

ELECTROLYTE DEPENDENCE OF AC ELECTRO-OSMOSIS

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ABSTRACT

This paper reports the first investigation of the dependence of AC electro-osmosis (ACEO) on the solution chemistry. It is argued that classical dilute-solution theory breaks down in ACEO, since the large applied voltage leads to ion crowding near the electrode surfaces. A modified theory is proposed with steric effects (finite ion sizes) and a charge-dependent viscoelectric effect, which predicts that ACEO flow depends on the salt concentration, ion sizes and valences. Experiments demonstrate significant variations in ACEO pumping upon varying salt concentration (μM – mM KCl) or ionic species (μM NaCl, CaCl_2 , MgCl_2 , KI, KOH), which merit further experimental and theoretical study.

Keywords: AC electro-osmosis, nonlinear electrokinetics, micropumps

1. INTRODUCTION

Nonlinear “induced-charge” electro-osmotic (ICEO) flows offer promising methods for manipulating fluids and colloids in portable or implantable microfluidic devices [1]. The potential advantages include the lack of moving parts or mechanical actuation, precise local flow control, ease of fabrication, and low voltage (a few volts) and low power (milliwatts), which could be provided by standard miniature batteries. In particular, the design of AC electro-osmotic (ACEO) pumps [2,3] has advanced to the point where fast mm/sec velocities are now possible at a few volts [4], at least in water [5] and dilute KCl [6].

Two prior experiments have shown the decay of ICEO flow with increasing salt concentration above 0.1 mM and effectively vanishing above 10 mM, which is not predicted by the existing theory. For ACEO pumps, this effect has only been reported once in KCl using an asymmetric planar electrode array at high voltage (>2 V) and high frequency (>10 kHz), where the flow is in the reverse direction from the theory [3]. Recently, a similar concentration dependence has been observed in NaCl in the induced-charge electrophoresis (ICEP) of metallo-dielectric Janus particles at lower voltages (< 0.5 V across the particles) and lower frequencies (< 1 kHz) [7]. It has been suggested that this concentration dependence is a universal feature of ICEO flows, associated with ion crowding in highly charged double layers [8]. The theory also predicts that ICEO flows depend on the ionic species, but this has never been studied experimentally.

2. THEORY

Classical Poisson-Boltzmann theory assumes a dilute solution of point-like ions in thermal equilibrium in the mean potential. There clearly exists a concentration c_{max} , which depends (at least) on the size a and valence z of each counter-ion, above which this approximation breaks down. This limit is reached at a diffuse-layer voltage $\psi_c = (kT/ze)\log(c_{\text{max}}/c)$ of order the thermal voltage $kT/e = 25$ mV, which is 100 times smaller than typical voltages applied to the double layer in ACEO. At such large voltages, ions become crowded in the double layer [9]. One consequence of steric repulsion is that

the differential capacitance decays at large voltage, the opposite prediction of PB theory (Fig. 1). This alters the “RC time” and thus the frequency dependence of ICEO flows in a way that depends on the counterion size and valence. Steric effects alone, however, cannot predict strong dependence on the salt concentration. This can be explained by postulating that the viscosity η increases (and permittivity ϵ decreases) with increasing counter-ion charge density ρ and diverges at close packing. The simplest assumption, $\epsilon/\eta \propto (1 - \rho/c_{\max})$, yields a modified induced electro-osmotic slip formula [8],

$$u_s = -\frac{\epsilon E}{\eta} \left(\psi - \text{sgn}(\psi) \frac{kT}{ze} \log \left[1 + 4 \frac{c}{c_{\max}} \sinh^2 \frac{ze\psi}{2kT} \right] \right) \sim -\text{sgn}(\psi) \frac{\epsilon kT}{\eta ze} E \log \frac{c_{\max}}{c} \quad (1)$$

in which the ICEO mobility saturates at large voltage as $u_s/E \propto \log(c_{\max}/c)/z$.

3. EXPERIMENTAL

Using the methods of Ref 6, ACEO pumps consisting of 5mm-long interdigitated Au electrode arrays of two designs (planar [3] and non-planar [6]) were tested using 20mm-long multilayer soft-lithographic loops, which served to isolate the pumps from external pressure gradients. Each electrolyte was prepared in reagent-grade de-ionized (DI) water (0.56 S/cm, pH=5). Each pump was operated in DI water at 2 Vpp, 1 kHz for 30 min prior to testing and for 2 min. between electrolytes. A dilute fluorescent bead solution was loaded and not allowed to reach the electrodes in each case. Digital movies were analyzed in custom PIV software built around the shareware uraPIV. The resulting parabolic flow profile was analyzed to determine peak mid-channel stream velocity reported in the figures.

