ELECTRIFICATION OF WEAKLY CONDUCTIVE LIQUIDS IN FLOW
WITHIN TUBES

Yu. D. Shikhmurzaev

It is well known that when weakly conductive liquids such as hydrocarbons flow within tubes they acquire a certain electrical charge [1-4]. As a result the danger of electrical discharge and explosion in tubes and reservoirs arises [1, 5]. In connection with this, it is of interest to determine the dependence of the maximum electrification current developed in flow of a weakly conductive liquid through a tube on the tube dimensions, liquid properties, and flow parameters.

The development of a space charge within the medium is connected with electrochemical reactions occurring on the tube surface, in which ions of an impurity with electrolytic nature, dissolved in the liquid, participate [2, 4]. Generally speaking, the electrification current, i.e., the charge removed by the liquid per unit time from a tube of given length depends on the rate constants of the surface reactions. The present study will consider the limiting case where ions of only one sign participate in the surface reactions and the reactions occur at an infinite rate. The electrification current will then be determined by the rate of ion supply to the tube surface. In [6] this problem was considered for small-diameter tubes, in which the characteristic thickness of the diffusion boundary layer which develops is small in comparison to the Debye radius of the liquid. It was shown that in this case in the zeroth approximation in the small parameter defined by the ratio of the diffusion boundary-layer thickness to the tube radius, the effect of electric field on ion motion can be neglected, and the problem reduces to solution of the convective diffusion equation.

The present study will consider electrification of a liquid when the diffusion boundary-layer thickness and the liquid Debye radius are of the same order of magnitude and the effect of the electric field developed on ion motion is significant. It will be assumed that the liquid's Debye radius r_D is small in comparison to the tube radius a, $\delta = r_D/a \ll 1$. Cases of complete and slight dissociation of the impurity will be considered. In the latter case it will be assumed that volume electrochemical reactions may occur in the liquid: dissociation of impurity molecules occurring at a constant rate and recombination of ions at a rate which is assumed proportional to the product of their concentrations.

It will be shown that in each of the cases considered there exist dimensionless variables in which in the zeroth approximation with respect to the parameter δ the dependence of maximum electrification current on problem parameters is describable by a universal curve. The form of this curve is obtained numerically for each case. The dependence of maximum electrification current on tube dimensions, liquid properties, and flow parameters will be analyzed. The limits of applicability of the solution obtained will be evaluated.

1. Formulation of the Problem. We will consider electrification of a weakly conductive liquid in a steady state flow within a semiinfinite grounded metallic tube, at the input of which the liquid is not charged. We assume that the liquid conductivity is caused by dissociation of impurity molecules [2, 3] and that electrification occurs due to oxidation-reduction reactions occurring on the inner surface of the tube [2, 4]. We will study the limiting case in which ions of only one sign (for definiteness, negative) react on the tube walls and the reaction occurs at an infinite rate.

We will describe the weakly conductive liquid using the model of a multicomponent mixture consisting of positive and negative ions, neutral electrolyte molecules, and molecules of the nonelectrolytic carrier liquid. We assume that the ion concentrations are much less than the carrier liquid concentration, so that the effect of ions on the motion of the medium may be neglected, taking the flow as known in solving the electrodynamic hydrodynamics problem.

We assume further that the liquid velocity profile is given by the Poiseuille expression, while the temperatures of the components are the same, and equal to the temperatures of the tube wall. With consideration of these assumptions, the system of equations and boundary conditions describing the process of liquid electrification during flow in the tube can be written in the form (using cylindrical coordinates x^*, r^*, with the x^* axis directed along the tube axis)

$$- D_\pm \Delta n_\pm^* \pm b_\pm \, \mathrm{div}\left(n_\pm^* \mathbf{E}^*\right) + u_{\max}\left(1 - \frac{r^{*2}}{a^2}\right)\frac{\partial n_\pm^*}{\partial x^*} = \gamma k_r \left(n_0^2 - n_+^* n_-^*\right); \tag{1.1}$$

