

## CALCULATION OF THE FORCES ACTING ON A POORLY CONDUCTING FLUID IN AN ELECTRIC FIELD\*

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On the basis of an asymptotic analysis of the equations describing the motion of charged components of a poorly conducting fluid in an electric field, a method is examined for computing the Coulomb forces due to the space charge. It is assumed that the rate of charged particle formation because of dissociation processes is dependent on the field strength. As experiments show [2-4], convective motion occurs in weakly conductive fluids subjected to Coulomb and polarization forces [1] in strong fields. Existing methods of computing the Coulomb forces that play a fundamental role in the actions on the fluid are based on using given dependences of the conductivity of the medium on the thermodynamic parameters and the field strength for calculating the magnitude of the space charge, and the contribution of the induced fields is not taken into account here. However, the conductivity in poorly conducting media is not a given transfer coefficient, and as is shown below, should be determined from the solution of the equations of motion of the charged components taking the boundary conditions on the fluid-solid interfacial surfaces into account.

1. Formulation of the problem. Two electrodes, between which an electric potential difference  $\varphi_w^*$  is produced, are placed in a weakly conductive fluid (such as transformer oil with weak electrolyte molecule impurities, etc.). One of the electrodes is a sphere of small radius  $R$ , while the second electrode is a grounded grid surrounding the sphere and pervious to the fluid. We consider the case when the spacing between the electrodes is  $L \gg R$ .

The distribution of positively and negatively charged particles and the electric potential must be found in the interelectrode spacing in order to compute the Coulomb forces in this domain. We shall use a three-constituent mixture of neutral particles and two species of ions, positive and negative, that comprise a small impurity in the carrying medium of neutral particles, as the model of the weakly conductive fluid under consideration.

Let bulk dissociation reactions proceed in the fluid with the formation of positive and negative ions and recombination. Let electrochemical reaction also proceed on the electrode surface, whereupon the neutral molecules will be transformed into positive or negative ions while the charged particles arriving at the surface from the bulk will become neutral. Since we are not interested in the chemical constitution of the ions, we shall use the effective parameters to describe them, such as the densities  $n_i^*, n_e^*$ , the mobility coefficients  $b_i^*, b_e^*$ , the ionization rate  $w^*$  and the recombination coefficient  $\alpha^*$  (the subscripts  $i$  and  $e$  refer to the positive and negative ions respectively).

The equations describing the stationary distributions of the dimensionless charged particle densities  $n_i, n_e$ , the electric potential  $\varphi$ , the field strength  $E$ , and the electric current densities  $j_i, j_e$  have the form

$$\delta b_e [r^2 (n_e' \pm \varphi_w n_e \varphi')] = r^2 (\alpha n_i n_e - w) \quad (1.1)$$

$$\kappa \varphi_w (r^2 \varphi') = r^2 (n_e - n_i), \quad E = -\varphi' \quad (1.2)$$

$$j_s = -b_e (\varphi_w^{-1} n_e' \pm n_e \varphi'), \quad s = i, e, \quad f' \equiv df/dr \quad (1.3)$$

Here the convective charged particle transport is neglected and by virtue of the condition  $L \gg R$ , spherical symmetry is assumed. The assumptions mentioned impose a lower constraint on the magnitude of the field strength. Dimensionless variables are introduced into (1.1)-(1.3) as follows:

$$r = \frac{r^*}{R}, \quad n_s = \frac{n_s^*}{n_0}, \quad \varphi = \frac{\varphi^*}{|\varphi_w^*|}, \quad E = \frac{E^* R}{|\varphi_w^*|} \quad (1.4)$$

$$j_s = \frac{j_s^*}{j_0}, \quad w = \frac{w^*}{w_0}, \quad \alpha = \frac{\alpha^*}{\alpha_0}, \quad b_s = \frac{b_s^*}{b_0}$$

$$n_0 = w_0^{-1/2} \alpha_0^{-1/2}, \quad j_0 = e_p n_0 b_0 |\varphi_w^*| R^{-1}$$

Here  $r^*$  is the distance from the centre of the spherical electrode,  $e_p$  is the charge on a proton, and  $k$  is Boltzmann's constant. The subscript zero denotes the characteristic values  
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of the parameters and the asterisk the dimensional variable.

