A Physicochemical Explanation for Flow Electrification in Low-Conductivity Liquids in Contact with a Corroding Wall

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Abstract—Electrification during flow of insulating liquids in pipes has been studied for a long time. Its dependence on flow parameters and pipe geometry has been modeled for many different cases and is quite well known. Even though different laws of flow electrification have been obtained empirically in terms of the pipe length, a complete analysis taking into account the electrochemical reactions at the pipe wall–liquid interface is lacking. In this paper, we present a model of the process in the case of a corroding wall and a liquid containing additives or impurities partially dissociated into positive and negative ions. We treat the case of laminar flow and an interfacial reaction whose conversion is small compared to the concentrations of positive and negative ions in the bulk solution. We compute the evolution of the space charge density in terms of the axial and radial coordinates, and the flow velocity. The boundary conditions on the wall are deduced from the kinetics of the wall surface reactions with the additives. Thus, analysis of these chemical reactions allows us to compute the net flux of electrical charge from the wall to the liquid. This flux is a function of the axial distance along the pipe and the mean flow velocity. Finally, comparison is made between our model and experiments on flow electrification for hydrocarbons liquids.

I. INTRODUCTION

WHEN an insulating liquid flows through a pipe or a porous medium, flow electrification occurs due to a streaming potential [1]–[9]. This phenomenon has created hazards for industry [10] as, in some cases, the electrical potential induced by the flow is very high, several tens of kilovolts or more. Thus, significant work has been done, sometimes empirically, to reduce flow electrification [11]. Also, fundamental research has been carried out for several decades in the Laboratory of Physics and Fluid Mechanics at the University of Poitiers, Poitiers, France, to understand the flow electrification phenomenon and to develop predictive models. First, the effect of Reynolds number has been studied, with emphasis on the transition from laminar to turbulent flow [12]. Then, the effects of radius and pipe length have been analyzed [13]. Finally, the effects of wall roughness have been investigated [14].

II. PHYSICOCHEMICAL REACTION

Even in carefully purified hydrocarbon liquid, some impurities remain. Additives are also used intentionally to reduce the electric resistivity of the liquid. In either case, some positive and negative ions exist inside a hydrocarbon liquid. In the bulk of the liquid and far from any solid surface, the densities of positive and negative charges are equal, i.e., the liquid is electrically neutral. For simplicity, let us assume that only a single impurity or additive $ALB_L$ exists in the liquid and is weakly dissociated

$$ALB_L \rightleftharpoons A_L^+ + B_L^-$$

(1)

where $k_1$ and $k_1^{-1}$ are the kinetic constants of the dissociation reaction. When an initially electrically neutral liquid comes into contact with a solid surface, a physicochemical reaction starts at the solid–liquid interface. This reaction depends on the nature of the solid and the liquid additive.

Here we assume that wall corrosion takes place. We also assume that the solid surface is partly or totally composed of atoms $CS$ and undergoes the following reaction in the presence of the liquid

$$CS \rightleftharpoons C_S^+ + e^-$$

(2)
with \( k_1 \) and \( k_{-2} \) representing the kinetic constants of wall corrosion reaction.

When the cations \( C_{S}^{+} \) and the solid contact anions \( B_{L}^{-} \) from the liquid impurity combine, a surface reaction may occur

\[
C_{S}^{+} + B_{L}^{-} \rightleftharpoons C_{S}B_{L}
\]

where \( k_3 \) and \( k_{-3} \) are now the kinetic constants of the ion recombination reaction. Thus, two kinds of impurities, \( A_{L}B_{L} \) and \( C_{S}B_{L} \), now exist in the liquid.

Reactions (1)–(3) are equivalent to a positive current at the solid–liquid interface, and they lead to an accumulation of positive ions in the liquid, while the negative ones react on the solid. The net reaction stops when the concentrations of anions \( B_{L}^{-} \) and cations \( C_{S}^{+} \) are such that the reaction (3) is in equilibrium at the interface. From an electrical point of view, this means that the space charge density in the liquid near the wall reaches a constant value. In the following section, we investigate this scenario.