$$\mathrm{div}\,\mathbf{E}^* = 4\pi e \varepsilon^{-1}\left(n_+^* - n_-^*\right), \quad \mathrm{rot}\,\mathbf{E}^* = 0; \tag{1.2}$$

$$n_\pm^* = n_0, \quad E_r^* = 0, \quad x^* = 0; \tag{1.3}$$

$$- D_+ \frac{\partial n_\pm^*}{\partial r^*} + b_+ n_+^* E_r^* = 0, \quad n_-^* = 0, \quad E_x^* = 0, \quad r^* = a, \tag{1.4}$$

$$\frac{\partial}{\partial x^*} n_\pm^*, \ E_x^* \to 0, \quad x^* \to +\infty.$$

Here $u_{\max}$ is the liquid velocity on the tube axis; a is the tube radius; $n_\pm^*$, $b_\pm$, $D_\pm$ are the concentrations and mobility and diffusion coefficients for positive and negative ions; $\mathbf{E}^*(E_r^*, E_x^*, 0)$ is the electric field intensity; k_r, n_0 are the recombination coefficient and equilibrium ion concentration; e is the absolute value of the ionic charge; and ε is the dielectric permittivity of the medium. The parameter γ is equal to zero for total dissociation and unity for weak dissociation. In the latter case the change in concentration of neutral electrolyte molecules due to volume reactions can be neglected and the dissociation rate assumed constant. For the future we will assume that $b_+ = b_- = b$, $D_+ = bkTe^{-1}$ (where k is Boltzmann's constant and T is temperature), $k_r = 8\pi e b \varepsilon^{-1}$, Langevin's relationship.

We dedimensionalize Eqs. (1.1), (1.2) and boundary conditions (1.3), (1.4) by introducing the following quantities:

$$n_\pm = n_\pm^*/n_0, \quad E_r = E_r^*/E_r^0, \quad E_x = E_x^*/E_x^0,$$
$$r = r^*/a, \quad x = x^*/(a\varkappa^3), \quad E_r^0 = 4\pi e n_0 \varepsilon^{-1} r_D,$$
$$E_x^0 = E_r^0 r_D/(a\varkappa^3), \quad r_D^2 = \varepsilon kT/(8\pi e^2 n_0),$$
$$\varepsilon_1 = \mathrm{Pe}^{-1/3} = (D/(a u_{\max}))^{1/3}, \quad \varkappa = \delta/\varepsilon_1, \quad \delta = r_D/a.$$

Here r_D is the liquid Debye radius, $a\varepsilon_1$ is the characteristic thickness of the diffusion boundary layer [6]; $\mathrm{Pe} = u_{\max} a D^{-1}$ is the diffusion Peclet number. After the dedimensionalization Eqs. (1.1), (1.2) and boundary conditions (1.3), (1.4) take on the form

$$- \delta^3 \left(\frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial n_\pm}{\partial r}\right) + \varkappa^{-6}\frac{\partial^2 n_\pm}{\partial x^2}\right) \pm \frac{\delta^2}{2}\left(\frac{1}{r}\frac{\partial}{\partial r}(r n_\pm E_r) + \right. \tag{1.5}$$

$$\left. + \delta\varkappa^{-6}\frac{\partial}{\partial x}(n_\pm E_x)\right) + (1 - r^2)\frac{\partial n_\pm}{\partial x} = \gamma\delta(1 - n_+ n_-);$$

$$\delta\left(\frac{1}{r}\frac{\partial}{\partial r}(r E_r) + \delta\varkappa^{-6}\frac{\partial}{\partial x}E_x\right) = n_+ - n_-, \quad \frac{\partial E_r}{\partial x} = \delta\frac{\partial E_x}{\partial r}; \tag{1.6}$$

$$n_\pm = 1, \quad E_r = 0, \quad (x = 0); \tag{1.7}$$

$$-2\delta\frac{\partial n_+}{\partial r} + n_+ E_r = 0, \quad n_- = 0, \quad E_r = 0 \quad (r = 1), \tag{1.8}$$

$$\frac{\partial}{\partial x} n_\pm, \ E_x \to 0 \quad (x \to +\infty).$$

We will study electrification in the initial section of the tube where $\varepsilon_1 \sim \delta \ll 1$, considering the asymptote of the solution of Eqs. (1.5)-(1.8) as $\delta \to 0$, $\kappa \equiv \delta/\varepsilon_1 = O(1)$. The case $\varepsilon_1 \to 0$, $\delta = O(1)$ was studied in [6].

