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pH Change in Electroosmotic Flow Hysteresis

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Author Contributions

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Notes

The authors declare no competing financial interest.

ABSTRACT: Electroosmotic flow (EOF) has been shown to exhibit hysteresis effect under displacement flow involving two solutions with different concentrations, i.e. the flow velocity for a high concentration solution displacing a low concentration solution is faster than the flow in the reverse direction involving the same solution pair. Based on our recent numerical analysis, pH change initiated at the interface between the two solutions has been hypothesized as the cause for the observed anomalies. We report the first experimental evidence on electro-osmotic flow hysteresis induced by pH change in the bulk solution. pH-sensitive dye was employed to quantify the pH changes in the microchannel during EOF. The electric field gradient across the boundary of two solutions generates accumulation or depletion of minority pH-governing ions such as hydronium (H_3O^+) ions, thus inducing pH variations across the microchannel. When a high concentration solution displaced a lower concentration solution, a pH increase was observed, while the flow in the reverse direction induced a decrease in pH. This effect causes significant changes to zeta potential and flow velocity. The experimental results show good quantitative agreement with numerical simulations. This work presents the experimental proof which validates the hypothesis of pH change during electroosmotic flow hysteresis as predicted by numerical analysis. The understanding of pH changes during EOF is crucial for accurate flow manipulation in microfluidic devices and maintaining of constant pH in biological and chemical systems under an electric field.

1 INTRODUCTION

2 Electroosmotic flow (EOF) or electro-osmosis is the flow of
3 liquid in a micro-/nano-sized channel or a porous medium under
4 an applied electric field. Typically, negative charges are formed
5 spontaneously on a solid surface when it is in contact with water
6 or aqueous solutions. The positive ions in the liquid are then at-
7 tracted to the charged surface while the negative ions are repelled
8 from it, forming a thin electrical double layer (EDL). When an
9 external electric field is applied parallel to the solid surface, the
10 positively-charged EDL is driven in the direction of the electric
11 field and the momentum is transferred to the bulk of the liquid
12 through viscous force to generate EOF. For a thin EDL in com-
13 parison to the size of the channel, the fluid flow velocity U is
14 given by the Helmholtz-Smoluchowski slip velocity equation: $U =$
15 $-\epsilon_0\epsilon_r E \zeta / \mu$ where E is the applied electric field, ϵ_0 and ϵ_r are the
16 permittivity of free space and the relative permittivity of the liquid
17 respectively, ζ is the zeta potential (electric potential developed at
18 the solid surface) and μ is the viscosity of the liquid.

19 EOF has found numerous applications in various fields includ-
20 ing manipulation of biomolecules^{1,2}, drug delivery^{3,4}, fuel cell^{5,6},
21 soil remediation^{7,8}, sludge treatment^{9,10}, biomedical diagnosis¹¹,
22 liquid pumping^{12,13} and mixing^{14,15} in micro-devices. In many
23 practical electrokinetic applications, two or more types of fluids

24 with different conductivities or concentrations are typically in-
25 volved. For example, electrokinetic instability mixing exploits the
26 high conductivity difference between two electrolytes to enhance
27 the mixing efficiency¹⁶. Transport and enrichment/stacking of
28 analytes can be achieved with EOF of sample and background
29 solution with large concentration difference¹⁷.

30 For EOF involving two solutions with different concentrations,
31 the EOF hysteresis effect, which is manifested by an observable
32 flow velocity difference between two opposing flow directions,
33 has been recently demonstrated in our previous experimental in-
34 vestigations¹⁸⁻²¹. The EOF hysteresis effect has been reported to
35 induce significant discrepancy in zeta potential values measured
36 with current monitoring method, for two opposing flow direc-
37 tions²². This EOF hysteresis could not be described by the existing
38 conventional model. Recently, we have developed a new theoretic-
39 al model to describe this phenomenon. Through numerical simu-
40 lations based on this new theoretical framework, we discover that
41 EOF involving two solutions with different concentrations induc-
42 es accumulation or depletion of minority pH-governing ions at the
43 bulk interface between the two solutions¹⁸. This effect causes
44 significant pH changes which affect the zeta potential and flow
45 velocity.