In the first experiment, the velocity versus frequency was carefully measured for a range of concentrations of KCl from 1.0 μM to 1.0 mM in a single planar device [3] at 3 Volt peak-to-peak (Vpp). In the second, preliminary set of experiments, the ionic species were varied at 1 μM in the sequence NaCl, CaCl_2 , MgCl_2 , KI, NaI, KOH, NaOH in a single non-planar 3D ACEO pump [6] with 3.0 μm step height at 2 Vpp. The NaI and NaOH data showed irregular scatter and were not included in the comparison in Figure 2.

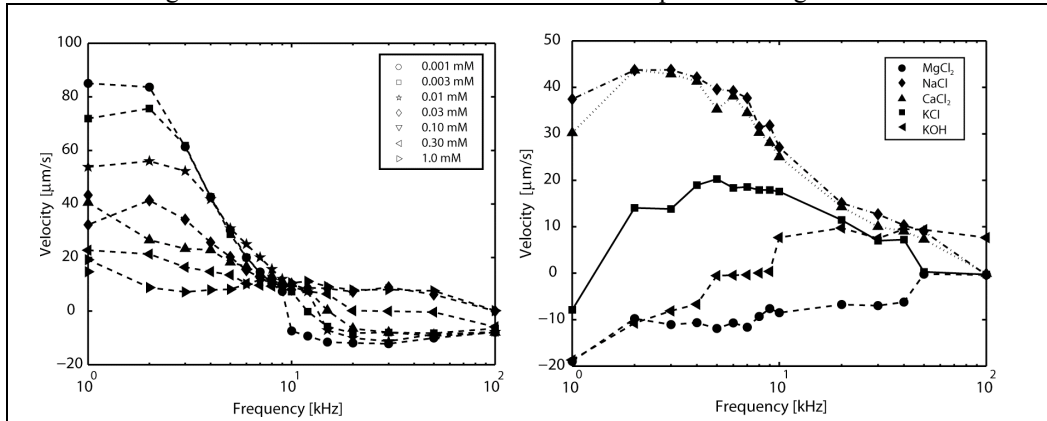


Figure 2. Left: Velocity from the planar ACEO pump [3] at 3 Vpp versus AC frequency in KCl at different concentrations, 1.0 μM – 1.0 mM, in DI water. Right: Velocity from the non-planar 3D ACEO pump [8] (3 μm steps) at 2 Vpp for different electrolytes at 1.0 μM .

4. RESULTS AND DISCUSSION

The KCl data for the planar pumps in Fig. 2 (left) is consistent with prior measurements [3]. At all concentrations, there is a single peak around 1 kHz with flow reversal at high frequency > 10 kHz, which can be reproduced in simulations using the nonlinear capacitance with steric effects in Fig. 1 [8]. The concentration dependence is roughly logarithmic for all frequencies, $u(\omega) \propto \log(c_{\max}/c)$, and extrapolates to zero around $c_{\max} \approx 10$ mM (similar to ICEP in NaCl [7]), as in the large-voltage limit of (1).

The second data set shows a strong dependence on the ionic species, but it is difficult to interpret. The data shows little difference between NaCl and CaCl₂, which were tested first; both exhibit a single peak of forward pumping, as expected for the non-planar pumps. The salt concentration is so low (1mM) that crowding effects could mainly involve the common H⁺ and OH⁻ ions, which are more abundant in the bulk at pH=5. The next electrolyte, MgCl₂, exhibited only reverse flow, inversely proportional to the frequency. Such low-frequency flow reversal is new and could be due to Faradaic reactions at the gold electrodes. Subsequent solutions either showed erratic flow (NaI, NaOH) or more low-frequency flow reversal (KI, KOH, KCl). Prior experiments in KCl [3,6] have not seen this behavior, which suggests that the electrodes may have been electrochemically altered.

5. CONCLUSIONS

We have shown that ICEO flow depends on solution chemistry, which can adversely affect microfluidic applications, such as ACEO pumps. More experiments are planned.

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