# SPECIAL FEATURES OF SPACE-CHARGE DISTRIBUTION IN THE DIFFUSION LAYER DEVELOPING DURING AN ELECTRODE PROCESS FOLLOWED BY A HOMOGENEOUS REACTION

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*The special features of space-charge distribution were analyzed which arise within the diffusion layer while cations and a neutral substance are reduced in parallel under steady-state conditions and the negatively charged products of the electrode reaction subsequently undergo a homogeneous reaction. It was shown that at certain values of the parameters, the space-charge distribution can develop a peak in the center of the reaction zone of the homogeneous reaction. The distrbutions of potential and electric field were obtained for the system being examined.*

A space-charge region is known to develop in the diffusion layer during current flow. The charge-density distribution in this region falls off with distance according to a power law, rather than exponentially as in diffuse layers [1]. The space-charge density next to the electrode increases drastically as the current density approaches a value corresponding to the limiting diffusion current; the sign of charge coincides with that of the electroactive ions.

It is of interest to find out how a homogeneous reaction involving solution ions and the charged electrode reaction products will influence the space-charge distribution in the diffusion layer. It must be pointed out that the space-charge region developing within the diffusion layer somewhat upsets the condition of local electroneutrality usually employed instead of the exact Poisson equation when solving electrodiffusion problems.

The solution found for the electrodiffusion problem with the electroneutrality condition can be used in finding the space-charge distribution when the spatial distribution of potential $\varphi$ that is obtained is used as zeroth approximation in the Poisson equation:

$$\rho=-\varepsilon\varphi''/4\pi. \tag{1}$$

Here $\rho$ is the charge density and $\varepsilon$ is the permittivity.

In the present work we analyze the character of space-charge distribution existing in the diffusion layer when two reactions occur in parallel at the electrode: the reduction of cations

$$A^{2+}+2e\rightarrow A^0 \tag{2}$$

and the reduction of oxygen which follows the scheme of

$$O_2+2H_2O+4e\rightarrow 4OH^- \tag{3}$$

and is followed by the homogeneous recombination of $OH^-$ and $H^+$ ions in the diffusion layer:

$$OH^-+H^+\rightarrow H_2O. \tag{4}$$

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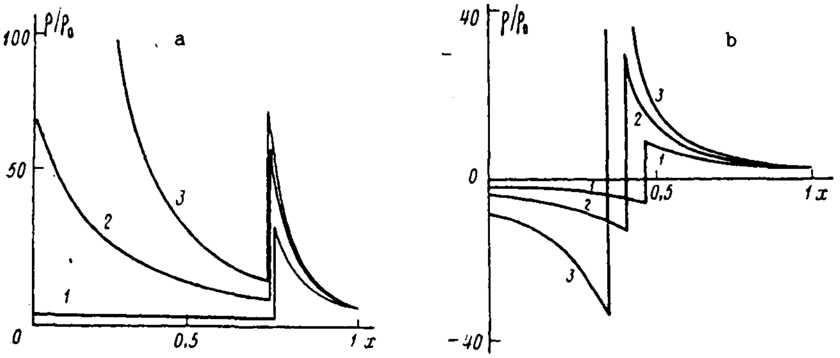

Fig. 1. Distribution of space-charge density according to relations (20) and (21) for $j_2 = 4$ and $v = 0.56$; (a) $k = 0.4$, the values of $j_1$: 1) 4.3; 2) 4.8; 3) 5; (b) $k = 0.8$, the values of j,: 1) 2; 2) 2.5; 3) 2.7.

