## ELECTRIFICATION OF LOW-CONDUCTIVITY LIQUIDS

## IN LAMINAR FLOW THROUGH TUBES

## AND CAPILLARIES

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One of the possible mechanisms of the electrification of low-conductivity liquids aiquid hydrocarbons, mineral oils, etc.) flowing through metal tubes and capillaries is the oxidation reduction reaction of impurity ions on channel walls [1-5]. This point of view was first considered in [2] on the basis of experimental data in [3], where it was shown that when a neutral liquid ( N -heptane) flows through a grounded metal capillary it emerges positively charged, and the charging current from the end of the capillary is steady for a steady flow of liquid.

In contrast with $[2,4,5]$ we assume here that the forward ion neutralization reaction rate is small in . comparison with the inverse reaction rate.

1. Statement of the Problem. In contrast with conventional approach to the phenomenon of electrification of low-conductivity liquids based on the concept of the generation of a charging current as a result of the removal of charges from the diffusion part of the electric double layer by hydrodynamic flow [6], Gavis and Koszman [2] present a new approach which in terms of chemical kinetics consists in the following. They assume that at the channel entrance (Fig. 1) the neutral liquid contains positive $B^{+Z_{1}}$ and negative $A^{-Z_{2}}$ impurity ions, where $z_{1}$ and $z_{2}$ are the valences of the ions. During the motion of the liquid partial or complete neutralization of negative ions occurs on the tube wall ( $r=R$ ) as a result of the reversible reaction

$$
\begin{equation*}
A^{-z_{2}}-m e^{-\frac{k_{f}}{\stackrel{k_{i}}{\rightleftarrows}}} A^{-\left(z_{2}-m_{i}\right)} \tag{1.1}
\end{equation*}
$$

where $k_{f}$ is the rate constant of the forward reaction and $k_{i}$ of the inverse reaction; $e^{-}$is the electron, and $m\left(m \leq z_{2}\right)$ is the number of electrons transferred from an $A^{-z_{2}}$ ion to the electrode. For $m=z_{2}$, neutral molecules $A$ are formed as a result of the reaction.

Since at the entrance $\Sigma_{0}(x=0)$ the concentration of $A^{-\left(z_{2}-m\right)}$ ions (or A molecules) is zero, the forward reaction will proceed more rapidly than the inverse near the entrance. As a result an excess of positive ions is formed in the liquid, i.e., it is electrified.

The boundary-value problem describing the charging of the liquid in reaction (1.1) has the following form:

$$
\begin{gather*}
\operatorname{div} \varepsilon \mathbf{E}=4 \pi e\left[z_{1} n_{1}-z_{2} n_{2}-\left(z_{2}-m\right) n_{3}\right], \mathbf{E}=-\nabla \psi ;  \tag{1.2}\\
\operatorname{div} \mathbf{i}_{k}=0 \quad(k=1,2,3), \mathbf{i}_{1}=-D_{1} \nabla n_{1}+b_{1} n_{1} \mathbf{E}+n_{1} \mathbf{v}, \mathbf{i}_{2}=  \tag{1.3}\\
=-D_{2} \nabla n_{2}-b_{2} n_{2} \mathbf{E}+n_{2} \mathbf{v}, \mathbf{i}_{3}=-D_{3} \nabla n_{3}-\gamma b_{3} n_{3} \mathbf{E}+n_{3} \mathbf{v}(0 \leqslant r \leqslant R ; \\
0 \leqslant x \leqslant \infty) ; \\
\sum_{0}(x=0): n_{1}=n_{1}^{0}, \quad n_{2}=n_{2}^{0}, \quad n_{3}=0, \quad z_{1} n_{1}^{0}=z_{2} n_{2}^{0} ;  \tag{1.4}\\
S(r=R): \mathbf{i}_{1} \mathbf{n}=0,\left(\mathbf{i}_{2}+\mathbf{i}_{3}\right) \mathbf{n}=0, \mathbf{i}_{2} \mathbf{n}=k_{f} n_{2}-k_{i} n_{3}, \psi=\psi_{0} ;  \tag{1.5}\\
\text { as } x \rightarrow \infty \mathbf{i}_{2} \mathbf{n}=0, n_{3} / n_{2}=k_{f} / k_{i}=K . \tag{1.6}
\end{gather*}
$$

