EXPERIMENTAL STUDY OF ELECTROLYTE DEPENDENCE OF AC ELECTROOSMOTIC PUMPS

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Abstract:
Recent studies indicate increased efficiency of microfluidic ac electro-osmotic pumps by utilizing broken symmetries with raised steps on the electrodes. An experimental study on the dependence of ac electroosmosis in microchannels on solution chemistry for the new fast aceo stepped pumps is reported. Micro PIV was used to determine peak velocities for $\mu M - mM$ concentrations of KCl, NaCl, CaCl$_2$ and MgCl$_2$ in a pumping loop for a spectrum (1 kHz- 100 kHz) of frequency for applied voltage. Experiments demonstrate significant variations in ACEO pumping upon varying salt concentration or ionic species, suggesting the need for further experimental and theoretical study for better design of biomedical microfluidic devices.

Keywords: Micropumps, ac electroosmosis, actuators

1. Introduction
Pressure based pumps for microfluidic fluid actuation suffer from various limitations such as unfavorable scaling with miniaturization due to large viscous forces. Electroosmotic flow, whereby a liquid can be made to slip past a solid surface by the application of an electric field due to charge distributions (the "double layer") close to the solid-liquid interface scale well with miniaturization and can be manufactured by relatively simpler microfabrication approaches.

AC electroosmotic (ACEO) pumps with broken symmetries offer innovative strategies for fluid manipulation in portable microfluidic devices. While, like DC electro-osmotic pumps, they have no moving parts and offer ease of fabrication, ACEO pumps require much lower voltages and power, suffer less from Joule heating (the same being critically important for biological samples in medical assay) and offer better localized and "tunable" flow control. Breaking of electrode symmetry by using nonplanar stepped electrode arrays is a relatively recent development [1, 2, 3], offering dramatically increased flow rates and reduced tendency for flow reversal, compared to asymmetric planar pumps [4].

The electrolyte dependence of ACEO has not been well characterized, particularly the effective vanishing of the flows at high salt concentration (>10 mM), and flow reversal at high frequencies (> 10 kHz), first observed in experiments with KCl [4]. The standard model of ACEO [8,9] and related induced-charge electrokinetic phenomena [10-11] is based on dilute-solution theory (point-like ions interacting through the mean field) and does predict any dependence on the solution chemistry. Recent extensions of the theory predict dependence on the salt concentration and ionic species [6], but these effects have not yet been studied systematically in experiments. Aside from our recent preliminary work [7], previous experiments on ACEO have used exclusively either KCl or water (tap, distilled, or de-ionized) [2, 3, 4,12].

In this work, the performance of the 3D aceo pumps has been studied for four different binary chloride solutions containing cations of varying size and charge: KCl, NaCl, CaCl$_2$ and MgCl$_2$. The electrolytes chosen are all

highly soluble in water and are expected to be completely dissociated at the concentrations of interest.In our first experiments with these solutions [7], we observed history dependence on the order of testing the electrolytes, as well as low-frequency flow reversal, which suggested that the Au electrodes were somehow electrochemically altered. Here, we have altered the protocol slightly, e.g. for a longer flush with de-ionized water between loading of different electrolytes, and fabricated new devices (using the same materials and procedures) with somewhat different geometries, but overall the experimental conditions are similar. In particular, the applied voltage is kept at 3 Volts peak to peak. Although the results do not show systematic trends, there is clearly strong dependence on the solution chemistry. These are the first studies of electrolyte dependence of ACEO, so the results are valuable both from a fundamental science perspective and to guide future design of microfluidics devices.
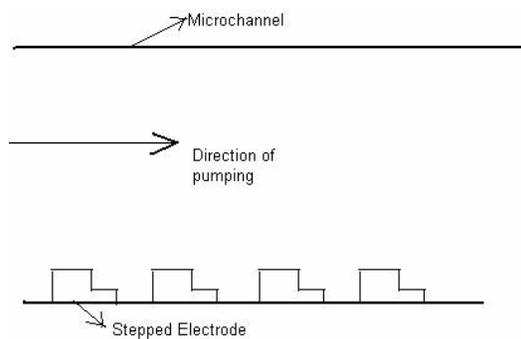

Fig 1. Side-view sketch of the stepped-electrode 3D ACEO pump used in our experiments. The expected direction of flow (for sufficiently tall steps) is indicated.