2. Approximate Solution of the Problem. We will seek a solution to the problem using the method of combining asymptotic expansions [7]. Taking the parameter $\delta = 0$ in Eqs. (1.5)-(1.8) and integrating the system thus obtained for the zeroth approximation of the external solution with consideration of the corresponding boundary conditions, we find

$$E_{r0}^{(e)} = 0, \ n_{\pm 0}^{(e)} = 1. \tag{2.1}$$

Here and below the superscripts (e) and (i) indicate parameters of the external and internal solutions, while the subscript 0 indicates that we are considering the zeroth (with respect to δ) approximation of the solution.

To obtain equations and boundary conditions for the internal solution, we substitute in Eqs. (1.5)-(1.8) the unknown functions, expressed in terms of series in powers of the parameter δ. After transformation to the new variables x, y = $(1 - r)/\delta$ we equate terms having equal powers of δ. The equations and boundary conditions for the zeroth approximation appear as follows

$$2 \frac{\partial^2 n_{\pm 0}^{(i)}}{\partial y^2} \pm \frac{\partial}{\partial y} \left(n_{\pm 0}^{(i)} E_{r0}^{(i)} \right) - 4y \frac{\partial n_{+0}^{(i)}}{\partial x} = 2\gamma \left(n_{+0}^{(i)} n_{-0}^{(i)} - 1 \right); \tag{2.2}$$

$$\frac{\partial E_{r0}^{(i)}}{\partial y} = n_{-0}^{(i)} - n_{+0}^{(i)}, \ \frac{\partial E_{r0}^{(i)}}{\partial x} = -\frac{\partial E_{x0}^{(i)}}{\partial y}; \tag{2.3}$$

$$n_{\pm 0}^{(i)} = 1, \ E_{r0}^{(i)} = 0 \ (x = 0); \tag{2.4}$$

$$2 \frac{\partial n_{+0}^{(i)}}{\partial y} + n_{+0}^{(i)} E_{r0}^{(i)} = 0, \ n_{-0}^{(i)} = 0, \ E_{x0}^{(i)} = 0 \quad (y = 0). \tag{2.5}$$

The conditions for merger of the zeroth approximations in the external (flow "core") an internal (boundary layer) regions have the form

$$n_{\pm 0}^{(i)} \to 1, \ E_{r0}^{(i)} \to 0 \quad (y \to +\infty). \tag{2.6}$$

It is evident from Eqs. (2.2), (2.3) and boundary conditions (2.4)-(2.6) that the functions $n_{\pm 0}^{(i)}$, $E_{r0}^{(i)}$ can be determined independently of the function $E_{x0}^{(i)}$, which is then found from the second expression of Eq. (2.3) using the last boundary condition of Eq. (2.5). The values of the function $E_{x0}^{(i)}$ on the external boundary of the boundary layer are boundary conditions for determining the zeroth approximation of E_x in the external region.

We note that in the case of weak dissociation of the impurity molecules with a recombination coefficient smaller than or of the order of the Langevin coefficient, the condition for electrochemical equilibrium in the boundary layer $n_0^2 = n_+^* n_-^*$ is in general not satisfied. This statement follows directly from the form of the electrodiffusion boundary-layer equations, Eqs. (2.2), (1.3).