Here $n_{i}, b_{i}$, and $D_{i}(i=1,2,3)$ are, respectively, the partial concentrations, the mobilities, and the diffusion coefficients of the $B^{+Z_{1}}, A^{-Z_{2}}$, and $A^{-\left(Z_{2}-m\right)}$ ions (or the $A$ molecules; $n_{1}^{0}$ and $n_{2}^{0}$ are the constant concentrations of the $B^{+Z_{1}}$ and $A^{-Z_{2}}$ ions at the channel entrance; $\varepsilon$ is the permittivity of the liquid; e is the charge of a proton; $\gamma=1$ for $z_{2}>m, n$ is the outward normal to $S$.

Equations (1.2) and (1.3) assume that the space charge $e\left[z_{1} n_{1}-z_{2} n_{2}-\left(z_{3}-m\right) n_{3}\right]$ formed in the electrification process, and the electric field induced by it, are so small that they do not affect the velocity distribution of the

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Fig. 1
liquid, i.e ${ }_{n} v=v_{0}(0,0, v(r))$ is a given function of coordinates, where $v_{0}$ is the velocity on the channel axis. The last of Eqs. (1.4) follows from the neutrality of the liquid at the entrance.

The first of Eqs. (1.5) states that there is no current of positive charges to the earth. The second equation represents the equality of the fluxes of $A^{-Z_{2}}$ and $A^{-\left(Z_{2}-m\right)}$ ions at the channel surface $S_{2}$ which is a consequence of the fact that each $A^{-\left(Z_{2}-m\right)}\left(A^{-Z_{2}}\right)$ ion can be formed on $S$ only as a result of the forward (inverse) reaction (1.1), and that they are not adsorbed on $S$. The third condition follows from the fact that the difference between the number $\mathrm{kfn}_{2}$ of $A^{-Z_{2}}$ ions neutralized and the number $\mathrm{k}_{\mathrm{i}} \mathrm{n}_{3}$ of $\mathrm{A}^{-\left(\mathrm{z}_{2}-m\right)}$ ions regenerated on S is equal to the influx of $A^{-z_{2}}$ (or $A^{-\left(z_{2}-m\right)}$ ) ions. Here it is assumed that (1.1) is a single-stage reaction [7]. The potential $\psi=\psi_{0}=$ const on S , since the channel wall is grounded.

Conditions (1.6) express the equilibrium of reaction (1.1) at a sufficiently large distance from the initial cross section $\Sigma_{0}$.

The charging current through an arbitrary cross section $\Sigma$ ( $x=$ const) is

$$
\begin{equation*}
I=e \int_{\Sigma}\left[z_{1} \mathbf{i}_{1}-z_{2} \mathbf{i}_{2}-\left(z_{2}-m\right) \mathbf{i}_{3}\right] \mathbf{e}_{x} d \Sigma \tag{1.7}
\end{equation*}
$$

2. Method of solution. Just as in [2,5], we make the following assumptions to simplify further study of the problem. First, we assume a sufficiently large average flow velocity of the liquid so that all quantities change much more slowly along the channel axis then in the radial direction. Hence, derivatives with respect to $x$ can be omitted in the Laplacian $\Delta$. Second, we assume that the fraction of converted $A^{-Z_{2}}$ ions is small in comparison with the unconverted ions in any cross section $\Sigma$. U nder this assumption the equilibrium constant $K$ of reaction (1.1) is small enough to permit the use of perturbation theory. Finally, we assume the equality of diffusion coefficients $D_{i}=D$ and mobilities $b_{i}=b(i=1,2,3)$.