### III. GENERAL EQUATIONS

In our model, we assume that the concentration of positive ions \( [C_{S}^{+}] \) at the wall–liquid interface is so large that there is always enough \( C_{S}^{+} \) for the wall reaction (3). In other words, the concentration of \( C_{S}^{+} \) is not rate controlling. We also assume that no \( C_{S}^{+} \) is in bulk liquid.

We shall call, respectively, \( n_{N} \) and \( n_{P} \) the time-dependent concentrations of negative and positive ions in the liquid near the interface. Thus

\[
N_{N} = [B_{L}^{-}] \quad \text{and} \quad n_{P} = [A_{L}^{+}]. \tag{4}
\]

Then, in accordance with our assumptions, the source \( \phi_{P} \) of positive charges per unit volume at the interface is given by reaction (3). Hence, as only the concentration of \( B_{L}^{-} \) is rate-controlling

\[
\phi_{P} = k_3[B_{L}^{-}] - k_{-3}[C_{S}B_{L}]. \tag{5}
\]

As \( [B_{L}^{-}] \) decreases with time due to the reaction at the interface, \( \phi_{P} \) decreases, and at equilibrium it finally vanishes for some \( [B_{L}^{-}]_{D} \), the index \( D \) referring to a fully developed double layer.

Let \( n_{P0} \) and \( n_{N0} \) be the concentrations of positive and negative ions, respectively, far from the interface or, equivalently, at the beginning of the contact. Then, a subtraction of mass balances on atoms \( A_{L} \) and \( B_{L} \) gives

\[
[C_{S}B_{L}] = (n_{N0} - n_{N}) + (n_{P} - n_{P0}). \tag{6}
\]

At equilibrium of reaction (1), we assume weak dissociation\[17\]

\[
n_{P}n_{N} \approx n_{P0}n_{N0}. \tag{7}
\]

Let us now introduce the space charge density \( \rho \) for ions with the same valence \( Z_{P} = Z_{N} = Z = 1 \), or

\[
\rho = e_{0}(n_{P} - n_{N}). \tag{8}
\]

\( e_{0} \) being the elementary charge. Then, assuming a low density of space charge, this implies

\[
(n_{P} - n_{N}) \ll (n_{P} + n_{N}). \tag{9}
\]

Equation (9) also implies that the conductivity remains nearly constant. In this case

\[
n_{P} + n_{N} \approx n_{P0} + n_{N0} \quad \text{and} \quad n_{P} - n_{P0} = n_{N0} + n_{N}. \tag{10}
\]

Thus, (5) becomes

\[
\phi_{P} = k_3n_{N} - 2k_{-3}(n_{N0} - n_{N}). \tag{11}
\]

Now, when \( n_{N} = n_{N0} \) and \( \phi_{P} = 0 \), then

\[
k_{-3} = k_3 \frac{n_{N0}}{2(n_{N0} - n_{N0})} \quad \text{and} \quad \phi_{P} = k_3 \left[ \frac{n_{N} - n_{N0} - n_{N}}{n_{N0} - n_{N0}} \right]. \tag{12}
\]

Rearrangement of (13) gives

\[
\phi_{P} = k_3 \frac{n_{N0}}{n_{N0} - n_{N0}}(n_{N} - n_{N0}). \tag{14}
\]

But, from (10), it is possible to write also

\[
n_{N} - n_{N0} = n_{P0} - n_{P} \tag{15}
\]

and (14) finally becomes

\[
\phi_{P} = \frac{k_3n_{N0}}{2(n_{N0} - n_{N0})e_{0}}(\rho_{WD} - \rho_{W}) \tag{16}
\]

with \( \rho_{W} \) being the space charge density near the interface, and \( \rho_{WD} \) the space charge density when the double layer is fully developed. Equation (16) can be then expressed in the form

\[
i_{W} = K(\rho_{WD} - \rho_{W}) \tag{17}
\]

\( i_{W} \) being the wall current density produced by the reaction at the interface, and \( K = \frac{k_{3}n_{N0}}{2(n_{N0} - n_{N0})e_{0}} \frac{V}{A} \) is an effective rate constant. Here \( V \) is the volume of the liquid in contact with the wall of surface area \( A \).