For total ($\gamma = 0$) or weak ($\gamma = 1$) dissociation of the impurity molecules, we can obtain an expression for the electrification current $J_y(L)$, i.e., the charge carried off by the flowing liquid per unit time from a section of tube of length L. This current is obviously equal but opposite in sign to the current flowing from the tube to ground, the value of which can be obtained by integrating the current density $j^* = eD \, \partial n_-^* / \partial r^* |_{r^*=a}$. Thus,

$$J_y(L) = -2\pi a e D \int_0^L \frac{\partial n_-^*}{\partial r^*} \Big|_{r^*=a} dx^* = (1 + O(\delta)) \frac{\varepsilon k T u_{max}}{4e} \int_0^{x_L} \frac{\partial n_{-0}^{(i)}}{\partial y} \Big|_{y=0} dx, \ x_L = L/(ax^3). \tag{2.7}$$

Equations (2.2), (2.3) and boundary conditions (2.4)-(2.6), which serve to determine the zeroth approximation of the solution in the boundary layer, contain a single parameter γ, which (assuming the Langevin dependence of recomination coefficient on mobility and charge of the ions and dielectric permittivity of the liquid) takes on two values. In view of this, for both total and weak dissociation of the impurity the integral on the right side of the last expression of Eq. (2.7) is a universal function of the upper limit, and is independent of the parameters. Introducing the notation $F_\gamma(x) = \int_0^x \partial n_{-0}^{(i)} / \partial x \, (0, x) \, dx$, to the accuracy of terms of the order of δ we can rewrite Eq. (2.7) in the form

$$J_\gamma(L) = \frac{\varepsilon k T u_{max}}{4e} F_\gamma \left(\left(\frac{8\pi n_0}{\varepsilon} \right)^{3/2} \frac{L a e^2 b}{(kT)^{1/2} u_{max}} \right) \equiv \frac{\varepsilon k T u_{max}}{4e} F_\gamma \left(\left(\frac{4\pi \sigma}{\varepsilon} \right)^{3/2} \frac{L a}{D^{1/2} u_{max}} \right) \tag{2.8}$$
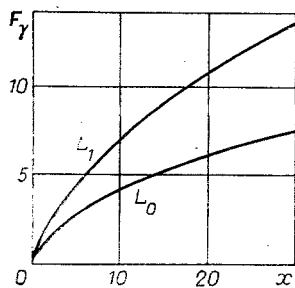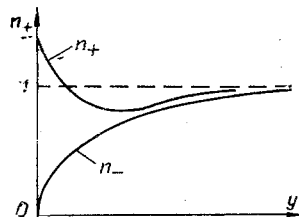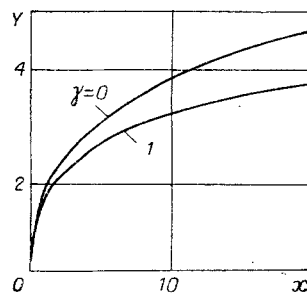
Fig. 1   Fig. 2   Fig. 3

(where σ is the equliibrium conductivity of the liquid).

The functions $F_\gamma(x)$ ($\gamma = 0$; 1) were obtained by numerical solution of Eqs. (2.2)-(2.6). Their curves are shown in Fig. 1, where L_0 and L_1 indicate total and weak dissociation, respectively. Having a known function $F_\gamma(x)$, it is possible to use Eq. (2.8) to clarify the dependence of electrification current on tube dimensions, liquid properties, and flow rate. To do this it is convenient to consider the dependence of log F_γ on log x. In logarithmic scale the angle formed by the tangent to the curve log F_γ(log x) to the axis log $F_\gamma = 0$ changes monotonically, tending downward to a value of 2/3 as log x → −∞ and to zero as log x → + ∞. From this and Eq. (2.8) it follows that the electrification current increases with increase in liquid temperature, flow rate through the tube, tube radius, length of the segment considered L, ion mobility, and ion concentration at the entrance to the tube. The dependence of electrification current on the ionic charge value is nonmonotonic. As is evident from Fig. 1, the electrification current is larger when the impurity electrolyte is weak.