In accordance with the perturbation method, we seek the solution in the form of series

$$
\begin{gather*}
n_{i}=n_{i}^{0}+n_{i}^{(1)}+n_{i}^{(2)}+\ldots, n_{3}=n_{3}^{(1)}+n_{3}^{(2)}+\ldots,  \tag{2.1}\\
\psi=\psi_{0}+\psi^{(1)}+\psi^{(2)}+\ldots \quad(i=1,2)
\end{gather*}
$$

After substituting (2.1) into (1.2)-(1.6), linearizing, and transforming to dimensionless variables by the formulas

$$
\begin{gathered}
q_{i}=n_{i}^{(1)} / n^{0}(i=1,2,3), \quad n^{0}=z_{1} n_{1}^{0}+z_{2} n_{2}^{0}, \\
\varphi=\psi^{(1)} \varepsilon / 4 \pi e n^{0}, r^{\prime}=r / R, x^{\prime}=x / R,
\end{gathered}
$$

we obtain

$$
\begin{gather*}
-L \varphi=q, L q_{3}-x v(r) \partial q_{3} / \partial x=0  \tag{2.2}\\
L q-\delta^{2} q-x v(r) \partial q / \partial x=0 \\
\text { at } x=0 q=q_{3}=0 ;  \tag{2.3}\\
\text { at } r=1 \frac{\partial q}{\partial r}+\delta^{2} \frac{\partial \varphi}{\partial r}=m\left(K_{f} \frac{\delta_{2}^{2}}{\delta^{2}}-K_{i} q_{3}\right)=m \frac{\partial q_{3}}{\partial r} \tag{2.4}
\end{gather*}
$$

Here

$$
\begin{gathered}
q=z_{1} q_{1}-z_{2} q_{2}-\left(z_{2}-m\right) q_{3} ; \quad L \equiv \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} ; \\
\delta_{2}^{2}=R^{2} / D \tau_{2}\left(\tau_{2}=\varepsilon / 4 \pi e b n_{2}^{0}\right) ; \delta^{2}=R^{2} / D \tau\left(\tau=\varepsilon / 4 \pi e b n^{0}\right) ; \\
\chi=v_{0} R / D ; K_{f}=k_{f} R / D ; K_{i}=k_{i} R / D
\end{gathered}
$$

and primes on the dimensionless coordinates have been omitted.
We assume a Poiseuille velocity profile $v(r)=1-r^{2}$. This approximation is valid when the characteristic length for the development of a parabolic profile $l \sim 0.16 \mathrm{v}_{0} \mathrm{R}^{2} / \nu$ [8], where $\nu$ is the kinematic viscosity, is appreciably shorter than the characteristic channel length $L$ over which the charging of the liquid takes place.

We solve problem (2.2)-(2.4) by taking Laplace transforms.

$$
q_{*}=\int_{0}^{\infty} q(r, x) \mathrm{e}^{-p x} d x
$$

Then we obtain the following problem for the transforms:

$$
\begin{gather*}
-L \varphi_{*}=q_{*}, \quad L q_{*}-\left[\delta^{2}+\beta^{2}\left(1-r^{2}\right)\right] q_{*}=0, \quad L q_{3^{*}}-\beta^{2}\left(1-r^{2}\right) q_{3 *}=0, \quad \beta^{2}=x p  \tag{2.5}\\
 \tag{2.6}\\
\frac{d q_{*}}{d r}+\delta^{2} \frac{d \varphi_{*}}{d r}=m\left(K_{f} \frac{\delta_{z}^{2}}{\delta^{2} p}-K_{i} q_{3^{*}}\right)=m \frac{d q_{3 *}}{d r}(r=1)
\end{gather*}
$$

which we solve by making the substitutions

$$
\begin{gathered}
q_{*}=A_{1} \mathrm{e}^{-z / 2} \Phi\left(\alpha_{1}, 1, z\right), \quad q_{3^{*}}=A_{2} \mathrm{e}^{-z / 2} \Phi\left(\alpha_{2}, \mathbf{1}, z\right), \\
\alpha_{1}=1 / 2+\left(\delta^{2}+\beta^{2}\right) / 4 i \beta, \quad \alpha_{2}=1 / 2+\beta / 4 i, z=i \beta r^{2}
\end{gathered}
$$