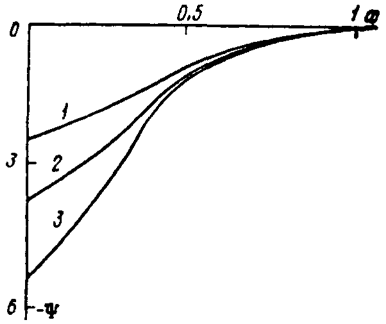

Fig. 2

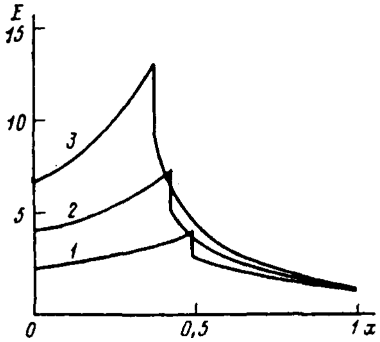

Fig. 3

Fig. 2. Potential distributions as described by relations (18) and (19). Curves *1-3* were calculated with the values of parameters $v, j_2$, k, and $j_1$ which correspond to curves *1–3* of Fig. lb.

Fig. 3. Distribution of electric field strength as described by relations (13) and (14). Curves *1-3* were calculated with the values of parameters $v, j_2$, k, and $j_1$ which correspond to curves *1–3* of Fig. lb.

The above reaction scheme (2) to (4) had been analyzed in detail in [2], where the mechanism of migration-current exaltation in acidic solutions was investigated.

It is a special feature of ionic transport processes in the system being examined that the fluxes of $H^+$ and $OH^-$ ions have opposite directions in the region where the homogeneous reaction (4) takes place. It can be expected that this pattern of the ionic fluxes will give rise to a space-charge distribution in the diffusion layer which exhibits a change of sign in the region where the homogeneous reaction takes place.

The system of electrodiffusion equations describing the distribution of component concentrations and potential in the diffusion layer is of the form of

$$\frac{dc_1}{dx} + c_1\frac{d\psi}{dx} = \frac{i_1 L}{FD_1c^0} = j_1, \tag{5}$$

$$\frac{dc_2}{dx} - c_2\frac{d\psi}{dx} = 0, \tag{6}$$

It can be seen that the conditions of

$$\nu j_2 \geqslant k j_1, \quad 0 \leqslant \theta \leqslant 1 \tag{17}$$

must be fulfilled so that the solutions reported may exist.

The potential distribution is found by integrating Eqs. (13) and (14), and given by the relations [2]

$$\psi(x) = \ln[1 + (x-1)(j_1 + \nu j_2)/2(1+k)] \quad \text{for} \quad \theta \leqslant x \leqslant 1, \tag{18}$$

$$\psi(x) = \psi_\theta + \frac{j_1 + j_2}{j_1 - j_2} \ln[1 + (x-\theta)(j_1 - j_2)/2G] \quad \text{for} \quad 0 \leqslant x \leqslant \theta, \tag{19}$$

where $\psi_\theta$ is the potential found from (18) for the point $\theta$: $\psi_\theta = \psi(\theta)$.

Substituting expressions (18) and (19) into (1) we obtain relations describing the spacecharge distribution in the two adjacent diffusion-layer regions:

$$\rho = -\rho_0 \frac{d^2\psi}{dx^2} = \rho_0 \left(\frac{d\psi}{dx}\right)^2, \quad \theta \leqslant x \leqslant 1, \tag{20}$$

$$\rho = -\rho_0 \frac{d^2\psi}{xd^2} = \rho_0 \frac{j_1 - j_2}{j_1 + j_2} \left(\frac{d\psi}{dx}\right)^2, \quad 0 \leqslant x \leqslant \theta, \tag{21}$$

where $\rho_0 = ec_0(l/L)^2$ and $l = (\varepsilon kT/4\pi e^2 c_0)^{1/2}$.

