Flow Electrification: a way to test the hypothesis of wall slip

Gerard Touchard
P' Institute
University of Poitiers, CNRS
Bd Marie & Pierre Curie, BP 30179
86962 Futuroscope Cedex, France
gerard.touchard@univ-poitiers.fr

Guillermo Artana
Facultad de Ingeneria
Universidad de Buenos Aires
Paseo Colon 850,
1063 Buenos Aires, Argentina
gartana@fi.uba.ar

Thierry Paillat
P' Institute
University of Poitiers, CNRS
Bd Marie & Pierre Curie, BP 30179
86962 Futuroscope Cedex, France
thierry.paillat@univ-poitiers.fr

***Abstract* -- For a liquid flowing inside a capillary of very small diameter, the no slip hypothesis on the wall seems to be questionable. Experiments to determine the validity of such hypothesis are very difficult to develop and results are often not that clear, especially because of the large number of parameters. Several techniques are used for this purpose without any one having a real supremacy on the others. Among the different technique some use the electrokinetic phenomena. In this paper we analyze some experiments made previously on streaming current in glass capillaries. In spite of a rather large dispersion it seems that a theoretical approach taking into account the wall roughness effect and a slip velocity is closer to the experimental results than the "classic Poiseuille flow".**

***Index Terms*—Flow electrification, Microfluidics, Slip condition.**

I. Introduction

For several decades experiments on flow electrification made in P' Institute (previously named L.E.A.) for very small diameter capillaries, show some deviations from what we could expect in such experimental conditions [1]. In another hand, fluid flow in micro capillaries has emerged as an important area of research. Indeed, numerous new technologies in biomedical, computer chips cooling, and chemical separations involve fluid transport in micro channels. Thus, many recent experiments were conducted in order to quantify the flow through micro system of pipes and channels. But the results obtained seem to question a fundamental hypothesis mostly used in Newtonian fluid flows: the non slip condition at the interface with the solid. The situation of apparent slip is commonly faced for flows of non-Newtonian fluids such as polymers. This particular situation is investigated for a long time and is of great practical importance. But, in the case of Newtonian fluids, in large channels the non-slip hypothesis at the interface permits to predict quite perfectly the flow experiments. In fact, this hypothesis seems to be questionable only for very tiny channels of width in the order of micro meters or smaller.

II. Slip or no-slip hypothesis

The slip or non-slip hypothesis at a solid-fluid interface is of major importance in fluid mechanics. However, this condition is an assumption that cannot be derived from first principles and could, in theory, be violated. A very complete analysis referring to a wide and exhaustive bibliography on the subject is given by E. Lauga [2]. From this study, as well theoretical and exploring results from experiments and from molecular dynamics simulations, slip seems to occur under certain conditions but the different experimental methods which are generally used to quantify the phenomenon seem to be all intrusive or not fully reliable. The concept of slip in the case of gas flow was first introduced by Maxwell [3] and is well known for rarefied gas. For air under standard conditions of temperature and pressure it is significant when the dimensions of the channels are of the same order than the mean free path of the gas molecules: around 0.1µm. By cons, in the case of Newtonian liquids the slip is function of numerous parameters such as surface roughness, gas bubbles at the interface, wetting, shear rate, electrical double layer, pressure [4-12]. Thus in spite of numerous investigations or opinions of great names in the field of physics since several centuries, including Bernouilli, Euler, Coulomb, Poisson, Navier, Hagen, Poiseuille, Darcy, Stokes, Helmoltz, Couette, Maxwell, Prandtl and Taylor, the hypothesis remains questionable.

The object of the present work is not to add a new study to enforce the slip or non-slip hypothesis, but taking into account the different research made on flow electrification in micro diameter capillaries to try to explain the deviations observed of our experiments from the "classic" predictions.