46

Figure 1. Experimental setups for (A) current monitoring method and (B) pH quantification of sample collected at different time instances during displacement flow

The prediction of pH changes in the bulk fluid is rather counter intuitive as EOF in a micro-channel is believed to be caused by surface phenomenon and the majority ions. Without direct experimental observation of pH changes as a result of EOF hysteresis, this prediction will remain as a hypothesis as it is deduced indirectly through numerical simulations. This investigation, therefore, focuses on the experimental observation of pH changes induced by EOF hysteresis, and their quantification for comparison with numerical simulations.

The pH change investigated in this study is distinct from other mechanisms which induce pH variations in EOF as reported in the literatures. EOF hysteresis presented here is caused by the stacking or depletion of pH-governing ions across two solutions with different conductivities. Electrolytic reactions at the electrodes can potentially induce pH and flow velocity changes during EOF^{23,24}. This effect was minimized in our experiments (see Supporting Information) and thus can be neglected. The development of pH gradient in EOF across nanopores has been observed due to ion concentration polarization (ICP) effect^{25,26}. However, the ICP effect is only significant when the EDL layers overlaps in nanochannels, and thus not relevant in this study.

EXPERIMENTAL SECTION

Current monitoring experiments. The EOF experiment was performed by applying a voltage of 1800V (CZE1000R, Spellman) across a glass micro-capillary (Polymicro Technologies, inner diameter 250μm, length 15cm) placed between two reservoirs with 0.2mM and 1mM potassium chloride (KCl) solutions (Fluka) (see Fig. 1A). The conductivities of 0.2mM and 1mM KCl

were measured to be 30.8μS.cm⁻¹ and 147.9μS.cm⁻¹ respectively (IONCheck 65, Radiometer Analytical). As the solution with a different concentration flows into the capillary, the solution which initially resides in it is displaced and the total resistance of the capillary is changed. The change of resistance is reflected as an observable current change, which was recorded by a picoammeter (Keithley 6458). The current values I enable the positions of the two-fluid interface along the capillary x to be determined and non-dimensionalized with the capillary length L as p (see Fig. 2A):

$$p = \frac{\sigma_1 \sigma_2}{\sigma_2 - \sigma_1} \left(\frac{EA}{I} - \frac{1}{\sigma_2} \right), \quad (1)$$

where $\sigma_{1/2}$ = conductivities of the two solutions, and A = cross-sectional area of capillary. The displacement flow experiments were conducted in both directions, i.e. 1mM KCl displaces 0.2mM and 0.2mM KCl displaces 1mM KCl, to investigate the difference in pH changes.

Figure 2. (A) Dimensionless interface positions during displacement flow process at $p = 0.2$, 0.6 and 1. Current-time curves showing currents I for dimensionless interface positions $p = 0.2$, 0.6 and 1 when (B) 1mM KCl displaces 0.2mM KCl, and (C) 0.2mM KCl displaces 1mM KCl.

1
2 **Figure 3.** pH versus (A) R (red), (B) G (green) and (C) B (blue) values curves. (D) Calibration curve for pH quantification, where C =
3 (R+G-B) represents RGB values.

4 **pH measurement.** The EOF was stopped at various interface
5 locations ($p = 0.2, 0.6, 1$) (see Fig. 2) by switching off the voltage.
6 The capillary was immediately detached from the reservoirs to
7 obtain “snapshots” of the pH in the capillary at various time in-
8 stances, and to prevent any diffusion of solutions into/out of the
9 capillary. The capillary was then connected to a syringe and the
10 liquid was pumped into a white nylon female luer lock coupler
11 (Cole-Parmer), which was capped with a male luer plug at one
12 end to form a small liquid container (see Fig. 1B). Each capillary
13 only contains approximately 7 μ L of liquid. The experiment was
14 conducted 11 times for each interface position to generate 70-80 μ L
15 of sample in the container. Due to potential fluid loss from the
16 capillary during the execution of this procedure, the exact amount
17 of sample was measured with a chemical balance (A&D GR-200).
18 Subsequently, 2% (based on volume of sample) of pH-sensitive
19 dye, 0.04wt% bromocresol purple (Sigma-Aldrich), was added to
20 the sample collected (2.0 μ L Microsyringe, Hamilton) and the
21 color change was captured with a color camera (Olympus SC30)
22 attached to a stereo microscope (Olympus SZX7). The entire pro-
23 cess was repeated 3 times for each interface position to ensure
24 consistency and reliability of results.

