Flow Electrification Process: the Physicochemical Corroding Model Revisited

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ABSTRACT

Though the phenomenon of flow electrification has been observed for several decades, the physicochemical process appearing at the solid/liquid interface creating the double layer is not yet totally understood. In particular, returns from experiments made with oil and pressboards do not follow the predictions [9]. However, even if the wall material is conductive and not porous, divergences appear with the classical physicochemical model predictions, while a model taking into account the effect of the wall shearing stress on the interfacial process seems to have a much better agreement with the experiments, especially, for high laminar Reynolds numbers.

Index Terms — Flow electrification.

1 INTRODUCTION

FLOW electrification phenomena have been observed and studied for a long time [1-5]. This phenomenon, first causing problems in the petroleum industry, appeared to be responsible for major incidents in power electric transformers, in which oil flow is used to cool the system, and remains an important problem faced by electrical supply industry. Concerning analysis of the phenomenon, its evolution in terms of flow and pipe geometry is now rather well understood and established. However, the physicochemical process at the origin of the phenomenon is still under investigation. Indeed, even if several models have been proposed [6-8], experiments made recently with oil flows past pressboards do not follow the predictions [9].

In this paper we analyze fundamental experiments made some years ago by Romat and Touchard and partly published [10, 11]. The liquid used was n-heptane flowing through a stainless steel capillary of varying length. The experimental setup is presented in figure 1.

Special care was taken in the design of the experimental equipment in order to avoid liquid pollution. That is the reason why the liquid is only in contact with materials and gas as inert as possible (P.T.F.E., glass, stainless steel, Viton joints and argon gas). Indeed, it is now clear that impurities or additives in liquid play an important role in the process even in a small amount such as ppm.

Thus, an argon compressed bottle (1) connected to a pressure reservoir (2) gives a quasi constant pressure to a pressurization vessel (3) pushing the liquid in a large inlet reservoir (4) connected to the capillary (5). This reservoir is used as a tranquilization vessel to ensure a neutrality of the liquid at the entrance of the capillary. After the liquid has flown in the capillary it is collected in the collecting vessel (6). The electric charge transported by the liquid due to the flow electrification process in the capillary is measured with a picommeter Keithley (11) connected to a recorder (12). Then, the liquid is emptied in the outlet reservoir (7) and can fill again the pressurization vessel. The collecting vessel is under an argon atmosphere and inside a faraday cage. The tranquilization vessel and the capillary are thermally insulated. The flow, measured with the flow meter (9), may be adjusted varying the pressure on the pressurization vessel. The temperature of the liquid is controlled with a thermometer (10). The electrical conductivity of the liquid is permanently recorded with the conductivity cell (8).

The experiments reported in this paper have been made for laminar flows with a stainless steel capillary of 0.24 mm in radius R and initially 4 m long. After a set of experiments the capillary was shortened. Thus, six capillary lengths have been tested: 4 m, 3 m, 2 m, 1 m, 0.5 m and 8 cm.

The electrical conductivity of the liquid has remained constant during all the set of experiments (σ = 4.15×10^{-12} Ω^{-1} m^{-1}), this means that the amount of impurities inside the liquid has mainly remained constant. However, the electrical conductivity is not a sufficiently sensitive parameter to detect a minor change in number and nature of impurities which, nevertheless, can change the interfacial physicochemical process.

The ionic mobility being equal to 6.13×10^{-8}, the diffusion coefficients are obtained from Einstein relation (D = kTμ / e0), thus: D = 1.55×10^{-9} m^2 / s . The relative permittivity is taken equal to 2 as normal n-heptane.

Finally the Debye length is computed (δ0 = ε D / σ = 7.98×10^{-5} m), this means that the radius of the capillary is around three times greater than the Debye length. Thus, an important part of the diffuse layer is transported by the flow.

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2 EXPERIMENTS

We can see in Figure 2 the space charge density transported by a laminar flow ($Q_l$) in terms of the Reynolds number ($Re$) for six different capillary lengths. The space charge density transported is obtained dividing the current by the flow rate.