III. Roughness effect

The global effect of roughness for laminar flows of liquids in µm diameters capillaries is not obvious. Generally two opposite effects exist due to roughness. Roughness enlarge the friction factor as pointed out by Croce [9], but under certain conditions, roughness can house micro bubbles on which the liquid slides [2,5], this is the well known "lotus-leaf effect". Indeed, surfaces covered with microstructures and nanostructures such as grooves, or holes can effectively trap bubbles. If the liquid surface is restricted to the top of the roughness the liquid will be in contact with the solid only on fraction of the surface, while the rest will be in contact to the gas phase with possibility of slip on it. Thus, the liquid moves over trapped bubbles with a significant reduction in friction.
Reasonably, probably, both phenomena exist very close to the interface. These two opposite phenomena are not easy to model at the same time, because, one corresponds to an increasing of the local apparent viscosity while the other corresponds to a lower viscosity in the very near vicinity of the wall.

IV. FLOW ELECTRIFICATION PROCESS

At a liquid/solid interface, due to a physico chemical process [13] an electrical double layer appears. This leads to electrical charge of one sign appearing in the liquid close to the interface and charges of opposite sign on the solid. It is usual to consider the Stern model for this double layer. Thus, in the liquid two layers composed the double layer. One very close to the solid is called the compact layer; the width of it is in the order of magnitude of molecular dimension and thus can not be affected by the flow of the liquid. Farther in the liquid a diffuse layer exists, the width of which (the so called "Debye length") is inversely proportional to the root square of the electrical conductivity of the liquid.

Considering the case of two kinds of ions in the diffuse layer: one positive and one negative with the same valence Z=1 and the same diffusion coefficient. After computation, in the case of weak space charge density (that is to say for $n_P - n_N \ll n_P + n_N$, n_P and n_N being respectively the number of positive and negative ions per unit of volume), the space charge density profile in a pipe of circular cross section is given by the following equation:

$$\rho = \rho_w \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)} \tag{1}$$

ρ_w being the wall space charge density, r the radial coordinate, R the radius of the pipe δ_0 the diffuse layer thickness (the Debye length) and I_0 the modified Bessel Function of zero order. Some remarks are needed concerning this relation. The value of ρ_w is only due to the physicochemical reaction at the interface solid liquid, ions or dissociated impurities of the liquid reacting with some components of the solid. Thus, obviously this reaction is independent of the radius of the pipe. This means that ρ_w is independent of the pipe radius but normally depends on the conductivity of the liquid which is in direct relation with the concentration of ions or dissociated impurities, as well the diffuse layer thickness (the Debye length). Indeed we have the following relation:

$\delta_0 = \sqrt{\frac{\varepsilon_e D_0}{\sigma}}$, ε_e being the electrical permittivity of the liquid, D_0 being the mean diffusion coefficient of ions (supposed to be the same for cations and anions) and σ being the electrical conductivity of the liquid.

A. *Space charge convected by laminar flow in smooth pipes and without slip*

We suppose that the length of the capillary is large enough in order to have a fully developed diffuse layer at the exit of the pipe and a Poiseuille velocity profile. As well, we consider the head loss at the entrance negligible. In such conditions the velocity is given by the following equation:

$$u(r) = -\frac{1}{4\mu}\left(R^2 - r^2\right)\frac{dP}{dX} \tag{2}$$

where μ is the dynamic viscosity of the liquid, R the radius of the capillary and dP/dx the pressure gradient along the capillary axis. A mean flow velocity can then be deduced:

$$U_m = -\frac{R^2}{8\mu}\frac{dP}{dx} \tag{3}$$

The electrical current generated by the flow of the charges transported, also called electrification current or streaming current, is then given by the following integral:

$$I = \int_0^R 2\pi\, r\, \rho(r)\, u(r)\, dr \tag{4}$$

Thus, taking into account the expression for the profile of the space charge density and the velocity, we find:

$$I = \int_0^R 2\pi \frac{1}{4\mu} r \left(R^2 - r^2\right)\frac{\Delta P}{L} \rho_w \frac{I_0(r/\delta_0)}{I_0(R/\delta_0)} dr \tag{5}$$

L being the length of the capillary and ΔP the pressure difference between the entry and the exit of the capillary. This integral has an analytical solution:

$$I = \frac{\pi}{\mu}\frac{\Delta P}{L}\rho_w \frac{R^2 \delta_0^2 I_2(R/\delta_0)}{I_0(R/\delta_0)} \tag{6}$$

I_2 being the modified Bessel function of second order.

