



# A simple electrochemical methodology for evaluation of the velocity of electroosmotic flow at the tip of polarized microcapillary



Barry R. Silver, Karel Holub, Vladimír Mareček<sup>\*,1</sup>

*J. Heyrovský Institute of Physical Chemistry of the ASCR, v. v. i., Dolejškova 2155/3, 182 23 Prague 8, Czech Republic*

## ARTICLE INFO

### Article history:

Received 29 May 2014

Received in revised form 24 July 2014

Accepted 25 July 2014

Available online 12 August 2014

### Keywords:

ion transport

electroosmotic flow

AC impedance

pseudo-inductive behaviour

microcapillary.

## ABSTRACT

A simple electrochemical methodology for evaluation of the velocity of electroosmotic flow at the tip of a polarized microcapillary is herein described. The methodology relies on the application of a composite, potentiostatically-controlled voltage signal which comprises both AC and DC polarization components. Subsequent analysis of the current-time response yields an approximation for the velocity of electroosmotic flow at the microcapillary tip. Using this methodology, it is also herein shown, that previously observed low-frequency pseudo-inductive behaviour is related to an accumulation of ions into the capillary tip region under an applied potential *via* a mechanism based on electroosmosis.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recently, we reported a procedure which enables the manufacture of robust and reusable glass capillaries with orifice diameters in the micron size range and below [1]. Moreover, using electrochemical impedance spectroscopy (EIS) in conjunction with these same capillaries, we observed an interesting low-frequency pseudo-inductive behaviour. The low frequency pseudo-inductive behaviour exhibits as a low frequency inductive loop on a Nyquist representation of the impedance spectra, possessing positive imaginary impedance [1,2]. The low frequency pseudo-inductive behaviour was found to manifest when conducting conventional EIS using capillaries which exhibited non-ohmic current–potential dependence [1,2].

Non-ohmic current–potential behaviour or ion current rectification, first observed by Wei et. al [3], has been the subject of much previous research and the reader is actively referred to previous works [3–7] for a more extensive introduction. For the sake of brevity, a small definition is included for the sake of the uninitiated reader. Ion current rectification has been found to manifest in glass nano- and microcapillaries as current which is of higher magnitude at one polarity of applied potential than at another. This is contradictory to behaviour predicted from Ohm's Law, which indirectly

states that the current magnitude should be equal at a particular potential, regardless of the polarity of the applied potential. The rectification of current, towards non-ohmic behaviour, is known to occur due to a number of factors which include the geometry of the capillary tip [5], the magnitude and polarity of the glass surface charge [5,7], the solution pH [8] and the electrolyte concentration and type [9].

Although work presented herein appears on the surface as closely related to other works concerning conventional ion current rectification, in this paper we have purposely chosen to focus (in a more in-depth nature) on the interesting, and not widely researched pseudo-inductive aspects. Moreover, we intend this paper to be an addition to our very recent previous work [1].

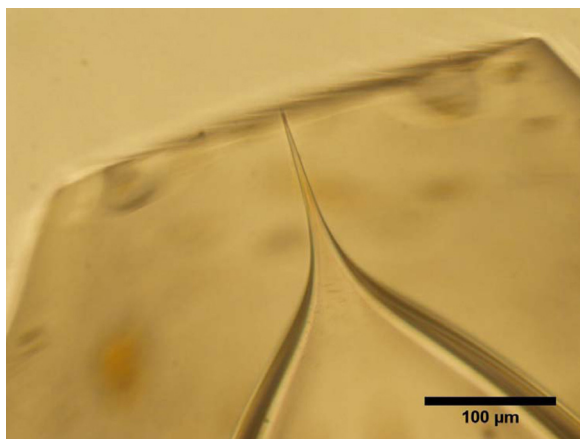
Upon closer inspection of the low frequency pseudo-inductive loop (on the Nyquist plot), one notes that solution conductivity is increasing with decreasing frequency [1]. Our previous work [1] suggested that such behaviour may have originated from an enhancement in ion transport (and hence conductivity) caused by a polarization of the electric double-layer in a longitudinal direction via the application of an AC signal [1]. The electric double-layer to which we immediately refer, is that which is formed between the negatively charged glass surface and the adjacent cations of the electrolyte.

In an attempt to circumvent possible errors in phase angle measurement using conventional EIS (with larger than prescribed signal amplitudes, as used in our previous study), we have herein introduced a novel experimental approach. Essentially herein, we measure only the average amplitude of the current response to

<sup>\*</sup> Corresponding author. Tel.: +420 266052073.

E-mail address: [vladimir.marecek@jh-inst.cas.cz](mailto:vladimir.marecek@jh-inst.cas.cz) (V. Mareček).

<sup>1</sup> ISE member



**Fig. 1.** An optical micrograph showing the tip capillary geometry. The inner orifice radius is ca 0.4  $\mu\text{m}$ .

the applied composite electrical perturbation signal over a three minute time period. The composite electrical perturbation signal comprises both AC and DC polarization components, with both components being potentiostatically controlled. In this way, we were able to detect the presence of electroosmosis and evaluate the velocity of electroosmotic flow at a glass microcapillary tip in a relatively simple and rapid manner.