where $\Phi(\alpha, 1, z)$ is the confluent hypergeometric function [9]. After determining the constants $A_{1}$ and $A_{2}$ from (2.6), and taking the inverse Laplace transforms, we obtain

$$
\begin{gather*}
q=\frac{m \delta_{2}^{2} K_{f}}{\delta^{2}} \frac{1}{2 \pi i} \int_{p_{0}-i \infty}^{p_{0}+i \infty} \frac{i \beta H(\beta) e^{\frac{i \beta\left(1-r^{2}\right)}{2}} \Phi\left(\alpha_{1}, 1, i \beta r^{2}\right)}{p H_{1}(\delta, \beta) H_{2}\left(K_{i}, \beta\right)} \mathrm{e}^{p x} d p\left(\operatorname{Re} p_{\theta}>0\right),  \tag{2.7}\\
H(\beta)=2 \alpha_{2} \Phi\left(\alpha_{2}+1,2, i \beta\right)-\Phi\left(\alpha_{2}, 1, i \beta\right), \\
H_{1}(\delta, \beta)=i \beta\left[2 \alpha_{1} \Phi\left(\alpha_{1}+1,2, i \beta\right)-\Phi\left(\alpha_{1}, 1, i \beta\right)\right]-\frac{\delta^{2}}{2} \int_{0}^{1} \mathrm{e}^{\frac{i \beta(1-\xi)}{2}} . \Phi\left(\alpha_{1}, 1, i \beta \xi\right) d \xi, \\
H_{2}\left(K_{i}, \beta\right)=K_{i} \Phi\left(\alpha_{2}, 1, i \beta\right)+i \beta H(\beta) .
\end{gather*}
$$

Using the theorem of residues [9], we can write (2.7) in the form

$$
\begin{equation*}
q=\frac{m \delta_{2}^{2} K}{4 \delta^{2}}\left(\frac{I_{0}(\delta r)}{\int_{0}^{1}\left(1-r^{2}\right) I_{0}(\delta r) r d r}-\sum_{k=1}^{\frac{2}{}} \sum_{n=1}^{\infty} a_{k n} \mathrm{e}^{\frac{p_{k n}\left(r^{2}-1\right)}{2}} \Phi\left(\alpha_{k n}, 1,-p_{k n} r^{2}\right) \mathrm{e}^{-\frac{p_{k}^{2} n}{x} x}\right) \tag{2.8}
\end{equation*}
$$

where $\alpha_{1 n}=1 / 2-\left(\hat{\delta}^{2}-p_{1 n}^{2}\right) / 4 p_{1 n} ; \alpha_{2 n}=1 / 2+p_{2 n} / 4 ; p_{1 n}$ and $p_{2 n}$ are the positive simple roots, numbered in ascending order, of the following equations:

$$
\begin{gather*}
h_{1}\left(p_{1 n}\right) \cong H_{1}\left(\delta, i p_{1 n}\right)=p_{1 n}\left[-2 \alpha_{1 n} \Phi\left(\alpha_{1 n}+1,2,-p_{1 n}\right)+\Phi\left(\alpha_{1 n}, 1,-p_{1 n}\right)\right]-\frac{\delta^{2}}{2} \int_{0}^{1} e^{\frac{p_{1 n}}{2}(\xi-1)} \Phi\left(\alpha_{1 n}, 1,-p_{1 n} \xi\right) d \xi=0  \tag{2.9}\\
h_{2}\left(p_{2 n}\right) \equiv H_{2}\left(K_{i}, i p_{2 n}\right)=K_{i} \Phi\left(\alpha_{1 n}, 1,-p_{2 n}\right)-p_{2 n}\left[2 \alpha_{2 n} \Phi\left(\alpha_{2 n}+1, \quad 2,-p_{2 n}\right)-\Phi\left(\alpha_{2 n}, 1,-p_{2 n}\right)\right]=0 . \tag{2.10}
\end{gather*}
$$