B. *Space charge convected by a laminar flow in rough pipe and with slip*

We consider capillaries with a wall roughness of same amplitude ε and we assume the hypothesis of a slip velocity on the wall due to the gas bubbles embedded inside the roughness. Thus close to the wall, in the roughness region, we suppose the velocity nearly constant due to an apparent high viscosity generated by eddies generated by the roughness, and as well we suppose a small slip velocity on the wall. Finally, the velocity profile is likely to that shown on Fig. 1.

Then, in order to get analytical calculus we approximate the velocity profile by a parabolic (Poiseuille profile) in the central region and a constant one near the wall (Fig. 2).
The velocity in the wall region is equal to the slip velocity U_S which can be computed in terms of the friction coefficient k :

$$U_S = -\frac{\varepsilon}{k}\frac{dP}{dx} \tag{7}$$

(the wall shearing stress $\tau = k\, U_S$)

ε being the wall region thickness (assumed to be in the order of magnitude of the roughness height) and $\frac{dP}{dx}$ the pressure gradient. It is usual to express k as follows : $k = \frac{\mu}{\ell}$, ℓ being a characteristic length [5].

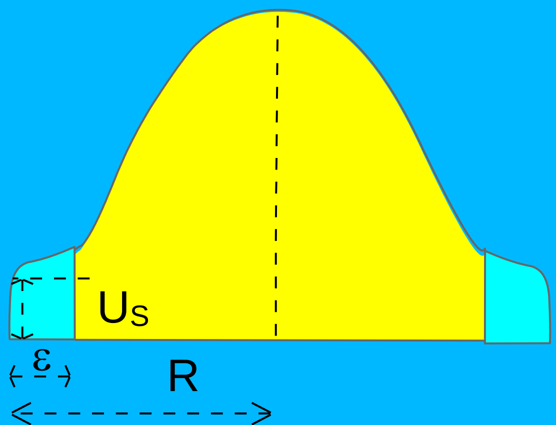

Fig. 1. Velocity profile

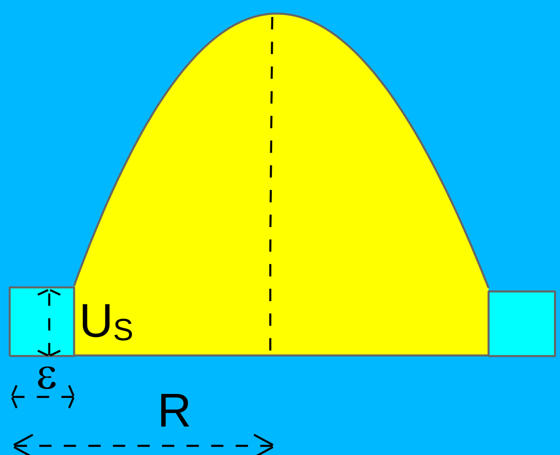

Fig. 2. Velocity profile approximated

Then we have two formulas for the velocity profile, depending on the region.

1) *central region* ($0 \le r \le R - \varepsilon$)

The velocity has a parabolic (Poiseuille) profile added with the sliding velocity: $U = U_P + U_S$

with :

$$U_{1P} = -\frac{dP}{dx}\left[\frac{(R-\varepsilon)^2}{4\mu}\left(1 - \frac{r^2}{(R-\varepsilon)^2}\right)\right] \tag{8}$$

and :

$$U_S = -\frac{1}{\mu}\frac{dP}{dx}\ell\varepsilon \tag{9}$$

2) *wall region* ($R - \varepsilon \le r \le R$)

The velocity is constant and equal to the sliding velocity:

$$U = U_S = -\frac{1}{\mu}\frac{dP}{dx}\ell\varepsilon \tag{10}$$

The streaming current generated by the flow of the charges transported is still given by the same integral:

$$I = \int_0^R 2\pi\, r\, \rho(r)\, u(r)\, dr \tag{11}$$

But the space charge density profile must take into account the effect of the roughness.