2. Experiments

2.1 Fabrication

The pumps were fabricated using photo-patterning, etching and electroplating, following the methods described in prior publications by our group [2,3,7]. Electron beam evaporation was used to deposit a 50nm adhesion layer of chrome, followed by a 50 nm layer of gold onto borosilicate glass wafers which had been precleaned in a piranha solution (1:3 solution of hydrogen peroxide and sulfuric acid) for 20 min and roughened in a barrel asher for 2 min. The precursor planar electrode structures were created using gold and chrome etchants using standard positive resist photolithography (OCG 825). A second mask was aligned to base features, and a thick photoresist (10 μm, AZ 4620) was patterned for electroplating. Steps were electroplated to a fixed, nearly uniform height (2.6 μM) using gold solution (Orotemp 24C, Technic, Inc.) and the residual photoresist was stripped using acetone and isopropanol. Bare copper leads were attached using conductive silver epoxy. The resulting heights of the three-dimensional structures were measured using a white light interferometer (Zygo Corp.). The array length was 5mm.

This micrograph in Fig. 2 shows that the tops of electroplated steps were slightly misaligned from with the flat electrodes on which they were grown by roughly 2 microns. To some extent this perception is due to tilting of the side surfaces of the steps by the electroplating process. The fabrication process may also have altered the gold surfaces at smaller scales. The chrome precursor layer was used not only for adhesion of the gold electrodes to the glass, but also to ensure good electrical connections to all electrodes during the electroplating to achieve nearly uniform step heights. However, the harsh chemicals used to remove the chrome from the gaps between the electrodes may alter the gold surfaces in ways that affect the experiments. Other fabrication methods will be explored in future work.
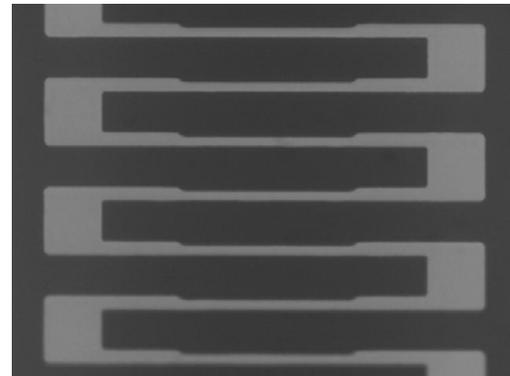

Fig 2. Micrograph of electrode array, showing the electroplated steps. For scale,

the underlying flat pattern has 5 micron wide gaps and 15 micron wide electrodes.

A microfluidic chip was fabricated as for previous aceo studies[3] similar to the loop described previously by Studer et al. and comprised of a base glass substrate with the electrodes described above, capped with a polydimethylsiloxane (PDMS) device [5]. Valves controlled by off chip pressure regulators isolate fluid flow from external disturbances. The loop had a perimeter of 20 mm. The device was fabricated using multilayer soft lithography (MSL) [5]. Internal interconnects between rectangular and rounded channels on two device layers (the flow loop and the valve control layer) enable rectangular channels on the base layer to be used to create "push-up" valves [6] to control fluid flow into the loop. A positive resist (AZ 4620, Clariant) was used to fabricate the injection layer mold. Rectangular cross sectioned channels were fabricated using flow molds created using negative photoresist (SU-8 2050, Microchem). The top layer was cast using the injection mold, and aligned over the thin partially cured lower layer which had been spun coat on the flow mold. Interconnects between the two layers were created by small cuts with a scalpel. Injection and flow channels were 10 μm and 80 μm tall respectively, and both were 100 μm wide. The ACEO substrates and the PDMS caps were aligned by hand under a microscope and plasma-bonded.

2.2 Measurements

Fluid intake and purging was software controlled using micro-solenoids connected to the integrated MSL valves [5]. Pressurized reservoirs of operating fluid (the electrolyte of interest; 1 M solutions of KCl, NaCl, $MgCl_2$ and $CaCl_2$, all Mallinckrodt Chemicals) were prepared in deionized water. The same was diluted down to concentrations of interest, and a solution containing 1:250 tracers (1.0 μm diameter fluorescent tracers, 505EX/515EM, Molecular Probes) in water (v/v) was connected to the microfluidic device via tygon tubing. As in [3] one input channel was used to load the electrolyte and another far from the pumps was used to load the tracer particles in order to eliminate electrophoretic effects over the pumps and

prevent contamination of the pumps. A signal generator (Agilent 3320A) was used to operate the pumps at various frequencies (1-100 kHz), at 3 V peak-to-peak (V p-p.). Movies of the fluid far from the electrodes were recorded using a camera (Sony XCD-V50 B/W, 640 × 480 pixels) under an inverted fluorescent microscope with a 20× objective at each driving frequency for each of the electrolytes. The focal plane of the microscope was set to the centerline of the microchannel to record the fastest moving particles.