25 The pH of the sample can be quantified by performing image
26 analysis on the color images. Similar approaches have been
27 adopted for non-destructive evaluation of chlorophyll content in
28 leaves²⁷⁻²⁹. The pH calibration curve was produced based on the
29 color images captured under the same optical parameters (expo-
30 sure time, illumination intensity, magnification etc) when bromo-
31 cresol purple was added to 7 calibration solutions, which were
32 pH-adjusted with sodium hydroxide (NaOH) and hydrochloric
33 acid (HCl). The pH of these calibration solutions were pre-
34 determined by a pH meter (FEP20, Mettler Toledo).

35 A program was written in MATLAB to extract the RGB (red,
36 green, blue) values from these color images. There was a strong

37 correlation between R, G, and B values of the solutions (see Fig.
38 3); R and G values are positively correlated to each other (correla-
39 tion coefficient of 1) while B value is negatively correlated to R
40 and G values (correlation coefficient of -1). This indicates that
41 they are not independent variables; indeed, their combination will
42 represent one independent variable. Therefore, a new variable, C
43 = (R+G-B) was created to represent the RGB values. C is re-
44 gressed on pH with a cubic curve (see Fig. 3D), which yields a
45 coefficient of determination of 0.97. The calibration curve enables
46 the quantification of the average pH for the sample collected at
47 different time instances during the flow process.

48 *In situ* measurement of pH change in microchannel with pH-
49 sensitive fluorescent dyes have been reported in the literatures<sup>30-
50 32</sup>. Due to the effect of electrophoretic movement and stack-
51 ing/depletion of dye, accurate pH quantification requires the addi-
52 tion of another control dye, which is insensitive to pH change³¹. In
53 our experiments, the pH sensitive dye was not added into the res-
54 ervoirs or the capillary as it could distort the experimental condi-
55 tions and variables that we intended to measure. Instead, after the
56 EOF was stopped, the content of the capillary was collected into a
57 separate container, where pH sensitive dye was added. This meth-
58 od allows the average pH measurement of the content in the capil-
59 lary without the interference of dye concentration stack-
60 ing/depletion during EOF. Therefore the dye color change ob-
61 served in our experiment is solely due to pH change, and not re-
62 lated to the dye concentration stacking/depletion.

63 **Numerical simulations.** To understand the trend and mechan-
64 ics of the observed pH change, numerical simulations were per-
65 formed with finite element method (FEM) software COMSOL
66 Multiphysics. We have reported a 2-D axisymmetric numerical
67 model which captures the fluid dynamics and reversible chemical
68 reactions during EOF in our previous paper¹⁸. In this study, we
69 simplify the model to a 1-D domain (a straight line) for better

1 computational efficiency to obtain the pH variation along the axial
2 direction (x -axis) of the capillary. The fluid velocity profile in the
3 radial direction is not simulated by Navier-Stokes and continuity
4 equations in this 1-D model, but it has been replaced by an aver-
5 age velocity which is calculated from the average zeta potential
6 (see Eq. (5)). The applied electric field, the main driving force of
7 EOF, has a negligible radial component as it is parallel to the
8 straight micro-capillary. The governing equations for the model
9 are:

$$10 \quad \frac{d}{dx} \left(\sigma \frac{dV}{dx} \right) = 0, \quad (2)$$

$$11 \quad \sigma = 2Fc_0u_{m0}, \quad (3)$$

$$12 \quad \frac{d\sigma}{dt} - D_0 \frac{d^2\sigma}{dx^2} + U_{ave} \frac{d\sigma}{dx} = 0, \quad (4)$$

$$13 \quad U_{ave} = -\frac{\varepsilon_0 \varepsilon_r \zeta_{ave} E_0}{\mu}, \quad (5)$$

$$14 \quad \sqrt{8c_0 \varepsilon_0 \varepsilon_r R T \sinh \left(\frac{F\zeta}{2RT} \right)} = \frac{-eN_{total}K_A}{K_A + [H_3O^+] \exp \left(\frac{-F\zeta}{RT} \right)}, \quad (6)$$

$$15 \quad \frac{dc_i}{dt} - D_i \frac{d^2c_i}{dx^2} - \frac{d}{dx} \left[u_{m(i)} c_i \frac{dV}{dx} \right] + U_{ave} \frac{dc_i}{dx} = R_i, \quad (7)$$