This effect is not obvious. We made in the past a study for periodic roughness of same amplitude, which seem to decrease the flow electrification because a part of the charge of the diffuse layer remains, in that case, prisoner between to successive roughness [14] . In the present case the roughness are not at all regular and periodic but fully random, thus we expect it generate a kind of mixing of the charges in the diffuse layer as act eddies or turbulence. In that case we consider that the diffuse layer thickness is enlarged by the roughness and instead of δ_0 the thickness will be supposed to be δ_r function of δ_0 but also of the roughness height ε .

Finally the streaming current generated can be computed:

$$I = \int_0^{R-\varepsilon} 2\pi r\rho_w \frac{I_0(r/\delta_r)}{I_0(R/\delta_r)} U_P\, dr + \int_0^{R-\varepsilon} 2\pi r\rho_w \frac{I_0(r/\delta_r)}{I_0(R/\delta_r)} U_S\, dr + \int_{R-\varepsilon}^{R} 2\pi r\rho_w \frac{I_0(r/\delta_r)}{I_0(R/\delta_r)} U_S\, dr \tag{12}$$

The first integral is called Int_1 , the second one Int_2 and the third one Int_3. Then integration of Int_2 gives two terms ($Int_2 = T_{22} - T_{21}$) (Barrow's rule), as well integration of Int_3 gives two terms ($Int_3 = T_{32} - T_{31}$).

But, $T_{21} = 0$ (because $I_1(0) = 0$) and $T_{22} = T_{31}$.

Finally, $I = Int_1 + T_{32}$, with:

$$Int_1 = -\frac{\pi}{\mu}\frac{dP}{dx}\frac{\rho_w}{I_0(R/\delta_r)}\delta_r^2 (R-\varepsilon)^2 I_2((R-\varepsilon)/\delta_r)$$

and

$$T_{32} = -2\frac{\pi}{\mu}\frac{dP}{dx}\frac{\rho_w}{I_0(R/\delta_r)}\delta_r R\ \ell\varepsilon\ I_1(R/\delta_r)$$

Thus the streaming current can then be expressed as following:

$$I = \frac{\pi}{\mu}\frac{\Delta P}{L}\rho_w \cdot \frac{(R-\varepsilon)^2\delta_r^2\ I_2((R-\varepsilon)/\delta_r) + 2\varepsilon\ell\ \delta_r R\ I_1(R/\delta_r)}{I_0(R/\delta_r)} \tag{13}$$

We will compare the two expressions for the current "without slip and roughness" (equation (6)) and "with slip and roughness" (equation (13)) with the experimental results.

V. EXPERIMENTAL SETUP

A grid of the experimental equipment is shown in Fig. 3. The glass capillary is mounted on a Teflon sample holder. A set of O-rings seals on the side of the capillary. The two chambers on both sides of the sample are bound by four tie rods and O-rings which seal the apparatus. The upstream chamber is connected to a liquid reservoir pressurized by means of a bottle of compressed nitrogen. The pressure is controlled by the pressure gauge and, for safety reasons, will be limited to 2 bars. The downstream chamber is connected to a calibrated glass tube for measuring the flow rate with a cathetometer. A metal electrode is immersed in each chamber. The whole assembly is put in a Faraday cage grounded. The electrode in the upstream chamber is grounded, while the electrode in the downstream chamber is connected to a Keithley 642 picoammeter of very high sensitivity which is itself connected to a data acquisition system.