Functions $\rho(x)$ determined with relations (20) and (21) for a number of values of the parameters $j_1, j_2$, and k are shown in Figs. 1a and 1b. It follows from Fig. 1*b* and from relations (20) and (21) that a discontinuous change in space-charge density attended by a change in sign of this space charge occurs at the point of $x = \theta$ for currents $j_1 < j_2$. At $j_1 > j_2$ and $k < \nu$, a discontinuous change in p is again observed at the point of $x = \theta$, but this is not attended by a change in sign of $\rho$ (Fig. 1a). It had been shown in [2] that in the system being examined, there are two possibilities for the development of a limiting current of cation discharge. When $\nu > k$, the limiting current of cation discharge, $j_1^l$, implies that the condition of $c_1(0) = 0$ is fulfilled. Then the rise of the current from $j_1$ to $j_1^l$ is attended by an increase in space-charge density at the electrode surface while the change in behavior of $\rho(x)$ around $x = \theta$ is insignificant (Fig. 1a). When $k > \nu$, a limiting current of cation discharge, $j_1^l$, implies that the concentration $c_1$ tends toward zero at $x = \theta$. Then the rise of current $j_1$ to the level of $j_1^l$ is attended by an increase of the discontinuous change in space-charge density at $x = \theta$, with $\rho(\theta - 0) \to -$w and $\rho(\theta + 0) \to +\infty$, while the change in p close to the electrode is insignificant.

The distributions of $\psi(x)$ and $E = -d\psi/dx$ for a number of values of $j_1$, $j_2$, and k are shown in Figs. 2 and 3. Functions $\psi(x)$ are smooth and continuous, and owing to the logarithmic divergence of $\psi$ which occurs when $x \to 0$, we find that $\psi(0) \to -\infty$ when $j_1$ tends towards $j_1^l$ in the case of $k < \nu$. When $j_1$ tends towards $j_1^l$ while $k > \nu$, the values of $\psi$ decrease everywhere within the region of $0 < x < \theta$ owing to the decrease of $\psi$ at $x \approx \theta$ (Fig. 2).

At $k > \nu$, the electrical field E decreases monotonically within the region of $0 < x < \theta$, then it increases monotonically within the region of $\theta < x < 1$, but there is no change in its sign. At $j_1$ coming close to $j_1^l$, function $E(x)$ asymptotically tends toward a vertical line of $x = \theta$ to the left and right of $x = \theta$ when $k < \nu$ (Fig. 3). Function $E(x)$ asymptotically tends toward a vertical line of $x = 0$ at $j_1$ coming close to $j_1^l$ when $k < \nu$.

Thus, the above analysis shows that the homogeneous recombination of $H^+$ and $OH^-$ ions occurring within the diffusion layer should lead to interesting peculiarities in the space-charge distribution.

A discontinuous change in the sign and magnitude of $\rho(x)$ occurs at the point of $x = \theta$ where the homogeneous reaction is centered. In the process discussed, the region where the homogeneous reaction takes place is concentrated in a point owing to the high value of its rate constant. In the more general case of moderate values of the rate constants, the reaction zone will be spread out, and the change from positive to negative values will occur smoothly, rather than discontinuously.

The result obtained can be explained qualitatively as follows. The region where the homogeneous reaction takes place can formally be visualized as the plane of an electrode to which $H^+$ ions are supplied from one side, and $OH^-$ ions from the other side. A space charge of positive sign develops — just as in ordinary binary electrolyte solutions — in the region of $\theta \leq x \leq 1$, where the $H^+$ ions are supplied. The space charge is negative in the region of $0 \leq x \leq \theta$, where the $OH^-$ ions are supplied. At

$$D_3\left(\frac{dc_3}{dx}-c_3\frac{d\psi}{dx}\right)-D_4\left(\frac{dc_4}{dx}+c_4\frac{d\psi}{dx}\right)=-\frac{i_2L}{Fc^0}=-D_3j_2. \tag{7}$$

$$c_3c_4=K_0, \tag{8}$$

$$c_2+c_3=c_1+c_4. \tag{9}$$

Here $c_1$, $c_2$, $c_3$, and $c_4$ are the concentrations of cations $A^+$, anions, $OH^-$ ions, and $H^+$ ions made dimensionless with the aid of the concentration, $c^0$, of $A^+$ ions in the bulk solution; $\psi = F\varphi/RT$ is the dimensionless electric potential, $x$ is the coordinate made dimensionless with the aid of diffusion-layer thickness L $(0 \le x \le 1)$; $i_1$ and $i_2$ are the current densities of cation discharge and oxygen reduction; and $K_0$ is the ionic product of water. Equation (9) is a statement of the condition of local electroneutrality.