16 where σ is the conductivity of KCl solution, V is the applied elec-
17 tric potential, F is the Faraday constant, c_0 is the bulk concentra-
18 tion of KCl solution, u_{m0} is the magnitude of ionic mobility for
19 potassium (K^+) or chloride (Cl^-) ion, D_0 is the diffusion coefficient
20 of K^+/Cl^- ion, U_{ave} is the average EOF velocity, ζ is the local zeta
21 potential, ζ_{ave} is the zeta potential averaged along the entire capil-
22 lary, R is the gas constant, T is the temperature, e is the elemen-
23 tary charge, N_{total} is the total number of surface site density for
24 silanol group ($SiOH$), K_A is the equilibrium constant for the
25 deprotonation of $SiOH$ group, $[H_3O^+]$ is the bulk concentration of
26 hydronium ion, c_i , D_i , u_{mi} and R_i are the concentration, diffusion
27 coefficient, ionic mobility and total reaction rate respectively, for
28 each ionic species (except for K^+ and Cl^-). The ionic mobility is
29 related to diffusion coefficient through the Einstein relation, $D_i =$
30 $u_{mi}k_B T / z_i e$, where k_B is the Boltzmann constant and z_i is the ionic
31 charge number.

32 Eq. (2) dictates the applied electrical potential distribution,
33 which is determined by the conductivity of KCl solution. It is
34 assumed that minority ions such as H_3O^+ and bicarbonate ions
35 (HCO_3^-) ions do not contribute to the conductivity of the solution
36 due to their low concentrations. The conductivity of the solution is
37 related to the concentration of KCl by Eq. (3). Instead of model-
38 ing the KCl solution with K^+ and Cl^- ions separately, a single
39 variable of conductivity σ is adopted¹⁶ because the diffusion coef-
40 ficient and magnitude of ionic mobility for both ions are almost
41 identical. The evolution of σ due to convection and diffusion is
42 given by Eq. (4). The EOF velocity is provided by the slip veloci-
43 ty equation (Eq. (5)), which is calculated based on the zeta poten-
44 tial averaged along the entire capillary at every time instance. The
45 local zeta potential is related to the bulk KCl concentration and
46 pH through Eq. (6), which is obtained by equating Grahame equa-
47 tion with charge regulation model^{18,33}. A series of Nernst-Planck
48 equations (Eq. (7)) provide the concentration evolution of each
49 minority ionic species under the effect of electromigration, diffu-
50 sion, convection and reaction. Various chemical equilibrium equa-
51 tions including the auto-ionization of water and equilibria of car-
52 bonic acid (carbon dioxide dissolved in water) were also included
53 (see Supporting Information). The values of all constants em-
54 ployed in the numerical simulations are listed in Table S1 in the
55 Supporting Information.

56 The 1-D simulation domain is a straight line with a length of
57 1cm. Although the 1-D simulation domain is 1cm, the simulation
58 results can be related to the experimental results (length of 15cm)

59 through the dimensionless interface position p as defined in Eq.
60 (1). The inlet and outlet boundary conditions along with initial
61 conditions are listed in Table 1. The applied voltage is set to 120V
62 over the 1cm domain to generate similar electric field magnitude
63 ($120Vcm^{-1}$) as the experiments. The initial concentrations of mi-
64 nority ions including H_3O^+ , OH^- , HCO_3^- , H_2CO_3 and CO_3^{2-} were
65 calculated based on the respective chemical equilibria (see Sup-
66 porting Information), and set as the boundary and initial condi-
67 tions. The pH values of 1mM and 0.2mM KCl are identical. The
68 conductivity conditions are set according to the flow scenario
69 based on the experiments. The line was meshed with 2000 ele-
70 ments. Convergence test was performed with higher number of
71 elements and the numerical error was found to be negligible for
72 this mesh selection. The maximum time step and total simulated
73 time was set to 0.005s and 22s respectively.