The coefficients $a_{1 \mathrm{n}}$ and $a_{2 \mathrm{n}}$ are found in the form

$$
\begin{equation*}
a_{1 n}=\frac{8 K_{i} H\left(i p_{1 n}\right)}{h_{1}^{\prime}\left(p_{1 n}\right) H_{2}\left(K_{i}, i p_{1 n}\right)}, \quad a_{2 n}=\frac{8 K_{i} H\left(i p_{2 n}\right)}{H_{1}\left(\delta, i p_{2 n}\right) h_{2}^{\prime}\left(p_{2 n}\right)}, \quad . \tag{2.11}
\end{equation*}
$$

where primes denote derivatives with respect to $p_{\text {in }}$ and $p_{2 n}$ respectively.
Using (1.7), and taking account of (2.8), we find the charging current

$$
\begin{gather*}
I=I_{\infty}\left[1-\sum_{n=1}^{\infty} a_{n} \exp \left(-\frac{p_{1 n}^{2} D}{v_{0} R^{2}} x\right)-\sum_{n=1}^{\infty} b_{n} \exp \left(-\frac{p_{2 n}^{2} D}{v_{0} R^{2}} x\right)\right] ;  \tag{2.12}\\
I_{\infty}=\frac{1}{2} m \pi t n_{2}^{0} v_{0} R^{2} K, \quad a_{n}=a_{1 n} c_{1 n}, \quad b_{n}=a_{2 n} c_{2 n}  \tag{2.13}\\
c_{k n}=\frac{1}{2} \int_{0}^{1}(1-\xi) \exp \left(\frac{p_{k n}}{2}(\xi-1)\right) \Phi\left(\alpha_{k n}, 1,-p_{k n} \xi\right) d \xi \\
(k=1,2, n=1,2,3, \ldots) .
\end{gather*}
$$

3. Results of Numerical Calculations. Equations (2.9) and (2.10) show that the $p_{\text {in }}$ depend only on the parameter $\delta^{2}$, and the $\mathrm{p}_{2 \mathrm{n}}$ on $\mathrm{K}_{\mathrm{i}}$. The results of numerical calculations of these dependences plotted in Figs. 2 and 3 show that as $\delta \rightarrow 0$ the roots $p_{1 n}$ approach constant values ( $p_{11} \rightarrow 5.0, p_{12} \rightarrow 9.1, p_{13} \rightarrow 12.5$ ), whereas as $\delta$

TABLE 1

| $\delta^{2}$ | 1 | 30 | 50 | 70 | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0,835 | 0,836 | 0,831 | 0,822 | 0,808 |
| $b_{1}$ | 0.97 | 0,095 | 0,095 | 0,095 | 0,094 |
| $b_{2}$ | 0,014 | 0,014 | 0,014 | 0,014 | 0,013 |
| $b_{3}$ | $0.28 \cdot 10^{-3}$ | $0,28 \cdot 10^{-4}$ | $0,15 \cdot 10^{-3}$ | $-0,0013$ | $0,5 \cdot 10^{-6}$ |
| $a_{1}$ |  |  |  |  |  |



Fig. 2


Fig. 3
increases, they increase; for $\delta>10$ we have $p_{11} \sim \delta$ (for $\delta^{2}=1,10,50$, and $100, p_{11}=5.16,5.97,8.72$, and 11.2, respectively). The roots $p_{2 n}$ also increase monotonically with increasing $K_{i}$, but, in contrast with the previous case, approach constant values as $K_{i} \rightarrow \infty$. Thus, for $K_{i} \geq 40$, the $p_{2 n}(n=1,2,3)$ change by a fraction of a percent, and their values for $\mathrm{K}_{\mathbf{i}}=10$ and $\mathrm{K}_{\mathbf{i}}=40$ differ by $3-4 \%$ (for $\mathrm{K}_{\mathrm{i}}=10, \mathrm{p}_{21}=2.51, \mathrm{p}_{22}=6.32, \mathrm{p}_{23}=10.12$; for $\mathrm{K}_{\mathbf{i}}=$ $40, \mathrm{p}_{21}=2.65, \mathrm{p}_{22}=6.59, \mathrm{p}_{23}=10.55$ ).