### IV. TIME EVOLUTION

From previous experiments\[18\], we know that the electrical current in (17) is very low. Thus, we may assume an equilibrium spatial profile of the diffuse layer during the flow, but with a time-dependent charge density. With this assumption different solutions can be found, depending on the geometry of the interface in the case of low space charge density and for a no fluid flow case.
A. Planar Electrode

In this case an analytical solution exists for a fully developed diffuse layer [3]

$$\rho = \rho_W \exp \left( -\frac{x}{\delta_0} \right)$$  \hspace{1cm} (18)

where \(x\) is the distance from the wall and \(\delta_0\) is the Debye length

$$\delta_0 = \sqrt{\frac{\varepsilon k T}{\varepsilon^2 (n_p + n_N^+)}} = \text{const.}$$  \hspace{1cm} (19)

Here \(\varepsilon\) is the dielectric permittivity of the liquid, \(k\) is the Boltzmann coefficient, and \(T\) is the absolute temperature. The Debye length is constant as is the permittivity and temperature and, therefore, \(n_p + n_N^+\) remains also constant.

The total charge in the diffuse layer is given by

$$q = \int_0^\infty \rho dx = \rho_W \delta_0.$$  \hspace{1cm} (20)

Thus, as

$$i_W = dq \frac{dt}{dt}$$ \hspace{1cm} (21)

and

$$\frac{d\rho_W}{dt} = K \frac{\delta_0}{\rho_{WD} - \rho_W}$$  \hspace{1cm} (22)

it follows that

$$\rho_W = \rho_{WD} \left[ 1 - \exp \left( -\frac{K t}{\delta_0} \right) \right].$$  \hspace{1cm} (23)

Finally

$$\rho = \rho_{WD} \left[ 1 - \exp \left( -\frac{K t}{\delta_0} \right) \right] \exp \left( -\frac{x}{\delta_0} \right).$$  \hspace{1cm} (24)

B. Two Parallel Plates

A similar analysis gives the following result [4]:

$$\rho = \rho_W \frac{\cosh(x/\delta_0)}{\cosh(a/\delta_0)}$$  \hspace{1cm} (25)

$$q = \rho_W \delta_0 \tan(a/\delta_0)$$  \hspace{1cm} (26)

$$\rho_W = \rho_{WD} \left[ 1 - \exp \left( -\frac{K}{\delta_0 \tanh(a/\delta_0)} t \right) \right]$$  \hspace{1cm} (27)

and

$$\rho = \rho_{WD} \left[ 1 - \exp \left( -\frac{K}{\delta_0 \tan(a/\delta_0)} t \right) \right] \frac{\cosh(x/\delta_0)}{\cosh(a/\delta_0)}$$  \hspace{1cm} (28)

where \(a\) is the channel half width.

\[
\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig1}
\caption{Time evolution of space charge density, \(R = 0.2\) mm, \(K = 0.75 \cdot 10^{-5}\) m/s.}
\end{figure}

\[
\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig2}
\caption{Time evolution of space charge density, \(R = 0.5\) mm, \(K = 0.75 \cdot 10^{-5}\) m/s.}
\end{figure}

C. Pipe of Circular Cross Section

For a tube of radius \(R\) [3], [4], the space charge density is given by

$$\rho = \rho_W \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)}$$  \hspace{1cm} (29)

$$q = 2\pi R \delta_0 \frac{\rho_W}{I_0(R/\delta_0)} I_1(R/\delta_0)$$  \hspace{1cm} (30)

and

$$\rho = \rho_{WD} \left[ 1 - \exp \left( -\frac{K I_0(R/\delta_0)}{2\pi R \delta_0 I_0(R/\delta_0)} t \right) \right] \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)}$$  \hspace{1cm} (31)

where \(I_0\) and \(J_1\) are the modified Bessel functions.

In Figs. 1–6, we plot the evolution of the space charge density profile for two different values of \(K\) and three radii taken in the range of our previous experimental results [19]. In these figures, \(\rho\) represents the calculated local space charge density in \(\mu C/m^3\), and the value of the Debye length is set.
at $\delta_0 = 7.98 \cdot 10^{-5}$ m. The large influence of pipe radius is evident as is the similarity of the profiles for the same values of the product of $K$ and time.