Three dimensionless parameters

$$\delta = \frac{kT^*b_0}{e_p R^2 (w_0 \alpha_0)^{1/2}}, \quad \alpha = \frac{\varepsilon kT^*}{4\pi e_p^2 n_0 R^2}, \quad \varphi_w = \frac{e_p |\varphi_w^*|}{kT^*} \quad (1.5)$$

occur in (1.1)–(1.3)

In a strong field the effective ionization rate can depend not only on the temperature  $T^*$  and density  $n_0^*$  of the dissociating particles (these quantities are considered constant) but also on the field strength  $/5, 6/$ . We write the quantity  $w$  in the form  $/6/$

$$w = w(n_0, T, 0) \exp(2\beta |E|^{1/2}), \quad \beta = e_p \varphi_w^{1/2} (ekT^*R)^{-1/2}, \quad (1.6)$$

Here  $w(n_0, T, 0)$  is the dimensionless ionization rate in the absence of a field (this quantity is considered given), and  $\varepsilon$  is the permittivity of the medium.

We write the boundary conditions for (1.1) and (1.2) on the surface of the spherical electrode in the form ( $s = i, e$ )

$$\begin{aligned} r = 1, \quad \varphi = \pm 1 \\ \lambda_s \delta^{-1} (k_s - v_s k_{rs} n_s) = b_s (-n_s' \mp \varphi_w n_s \varphi') \\ k_s = \frac{k_s^*}{k_{s0}}, \quad k_{rs} = \frac{k_{rs}^*}{k_{rs0}}, \quad \lambda_s = \frac{k_{s0}}{w_0 R}, \quad v_s = \frac{k_{rs0} n_0}{k_{s0}} \end{aligned} \quad (1.7)$$

Here  $k_s^*, k_{rs}^*$  are the effective parameters of surface electrochemical reactions of the type  $A^+ + e \rightleftharpoons A, B^- - e \rightleftharpoons B$ . The quantities  $k_s, k_{rs}$  are later considered given. The upper sign on the left side of (1.1), on the right sides of (1.3) and the third relationship (1.7) corresponds to positive ions ( $s = i$ ). The selection of the sign in the second relationship of (1.7) is governed by the sign of  $\varphi_w^*$ .

By virtue of the assumption  $L \gg R$ , we replace the condition on the outer electrode by the asymptotic conditions

$$r \rightarrow \infty, \quad \varphi \rightarrow 0, \quad n_i \rightarrow (w/\alpha)^{1/2}, \quad n_e \rightarrow (w/\alpha)^{1/2} \quad (1.8)$$

It is here assumed that the medium is quasineutral fairly far from the electrodes, the electric fields is small (because of the spherical geometry of the problem), and the charged particle densities are governed by the chemical equilibrium conditions.

Eqs. (1.1)–(1.3) and boundary conditions (1.7)–(1.8) enable us to find the charged particle density, the electric potential, and the field strength distributions in the neighbourhood of the spherical electrode, and to compute the magnitude of the Coulomb forces acting on the fluid in the interelectrode space by means of these distributions.

The physical mechanism resulting in the appearance of a space charge (SC) in the initially neutral dissociating medium during current passage through a domain with a non-uniform electrical field distribution is examined in  $/7/$ . Estimates in general form were carried out there for the limits of applicability of the relationships used to compute the Coulomb forces by means of a given dependence of the conductivity of the medium on the field and other parameters.

An asymptotic analysis of the problem formulated in the case when the parameters are  $\delta \ll 1, \varphi_w \gg 1, \delta \varphi_w \gg 1, \alpha \varphi_w \gg 1$ , and the ionization rate is independent of the field, was performed in  $/8/$ . It has been shown that for a certain relationship between the parameters of the surface electrochemical reactions the problem has a solution describing the bipolar structure of the SC domain near the electrode, which was observed in the experiment (the sign of the SC in the diffusion boundary layer agrees with the sign of the electrode charge and the Coulomb force is directed from the electrode; a SC of opposite sign, whose density decreases monotonically to zero with distance from the electrode, is formed outside the diffusion layer, and the Coulomb force acts in the direction of the electrode in this domain).