75 **Table 1: Boundary and initial conditions for 1-D numerical**
76 **simulations for 0.2mM displacing 1mM KCl (LH) and 1mM**
77 **displacing 0.2mM KCl (HL).**

Variables	Boundary conditions		Initial conditions
	Inlet	Outlet	Domain
V	120V	0	120 ($L - x$)
c_i	Initial concentration of minority ions for KCl		
LH : 0.2mM displacing 1mM KCl			
σ	Conductivity of 0.2mM KCl	Conductivity of 1mM KCl	
HL : 1mM displacing 0.2mM KCl			
σ	Conductivity of 1mM KCl	Conductivity of 0.2mM KCl	

78

79 RESULTS AND DISCUSSION

80 Fig. 4A shows the experimental average pH variations at dif-
81 ferent interface positions for the two opposing flow directions.
82 When 1mM KCl displaces 0.2mM KCl, the average pH increases
83 from 5.64 (initial pH of KCl solutions) to 6.07 throughout the
84 displacing process. In the reverse flow direction, i.e. 0.2mM KCl
85 displaces 1mM, the average pH decreases from 5.64 to a mini-
86 mum of 5.24 before increasing to 5.44 at the end of the displace-
87 ment. Despite the increase from minimum pH, the final pH was
88 still below the initial pH of 5.64.

89 A control experiment was conducted by filling both reservoirs
90 with a solution of 0.6mM KCl (average of 1mM and 0.2mM). The
91 control experiment only demonstrated a low pH increase of 0.1
92 (see Supporting Information) in comparison to the ± 0.4 pH
93 changes in the displacement flow of 1mM and 0.2mM KCl. The
94 slight pH increase is potentially due to electrolytic reactions of
95 water at the electrodes. Precautionary measures such as employ-
96 ing low solution concentration and large reservoirs (4ml) have
97 been adopted to minimize the pH variation in micro-capillary due
98 to electrolysis³⁴. In conclusion, the experimental results demon-
99 strate the definite dichotomic pH changes in micro-capillary de-
100 pending on the flow directions, i.e. pH increases when a high
101 conductivity solution displaces a low conductivity solution while
102 pH decreases when a low conductivity solution displaces a high
103 conductivity solution.

104 The numerical simulation reveals the mechanism for the pH
105 change during the displacement flow of two solutions with differ-
106 ent concentrations. The electric field distribution across the two
107 solutions is determined by the conductance ratio between the two
108 segments of fluid. The pH-governing minority ions are forced to

1 migrate across the interface between the two solutions under the
2 applied electric field. When a high concentration solution displac-
3 es one with a lower concentration, the pH increase is caused by
4 the depletion of H_3O^+ and accumulation of HCO_3^- across the inter-
5 face. On the contrary, when a lower concentration solution displac-
6 es one with a higher concentration, the pH decrease is caused
7 by the accumulation of H_3O^+ and depletion of HCO_3^- across the
8 interface. The distributions of these pH-governing minority ions
9 are determined by the interplay between acid-base equilibria,
10 electromigration, diffusion and convection effects. Subsequently,
11 the pH depletion or accumulation zones expand outwards to other
12 parts of the solution, driven by electromigration effect.

13 The simulated pH is averaged along the capillary and compared
14 with the experimental results (see Fig. 4A). The diffusion coeffi-
15 cient of hydrogen ion in water is typically cited as $9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
16 ³⁵. With this value, it is found that the curves obtained from nu-
17 merical simulation have large discrepancies with the experimental
18 data points, beyond the limit of experimental error.

19

20

21 **Figure 4.** (A) Experimental and numerical average pH varia-
22 tions at different dimensionless interface positions p for 1mM KCl
23 displaces 0.2mM KCl (HL), and 0.2m M KCl displaces 1mM KCl
24 (LH). $D_{\text{H}_3\text{O}^+}$ is the diffusion coefficient of hydronium ion. (B)
25 Simulated local pH distribution along the micro-capillary at vari-
26 ous interface positions, which are marked with short vertical line

27 ($p = 0.2, 0.6, 1$), for displacement flows in HL and LH directions,
28 assuming $D_{\text{H}_3\text{O}^+} = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

29

30 Indeed, the anomalously high value of diffusion coefficient for
31 hydrogen ions has been a topic for intense research and debate for
32 decades^{36,37}, where various theories have been proposed to ex-
33 plain the phenomenon. One of the theory suggests that the majori-
34 ty of the diffusion coefficient value is attributed to Grotthuss
35 mechanism^{38,39} (also known as structural diffusion), which in-
36 volves the rapid exchange of proton (H^+) between adjacent H_3O^+
37 and water molecule (H_2O). However, the carriers, i.e. H_3O^+ , also
38 experience ordinary diffusive or electromigration movement and
39 contribute partially towards the apparently movement of H^+ in
40 water.