The boundary conditions at $x = 1$ (the diffusion-layer boundary on the side of the bulk solution) are of the form of

$$c_1(1)=1,\quad c_2(1)=1+k,\quad c_3(1)=0,\quad c_4(1)=k,\quad \psi(1)=0. \tag{10}$$

The current for reduction of the neutral substance (here $O_2$) is independent of the rate of reduction of other substance.. Thus, the limiting value of current density $i_2$ depends only on the $O_2$ concentration in the part of the solution that is stirred, and in the present context is regarded as an extraneous, given parameter.

The water recombination reaction (4) is very fast, and the equilibrium constant K $\ll$ 1; we can assume, therefore, that at any point within the diffusion layer we shall find, either $OH^-$ ions or $H^+$ ions, but never both at the same time. Then the diffusion layer as a whole is split into two regions, $0 \le x \le \theta$ and $\theta \le x \le 1$, by the point of recombination of the $H^+$ and $OH^-$ ions, $x = \theta$. In the region to the right of $x = \theta$, it can be assumed that $c_4 > 0$ and $c_3 = 0$, while in the region to the left it can be assumed that $c_3 > 0$ and $c_4 \approx 0$. Using these approximations we can change from Eq. (7) describing the overall flux of the $H^+$ and $OH^-$ ions to the two equations

$$\frac{dc_3}{dx}-c_3\frac{d\psi}{dx}=-\frac{i_2L}{FD_3c^0}=-j_2,\qquad 0<x<\theta, \tag{11}$$

$$\frac{dc_4}{dx}+c_4\frac{d\psi}{dx}=\frac{i_2L}{FD_4c^0}=j_2\nu,\qquad \theta<x<1, \tag{12}$$

where $\nu = D_3/D_4$. We point out that the dimensionless fluxes $j_1$ and $j_2$ introduced in (5) and (7) are positive.

In [2] an analytical solution to the above system of equations was described, and the distributions of potential and of the concentrations of all components were found. The distribution of electric field strength within the diffusion layer obtained in [2] can be described by the relations

$$-\frac{d\psi}{dx}=-\frac{j_1+\nu j_2}{2(1+k)+(j_1+\nu j_2)(x-1)}\quad \text{for. } \theta\leqslant x\leqslant 1, \tag{13}$$

$$-\frac{d\psi}{dx}=-\frac{j_1+j_2}{(j_1-j_2)(x-\theta)+2G}\quad \text{for } 0\leqslant x\leqslant\theta. \tag{14}$$

Here G is the concentration found at point $x = \theta$ for the cations undergoing discharge:

$$G=c_1(\theta)=\sqrt{(1+k)(1-j_1k/\nu j_2)}. \tag{15}$$

The value of $\theta$ has also been found by solving

$$\theta=1-2(1+k)\left[1-\sqrt{(1-j_1k/\nu j_2)/(1+k)}\right]/(j_1+\nu j_2). \tag{16}$$

the plane of $x = \theta$ itself, the charge density should change discontinuously, and in the more general case of a distributed homogeneous reaction, a transition zone will exist where the space charge changes sign.

In the above analysis, the set of two parallel electrode reactions (2) and (3) followed by the homogeneous reaction (4) was considered for which a solution to the electrodiffusion problem had been obtained previously in the approximation of local electroneutrality [2]. Setting $j_1 = 0$ in all of the above relations we arrive at the case of a single electrode reaction (3) that is followed by the homogeneous reaction. In this situation the ions with concentrations $c_1$ and $c_2$ function as the base electrolyte. It is easily seen that again a discontinuous change in the size and sign of space-charge density should occur within the diffusion layer. This effect is the more pronounced the lower the base-electrolyte concentration and the less suppressed are the effects of the migration current.

We point out in conclusion that peaks in the space-charge distribution, including those attended by a change in sign of the space charge, had been predicted in [3, 4] for systems where fixed charges exist in addition to the mobile ions, and also for membrane systems within which homogeneous chemical reactions involving charged reactants take place [5].

## LITERATURE CITED

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