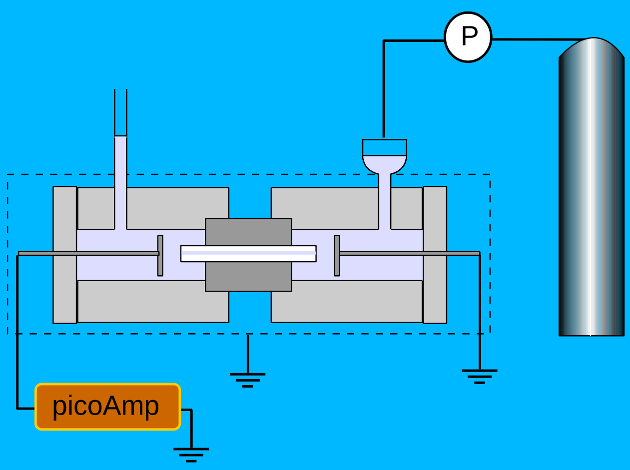

Fig.3. Experimental equipment

VI. MEASUREMENT PROTOCOL AND EXPERIMENTAL CONDITIONS

When the cell is mounted, three to four hours are needed to reach a physicochemical equilibrium. When this equilibrium is reached, a flow of liquid through the capillary is made to eliminate the standing water.
The measurements are then performed. The pressure difference generated between the two chambers causes the water flow through the capillary. The current due to the flow electrification is then measured and recorded. This pressure difference is maintained for two to three minutes. The pressure is then released. The operation is repeated for differences in pressure ranging from 0.3 to 2 bar.
This experiment is carried out for 6 capillaries of different diameters and for several electrical conductivities of deionised water.

A. *Capillaries used*

Six capillaries were used. They have the same length (L = 7cm), the same external diameter (4.5 mm) and the same chemical composition. Their inner diameter is 20µm, 50µm, 60µm, 100µm, 150µm and 200µm. They seem to have the same roughness on the inner wall that we estimate with a SEM to 0.5 µm.

B. *Liquid used*

We used deionised water with different concentration in carbon dioxide, thus with different conductivity that we control all along the experiments.

C. *Water parameters*

From literature we took the following parameters.

Dynamic viscosity: $\mu = 1 \cdot 10^{-3}\,P$

Electrical permeability: $\varepsilon_e = \varepsilon_{er} \cdot \varepsilon_{e0} = 78.3 \cdot \frac{1}{36\pi} 10^{-9}\,Fm^{-1}$

Mean ionic diffusion coefficient: $D_0 = 6.3\,10^{-9}\,m^2 s^{-1}$

We assume, as we experimentally found in different studies [15], that the space charge density on the wall is proportional to the electrical conductivity. This means that the physicochemical process on the wall is, as the conductivity, proportional to the concentration of impurities inside the water.

VII. RESULTS ANALYSIS

The streaming current recorded divided by the applied pressure is plotted Fig. 4 to Fig.9 for the different capillaries and for a set of water conductivities. The different points for a given conductivity correspond to the different applied pressure. Theoretical predictions are also plotted on the same graphs. These theoretical values are computed in order to fit the mean experimental value obtained for one water conductivity ($\sigma = 10^{-3} \cdot \Omega^{-1} m^{-1}$). The black solid line correspond to the theoretical predictions issued from the "without roughness and without slip" analysis (equation (6)), while the red line correspond to the theoretical predictions issued from the "with roughness and with slip" analysis (equation (13)). For these last theoretical predictions the roughness influence on the enhancement of the diffuse layer thickness was taken as follows: $\delta_r = \delta_0 + 0.25\,\varepsilon$. The length ℓ which characterise the slip velocity was taken as: $\ell = 2.65 \cdot 10^{-7}\,m$. These two quantities δ_r and ℓ was adjust to fit better one experimental point in terms of radius (see below). The values of ℓ and ε correspond to a slip velocity U_S =0.19 mm/s while the mean velocity is U_m =17.9 mm/s for the capillary of 20µm in diameter and U_m =1.79 m/s for the capillary of 200µm in diameter. Thus, such slip velocity is in all cases much smaller that the mean velocity and very difficult to observe from flow rate experiments.