From this set of experimental results it seems that when the capillary is 4 m long the diffuse layer is fully developed at the exit of the tube for Reynolds numbers lower than 200. Indeed, in that case the space charge density transported remains constant (~127 $\mu$C/m$^3$). From this result and with the assumption of weak space charge density [10] it is then possible to compute the wall space charge density in a fully developed diffuse layer:

$$\rho_{WD} = \frac{Q_l}{8} \frac{I_0(R/\delta_0)(R/\delta_0)^2}{I_2(R/\delta_0)}$$

where $I_0$ and $I_2$ are the modified Bessel functions of 0 and 2 order.

We find $\rho_{WD} = 311 \mu$C/m$^3$.

3 THE CORRODING MODEL

This model [8] assumes that only a single impurity or additive $A_L B_L$ is very weakly dissociated inside the liquid.
Thus, we have the following equation

\[ A_l B_L \xrightarrow{k_1} A_l^+ + B_L^- \]  

where \( k_1 \) and \( k_1^- \) are the kinetic constants of the dissociation reaction. It is also assumed that the solid surface is partly or totally composed of atoms \( C_S \) and undergoes the following reaction in presence of the liquid

\[ C_S \xrightarrow{k_2} C_S^+ + e^- \]  

where \( k_2 \) and \( k_2^- \) are the kinetic constants of the wall corrosion reaction. Then when the ions \( C_S^+ \) are in contact with anions of the liquid \( B_L^- \), a surface reaction can occur

\[ C_S^+ + B_L^- \xrightarrow{k_3} C_S B_L \]  

where \( k_3 \) and \( k_3^- \) are the kinetic constants of the ions recombination reaction.

### 3.1 Assumptions of the Model

This model makes three important assumptions:

- Concentration of \( C_S^+ \) is not rate controlling and independent of the wall shearing stress.
- Weak space charge density in the whole diffuse layer.
- Space charge density profile is that of an equilibrium diffuse layer all along the axis.

The last assumption could be justified by a very slow interfacial reaction compared to the diffuse layer rearrangement. In fact, it has been shown that the time constant in both cases is not so different [9].

The second assumption is obviously false as the non dimensional space charge density on the wall [10] \( \rho_{WD+} = 4.59 \) while this assumption supposes the non dimensional space charge density much lower than 1. In fact, the error made with this assumption does not change the behavior of the charge transported in terms of the Reynolds number upon which we are interested in this paper.

The questionable assumption in this paper is the first one. Indeed, we will see that, even for conductive and not porous pipe wall as it is the case for stainless steel capillary tube, \( C_S^+ \) concentration varies with the wall shearing stress.

### 3.2 Theoretical Predictions of the Model

The corroding model, as well as, other previous models [6-8] predict that the wall current density at a given axial coordinate \( z \) of the tube is given by the following equation

\[ i_W(z) = K[\rho_{WD} - \rho_W(z)] \]  

where \( K \) is a constant and \( \rho_W(z) \) is the space charge density on the wall at the axial coordinate \( z \).

Then, the space charge density on the wall and the space charge density transported can be computed in terms of \( z \) and the Reynolds number \( R_e \) by the following calculus:

\[
d \left( \frac{2 \pi \rho(r, z) U(r) r \, dr}{dz} \right) = 2 \pi R_i W(z)
\]

where \( U(r) \) is the axial velocity in a cross section

\[
\rho(r, z) = \rho_W(z) \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)}
\]

\[
\int_0^R 2 \pi \rho(r, z) U(r) r \, dr = 8 \pi \rho_W(z) \delta_0^2 U_m \frac{I_2(R/\delta_0)}{I_0(R/\delta_0)}
\]

\[
U_m \text{ being the flow velocity, then:}
\]

\[
i_W(z) = \frac{d\rho_W(z)}{dz} \frac{4 \delta_0^2 U_m}{R} \frac{I_2(R/\delta_0)}{I_0(R/\delta_0)}
\]

Then from equation 5 we find:

\[
\rho_W(z) = \rho_{WD} \left[ 1 - \exp \left( -\frac{K(R/\delta_0)^2 I_0(R/\delta_0)}{2 Re \nu I_2(R/\delta_0)} z \right) \right]
\]

\[
Q_1(z) = 8 \rho_W(z) I_2(R/\delta_0) \frac{I_0(R/\delta_0)}{(R/\delta_0)^2 I_2(R/\delta_0)}
\]

where \( \nu \) is the kinematic viscosity of the liquid.