An asymptotic analysis of the problem is performed below under the conditions when the parameters are  $\delta \ll 1, \varphi_w \gg 1, \delta \varphi_w \ll 1, w = w(E)$ . It is shown that the domain outside the diffusion boundary layer also has a bipolar structure; the SC of the medium changes sign with distance from the diffusion layer boundary, and a domain occurs with the same named charge as the electrode. In this domain the Coulomb force is again directed from the electrode. A numerical solution is also obtained for the problem in the complete formulation for values of the parameters corresponding to real weakly conductive fluids.

**2. Asymptotic analysis of the problem in a diffusionless approximation.** We will investigate the behaviour of solutions of the problem formulated above in the domain outside the diffusion boundary layer under conditions when the parameters are  $\delta \ll 1, \varphi_w \gg 1$ . To simplify the calculations we consider the case when the charged particle mobility coefficients are identical ( $b_i^* = b_e^*$ ), the recombination coefficient is calculated by the Langevin formula, and the quantities  $w(n_0, T, 0), k_s^*, k_{rs}^*$  are constants. For an appropriate selection of the characteristic values of the parameters we can evidently set  $b_i = b_e = 1, \alpha = 1, k_s = k_{rs} = 1, w = \exp(2\beta |E|^{1/2})$ . We introduce the new variables

$$q = n_i - n_e, \quad \sigma = n_i + n_e \quad (2.1)$$

The quantities  $q$  and  $\sigma$  are the dimensionless space charge density and conductivity of the medium. Using these variables we write (1.1)–(1.3) by neglecting components describing the diffusion transport of charged particles

$$\begin{aligned} \mu\sigma' &= -\frac{\sigma q}{2E}, \quad \mu E' = \frac{1}{2}q - \frac{2\mu E}{r} \\ \mu q' &= \frac{1}{E} \left[ 2 \exp(2\beta |E|^{1/2}) - \frac{\sigma^2}{2} \right], \quad \mu = \delta\varphi_c \end{aligned} \quad (2.2)$$

In the zeroth approximation in the small parameter  $\delta$ : the equations (2.2) yield the parameter distributions for the medium in the domain outside the diffusion boundary layer.

To be specific, we consider the case of a negatively charged electrode ( $\varphi_w^* < 0$ ). The boundary conditions for (2.2) have the form /8/

$$\begin{aligned} r = 1, \quad 1/2\mu(\sigma - q)E &= \lambda_e [1/2v_0(\sigma - q) - 1] \\ r \rightarrow \infty, \quad E \rightarrow 0, \quad q \rightarrow 0, \quad \sigma \rightarrow 2 \end{aligned} \quad (2.3)$$

$$\int_1^\infty E dr = -1 \quad (2.4)$$

The diffusion component is omitted in the second relationship in (2.3) and it is here considered that the parameter  $\lambda_e > \delta$ . It follows from the first two equations of (2.2) that

$$r^2\sigma E = j = \text{const} \quad (2.5)$$

The constant of integration  $j$  is the total current density on the electrode in the approximation under consideration. After solving problem (2.2), (2.3) by using condition (2.4), a relation can be found between the current on the electrode  $j$  and the applied potential difference  $\varphi_w^*$ , the current-voltage characteristic of the electrode.

The parameter  $\mu$  in system (2.2) can be represented in the form of the relationship  $\mu = \tau_{c,h}/\tau_E$ , where  $\tau_{c,h} = (w_0\alpha_0)^{-1/2}$  is the characteristic time of the change in the charged particle density because of the bulk chemical reactions, and  $\tau_E = R^2(b_0|\varphi_w^*|)^{-1}$  is the characteristic time of ion drift in the electric field. We will perform an asymptotic analysis of the problem for conditions when the charged particle motion under the effect of the field disturbs the chemical equilibrium slightly; here  $\mu \ll 1$ . The parameter  $\mu$  is contained in the equations as a factor in front of the derivatives, for small  $\mu$  the problem is singularly disturbed, consequently, the method of boundary layer expansions /10/ can be utilized.

We introduce the boundary-layer (BL) variable  $\tau = (r-1)\mu^{-1}$  and we seek the solution in the form of expansions in the parameter  $\mu$  that consist of a smooth part (dependent on the variable  $r$ ), and a BL part (dependent on the variable  $\tau$ )

$$f = f_0(r) + \mu f_1(r) + \dots + F_0(\tau) + \mu F_1(\tau) + \dots$$

where  $f = q, \sigma, E$ . We substitute these expansions into (2.2) and equate terms with identical powers of  $\mu$ , where the terms dependent on  $r$  and  $\tau$  are, according to /10/, equated separately. The non-linear terms containing the products of the smooth and BL functions refer to the BL equations, and the smooth functions therein are expanded in Taylor series in the neighbourhood of the point  $r = 1$ .