In spite of a rather large dispersion it seems that the predictions with slip and taking into account the influence of the roughness are more in agreement with the experimental result.

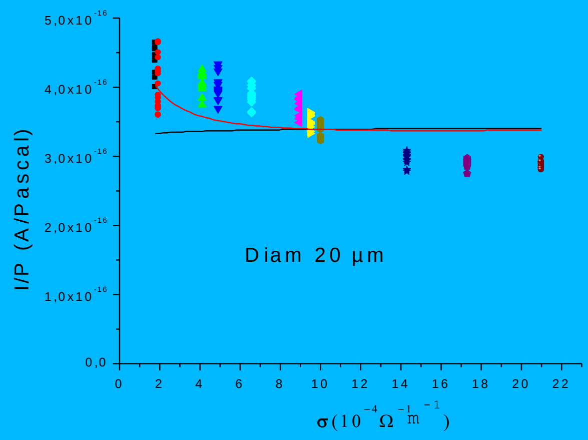

Fig. 4. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 20 µm in diameter

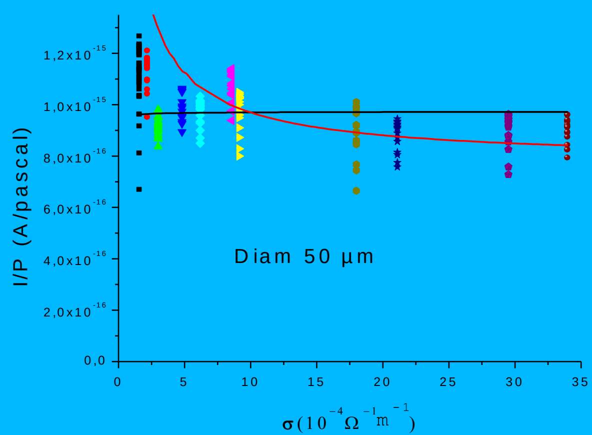

Fig. 5. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 50 µm in diameter

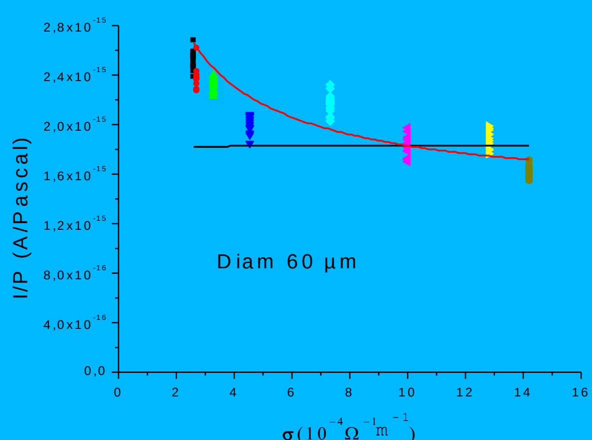

Fig. 6. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 60 µm in diameter

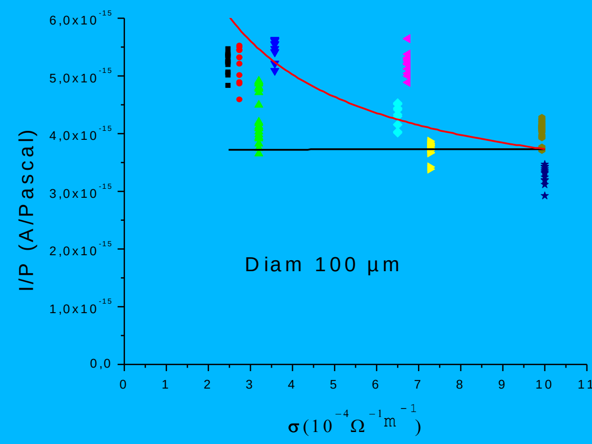

Fig. 7. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 100 µm in diameter

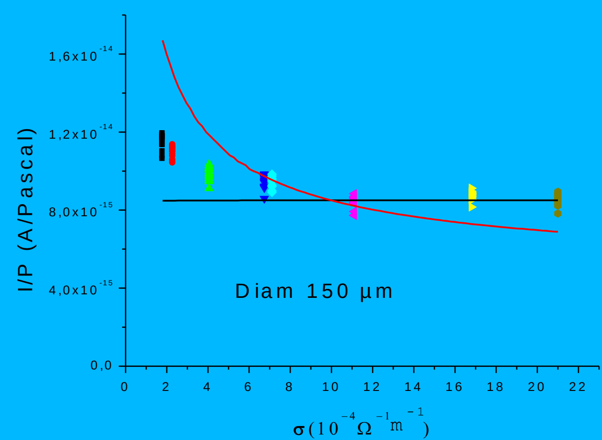

Fig. 8. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 150 µm in diameter

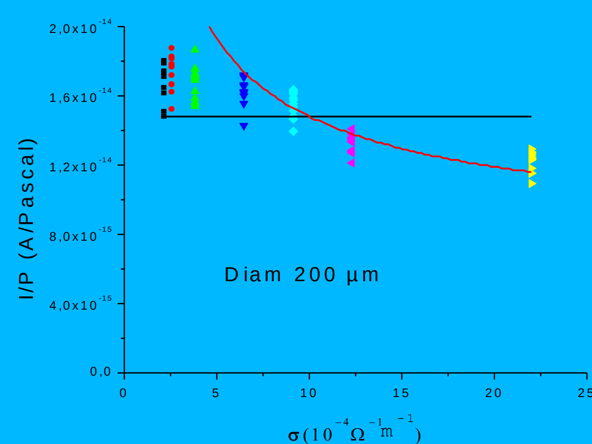

Fig. 9. Ratio of streaming current on applied pressure in terms of water conductivity for a capillary of 200 µm in diameter

In Fig.10 the ratio of the streaming current divided by the applied pressure is plotted for a given water conductivity ($\sigma = 10^{-3} \cdot \Omega^{-1} m^{-1}$) in terms of