

# Study on Faradaic and Coulombic interactions at microelectrodes utilized in AC electroosmotic micropumps

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## Abstract

Alternating current (AC) electroosmotic micropumps are suggested to be powerful tools for electrolyte dosing in various micro and nanofluidic systems. These pumps are able to manipulate small volumes of liquid samples and involve no moving parts. The pumps find their use in a variety of bioapplications or clinical diagnostics.

The micropump is realized by an array of microelectrodes coated along the microchannel, on which an ac electric field is applied. The ac voltage is typically in the range of few volts. Theoretical models describing the ac electroosmotic transport usually consider the Coulombic polarization of the microelectrodes. However, Faradaic currents can occur in such systems as a result of electrochemical reactions. Here we present a mathematical model of an ac electroosmotic system with electrochemical reactions. The model is based on the balances of mass and electric charge and the kinetic equations for the electrode reaction.

The theory of the electrolyte dynamics at polarized surfaces for larger applied voltages taking into account the steric effects (formation of condensed ionic layers) has been also published by other authors. The aim of our future work is to study the effect of Faradaic currents on the behavior of the ac electroosmotic micropumps and compare the obtained predictions with those given by the models considering the condensed layer formation.

## I. INTRODUCTION

Increasing complexity of microfluidic devices enforces the need for integrated local fluid control in microchannels. Electric fields applied on microelectrodes can induce electrokinetic pumping of electrolytes. The electrically induced pumping systems are mostly based on DC electroosmotic phenomena that usually require high voltages. Integration of electrodes in microfluidic channels for standard DC EO pumping is seriously limited by undesirable effects related to high voltages, such as heating, significant changes of the electrolyte composition, and bubble formation. A promising alternative to the classical electroosmotic pumps relies on microelectrode fluidic systems that exploit AC signals with very low amplitude, Fig 1.

The first design of the AC electrokinetic micropumps was proposed by Ajdari [1]. The micropump can be constructed by means of arrays of asymmetric pairs of co-planar microelectrodes deposited on a dielectric substrate. It was expected that the asymmetry of the electric field will lead to a net flow of the electrolyte. His predictions were verified by several experimental and theoretical works, e.g., [2–6].

There are many theoretical models describing the AC electroosmotic pumping [4, 7–9]. In our group, we progressively develop and analyze a nonlinear and nonequilibrium mathematical model based on Poisson-Navier-Stokes-Nernst-Planck approach [10–14]. The model should be valid at least up to the AC amplitude equal to several hundreds of millivolts. The model also describes the fields of model variables in the entire space and time domain for arbitrary AC frequency. Numerical analysis of the model equations is difficult due to the presence of different characteristic space dimensions (the EDL thickness, the geometry scale).

The nonlinear phenomena related to the surface polarization for larger AC amplitudes (higher than  $\approx 25$  mV) were also advanced in [15–17]. Kilic et al. [15] noted that the formation of so called "condensed layer" of ions emerges above a certain voltage limit due to the steric hindrance of solvated ions, i.e. the theory for dilute solutions is not longer valid. Hence, the authors introduce an additional term in the classic Nernst-Planck equation describing the ion transport in dilute solutions [16]. The developed mathematical model was able to predict physically relevant ion concentrations at polarized boundaries. Formation of condensed layers of ions was predicted for voltages above few hundreds of millivolts.

Most of the theoretical studies of ac electroosmosis have been performed for electrodes with zero electric charge transfer, i.e., with no Faradaic interactions. Indeed, the bubble formation and electrode dissolution at low AC frequencies and high amplitudes were observed by many experimentalists, which indicates that electrode reactions are actually taking place in such systems [5, 6, 18]. It was experimentally found that intensive Faradaic interactions in AC micropumps are usually important above the voltage  $3V_{rms}$ . Under such conditions bubbles of the electrode gas quickly fill microchannels and/or the forcing



Fig. 1. The asymmetric arrangement of AC electroosmotic pumps

microelectrodes are destroyed. However, Studer *et al.* [6] showed that an AC pump can operate above  $10V_{rms}$ . The same findings was reported by Lastochkin *et al.*[19].