We note that at $x_L \ll 1$, i.e., when the diffusion layer thickness is much less than the liquid's Debye radius, calculation by Eq. (2.8) gives the same results as the expression for electrification current obtained in [6].

Ion concentration profiles (for $\gamma = 0$) are shown in Fig. 2. These show that just as in the case $\varepsilon_1 \to 0$, $\delta = O(1)$ [6], the space charge is mainly concentrated in a narrow layer near the wall. The positive ion concentration profile at some distance from the tube surface has a minimum, where the diffusion component of the radial positive ion flux changes sign. The migration component is directed along the radius everywhere. This changes in sign of the diffusion component of the radial positive ion flux is related to the effect of the tube wall, on which the diffusion component compensates the migration one, while far from the tube surface the migration flux of positive ions leads to a reduction in their concentration in the radial direction, i.e., to the appearance of a diffusion flux directed along the radius. At $\gamma = 1$ the space charge is also concentrated in a narrow layer near the wall, but the positive ion concentration increases monotonically with decrease in distance to the wall.

We will estimate the maximum length of the tube segment over which the electrification current can be calculated with Eq. (2.8). We will term the quantity $\delta_{ef}(x)$, defined by the equation

$$\max \left[|1 - n_+(x, 1 - \delta_{ef}(x))|, \ |1 - n_-(x, 1 - \delta_{ef}(x))| \right] = 0.05,$$

the dimensionless "effective thickness" of the electrodiffusion boundary layer. Equation (2.8) can be used for calculation if $\delta_{ef}(x_L) \ll 1$. Figure 3 shows a graph of the function $Y(x) = \delta_{ef}(x)/\delta$, obtained numerically, which for a given value of the parameter δ allows estimation of the "effective thickness" of the electrodiffusion boundary layer.

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HYDRODYNAMIC MECHANISM OF SPONTANEOUS RETARDATION
OF AN ENDOTHERMIC REACTION

V. I. Naidenov

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It is known that the steady operating regimes of continuous reactors for endothermic reactions are generally stable. This is true if the velocity of the reacting mixture is not dependent on temperature and concentration. However, as was shown in [2-4], allowing for the dependence of the viscosity of the fluid and, thus, the flow velocity on the governing factors of the process (temperature, degree of conversion) leads to qualitative changes in the processes of chemical conversion, heat and mass transfer, and motion. The studies [5-7] examined nonlinear effects in media in the case of volumetric heat adsorption, these effects having been due to the temperature dependence of the thermal conductivity and the capacity of the heat sink.

Here we describe the hydrodynamic mechanism of spontaneous retardation of an endothermic reaction occurring in a moving homogeneous fluid. It should be noted that the results obtained are also valid for other manufacturing processes which involve the motion of a fluid with variable viscosity.

We will examine the laminar flow of a viscous fluid in a circular tube of radius a and length L under the influence of an applied pressure gradient p. For simplicity, we will assume that there is no heat transfer through the tube wall and that an endothermic reaction with an activation energy E_2 and a thermal effect q is occurring in the fluid. We further assume that the absolute viscosity of the fluid is determined by the Arrhenius dependence on absolute temperature

$$\mu = \mu_0 \exp \frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where μ_0 and T_0 are the viscosity and temperature of the fluid at the inlet; E_1, activation energy for viscous flow; R, gas constant.

Assuming the Reynolds number to be small (Re $= Q\rho/\pi a\mu_0$), we use a hydraulic approximation of the equations of motion and heat transfer

$$p = 8\mu_0 e^{\frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \frac{Q}{\pi a^4}, \tag{1}$$

$$\frac{dT}{dt} + \frac{Q}{\pi a^2 L \rho c_p}(T - T_0) = -\frac{q}{\rho c_p} e^{-\frac{E_2}{RT}} + \frac{\mu_0 Q^2}{\pi^2 a^6 \rho c_p} e^{\frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)},$$

where Q is the fluid flow rate; ρ and c_p are the density and specific heat of the fluid. System (1) in essence describes the processes of motion and heat transfer in an ideal-