the capillaries diameter. As well, the theoretical predictions for the two different analyses are also plotted fitting with the experimental value for the smaller diameter (20 µm). The black line correspond to the "without roughness and without slip" analysis (equation (6)), while the red line corresponds to the "with roughness and with slip" (equation (13)).

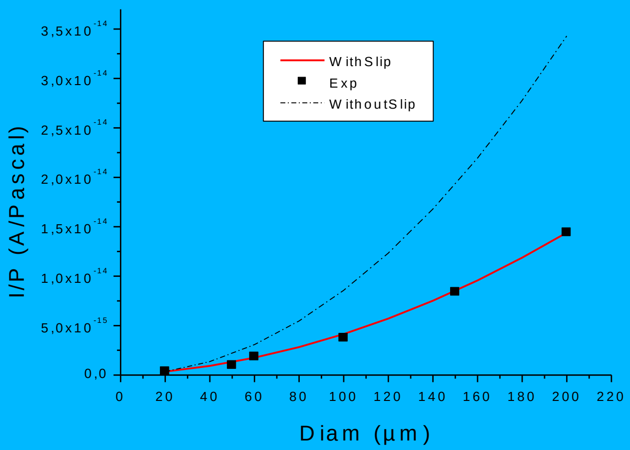

Fig. 10. Ratio of streaming current on applied pressure in terms of the capillaries diameter and for a water conductivity ($\sigma = 10^{-3} \cdot \Omega^{-1} m^{-1}$)

In both theoretical analysis the wall space charge density on the wall was assume to be independent of the radius of the capillary as it relates the physicochemical process intensity which is only function of the characteristics of the materials in contact.

Clearly, the "classic" predictions which does not take into account the roughness effect and a slip velocity on the wall does not fit well the experiments. This was, indeed, the reason of the present study.

How was done the fitting with experiment for the theoretical approach with slip and roughness effect ?