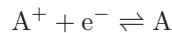
Olesen *et al.* [8] included the effect of Faradaic currents on microelectrodes using the Butler-Volmer reaction kinetics for electrochemical interactions. They carried out the analysis of the ac electroosmotic microsystems based on an array of asymmetric coplanar electrodes. They used the following approximations [9,20]: (i) The Debye layer is assumed to be in local equilibrium, such that the electric charge distribution and electric potential variation in the Debye layer can be described by the Gouy-Chapman theory. (ii) The fluid motion is described by the Stokes equation together with a slip boundary conditions. Their study was also restricted only to the case of when the electric field frequencies are much smaller than  $\sigma/\epsilon$ , which means that the electric double layer is fully relaxed. In their study, the effect of the mass transfer between the bulk and the Debye layer on the effective reaction kinetics was not included. Afterwards, Olesen included this effect in his dissertation thesis [21].

Ramos *et al.* [22] studied the effect of Faradaic currents in the traveling-wave electroosmotic pumps taking into account mass transfer effects (including the Warburg impedance representing a kind of resistance to mass transfer) under the linear and thin-layer approximations. At signal frequencies much smaller than  $\omega \ll \sigma/\epsilon$  (relaxed electric double layer), the predicted flow is always driven in the direction of the traveling-wave potential. Only for very fast reaction kinetics a fluid reversal was found at high frequencies,  $\omega \approx \sigma/\epsilon$ , and this flow was characterized by small net velocities. The effect of Faradaic currents is basically to decrease the slip velocity at the electrode surfaces. One of the motivations for studying the effect of Faradaic currents in the ac electroosmotic systems was that in experiments at somewhat higher voltages and higher frequencies, the electrolyte was found to move in the opposite direction than the forcing electric potential wave. It has been proposed that Faradaic currents are responsible for this flow reversal [19].

Recently, we have published a few theoretical papers dealing with ac electroosmotic micropumps using the Poisson-Navier-Stokes-Nernst-Planck analyses of various electroosmotic micropumps. However, no Faradaic charge injection was considered. In this work we present a simple kinetic model of Faradaic reactions on microelectrodes. The Poisson-Nernst-Planck approach is employed to study the transport processes between the electrode surface and the electrolyte bulk. We show the spatial profiles of model variables for different values of surface charge density and kinetic parameters. The polarization curves (current-voltage characteristics) are also shown. The kinetic parameters of this model will be fitted to real experimental results in the next step. The main aim of our future work is to connect this electrostatic part of the problem to the hydrodynamic part in order to obtain more realistic characteristics of the AC electroosmotic micropumps.

## II. MATHEMATICAL MODEL

We present 1D mathematical model based on the molar balances of chemical components ( $A^+$ ,  $B^-$ ), the Poisson equation and the kinetic model for an electrode reaction. A one electron cathodic reaction is considered



### A. Model equations

The molar balances of all species in the steady state are written in the form of the Nernst-Planck equation

$$\frac{d}{dx} \left( -D_i \frac{dc_i}{dx} - \frac{z_i D_i F}{RT} c_i \frac{d\varphi}{dx} \right) = 0 \quad i = A^+, B^- . \quad (1)$$

The convective terms have not been included as we limited our study to a one-dimensional problem.