V. LAMINAR FLOW ELECTRIFICATION IN A PIPE OF CIRCULAR CROSS SECTION

We still assume a low space charge density and a small wall current such that the profile of the space charge density is that of an equilibrium double layer along the pipe but with a time-varying amount of charge. At the pipe entrance, we assume that the space charge density is equal to zero in the entire cross section. As a first approximation, we also assume a fully developed laminar flow at the pipe entry. Thus, the laminar flow velocity is given by the following equation everywhere:

$$U = 2U_m \left( 1 - \frac{r^2}{R^2} \right)$$

with $U_m$ representing the mean axial velocity, $r$ the radial coordinate, and $R$ the radius of the pipe.

The profile of the space charge density is still given by (29), in which we compute the evolution of $\rho_w(z)$ along the pipe at a given time, $z$ being the axial coordinate. For a given $z$, the wall current is equal to the divergence of the space charge density convected

$$2\pi R i_w = \frac{d}{dz} \int_0^R 2\pi pU r dr$$

$$2\pi R i_w = \frac{d}{dz} \int_0^R 4\pi U_m \frac{\rho_w(z) I_0(r/\delta_0)}{I_0(R/\delta_0)} \left( 1 - \frac{r^2}{R^2} \right) r dr$$

$$i_w = \frac{4RU_m}{(R/\delta_0)^3 I_0(R/\delta_0)} \left[ (R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0) \right] \frac{d\rho_w(z)}{dz}.$$

\[33\] \[34\] \[35\]
Finally, using (17), we find that

\[
\rho_{W}(z) = \rho_{WD} \left[ 1 - \exp \left( - \frac{K (R/\delta_0)^3 I_0(R/\delta_0)}{4 R U_m [(R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0)]} \right) \right] \tag{36}
\]

and, further, from (29)

\[
\rho(r, z) = \rho_{WD} \left[ 1 - \exp \left( - \frac{K (R/\delta_0)^3 I_0(r/\delta_0)}{4 R U_m [(R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0)]} \right) \right] \times \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)}, \tag{37}
\]

This evolution is plotted in Figs. 7–9 again for parameter values corresponding to our previous experiments [19]. \( Re \) is the Reynolds number: \( Re = \frac{2 R \nu \rho}{\mu} \), \( \nu \) being the kinematic viscosity. From these figures, we see that the space charge development is a function of both the pipe radius and the Reynolds number for small values of \( z \). But, with the increasing pipe length and radius, the influence of the Reynolds number becomes very small.

The convected space charge density is obtained by integrating equation (37) over the pipe cross section

\[
Q(z) = 8 \frac{\rho_{W}(z)}{(R/\delta_0)^3 I_0(R/\delta_0) [(R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0)]}.
\] \tag{38}

The total current for a given Reynolds number \( Re \) and a given \( z \) is

\[
I(z) = 4 \pi \rho_{W}(z) R \nu \frac{(R/\delta_0)^3 I_0(R/\delta_0) [(R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0)]}{(R/\delta_0)^3 I_0(R/\delta_0) [(R/\delta_0) I_0(R/\delta_0) - 2 I_1(R/\delta_0)]}.
\] \tag{39}

We now compare the predictions given by (38) with previous experiments [19]. These experiments were performed with liquid heptane with the electrical conductivity \( \sigma = 4.15 \times 10^{-12} \Omega^{-1} \text{m}^{-1} \), and with the diffusion coefficients (obtained from mobilities) \( D_N = D_P = D = 1.55 \times 10^{-9} \text{m}^2/\text{s} \), giving a Debye length of \( \delta_0 = 7.98 \times 10^{-5} \text{m} \).

In order to make this comparison, we need two other parameters. The first parameter is the space charge density near the wall for a fully developed diffuse layer \( \rho_{WD} \). We determine \( \rho_{WD} \) from the value of the space charge density convected for a single low Reynolds number and in the region where the space charge density convected is independent of the Reynolds number. This was done in a 4-m-long pipe of 0.24-mm radius.

The second parameter is the reaction rate constant \( K \) that determines the rate of development of the wall space charge density. \( K \) is obtained from the higher Reynolds number flow, corresponding to a fully developed diffuse layer (the maximum Reynolds number for which we still have a constant value of the space charge density convected). This again was done in a 4-m-long pipe of 0.24-mm radius. The fitting of experimental
that quantitatively represent experimental data. We assert that wall corrosion is the physical basis of flow electrification.

REFERENCES

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