

SURFACE CHARGE STABILIZATION IN MICROFLUIDIC CHIPS : A HYSTERESIS BASED METHOD

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ABSTRACT

Major improvement of the reproducibility and resolution of on-chip electrokinetic separations are expected from the understanding and correction of channel surface instabilities. In this paper, we report more than one thousand electroosmotic mobility measurements performed under various conditions to achieve this goal. The surface instabilities were investigated within a microfluidic Wheaton Bridge (μ FWB) through surface charge hysteresis cycles, where the surface pretreatments, buffer pH, ionic strength and ionic composition were varied. Hysteresis cycles provided powerful insights on the origin of surface charge variability in microfluidic devices.

KEYWORDS: Electroosmotic Mobility, Surface Pretreatment, Hysteresis, Microfluidic Wheatstone Bridge

INTRODUCTION

Interface instabilities are one of the most detrimental effects for the development and wide spreading μ TAS. Especially, the control of surface charge inside the separation channel is essential to get high resolution and reproducible analytical experiments based on electrokinetic migration. In order to provide stable electroosmotic flows (EOF), empiric protocols have been developed according to the literature dedicated to analysts [1]. However, those procedures cannot be directly adapted to microchips as they are both sample and material dependant. Besides, there is no clear evidence of the benefit of acid, or base or any other pretreatment on surface stability. This poor fundamental understanding is mainly due to the lack of versatile instrument for surface charge investigation.

EXPERIMENTAL

In this context we propose a novel approach to study surface instabilities in microchannels. This study was achieved using a microfluidic Wheaton bridge technique [2]. Based on particle anemometry technique and a specifically designed microfluidic chip, this platform enabled us to perform fast and accurate EOF measurements as a function of electrolyte pH or ionic strength. When varying these parameters rapidly, surface charge instabilities can be clearly observed through the analysis of the hysteresis factors. This phenomenon was previously observed in standard capillary electrophoresis systems [3] but could not be properly explained.

A glass PDMS glass technology was used to fabricate sandwich microchips in a clean room. A 100 volt electrical field has been applied to measure the EOF after a 10 minute flush with specific solution. $1\mu\text{m}$ polystyrene fluorescent beads from Estapor have been spread across the microchannels to perform particle anemometry. All error bars of the figures correspond to the relative standard deviation of a minimum of five measurements.

RESULTS AND DISCUSSION

We first demonstrated that this phenomenon depended on surface pretreatment by studying the ionic strength hysteresis factor H_f of the glass water interface. Different solutions of HCl, NaOH and water have been employed as surface preconditioning before varying KCl concentrations (Figure 1 a). The hysteresis factor was deduced from the EOF mobility difference of the surface at low ionic strength before ionic strength increase (μ_I) and after ionic strength was decreased back (μ_F):

$$H_f = \frac{2|\mu_I - \mu_F|}{|\mu_I + \mu_F|}$$

EOF mobility instability was reduced by treating the chip with stagnant water, whereas HCl and NaOH solutions favored high hysteresis factor (see figure 1.b). We assume that stagnant water favors the rebuilding of a stable SiO_2 layer at the interface [4] that inhibits the K^+ and Cl^- irreversible adsorption / desorption processes.

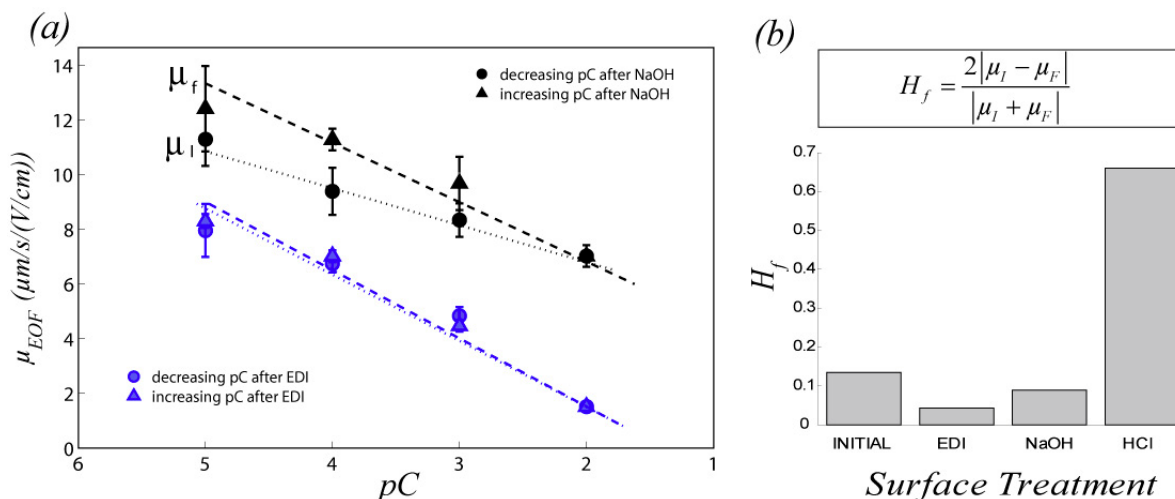


Figure 1. (a) EOF mobility as a function of the negative log of the concentration of KCl. The hysteresis parameter is defined as the relative difference of EOF surface mobility at 10^{-5} mol/L of KCl after increasing and then decreasing the KCl concentration. (b) Hysteresis parameter values as measured immediately after chip fabrication, after a 12 hours contact with stagnant deionised water then 10 minutes with 1 mol/L NaOH and 10 minutes with 1 mol/L of HCl treatments. All hysteresis measurements were done after surface mobility stabilization at 10^{-5} mol/L during 10 minutes.

pH hysteresis was also investigated under separation buffers. The popular phosphate buffer was employed at three different ionic strengths after the stagnant water preconditioning. Figure 2 shows that increasing ionic strength leads to an important EOF increase, which can only be explained by the adsorption of multivalent phosphate anions onto the glass surface. The hysteresis amplitude was also shown to increase with the phosphate buffer concentration which confirms the implication of ionic adsorption in the surface charge instability. As a consequence, we developed a simple model combining the anionic enrichment due to adsorption at the interface and the anionic exclusion due to surface potential repulsion. This competitive model showed that two stable surface charges can be generated by the same interface. This explained the hysteresis phenomenon, while showing that a stable surface can exhibit different surface charges depending on its initial pretreatment (acidic or basic).