For the initial approximations of the smooth part of the expansions after the calculations, we will have

$$\begin{aligned} q_0 &= 0, \quad r^2 E_0 = \frac{1}{2} j_{w0} \exp(-\beta |E_0|^{1/2}) \\ \sigma_0 &= 2 \exp(\beta |E_0|^{1/2}), \quad q_1 = \frac{2\beta E_0 |E_0|^{1/2}}{r(1 + 1/2\beta |E_0|^{1/2})} \end{aligned} \quad (2.6)$$

Here  $j_{w0}$  is the constant of integration that represents the zeroth term of the expansion of the total current density on the electrode in the parameter  $\mu$ . It is seen from the second equation in (2.6) that  $E_0$  is a function decreasing monotonically in absolute value as  $r$  increases. The quantity  $\sigma_0 \rightarrow 2$  as  $r \rightarrow \infty$ . The sign of  $q_1$  agrees with the sign of  $E_0$  and does not change in the whole domain; here  $q_1 \rightarrow 0$  for  $r \rightarrow \infty$ . It is seen that the functions of the zeroth and first approximation of the smooth part of the solution satisfy the asymptotic conditions (2.3) as  $r \rightarrow \infty$ .

The second equation of (2.6) yields  $j_{w0} = 2E_{01} \exp(\beta |E_{01}|^{1/2})$ , where  $E_{01} = E_0(1)$ . In the zeroth approximation in  $\mu$  a relationship that agrees with (2.4) is obtained for the function  $E_0(r)$ , therefore  $E_0(r) < 0$ ,  $j_{w0} < 0$ . Substituting  $E_0(r)$  into (2.4), and integrating by using the second equation in (2.6), we obtain

$$4\beta^{-1}t + t^2 - 4\beta^{-1}t \exp(1/2\beta t) = -1, \quad t = |E_{01}|^{1/2} \quad (2.7)$$

It is seen from (2.7) that the quantity  $|E_{01}|$  decreases monotonically as  $\beta$  increases, hence  $|j_{w0}|$  grows. For  $\beta = 0$  the quantity  $j_{w0} = -2$ , as  $\beta \rightarrow \infty$  the asymptotic form of the current density is given by the relationship  $j_{w0} = -\beta^2/8$ . In dimensional variables we have

$$j_{w0}^* = \frac{2e_p n_0 b_0 \varphi_{w0}^*}{R}, \quad \beta \ll 1 \quad (2.8)$$

$$j_{w0} = -\frac{e_p^4 n_0 b_0 \varphi_{w0}^{*2}}{8 \cdot (kT^*)^2 R^2}, \quad \beta \gg 1$$

We note that this result agrees qualitatively with experimental data according to which the current density for small field intensities is proportional to the applied potential difference while the current dependence on the potential difference is quadratic in strong fields /11/.

The equations for the functions  $F_0, Q_0, S_0$ , that represent the zeroth approximation of the BL part of the expansions for the quantities  $E, q, \sigma$ , respectively, have the form

$$\frac{dF}{d\tau} = \frac{1}{2} Q_0, \quad \frac{dQ_0}{d\tau} = \frac{1}{F} \left[ 2 \exp(2\beta |F|^{1/2}) - \frac{j_{w0}^2}{2F^2} \right] \quad (2.9)$$

$$S_0 = j_{w0} \left( \frac{1}{F} - \frac{1}{E_{01}} \right), \quad F = F_0 + E_{01} \quad (2.10)$$

The existence of solutions of BL type (tending asymptotically to zero as  $\tau \rightarrow \infty$ ) follows from an analysis of the integral curve pattern for (2.9) in the phase plane  $(F, Q_0)$ . The point  $(E_{01}, 0)$  whose coordinates correspond to asymptotic values of the desired functions is a saddle-point singularity for the equation

$$\frac{dQ_0}{dF} = \frac{4F^2 \exp(2\beta |F|^{1/2}) - j_{w0}^2}{Q_0 F^3} \quad (2.11)$$