The coefficients $a_{n}$ and $b_{n}$ in series (2.12) found by using these numerical values in Eqs. (2.11) and (2.13) are listed in Table 1. Calculations showed that the $b_{n}$ are positive and decrease rapidly with increasing $n$ (for $n=1,2,3$ approximately by an order of magnitude when $n$ increases by unity (Table 1)); the coefficient $b_{1}$, which makes the main contribution to the series sum, decreases slowly and monotonically with increasing $\delta$ the values of $b_{1}$ for $\delta^{2}=1$ and $\delta^{2}=100$ differ by $2 \%$ ). The coefficients $a_{n}$ may change sign, but their absolute values are small for $\delta^{2} \leq 100:\left|a_{n}\right| \ll b_{n}(n=1,2,3)$. Calculations also showed that for $n=1,2,3$ the absolute values of the $a_{\mathrm{n}}$ can be of the same order of magnitude.

Thus, for $\delta^{2} \leq 100$ and $\mathrm{K}_{\mathrm{i}} \geq 40$, the expression for the charging current, to within terms $0\left(10^{-3}\right)$, can be written in the form

$$
I=I_{\infty}\left[1-\sum_{n=1}^{3} b_{n} \exp \left(-\frac{\pi p_{2 n}^{2} D}{2 Q} x\right)\right] \quad\left(I_{\infty}=e m n_{2}^{0} Q K\right)
$$

where $\mathrm{G}_{4}=(\pi / 2) \mathrm{v}_{0} \mathrm{R}^{2}$ is the liquid flow rate; $\mathrm{p}_{21}^{2}=6.7 ; \mathrm{p}_{22}^{2}=43.5 ; \mathrm{p}_{23}^{2}=111$.
Table 1 shows that as the parameter $\delta$ is increased, the coefficients $b_{n}$ decrease, and the $\left|a_{n}\right|$ increase. Thus, as $\delta \rightarrow \infty$ one might assume that the series with the coefficients $a_{\mathrm{n}}$ will play the main role in Eq. (2.12) for the charging current. We could not test this assumption by numerical computer calculations, however, because of the poor convergence of the series for the confluent hypergeometric function and the presence of the rapidly varying exponential factor in the integrands in (2.9) and (2.13). On the other hand, for very large $\delta$ the condition for the asymptotic convergence of (2.1), which can be written in the form $\delta \mathrm{K} \ll 1$, is violated, and therefore the asymptotic solution obtained from (2.7) as $\delta \rightarrow \infty$ has no meaning.

Thus, the analysis given is valid for sufficiently small equilibrium constants $K \ll 1$, and $K_{i}$, and $\delta^{2} \ll K^{-2}$.
Analysis of the Solution. Equation (3.1) shows that the charging current increases monotonically with increasing flow rate $Q$, and for small values of $Q\left(Q \ll 2 \pi p_{23}^{2} \mathrm{Dx}\right)$ it varies linearly ( $\mathrm{I}=\mathrm{emn}_{2}^{0} \mathrm{KQ}$ ). In the limit as $Q \rightarrow \infty$ the current approaches saturation:

$$
I \rightarrow I_{0}=\frac{\pi}{2}\left(b_{1} p_{21}^{2}+b_{2} p_{22}^{2}+b_{3} p_{23}^{2}\right) e m n_{2}^{0} D K x
$$