For a given value of δ_r we determine the value of ℓ which give a good agreement with experimental results for the larger diameter (200µm). The value of δ_r is arbitrary but when it is determined, then, only one value of ℓ gives the good fitting. The influence of ε on δ_r was estimated from the comparison of the relaxation velocity of the diffuse layer with the radial velocity generated by roughness of height ε .

What seems interesting is that the experimental values obtained for the four intermediate diameters fit well with these predictions. Thus, even if, of course, there is a fitting, it seems that the hypothesis taking into account a slip velocity on the wall and the influence of the roughness leads to a much better agreement with our experiments than the "classic" predictions.

Acknowledgment

The present study has been made as part of researches of the L.I.A. of Physics and Fluid Mechanics supported by both Argentina and French Foreign office.

References

[1] T. Paillat, G. Touchard, E. Moreau, "Streaming Current Generated by a Deionized Water Flow through Glass Capillaries of Different Radii", in *Proc. ESA-IEJ Joint Symposium*, pp. 26-40, 1998.

[2] Eric Lauga, Michael P. Brenner and Howard A. Stone, "Microfluidics: The No-Slip Boundary Condition", Ch 15 *Handbook of Experimental fluid Dynamics*, Springer New-York, 2005.

[3] J. C. Maxwell, *Philosophical Transactions of the Royal Society of London, A 170*, p.213, 1879.

[4] Hui Zhao, "Electro-osmotic flow over a charged superhydrophobic surface", *Physical Review*, E 81, pp. 066314-1 066314-9, 2010.

[5] P.G. de Gennes, "On fluid/wall slippage", *Langmuir* Volume 18, Issue 9, 30 April 2002, pp. 3413-3414, 2002.

[6] J. Judy, D. Maynes, B.W. Webb "Characterization of frictional pressure drop for liquid flows through microchannels", *International Journal of Heat and Mass Transfer*, 45, pp. 3477-3489, 2002.

[7] David Erickson and Dongqing Li, "Streaming Potential and Streaming Current Methods for Characterizing Heterogeneous Solid Surfaces", *Journal of Colloid and Interface Science*, 237**,** pp. 283–289, 2001.

[8] Todd M. Squires, "Electrokinetic flows over inhomogeneously slipping surfaces", *Physics of Fluids*, 20, pp. 092105-1 to 10, 2008.

[9] Giulio Croce and Paola D'Agaro, "Numerical simulation of roughness effect on microchannel heat transfer and pressure drop in laminar flow", *J. Phys. D: Appl. Phys.*, 38, pp. 1518–1530, 2005.

[10] G. Gamrat, M. Favre-Marinet, S. Le Person, R. Bavière and F. Ayela , "An experimental study and modelling of roughness effects on laminar flow in microchannels", *J. Fluid Mech.*, vol. 594, pp. 399–423, 2008.

[11] Gh Mohiuddin Mala, Dongqing Li, "Flow characteristics of water in microtubes", *International Journal of Heat and Fluid Flow*, 20, pp. 142-148, 1999.

[12] N. V. Churaev, V. D. Sobolev, and A. N. Somov, "Slippage of Liquids over Lyophobic Solid Surfaces", *Journal of Colloid and Interface Science*, Vol 97, No. 2, pp. 574-581, 1984.

[13] G. Touchard, T. W. Patzek, C. J. Radke, "A physicochemical explanation for flow electrification in low-conductivity liquids", *IEEE Transactions on Industrial Applications*, vol. 32, n° 5, pp. 1051-1057, 1996.

[14] G. Touchard, M. Benyamina, J. Borzeix, H. Romat, "Static electrification by laminar flows through artificially roughed pipes", *I.E.E.E., I.A.S.*, vol. 25, n° 6, pp. 1067-1072, 1989.

[15] E. Moreau, T. Paillat, G. Touchard, "Space charge density in dielectric and conductive liquids flowing through a glass pipe", *Journal of Electrostatics*, Vol. 50-51, pp. 448-454, 2001.