Therefore, two singular integral curves exist that pass through the point  $(E_{01}, 0)$ . The quantities  $Q_0$  and  $F$  are connected on these curves by the relationship

$$\frac{Q_0}{4} = \frac{j_{w0}^2}{4} \left( \frac{1}{F^2} - \frac{1}{E_{01}^2} \right) + 2 \int_{E_0}^F \frac{1}{F} \exp(2\beta |F|^{1/2}) dF \quad (2.12)$$

The singular integral curves have just one point of intersection with the line  $Q_0 = 0$  since  $dQ_0/dF \neq 0$  thereon. Consequently, the quantity  $Q_0$  does not change sign in the BL domain.

We will examine the boundary conditions on the electrode surface. The second relationship in (2.3) contains the parameters  $\lambda_e$  and  $v_e$  whose order can generally be different relative to the parameter  $\mu$ . In conformity with this, the boundary conditions for the BL functions take a different form. For instance, we examine the case when the parameters  $\lambda_e \sim \mu, v_e \sim 1$ . In the zeroth approximation in  $\mu$  we have

$$\tau = 0, \quad \frac{\eta_e}{2} \left[ \frac{j_{w0}}{F(0)} - Q_0(0) \right] F(0) = -1 + \frac{v_e}{2} \left[ \frac{j_{w0}}{F(0)} - Q_0(0) \right], \quad \eta_e = \frac{\mu}{\lambda_e} \quad (2.13)$$

Together with (2.13), relationship (2.12) written at the point  $\tau = 0$  yields the boundary conditions for (2.9).

We will now examine the qualitative pattern of the parameter distributions in the neighbourhood of the electrode. In the case of a negatively charged electrode ( $\varphi(1) = -1$ ), the quantity  $F(0) < 0$ , and here it follows from the conditions for the BL solutions of (2.9) to exist that we should have  $Q_0 > 0$ . For  $\mu \ll 1$  the main contribution to  $q$  in the BL domain is introduced by  $Q_0$ . Therefore, a positive space charge (SC) is generated near the electrode in a layer of thickness of the order of  $\mu$ . This charge occurs under the action of a field attracting positive charges to the electrode. We note that surface electrochemical processes in which the negative ions participate exert an influence on the SC magnitude in the positively charged layer since the distribution of  $q$  here depends on the values of  $Q_0(0)$  and  $F(0)$ . Outside the BL domain  $Q_0, Q_1 \rightarrow 0$  and the main contribution to the space charge of the medium is introduced by  $q_1$ . As already noted, the sign of  $q_1$  agrees with the sign of  $E_0$ . In turn, the sign of  $E_0$  is identical with the sign of the electrode. The formation of a negative SC outside the BL domain is associated with the progress of the electric current in the dissociating medium in the presence of a non-uniform field.

Therefore, within the framework of the diffusionless model under conditions when the dissociation rate depends on  $E$ , the following structure of the near-electrode domain can be described. Near the electrode surface there is a positive SC layer which is replaced by a more extensive domain with negative SC with distance from the electrode, here the maximum value of  $q$  in the positively charged domain is substantially greater than the maximum value of  $|q|$  in the negative SC domain. The Coulomb force in the domain where  $q < 0$  is directed from the electrode.

We note that a situation is possible when  $Q_0(0) = 0$  on the electrode surface because of (2.12) and (2.13). The SC part of the solution is missing here and the negative SC domain governed by the smooth part of the solution propagates down to the electrode surface (more accurately, to the diffusion layer boundary). Only for such a situation are the representations developed in /12/ valid.

We calculate the total space charge  $Q$  that occurs in the fluid under the action of the mechanisms under consideration. Integrating  $q$  over the whole space occupied by the medium, we will have to terms in  $\mu^2$

$$\begin{aligned} Q &= Q_p + Q_n, \quad Q_p = -8\pi\mu F_0(0) \\ Q_n &= 8\pi\mu E_{01} [\exp(\beta |E_{01}|^{1/2}) - 1] \end{aligned} \quad (2.14)$$

The quantity  $Q_p$  yields the total positive SC that occurs in the medium under the effect of a field directed to the electrode and the surface electrochemical reactions with the participation of negative ions. The quantity  $Q_n$  yields the total negative SC that is formed during current progress through a domain with inhomogeneous  $E$  under conditions when the field accelerates the bulk dissociation process. Both charges are of order  $\mu$ . This is explained by the fact that the positively charged layer where  $q \sim 1$  has a thickness of the order of  $\mu$  while the extent of the negatively charged layer where  $|q| \sim \mu$  is on the order of one.