We note that this dependence of I on the average velocity of laminar flow in a capillary is observed in experiments [3] (for turbulent flow $I \sim V_{0}{ }^{15 / 8}$ at low velocities, and $\left[\sim V_{0}{ }^{7 / 8}\right.$ at high velocities [3]). The dependence of I on the ion concentration at the capillary entrance is generally treated as a dependence on conductivity. In this sense (3.1) gives a linear law, which is observed in experiments at sufficiently low conductivity [3]. However, in the light of modern concepts of the conductivity of liquid dielectrics [10, 11], a steady current is
not ensured by impurity ions, but by injection (or regeneration [10]) processes at the electrode-liquid contact, which are determined by the physical and chemical properties of the electrode, the liquid, and the impurity component. The last, according to data on electroconvective flows, must be neutral [11]. Thus, all one can say is that the conductivity of a neutral liquid is proportional to the ion concentration in it. Therefore, to explain the experimentally observed decrease in the charging current with an increase in conductivity for sufficiently high values of them, it is necessary to consider the interaction of the electrode surface not only with the impurity ions, but also with the neutral impurity component. Thuss for a sufficiently high concentration $c_{X}$ of impurity $X$ (i.e., high conductivity), their adsorption on the capillary surface can lead to a slowing down of the rate of neutralization of negative ions, i.e., to a decrease in the charging current. Analytically this indicates that for sufficiently large $c_{x}$ the limiting charging current $\mathrm{I}_{\infty}$ becomes a monotonically decreasing function of $c_{X}$. These arguments are confirmed experimentally in [3] where it was shown that as long as $\sigma<\sigma_{0}$ the limiting current $\mathrm{L}_{\infty}$ remains constant as $\sigma$ is increased, and begins to decrease only for sufficiently large $\sigma>\sigma_{0}$. From a quantitative point of view this can be described in the following way. If we assume that on that part of the surface where X was adsorbed the neutralization of negative ions (1.1) does not occur, the third condition in (1.5) takes the form

$$
\mathbf{i}_{2} \mathbf{n}=(1-\lambda)\left(k_{f} n_{2}-k_{i} n_{3}\right)_{2}
$$

where $\lambda$ is the area occupied by the adsorbate $X$ per unit area of the capillary surface. For example, if adsorption is described by the Langmuir isotherm, $\lambda=\beta c_{X} /\left(1+\beta c_{X}\right)$, where $\beta$ is a physical constant depending on the electrode material and the kind of impurity $X$. In this case the charging current will also be determined by (2.12), where $I_{\infty}=1 / 2 \mathrm{~m} \pi(1-\lambda) \mathrm{en}_{2}^{0} \mathrm{v}_{0} R^{2} \mathrm{~K}$. Since $c_{x}$ and $\lambda$ are proportional to the conductivity of the liquid, as $\sigma \rightarrow 0, \lambda \rightarrow 0$, and as $\sigma \rightarrow \infty, \lambda \rightarrow 1$. Therefore, for small conductivities the charging current varies linearly with $\sigma$, while for large conductivities it decreases with increasing $\sigma$.

The modern point of view on the conductivity of liquid dielectrics makes it possible to propose a fundamentally different electrification mechanism. Thus, if the electrode atoms (molecules) M manifest positive or negative electronegativity [12] with respect to the liquid molecules A (impurity $X$ ), positive or negative ions may be formed on the electrode surface which migrate into the depths of the liquid by convection or diffusion and electrify it. This mechanism of ion formation on the electrode surface is based on the concept of the conductivity of liquid dielectrics in [13].

It follows from (3.1) that for large enough $x\left(x \gg 2 Q / \pi p_{21}^{2} D\right.$ ) the charging current is independent of the length of the capillary and is equal to $\mathrm{I}=\mathrm{I}_{\infty}=\mathrm{emn}_{2}^{0} \mathrm{QK}$. The characteristic length L (electrification length) over which the limiting current $I_{\infty}$ can be reached is estimated as $L=v_{0} R^{2} / p_{21}^{2}$. For typical values $D=10^{-5} \mathrm{~cm}^{2} / \mathrm{sec}$ under the conditions of the experiments with heptane [3] ( $\mathrm{v}_{0}=100 \mathrm{~cm} / \mathrm{sec}, \mathrm{R}=0.016 \mathrm{~cm}$ ), we have $L=400 \mathrm{~cm}$. Such large values of the electrification length can be accounted for as follows. The electrification process ceases when reaction (1.1) comes to equilibrium. This equilibrium is reached when the concentration $n_{3}$ of $A^{-\left(z_{2}-m\right)}$ ions becomes uniform over the whole volume and equal to $n_{3}=\mathrm{Kn}_{2}^{0}$. Within the framework of the approximation considered, this process is determined by diffusion only (2.2). For high liquid velocities ( $\mathrm{V}_{0} \geq 100$ $\mathrm{cm} / \mathrm{sec}$ ) the convective flux is appreciably larger than the diffusion flux, which also leads to larger values of L. The smallest length $L_{m}$ for which significant electrification ( $\left[\simeq 0.1 \mathrm{I}_{\infty}\right.$ ) is possible is estimated as $\mathrm{L}_{\mathrm{m}}=$ $v_{0} R^{2} / p_{23} D$. For the values of $v_{0}, R$, and $D$ given above we have $L_{m}=25 \mathrm{~cm}$. We note that in experiments [3] the length of capillaries in which appreciable electrification was observed was $4-40 \mathrm{~cm}$, which agrees with the above estimate.

