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Experimental study of difference between streaming current and electroosmosis in single fused silica capillaries

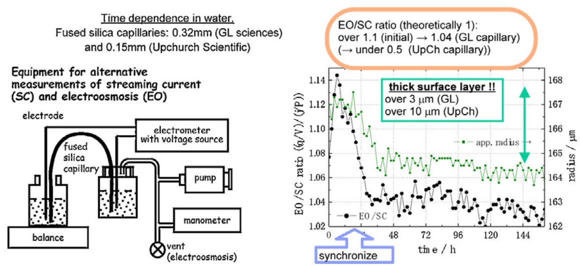
Takeshi Nashima *

National Metrology Institute of Japan, AIST Tsukuba, Umezono 1, Tsukuba, 305-8563, Japan

HIGHLIGHTS

- ► It is concluded that electroosmosis and streaming current are not identical.
- ► Using fused silica capillary–water system, long time tests were carried out.
- ► The surface of fused silica capillary is varied and reduces the radius slowly.
- ► The electroosmosis values are about 10% larger for non-varied capillaries.
- ► Electroosmosis is seriously affected by the variation of the surface of capillary.

GRAPHICAL ABSTRACT



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ABSTRACT

Two electrokinetic phenomena, electroosmosis and streaming current are compared and examined whether these two are identical as the measuring methods of zeta potential, using a single capillary method. In addition of zeta potentials by both methods, variation of apparent radius of fused silica capillaries, which were used in this study, were measured with time for a long period. Two sort of experimental results were obtained. First, it was revealed that the capillary radius reduces in order of day. The extent of the change was as huge as exceeding micrometers. This origin is speculated to be a sort of soft substances, which may be a silicate polymer, generating on the surface. This may be reflecting difference of the surface properties, that is, difference of materials. And second, it was found that there exists a difference between electroosmosis and streaming current measurements. The electroosmosis values are about 10% larger than the streaming potential values for non-varied capillaries. When the surface is varied and capillary radius is reduced, the electroosmosis is affected more seriously than the streaming current.

1. Introduction

When a fluid flows in a capillary channel, zeta potential is derived from the streaming current and the flow rate, and also, viscosity from the pressure difference and the flow rate. When voltage is applied to the same channel so that the electroosmosis is generated, zeta potential will be similarly derived from the potential gradient and the flow rate. These two electrokinetic phenomena are recognized as a good specimen of Onsager's reciprocal theorem, and represent the same physical properties theoretically. The objective of this study is to verify whether these two measuring methods of zeta potential are the identical. Although there have been reported the comparison of the streaming current or streaming potential and an electroosmosis [1,2], only the work of Ballaistre et al. [3] is comparable with this study, and it is reported that there is certain difference, in which electroosmosis becomes larger. Bellow, comparative experiments are conducted using single intact fused silica capillaries.

Zeta-potential is expressed as $\zeta = j_{SC} r^2 / 8\varepsilon q$ as to the streaming current method (SC). This becomes to $\zeta = l\, j_{SC} \eta / \pi r^2 \varepsilon P$ if q is

* Corresponding author. Tel.: +81 29 861 4067; fax: +81 29 861 4280.
E-mail address: t.nashima@aist.go.jp

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eliminated using the Hagen–Poiseuille's equation ($\eta = \pi r^4 P/8lq$). As to the electroosmosis method (EO), it is $\zeta = \eta q_{EO}/\pi r^2 \varepsilon E$. Then, with replacing by $E = lV$, the experimental formula in this study are obtained, that is,

$$\frac{j_{SC}}{P} = \frac{q_{EO}}{V} = \frac{\pi r^2 \varepsilon \zeta}{l\eta} \quad (1)$$

So, by testing these four measurable quantities, that is, j_{SC}, P, q_{EO}, and V, the equivalence of two methods will be examined. By alternating two methods in a short time, the experiment will be able to accept the varying condition of the testing capillaries. Defining EO as q_{EO}/V, and SC as j_{SC}/P, the EO–SC ratio (EO/SC), that should be unity theoretically, represents the divergences which is independent of variations of the quantities of the right side of the Eq. (1).

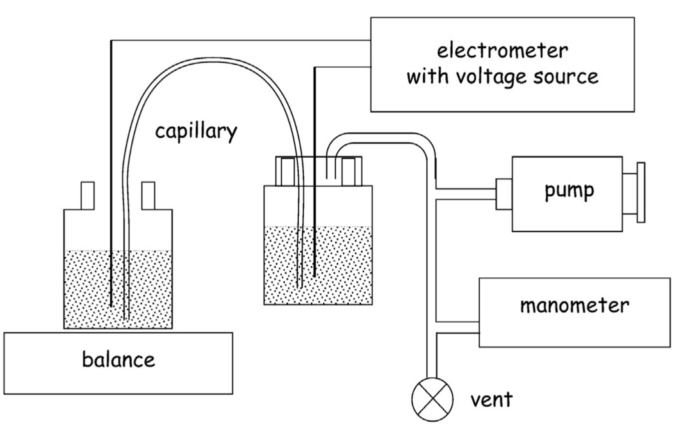
If the flow rate is measured with the measurement of streaming current, viscosity of sample can be measured simultaneously from the relation between the flow rate and pressure using the Poiseuille's formula as expressed above. However, in this study, it is not for measurement of viscosity, but used to obtain the capillary radius for given sample viscosity. This is because the phenomenon was found in which the apparent radius of the fused silica capillary changed in the long-term measurements.