We will project the Coulomb force acting on the medium at each point along the radius in some isolated direction and integrate over the appropriate half-space. To terms of the order of  $\mu^2$  an expression can be obtained for the total force  $P$

$$\begin{aligned} P &= P_a + P_r, \quad P_a = -2\pi\mu F_0(0) [F_0(0) + 2E_{01}] \\ P_r &= 4\pi\mu [|j_{w0}| \beta^{-2} - |E_{01}| (|E_{01}| + 2|E_{01}|^{1/2}) \beta^{-1} + 2\beta^{-2}] \end{aligned} \quad (2.15)$$

The quantity  $P_a$  yields the force that acts in the positive SC layer and squeezes the fluid to the electrode. The quantity  $P_r$  describes the repulsive force acting in the negatively charged layer. Both parts of the force are of the order of  $\mu$ . It is seen that the repulsive force  $P_r$  is governed just by the value of  $\beta$ . For  $\beta = 0$  when the field does not affect dissipation,  $P_r = 0$ . For  $\beta \gg 1$  the asymptotic value is  $P_r = 1/2\pi\mu$ . In dimensional variables this quantity is  $P_r^* = \epsilon\varphi_w^{*2}/16$ . We note that the dependence of  $P_r$  on  $\beta$  is not monotonic. The maximum value  $P_r \approx 0.7\pi\mu$  is reached for  $\beta \approx 10$ .

We will estimate the magnitude of the velocity which the repulsive force  $P_r$  can produce in the fluid. In dimensional variables, the extent of the domain with negative space charge is of the order of the electrode radius  $R$ . For sufficiently small  $R$  the force  $P_r$  can be considered as a point. Using the solution of the problem on the flow subjected to a point force, we write

$$v^* = \frac{P_r^*}{4\pi\eta^*z^*} \approx \frac{\epsilon\varphi_w^{*2}}{64\pi\eta^*z^*}, \quad \beta \gg 1$$

Here  $v^*$  is the fluid velocity in the direction of action of the point force  $P_r^*$ ,  $\eta^*$  is the dynamic viscosity of the fluid, and  $z^*$  is the distance from the point of application of the force. The estimate obtained for  $v^*$  agrees qualitatively with experimental results [2, 11] where a quadratic dependence of the velocity on the applied potential difference was also observed for high field intensities.

3. Solution of problem (1.1)–(1.3), (1.7), (1.8) for intermediate values of the parameters. The numerical solution of problem (1.1)–(1.3), (1.7), (1.8) in the complete formulation, obtained by the method of build-up by an implicit difference scheme using vector factorization for the solution of the difference equations linearized by using iteration, confirms the qualitative pattern described above for the parameter distributions of the medium in the neighbourhood of the electrode. The computations were performed for the following values of the quantities in the problem  $R = 10^{-4}$  m,  $b_0 = 3.87 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ,  $b_i = 1$ ,  $b_e = 2$ ,  $w_0 = 2.7 \times 10^{16} \text{ m}^{-3} \text{ sec}^{-1}$ ,  $\alpha_0 = 7 \times 10^{-15} \text{ m}^3 \text{ sec}^{-1}$ ,  $w(n_a, T, 0) = 1$ ,  $\alpha = 1$ ,  $T^* = 300$  K,  $n_0 = 1.96 \times 10^{15} \text{ m}^{-3}$ ,  $\epsilon = 2$ , and  $\beta\varphi_w^{-1/2} = 0.033$ . These values correspond to a fluid with characteristic conductivity  $1.03 \times 10^{-9}$  s/cm (such as transformer oil not subjected to any special refining). The characteristic value of the mobility coefficient corresponds to a diffusion coefficient of  $10^{-9} \text{ m}^2/\text{sec}^{-1}$ , and the value of  $\alpha_0$  is calculated from Langevin's formula. The characteristic value of the dissociation rate  $w_0$  is taken on the basis of data obtained in [13] by processing experimental current-voltage characteristics. The dimensionless parameters are  $\delta = 10^{-2}$  and  $\kappa = 6.8 \times 10^{-2}$ . The parameter  $\mu = \delta\varphi_w$  varied in the range  $10^{-2} \leq \mu \leq 780$  as the electrode potential  $\varphi_w^*$  varied between values of the order of  $-1$  V to  $-2 \times 10^3$  V. The small value of  $R$  selected simulates a needle electrode.