41 In this investigation, we assume that the formation of ion ac-
42 cumulation/depletion zone is caused by the ordinary eletromigra-
43 tive movement of H_3O^+ (without Grotthuss mechanism), which is
44 expected to exhibit similar diffusive properties as H_2O . With this
45 assumption, the diffusion coefficient of H_3O^+ is set to 2.3×10^{-9}
46 $\text{m}^2 \text{ s}^{-1}$, similar to the diffusion coefficient of H_2O instead. Interest-
47 ingly, the numerical results obtained with this value agree very
48 well with the experimental results.

49 When 1mM KCl displaces 0.2mM KCl, the average pH in-
50 creases initially up to 6.06 at $p = 0.8$ before decreasing to 5.98 at p
51 $= 1$. In the reverse flow direction, the average pH decreases ini-
52 tially to 5.21 at $p = 0.53$ before increasing to 5.57 at $p = 1$. The
53 initial pH increase/decrease is due to the expansion of H_3O^+ de-
54 pletion/accumulation zone which is leading the interface of the
55 two KCl solutions. Therefore, the higher value of mobility for
56 H_3O^+ (for $D_{\text{H}_3\text{O}^+} = 9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) employed in the simulations
57 predicted the accelerated expansion of ion depletion/accumulation
58 zone and an average pH value indicated in Fig. 4 (for both flow
59 directions) which deviates noticeably from the experimental val-
60 ues. As the H_3O^+ depletion/accumulation zone reaches the end of
61 the capillary, the trend of the pH change is reversed due to the
62 convective displacement of unaffected fluid zone from the inlet.

63 The numerical simulations also provide further insight on the
64 local pH distribution and evolution, which cannot be captured by
65 our experiments. The local pH changes are much higher than the
66 average pH changes which are approximately ± 0.4 (see Fig. 4A).
67 When 1mM KCl displaces 0.2mM KCl, the maximum local pH is
68 7.73 while the minimum local pH in the reverse flow direction is
69 4.86 (see Fig. 4B). The significant local pH change affects the
70 zeta potential and EOF velocity as reported in our previous inves-
71 tigation¹⁸⁻²¹. Furthermore, the pH change might be detrimental to
72 chemical and biological systems in lab-on-a-chip devices. Appro-
73 priate buffer solutions should be employed to minimize the pH
74 changes to achieve accurate flow control and maintain a constant
75 pH in the microfluidic chip under EOF.

76 CONCLUSION

77 In conclusion, we have presented conclusive evidence for the
78 pH change during EOF involving two solutions with different
79 concentrations. The average pH in micro-capillary was quantified
80 with a pH-sensitive dye through color image processing. When a
81 higher concentration solution displaced a lower concentration
82 solution, a pH increase was observed, while the flow in the re-
83 verse direction caused a decrease in pH. pH-governing minority
84 ions such as H_3O^+ and HCO_3^- are depleted or accumulated at the
85 interface between two solutions due to electromigrative flux im-
86 balance, causing significant pH changes. The experimental results
87 agree well with 1-D numerical simulations. The understanding of
88 pH changes during EOF is important for accurate flow manipula-

tion in microfluidic channels and maintaining of constant pH in biological and chemical systems under an electric field.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX.

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76

FOR TOC ONLY

Supporting Information

pH change in Electroosmotic Flow Hysteresis

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Table of contents:

Minimizing Joule heating & electrolysis -----	S-2
Symbols and values of constants used in numerical simulations-----	S-3
Reversible acid-base equilibria included in numerical simulations-----	S-5
Control experiments -----	S-7

Minimizing Joule heating & electrolysis

Undesirable effects during electroosmotic flow (EOF) such as Joule heating and electrolysis at electrodes can potentially alter the experimental conditions and parameters such as pH, zeta potential, conductivity etc. Various precautions have been adopted in this investigation to minimize the effect of Joule heating and electrolytic reactions.