1.1. Symbols

ζ: zeta potential, j_{SC}: streaming current, q_{EO}: volume flow rate of electroosmosis, q: volume flow rate, r, l: radius and length of capillary, ε (=$\varepsilon_0\varepsilon_r$): permittivity, η: viscosity, E: electric field, V: applied voltage, P: applied pressure

2. Experimental

Equipment is constituted as described in Fig. 1. The flow rate was calculated by weighing the mass of a open-air bottle with an electronic balance. The both ends of the capillary are directly dipped in the sample in bottles with the electrodes. For the SC measurement, pressure difference is generated by the plunger pump which carries out both-way operation. About for the EO measurement, the voltage generating function of an electrometer is used and at the same time, the vent is opened for both bottles are in the air release.



- syringe pump (pressure generation)
- electrometer (Keithley 6517: current measurement and 1000V voltage source)
- balance (Mettler AT250: flow rate measurement; sensitivity= 0.01mg)
- manometer (Yokogawa MT210: pressure measurement; sensitivity= 0.1Pa)
- Pt/Pt-black electrode
- air tight and open-air PET bottles
- vent (for EO measurement)
- simple booth (with temperature control by Peltier modules)

Fig. 1. Schematic drawing of equipment.

Table 1
Capillaries (fused silica capillary).

Name	Diameter (μm)	Length (mm)	Treatment
GL#1100[a]	320	275.3	Chromic acid mixture
GL#1101	320	283.2	Chromic acid mixture
GL#1102	320	258.5	Nitric acid
UpCh150[b]	150	266	Nitric acid

[a] GL: GL Sciences.
[b] UpCh: Upchurch Scientific.

Fused silica capillaries of nominal inner diameter of 0.32 mm and of 0.15 mm were used, which were purchased from two different companies. Each capillary was used after washing and rinsing treatment. It is shown in Table 1 for details. The sample liquid is distilled and highly deionized water that had been stored in a polyethylene bottle after making by a system (ADVANTEC GSH-200). It is thought that stored period is sufficiently long to reach equilibrium with carbon dioxide in the air. The temperature was controlled in a simple booth that enables heating or cooling by Peltier devices.

The method for one point of measurement value was as follows.

1. About the drive of a syringe pump, move from the minimum position to the maximum position by a constant speed over one eighth of the time of a both-way cycle, and three eighths carries out a time stop, and carry out a reverse motion in time of the remaining half. Measurements are performed in two eighths of the time of the second half, after the pump stops.
2. Repeating this 5 terms, measurement data of the latter three cycles is adopted, and a drift is compensated using these three data sets (Fig. 2).
3. Calculate the pressure difference, the flow rate difference and the streaming current difference from these cyclic measurements. As for pressure and the streaming current, they are mean values and for the flow rate, it is inclination of linear regression analysis of the readings of weighing. Note that the density of water for converting mass flow rate into volume rate uses the steady value of 0.997.

In the measurement of electroosmosis, unlike a pump drive, voltage becomes a preset value immediately, but data acquisition is performed similarly to the streaming current measurement in latter two eighths of time after the changing voltage.

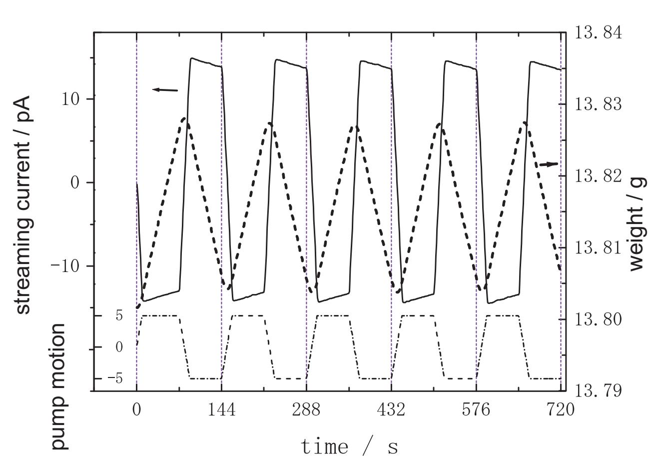


Fig. 2. An example of operation scheme for single data and output for the streaming current measurement.