The electric potential satisfies the Poisson equation

$$\varepsilon \frac{\partial^2 \varphi}{\partial x^2} = -q = -F \sum_i z_i c_i \quad i = A^+, B^- . \quad (2)$$

### B. Boundary conditions - the electrolyte/electrode boundary

The boundary condition without a reaction term is used for the component  $B^-$  which doesn't participate in the electrode reaction

$$0 = -D_{B^-} \frac{dc_{B^-}}{dx} - \frac{z_{B^-} D_{B^-} F}{RT} c_{B^-} \frac{d\varphi}{dx} . \quad (3)$$

The molar flux of the component  $A^+$  that participates in the electrode reaction on the electrode boundary is equal to the Faradaic current passing through the interface

$$-\frac{j}{zF} = -D_{A^+} \frac{dc_{A^+}}{dx} - \frac{z_{A^+} D_{A^+} F}{RT} c_{A^+} \frac{d\varphi}{dx} \quad (4)$$

The faradaic current density is defined by rate equation

$$j = F(K_1 - k_2 c_{A^+} |\sigma|) . \quad (5)$$

where  $\sigma$  is the surface charge density on the electrode surface. The component A is considered as an electrode material and its concentration remains constant, thus the reaction rate of forward reaction is defined by the constant  $K_1$ .

An additional boundary condition is needed to fully define the mathematical problem at the electrode-electrolyte boundary. The electric potential is defined using surface charge density  $\sigma$

$$\frac{\partial \varphi}{\partial x} = -\frac{\sigma}{\varepsilon} . \quad (6)$$

### C. Boundary conditions - the boundary for electrolyte bulk

The concentrations of components on the electrolyte bulk boundary are equal to their bulk values and the electric potential is fixed on zero reference value

$$c_{A^+} = c_0, \quad c_{B^-} = c_0, \quad \varphi = 0 . \quad (7)$$

## III. NUMERICAL ANALYSIS

Numerical analysis of the mathematical model was carried out in the Comsol Multiphysics software. The mathematical model consists of eqs. (1)-(2) and the boundary conditions (3),(4),(6),(7). The stationary analysis of the model equations was carried out using standard *femlin* procedure. The Comsol Multiphysics software requires discretization of the spatial computation domains into a set of finite elements. We used a highly non-uniform mesh with a high density in the electric double layer.

## IV. RESULTS

The model simulations were carried out for different values of kinetic parameters and the surface charge density. The concentrations of the cation and anion over electrical double layer is depicted in Figs. 2, 3 for selected values of parameters. The concentration of the anion falls to zero while the concentration of the cation with an increasing negative electric charge density on the electrode surface.

The electric potential field is plotted in Figs. 4-5. In Fig. 4, the rapid decrease of electric potential over EDL is shown. The ohmic losses through electrolyte bulk are illustrated in Fig. 5 by the linear increase of the electric potential out of the electric double layer.

The current-voltage characteristics (polarization curves) computed for different values of kinetic constant  $k_2$  are depicted in Fig. 6. The characteristics have an exponential shape which is in agreement with classical electrochemical theory. It can be seen that the amplitude of the current density increases with increasing value of the constant  $k_2$ .

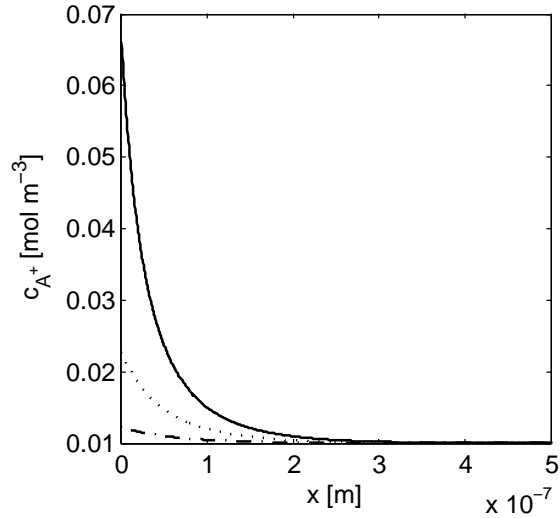


Fig. 2. The profile of cation concentration over electric double layer for different values of surface charge density,  $c_0 = 0.01 \text{ mol m}^{-3}$ ,  $K_1 = 1 \times 10^{-10}$ ,  $k_2 = 1 \times 10^{-7}$ , dash-dotted line -  $-5.3 \times 10^{-5} \text{ Cm}^{-2}$ , dotted line -  $-2.2 \times 10^{-4} \text{ Cm}^{-2}$ , solid line -  $-5.7 \times 10^{-4} \text{ Cm}^{-2}$