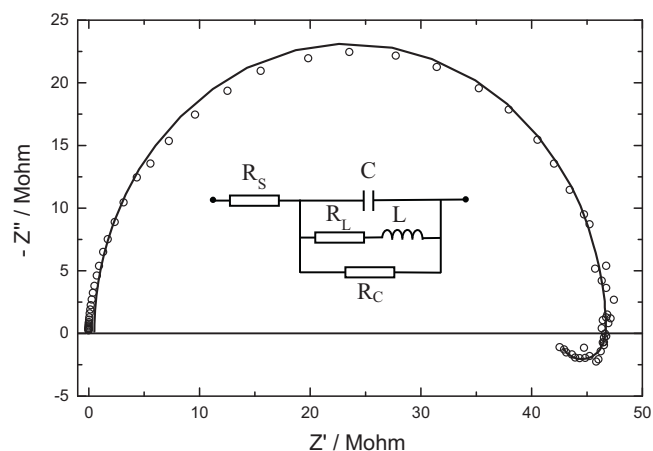
Additionally, we found that previously observed low-frequency pseudo-inductive loop behaviour [1,2] was not an experimental artifact, but rather a consequence of an electrolyte accumulation process in the capillary tip region caused *via* a mechanism based on electroosmosis.

## 2. Experimental

All solutions used in this paper were prepared using deionized water (conductance  $<0.1 \mu\text{S cm}^{-1}$ , Goro, Czech Republic). A glass microcapillary (Fig. 1) was filled with a solution of 10 mM LiCl (Fluka, Biochemika, 62476, >99% purity). The microcapillary was manufactured in the same manner as previously described [1]. A three electrode cell with two Ag/AgCl reference electrodes (one electrode located inside the capillary) was used throughout. A silver wire served as a counter electrode in the bulk solution. The entire electrochemical cell was placed within a grounded Faraday cage. Positive potentials refer to positive polarization of the Ag/AgCl electrode located inside the capillary.

Conventional EIS and linear sweep voltammetry experiments were conducted in a conventional manner using a CHI 660c Electrochemical Workstation (CHI Instruments, USA). The current response of the entire electrochemical cell to the composite perturbation signal was measured in a separate experiment.

The composite perturbation signal consisted of a low frequency AC signal (0.1 to 20 Hz, 0.2 V peak-peak amplitude) from a function generator DS340 (Stanford Research System) superimposed onto a DC signal generated using a PAR 263A potentiostat (EG&G Princeton Scientific Research). AC currents thus produced, were monitored and averaged using a LeCroy LT322 Waverunner oscilloscope (Teledyne LeCroy) over a 3 minute polarization cycle. The electrochemical system was then “left to rest” at open-circuit potential for a total of 3 minutes prior to initiating another polarization cycle at a different frequency. The first 3 minute polarization cycle began at a frequency of 20 Hz and proceeded towards lower frequencies in a sequential manner.



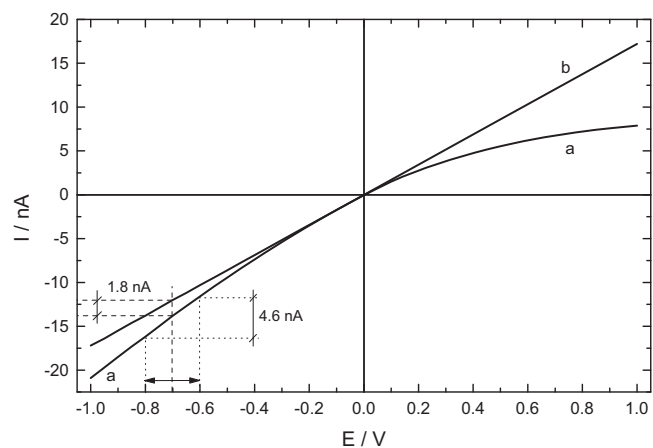
**Fig. 2.** Nyquist plot showing EIS data (dots) exhibiting low frequency pseudo-inductive behaviour. The equivalent circuit used to model and fit (solid line) the experimental impedance spectra is given in the inset.

## 3. Results and discussion

Fig. 2 illustrates a Nyquist representation of a measured impedance spectrum. This impedance spectrum was obtained using conventional potentiostatic EIS with a larger than normal perturbation amplitude ( $-0.7 \text{ V}$  bias, 0.2 V peak-peak amplitude, 10 kHz to 0.1 Hz frequency range). At frequencies lower than 3.7 Hz, the imaginary impedance becomes positive, and a pseudo-inductive loop appears. An equivalent circuit used to model and to fit the spectra was of the same type as one employed previously [1], and is represented in inset (Fig. 2).

Notably, conventional impedance spectra obtained at 0 V DC polarization (20 mV amplitude, 10 kHz to 0.1 Hz, not shown) exhibited no pseudo-inductive feature, and could therefore be analyzed using a simple Randles equivalent circuit to obtain the capillary tip resistance ( $R_c = 58.1 \text{ M}\Omega$ ) under non-polarized conditions [1]. The value of the capillary tip resistance under non-polarised conditions was used to construct a theoretical ‘ohmic’ line representing strictly ‘ohmic’ I-V behaviour of the microcapillary system (line b, Fig. 3). This theoretical line, is in essence, an idealised ohmic reference line against which ‘non-ohmic’ experimental data (obtained at a scan rate of  $2 \text{ mV s}^{-1}$ , starting at 0 V, line a in Fig. 3) can be usefully compared.

In Fig. 3, the enhancement in current above that of the theoretical ‘ohmic’ value at  $-0.7 \text{ V}$  is 1.8 nA, or approximately 15% on a



**Fig. 3.** (a) experimental I-V curve ( $2 \text{ mV s}^{-1}$ ), (b) theoretical ‘ohmic’ I-V curve plotted using a single resistance value  $R = 5.8 \times 10^7 \Omega$ .

Download English Version:

<https://daneshyari.com/en/article/184534>

Download Persian Version:

<https://daneshyari.com/article/184534>

[Daneshyari.com](https://daneshyari.com)