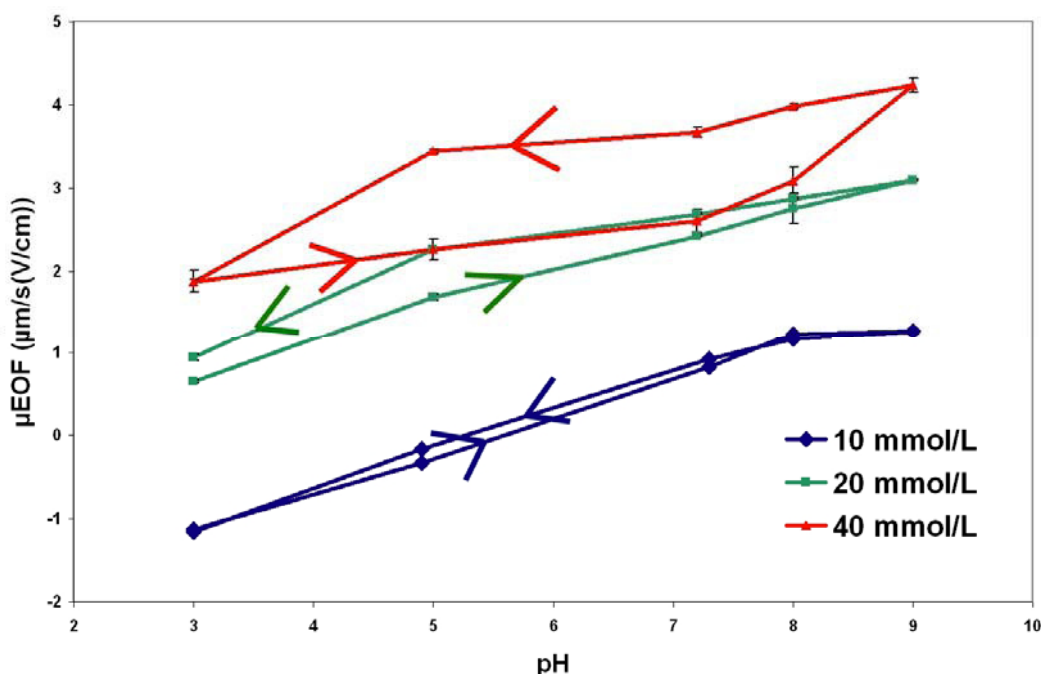


Figure 2. pH hysteresis cycles obtained by measuring the EOF mobilities at different pH of three ionic strength phosphate buffers: 10mmol/L, 20mmol/L and 40mmol/L. The arrows on the cycles have been drawn as a guideline for the reader to follow the measurement progression (the starting points of all cycles is pH=3).

The stability of the EOF hysteresis was also proved to decrease with phosphate concentrations. At 10 mM, successive hysteresis cycles completely overlap while at 40mM, the surface charge still fluctuated after three successive hysteresis cycles. It is not clear today if this “long term” surface instability can be explained by a chaotic transition due to the competition between adsorption, acido-basic reactions and interfacial electrostatic forces or if the chemical structure

of the stabilized hydrated layer is mainly affected by the phosphate ions at higher concentrations. In the first case, the instability is due to the buffer and cannot be solved by surface pretreatments, which means that phosphate buffers above 40mmol/L will always lead to surface instabilities. In the second case, a modification of the surface by pretreatments or specific coatings should overcome the surface stability.

CONCLUSION

In the last decade, efforts have been done to adapt the conventionnal lab-based protocol of macroscopic instruments to microfluidic. There is still today an urgent need to closely study the interfacial phenomena which lead to surface instabilities in microsystems.

The microfluidic Wheatston bridge is to our knowledge the best tool to evaluate the surface instabilities by measuring EOF mobility since this approach is fast and accurate. We found that pretreatments with highly concentrated (1 mol/L) acidic or basic solutions increase the hysteresis factor compared with a stagnant water pretreatment, which enables to create a SiO₂ stable interface that sustains reversible adsorption of ions.

This stabilized interface was shown to resist only to low concentration of phosphate buffers. The pH hysteresis observed with phosphate buffers can be explained by a simple competitive model between the adsorption of anionic phosphate and the negative surface potential of the interface. When phosphate buffer concentration is increased, the SiO₂ interface become unstable, the surface charge increases together with the hysteresis phenomenon. Alternative surface pretreatments or specific coatings are now under investigation in order to better understand the mechanism of interface instabilities and parameters that may contribute to limit them. The main question today is to understand whether the long term instability is due to interface chemical restructuration or is inherent to the competition of adsorption and electrostatic processes.

ACKNOWLEDGEMENTS

All authors would like to thank DGA (Direction Générale pour l'Armement-French ministry of Defence), ANR (Agence Nationale de la Recherche-P3N DIMIPOLE project) and PRES (Pôle de Recherche et d'Enseignement Supérieur UniverSud Paris-NANOMEDITOX project) for financial support. The authors are also grateful to C. Nanteuil, and J. Gamby for fruitful discussions.

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