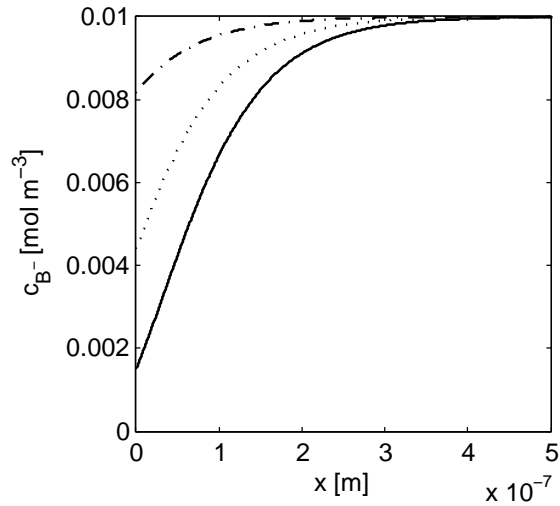


Fig. 3. The profile of anion concentration over electric double layer for different values of surface charge density,  $c_0 = 0.01 \text{ mol m}^{-3}$ ,  $K_1 = 1 \times 10^{-10}$ ,  $k_2 = 1 \times 10^{-7}$ , dash-dotted line -  $-5.3 \times 10^{-5} \text{ Cm}^{-2}$ , dotted line -  $-2.2 \times 10^{-4} \text{ Cm}^{-2}$ , solid line -  $-5.7 \times 10^{-4} \text{ Cm}^{-2}$

## V. CONCLUSION

We present a nonequilibrium 1D mathematical model consisting of the Poisson equation, the molar balances of chemical components, and the Faradaic charge injection from the electrode surface. We are able to study the nonequilibrium transport and reaction processes at an electrode surrounded by an uni-univalent electrolyte. We computed the current voltage characteristics of the model system and the profiles of the model quantities for some values of the kinetic parameters are shown. We are planning to find such kinetic parameters of the electrochemical reaction that will enable to fit experimental current-voltage characteristic for particular electrochemical systems. We will probably have to suggest a more complex kinetic scheme of the electrode reaction. In principle, the mathematical model does not contain the electrochemical equilibrium assumption at the electrode/electrolyte interface. We believe that such a model will be useful for dynamical studies of these systems. Our future aim is involving this or a modified kinetic model of the electrode reaction to our Poisson-Navier-Stokes-Nernst-Planck model of the AC electroosmotic micropump. We will also study the influence of the Faradaic current on the global characteristics of the electroosmotic pumps.

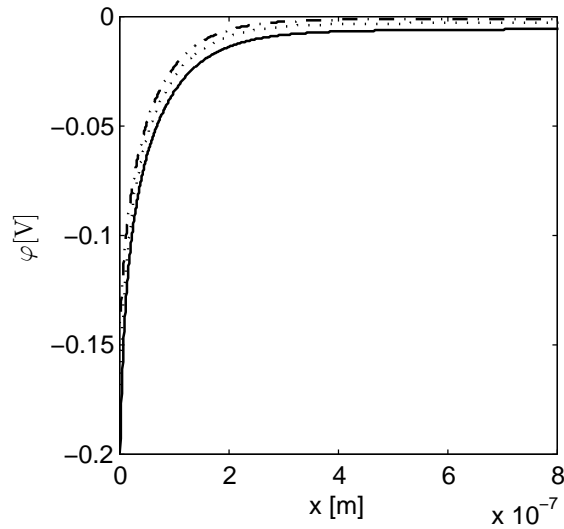


Fig. 4. The electric potential profile over electric double layer for different values of surface charge density,  $c_0 = 0.01 \text{ mol m}^{-3}$ ,  $K_1 = 1 \times 10^{-10}$ ,  $k_2 = 1 \times 10^{-7}$ , dash-dotted line -  $-0.0039 \text{ C m}^{-2}$ , dotted line -  $-0.0062 \text{ C m}^{-2}$ , solid line -  $-0.01 \text{ C m}^{-2}$