Parameter distributions of the medium are presented below for the case when the charged particles on the electrode surface recombine at an infinite rate ( $\nu_s = \infty$ ), here  $n_i(1) = n_e(1) = 0$ . The boundary value is  $q(1) = -1$  (negatively charged electrode).

Profiles of the ion densities  $n_i$  (the solid lines) and  $n_e$  (the dashed lines) are represented in Fig. 1 for values of the parameters  $\varphi_w = 3.8 \times 10^4$  (curve 1) and  $\varphi_w = 7.8 \times 10^4$  (curve 2). The value of the parameter is  $\mu \gg 1$ ; here the field in the neighbourhood of the electrode strongly disturbs the equilibrium of the bulk chemical reactions.

Computations show that in the immediate proximity to the electrode surface there is a thin diffusion boundary layer with a thickness of less than  $10^{-3} R$ , where the positive ion density grows abruptly (for  $\varphi_w = 7.8 \times 10^4$  the quantity  $n_i$  reaches the value 5.45 in this layer), while

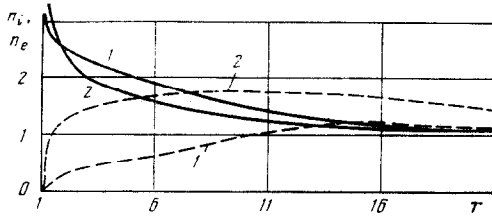


Fig. 1

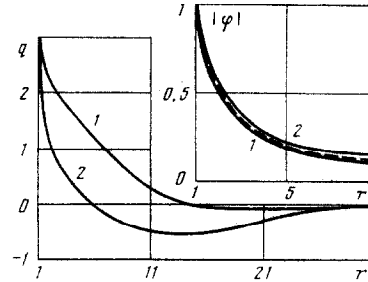


Fig. 2

the negative ion density changes slightly. Furthermore, there is a positive SC layer (the usual double layer on a negatively charged electrode) with a thickness of the order of  $14R$  for  $\varphi_w = 3.8 \times 10^4$  and  $5R$  for  $\varphi_w = 7.8 \times 10^4$ . We note that the double-layer thickness in intense fields substantially exceeds the Debye length  $R_d$  ( $R_d = 0.26 R$  in the case under consideration). The diminution in the double-layer thickness as the field grows is associated with the strong dependence of the ionization rate on the field. Furthermore there is a negative SC layer whose thickness grows as the field strength increases. For  $\varphi_w = 7.8 \times 10^4$  the thickness of this layer reaches approximately  $20 R$ .

The SC and electrical potential distribution is shown in Fig. 2 for  $\varphi_w = 3.84 \times 10^4$  (curve 1) and  $\varphi_w = 7.8 \times 10^4$  (curve 2). It is seen that as  $\varphi_w$  grows the maximum values of  $|q|$  in the double layer and in the negative SC layer will increase. The dashed line yields the potential distribution in the case when  $q \equiv 0$  (external field). For  $\varphi_w = 7.8 \times 10^4$  ( $\varphi_w^* = -2 \text{ kV}$ ) the maximum value of the field strength reaches  $1.6 \times 10^4 \text{ kVm}^{-1}$ .

The electrode current-voltage characteristic is linear ( $j \sim \varphi_w$ ) for  $\varphi_w \leq 3 \times 10^4$ , and a weak non-linearity ( $j \sim \varphi_w^{1.12}$  for  $\varphi_w \leq 7.8 \times 10^4$ ) starts to appear as  $\varphi_w$  increases further.

The pressure drop which should equalize the repulsive force so that the fluid remains fixed can be calculated using the hydrostatic equations. For  $\varphi_w = 7.8 \times 10^4$  the pressure drop is  $0.03 \text{ Pa}$ . Such a pressure drop value can cause a flow velocity of the order of  $10^{-2} \text{ m/sec}^{-1}$  in a stream tube of incompressible fluid. Flows with such velocities have been observed experimentally [11/.

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