Two devices were used in this study, one for various concentrations of $CaCl_2$ (Device 1), and another device (Device 2) for the full range of electrolytes (KCl, NaCl, $CaCl_2$, $MgCl_2$). On device 1, the full frequency spectrum was run at each concentration of $CaCl_2$ in order of increasing concentration. Device 2 was run for all the electrolytes at the low concentration in the order KCl, NaCl, $MgCl_2$, $CaCl_2$ before proceeding to the next higher concentration in the same order.

In order to achieve repeatable results and minimize history effects on pumping both devices were first conditioned by running the pump with DI water at 3V p-p 5 k Hz frequency for 60 minutes before testing. The same is a change from the preliminary work of [7] where the frequency was 1 k HZ, assuming that an increased frequency (and hence pumping velocity) would further decrease effects of history. Between changes of solutions, the devices were flushed for three minutes by pressure driven flow with deionized water. The flushing time in the preliminary experiments [7] was one minute, which was increased for this work so as to ensure that no ionic species from previous tests remained within the device.

3 Results

The results of the experiments are summarized in the figures. The data demonstrates that the flow rate is sensitive to the solution chemistry, although further experiments will be required to clarify the trends. Figure 3 shows the velocity versus frequency at different concentrations of $CaCl_2$ (0.01 – 1.0 mM) in Device 1 (which was not used for any other electrolytes). The

results are quite similar to previous data for KCl in planar pumps [4,7]. The flow rate generally decreases with increasing salt concentration; it drops quickly from 0.1 mM to 1 mM and is difficult to observe at higher concentrations. This phenomenon is not predicted by the standard model and has recently been attributed to increased viscosity in the double layer upon crowding of the ions [6].

The dependence of the pumping velocity on the ionic species from Device 2 is shown in Figure 4 for two different bulk salt concentrations (0.01 mM and 0.1 mM). Pumping is observed for all electrolytes at both concentrations, mostly in the expected "forward" direction shown in Figure 1. The low frequency flow reversal observed for some electrolytes in our first experiments [7] was not observed here, which could mean that our improved protocol helped to avoid electrochemical altering of the electrodes (e.g. by Faradaic reactions).

The peak frequency occurs in the range 1-10 kHz under most conditions, consistent with capacitive double-layer charging. The peak velocities are in the range 80-180 μm/sec for all solutions, with the exception of $MgCl_2$ at the higher concentration, which was much slower. Since only 20% of the microfluidic loop contains the ACEO pump, five times larger peak velocities in the range 0.4-0.9 mm/sec should be observed in a loop 100% covered by the pump without any extra hydraulic resistance. These flow rates are comparable with previous experiments on KCl with 3D ACEO pumps in a similar device [3], although the velocity for KCl here is several times slower, perhaps due to the geometrical differences noted above.

At the lower concentration (0.01 mM), all electrolytes exhibit weaker reverse flows at high frequency, above 10 kHz. In Device 2 (Fig 4) the effect is strongest for $CaCl_2$, and in Device 1 (Fig 3) the same reversal is seen at all concentrations. In the planar geometry, high-frequency flow reversal has recently been attributed to steric effects on the double-layer capacitance at large voltages ($\gg kT/e = 25$ mV), which depend on the ionic sizes and charges [6]. However, this theory has not yet been applied to 3D ACEO pumps such as ours, which should not reverse according to the standard low-

voltage theory, if the steps are tall enough [1]. Experiments with 3D ACEO pumps in KCl have shown that robust forward pumping without reversal can be obtained with sufficiently large steps (>2.5μm in this geometry) [3], large enough to create a "fluid conveyor belt" [1]. Our step heights are only slightly into this range, and together with the misalignment discussed above (Figure 2), this may explain why we observed high-frequency flow reversal with a non-planar geometry.