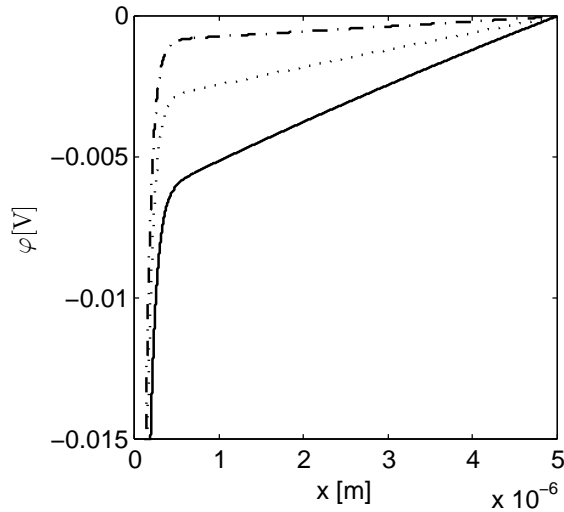


Fig. 5. The electric potential profile over electrolyte bulk for three values of surface charge density,  $c_0 = 0.01 \text{ mol m}^{-3}$ ,  $K_1 = 1 \times 10^{-10}$ ,  $k_2 = 1 \times 10^{-7}$ , dash-dotted line -  $-0.0039 \text{ C m}^{-2}$ , dotted line -  $-0.0062 \text{ C m}^{-2}$ , solid line -  $-0.01 \text{ C m}^{-2}$

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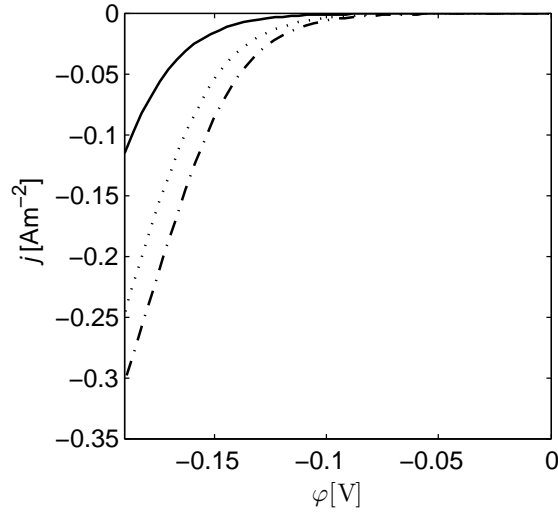


Fig. 6. The polarization curves (the current-voltage characteristics) for different values of kinetic constant  $k_2$ , dash-dotted line -  $7 \times 10^{-7}$ , dotted line -  $4 \times 10^{-7}$ , solid line -  $1 \times 10^{-7}$ ,  $c_0 = 0.01 \text{ mol m}^{-3}$ ,  $K_1 = 1 \times 10^{-10}$

TABLE I  
LIST OF SYMBOLS

symbol	quantity
$c$	concentration [ $\text{mol m}^{-3}$ ]
$D$	diffusivity [ $\text{m}^2 \text{ s}^{-1}$ ]
$F$	the Faraday constant [ $\text{C mol}^{-1}$ ]
$R$	molar gas constant [ $\text{JK}^{-1} \text{ mol}^{-1}$ ]
$T$	temperature [K]
$x$	spatial coordinate [m]
$j$	current density [ $\text{A m}^{-2}$ ]
$q$	electric charge density [ $\text{C m}^{-3}$ ]
$\varepsilon$	electrolyte permittivity [ $\text{F m}^{-1}$ ]
$\sigma$	surface charge density [ $\text{C m}^{-2}$ ]
$\varphi$	electric potential [V]

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