1 = 2$, $\bar{z}_2 = \bar{z}_3 = \bar{z}_4 = \bar{z}_5 = 1$) one can find the regions of values of j_1 and j_2 where it is possible for reaction (1) to occur in parallel with reactions (2) and (3) (region III) or with reaction (4) (regions I and II). Figures 2a and 2b show possible versions of the relative location of curve $j_1(j_2)$ corresponding to the condition of $c_3(0) = 0$ as described by relation (41) when the reactions follow the scheme of (1) to (3) (curve 4), as well as to the same condition of $c_3(0) = 0$ in the case where the reactions follow the scheme of (1) and (4) (curve 3, which has a break). Moreover, for the latter scheme curves $j_1(j_2)$ are reported which correspond to other possibilities for the advent of limiting currents: $c_2(0) = 0$ (curve 2) or $c_1(0) = 0$ (curve 1).

We notice that the process investigated in the present work, which comprises a homogeneous recombination reaction, can be realized in region III which is to the left of the curve 4 described by relation (41) and to the right of curve 2 corresponding to the condition of $\theta = 0$. This region supplements the regions I and II in Fig. *2a* where the processes can follow the scheme of (I) and (4), and it may join up with region I (Fig. 2b) at sufficiently small values of the parameter *k* when curves 2 and *3* intersect.

Thus, the complete picture for metal deposition and simultaneous anion reduction involving hydrogen ions looks as follows. The fact that said electrode processes occur in parallel in regions I and II gives rise to their mutual dependence. A stationary mode which corresponds to region Il cannot be attained when the currents of both reactions increase monotonically. Region III which corresponds to the additional homogeneous process occurring in the diffusion layer can either exist in isolation or have a common boundary with region I, and a change in reaction mechanism occurs when this boundary is crossed.

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