### 4 Model Predictions and Experiments Comparison

Reversing the calculus, experimental value of \( K \), can be computed with equations (6) and (7) from the experimental space charge density transported shown in figure 2

\[
K = \frac{-2 \nu Re I_2(R/\delta_0)}{(R/\delta_0)^2 I_0(R/\delta_0)} \ln \left[ 1 - \frac{Q_1}{8 \rho_{WD} I_2(R/\delta_0)} \right]
\]

These values of \( K \) are plotted in terms of \( \text{Re} \) for different \( z \) in Figure 3 (excluding data of fully developed layer).

Obviously, \( K \) is not constant as it was predicted by the model but seems to have a linear evolution in terms of \( \text{Re} \), thus, in terms of the wall shearing stress. That is the reason why we have tried to find a new model more realistic.
5 NEW CORRODING MODEL

The fact that \( K \) would depend on the Reynolds number means that the concentration of \( C^+ \) on the wall would be reinforced by the wall shearing stress. In other words the corrosion would be reinforced by the flow, which can be understandable. This behavior of \( K \) would explain why, in figure 2, the space charge density transported is generally not constantly decreasing with the Reynolds number but seems to reach an asymptotic value for large laminar Reynolds number. We have, then, tried to find an evolution of \( K \) in terms of \( Re \) which gives the best agreement with the experiments.

A rather good agreement can be found with the following value of \( K \):

\[
K = 1.35 \times 10^{-8} Re + 4.75 \times 10^{-6}
\]  

(9)

This \( K \) behaviour gives a good relative evolution of \( Q_l \) in terms of \( Re \) for Reynolds numbers in the range (200, 2000) and for the different values of \( z \). However, to have a good absolute fitting it is needed to consider that the space charge density on the wall varies with the different sets of experiments corresponding to the different values of \( z \). Considering that the time between the sets of experiments is generally several weeks, and in spite of very careful experimental process it is not totally surprising that this parameter can change. Thus, computation of theoretical evolution has been made with \( K \) given by equation (9) and the following space charge density on the wall (\( \mu C / m^3 \)).

We can see in figures 4 to 9 a comparison of the experiments and the two theoretical cases:

- \( K \) constant (\( 1.156 \times 10^{-5} \)) and \( \rho_{WD} = 311 \cdot \mu C / m^3 \) as it was found in the previous model [8]
- \( K \) given by equation (9) taking into account space charge densities on the wall given by Table 1

This new model gives a rather good agreement with experiments. Then experimental values of \( K \) are again computed with equation (8) and taking into account space charge densities on the wall given by Table 1. We can see in Figure 10 these experimental values compared to the evolution of \( K \) given by equation (9), the agreement is rather good as it could be predicted instead of the case of experiments made with a 4 m long capillary tube for large Reynolds number. We do not know exactly why the agreement is not good in that case, but we suspect a change in the liquid as these experiments was the first and may be the liquid had not yet reach equilibrium in the circuit.

6 CONCLUSION

Analyzing experiments made in a metallic capillary it appears that the constant \( K \) of the process must be a linear function of the wall shearing stress. This means that the corrosion process on the wall must also be a linear function of the wall shearing stress and not only a chemical reaction.
Figure 10. K evolution in terms of Re and z.

REFERENCES


Thierry Paillat was born in France, in 1971. He graduated in physics and electrical engineering and received the Ph.D. degree from the University of Poitiers, France in 1998. Since 1998, he has been an Associate Professor and works in the Electrofluidodynamic team in the "Laboratoire d'Etudes Aérodynamiques", in Poitiers University, France. His thematic research focuses on electrostatic hazards by flow electrification of fluids and fundamental aspects of electrical double layer.

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