The concentrations and conductivities of the solutions were kept low ($30.8 \mu\text{S}\cdot\text{cm}^{-1}$ and $147.9 \mu\text{S}\cdot\text{cm}^{-1}$ for 0.2 mM and 1 mM KCl respectively) to ensure that the effect of Joule heating is negligible¹. A conservative estimate of Joule heating can be calculated from the energy balance between the energy generation and the energy storage in the liquid². For the worst case scenario in our experiments (applied electric field = $120 \text{ V}\cdot\text{cm}^{-1}$, solution conductivity of 1mM KCl = $147.9 \mu\text{S}\cdot\text{cm}^{-1}$, capillary diameter = $250 \mu\text{m}$ and experimental duration = 5 min), the temperature increase is in the range of 0.1°C .

Various measures have been implemented to minimize the pH changes in the reservoirs due to the production of hydronium (H_3O^+) and hydroxide (OH^-) ions from the undesirable electrolytic reactions at the electrodes³. The reservoirs (4 ml) were designed to be significantly larger than the volume of the capillary ($7.4 \mu\text{L}$) to dilute the concentrations of H_3O^+ and OH^- ions produced at the electrodes⁴. In addition, the electrodes were positioned far (2cm away) from the inlet/outlet of the capillary to minimize the diffusion of these ions into the microchannel⁵. More importantly, the current across the capillary was maintained at low values ($1.8 - 8.6 \mu\text{A}$) to minimize electron transfer at the electrodes, thus reducing the production of H_3O^+ and OH^- ions at the electrodes. This was achieved by employing solutions with low conductivities ($30.8 - 147.9 \mu\text{S}\cdot\text{cm}^{-1}$) and a long capillary (15 cm) with a small diameter ($250 \mu\text{m}$).

Symbols and values of constants used in numerical simulations

The symbols and values of all constants employed in the numerical simulations are listed in Table S1.

Table S1. Symbols and values of constants used in numerical simulations.

Parameter	Symbol (Unit)	Value
Permittivity of free space	ε_o (C.V ⁻¹ .m ⁻¹)	8.85 x 10 ⁻¹²
Relative permittivity	ε_r	80
Viscosity of water	μ (kg.m ⁻¹ .s ⁻¹)	8.90 x 10 ⁻⁴
Density of water	ρ (kg.m ⁻³)	1000
Faraday constant	F (C.mol ⁻¹)	96485
Gas constant	R (J.mol ⁻¹ .K ⁻¹)	8.314
Boltzmann constant	k_B (J.K ⁻¹)	1.38 x 10 ⁻²³
Temperature	T (K)	298
Electron charge	e (C)	1.602 x 10 ⁻¹⁹
Diffusion coefficient of K ⁺ /Cl ⁻ ion ^a	D_0 (m ² .s ⁻¹)	1.957 x 10 ⁻⁹
Diffusion coefficient of H ₃ O ⁺ ion	$D_{H_3O^+}$ (m ² .s ⁻¹)	9.3 x 10 ⁻⁹ /2.3 x 10 ⁻⁹
Diffusion coefficient of OH ⁻ ion	D_{OH^-} (m ² .s ⁻¹)	5.26 x 10 ⁻⁹
Diffusion coefficient of H ₂ CO ₃	$D_{H_2CO_3}$ (m ² .s ⁻¹)	1.3 x 10 ⁻⁹
Diffusion coefficient of HCO ₃ ⁻ ion	$D_{HCO_3^-}$ (m ² .s ⁻¹)	1.105 x 10 ⁻⁹
Diffusion coefficient of CO ₃ ²⁻ ion	$D_{CO_3^{2-}}$ (m ² .s ⁻¹)	9.2 x 10 ⁻¹⁰
Magnitude of ionic mobility ^b of K ⁺ /Cl ⁻ ion	u_{m0} (m ² .V ⁻¹ .s ⁻¹)	7.621 x 10 ⁻⁸
Ionic mobility of H ₃ O ⁺ ion	$u_{m(H_3O^+)}$ (m ² .V ⁻¹ .s ⁻¹)	3.622 x 10 ⁻⁷ /8.957 x 10 ⁻⁸
Ionic mobility of OH ⁻ ion	$u_{m(OH^-)}$ (m ² .V ⁻¹ .s ⁻¹)	-2.048 x 10 ⁻⁷
Ionic mobility of HCO ₃ ⁻ ion	$u_{m(HCO_3^-)}$ (m ² .V ⁻¹ .s ⁻¹)	-4.303 x 10 ⁻⁸
Ionic mobility of CO ₃ ²⁻ ion	$u_{m(CO_3^{2-})}$ (m ² .V ⁻¹ .s ⁻¹)	-7.166 x 10 ⁻⁸
Ionic charge number of K ⁺ /Cl ⁻ ion	z_{K^+}/z_{Cl^-}	+1/-1