At the higher concentration (0.1 mM), we did not observe flow reversal with any of the electrolytes in Device 2. The peak frequency also consistently shifted upward, roughly from 1 to 10 kHz. The theory in [6] predicts that steric effects leading to flow reversal should increase with concentration, so this behavior is hard to understand. It may be that our low-concentration, high-frequency flow reversal is due to a larger role played by water ions, H^+ and OH^-, since similar flow reversal has also been observed in pure water in a different non-planar geometry [2]. Since the higher concentrations were tested later in the same device, however, there may also have been electrochemical modification of the electrodes from switching electrolytes and operating at 3 V.

Support for this hypothesis comes from the 0.1 mM $CaCl_2$ data in Figure 3 (Device 1), which is very different from that in Figure 4 (Device 2) at the same concentration and resembles the 0.01 mM frequency spectrum at all concentrations. Since the Figure 3 data also resembles results from previous experiments on KCl [4,7], it is probably more reliable than the data in Figure 4. As in our first paper [7], switching electrolytes in the same device seems to significantly affect the flows. This effect may be enhanced by the large voltage (3 V pp), which is not far outside the "electrode damaging zone", where gas bubbles from electrolysis can be observed at low frequency [4]. For a systematic understanding of electrolyte effects on ACEO flow, future experiments should explore different switching protocols, use separate devices with reproducible geometries, apply lower voltages, and work with taller steps to enhance the robust

forward flow associated with the "fluid conveyor belt" [1-3].

Trends with ionic properties are not clear at this point. In both devices, the fastest flows were observed in $CaCl_2$, which has the larger, divalent cation. The slowest flows (from Device 2 only) were observed in $MgCl_2$, which has a smaller, divalent cation. Among the monovalent solutions in Device 2, the one with the larger cation (NaCl) was somewhat faster than the smaller (KCl). There is no clear correlation with size or charge alone, however, since $MgCl_2$ was much slower than all three of the other solutions. Other large-voltage effects, such as Faradaic reactions, may be masking the underlying trends.

In summary, using four binary chloride solutions with different cations, we have shown that ACEO flow depends on the solution chemistry, as well as on the history of device loading and operation. The flow generally decays with increasing salt concentration from 0.01 to 1 mM. In many cases, especially at low concentration, there is significant, reproducible flow reversal at high frequency (> 10 kHz). At least for dilute solutions of simple binary salts (< 0.1 mM), our experiments support previous conclusions that reliable pumping velocities of order mm/sec are possible with only a few volts. More experiments are needed, however, to clarify the effects of changing the solution chemistry, which will be important for manipulating complex biological solutions.
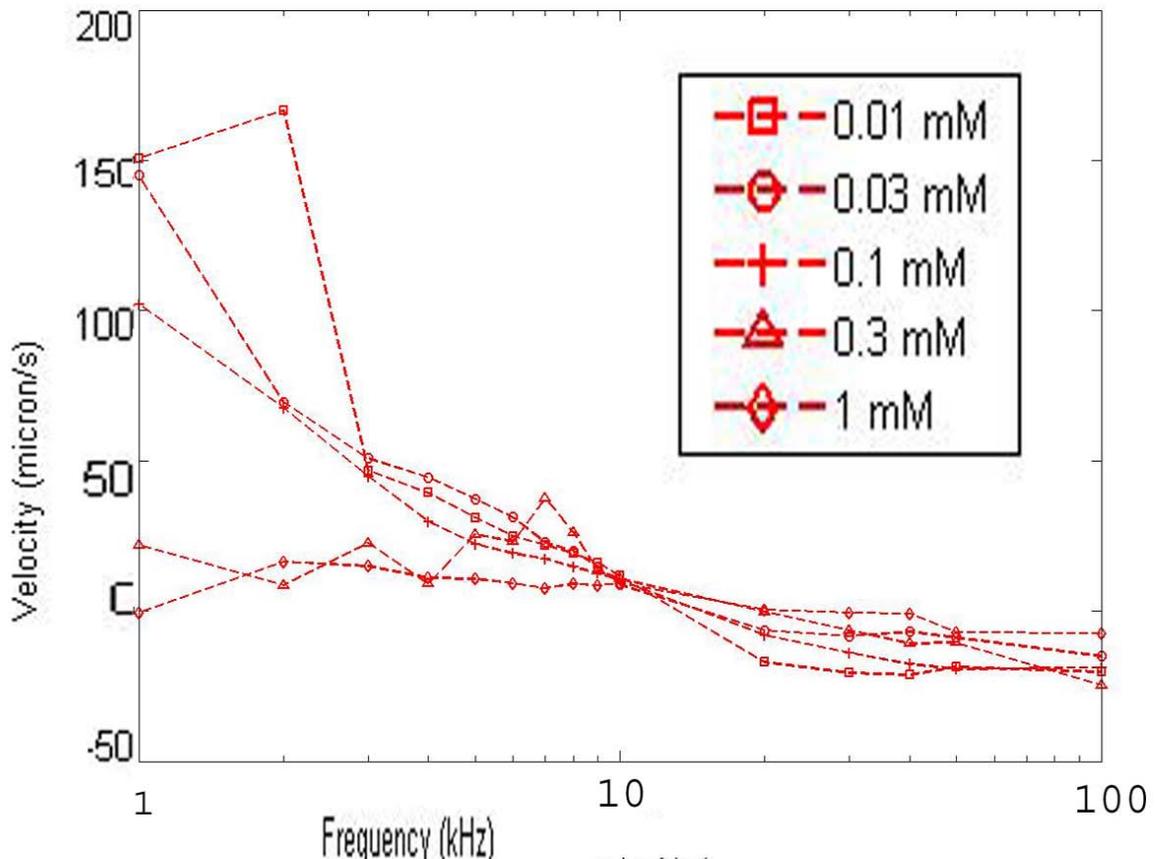