Thus, for low conductivity there is qualitative agreement of (3.1) with the experimental data of [3]. For a quantitative test of (3.1) and qualitative agreement for high conductivities, further experimental research is necessary to determine the components of the reaction (1.1), to measure the reaction rate constants (equilibrium constants K ), and to study the role of neutral impurities.

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INITIAL ASYMPTOTE TO THE SOLUTION
OF TEE PROBLEM OF DROPLET INCIDENCE
ON A PLANE
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The initial stage of collision of a spherical droplet on a solid plane is considered. It is assumed that the droplet liquid is ideal and incompressible, and that surface tension and external mass forces are absent.

This problem is closely related to that of entry of a blunt body into a liquid, which was first considered in [1]. The method for calculation of the resistive forces, developed in [1], is based on the assumption that the velocity distribution on the free surface at each moment is the same as that obtained directly after collision of a floating plate of the same dimensions.

These problems have the following unique features: 1) the flow region $\Omega_{t}$ is unknown; 2) the contact line between free liquid surface and the solid must be determined at the boundary of the flow region; 3) singularities may appear in the solution on this line.

A new approach to problems of this kind is the introduction of Lagrangian coordinates [2,3], in which the flow region is fixed.

1. At time $t=0$ a liquid sphere of radius $a$ is tangent upon a solid plane, which moves along the $z$ axis at velocity $v$. We must find the liquid motion which then occurs. In the space formed by Lagrangian Cartesian coordinates $\xi, \eta, \zeta$ the region occupied by the liquid is known, being a sphere of radius $a$ with center at the origin. We denote this region by $\Omega_{0}$. The variables $x, y, z$ denote the corresponding Euler coordinates, $\Gamma$ is the free surface of the liquid, and $\Sigma$ is the contact spot between droplet and solid plane. The Euler equations, written in Lagrangian coordinates, have the form [3]

$$
\begin{equation*}
M_{0}^{*} \mathrm{x}_{t t}+\frac{1}{\gamma} \nabla_{\mathrm{s}} p=0, \quad \operatorname{det} M_{0}=1 \text { in } \Omega_{0} \tag{1.1}
\end{equation*}
$$

with boundary conditions $\left.p\right|_{\Gamma}=0,\left.z_{t}\right|_{\Sigma}=v$ and initial conditions $x\left|t=0=\xi, x_{t}\right| t=0$, where $x=(x, y, z) ; \xi=(\xi, \eta$, ૬) ; $M_{0}=\partial(\mathbf{x}) / \partial(\xi) ; \quad M_{0}^{*}$ is the matrix conjugate to $\mathrm{M}_{0}$ and p is the pressure. The problem is a complex one because of its nonlinearity and the existence of the unknown line on the sphere boundary $\partial \Omega_{0}$, dividing $\Gamma$ and $\Sigma$.
2. We will linearize Eq. (1.1) for the initial rest state, keeping terms of zeroth- and first-order smallness in displacement. For the linearized problem we can introduce a displacement potential $\Phi=\Phi(\xi, \eta, \zeta, t)$, which in view of the continuity equation, will be a function harmonic in $\Omega_{0}$. From the momentum equation follows that

$$
\begin{equation*}
p=-\gamma \Phi_{i t} \tag{2.1}
\end{equation*}
$$

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