Fig 3. Pumping Velocity versus Frequency for various $CaCl_2$ concentration solutions at 3 V pp applied ac voltage for a 2.6 micron step height device.
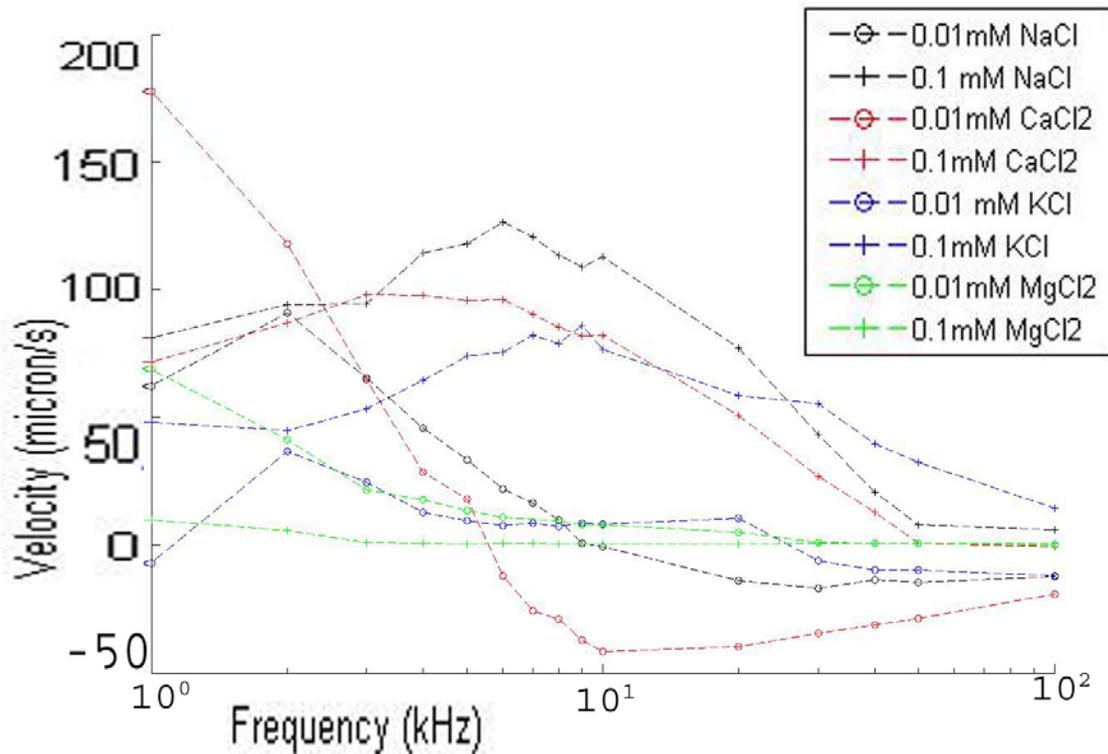
Fig 4. Pumping Velocity versus Frequency for various electrolyte solutions at 3 V pp applied ac voltage for a 2.6 micron step height device.

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