Ionic charge number of H_3O^+ ion	$z_{\text{H}_3\text{O}^+}$	+1
Ionic charge number of OH^- ion	z_{OH^-}	-1
Ionic charge number of HCO_3^- ion	$z_{\text{HCO}_3^-}$	-1
Ionic charge number of CO_3^{2-} ion	$z_{\text{CO}_3^{2-}}$	-2
Equilibrium constant of SiOH deprotonation reaction	K_A	6.310×10^{-8}
Total number site density of SiOH	$N_{\text{Total}} (\text{m}^{-2})$	8×10^{18}
Partial pressure of carbon dioxide	$PCO_2 (\text{atm})$	3.5×10^{-4}
Henry's law constant	$K_H (\text{L.atm.mol}^{-1})$	29.76
Apparent specific forward rate constant of water	$K_{fw} (\text{mol.dm}^{-3}.\text{s}^{-1})$	1×10^{-4}
Water ionization constant	$K_w (\text{mol}^2.\text{dm}^{-6})$	1×10^{-14}
Apparent specific forward rate constant of carbonate system 1	$K_{fC1} (\text{s}^{-1})$	4.45
Equilibrium constant of carbonate system 1	$K_{C1} (\text{mol.dm}^{-3})$	4.45×10^{-7}
Apparent specific forward rate constant of carbonate system 2	$K_{fC2} (\text{s}^{-1})$	0.469
Equilibrium constant of carbonate system 2	$K_{C2} (\text{mol.dm}^{-3})$	4.69×10^{-11}

^aDiffusion coefficient of K^+ is used to model a single variable of conductivity ($\sigma = 2Fc_0u_{m0}$, where c_0 is the bulk concentration of KCl) as the diffusion coefficient and magnitude of ionic mobility for both K^+ and Cl^- ions are almost identical.

^bIonic mobility is related to diffusion coefficient through the Einstein relation, $D_i = (u_{mi}k_B T)/(z_i e)$.

Reversible acid-base equilibria included in numerical simulations

The auto-ionization of water (H_2O):

where OH^- and H_3O^+ represent the hydroxide and hydronium ions. The rate of the forward reaction r_{fw} is

$$r_{fw} = K_{fw} [\text{H}_2\text{O}]^2, \quad (\text{S2})$$

where K_{fw} is the apparent specific rate constant for the forward reaction. The expression for the equilibrium constant (also known as the water ionization constant) is

$$K_w = [\text{OH}^-] [\text{H}_3\text{O}^+], \quad (\text{S3})$$

for which the value of $[\text{H}_2\text{O}]$ is assumed to be a constant, and takes the value of 1.

The dissolved carbon dioxide in equilibrium with the carbonic acid, represented by H_2CO_3^* , undergoes deprotonations through the following acid-base equilibria:

The rate of the forward reaction r_{fC1} for carbonate system 1 (Equation S4) is

$$r_{fC1} = K_{fC1} [\text{H}_2\text{CO}_3^*] [\text{H}_2\text{O}], \quad (\text{S6})$$

where K_{fC1} is the apparent specific forward rate constant of carbonate system 1. The equilibrium constant for carbonate system 1 is defined as:

$$K_{C1} = [\text{HCO}_3^-] [\text{H}_3\text{O}^+] / [\text{H}_2\text{CO}_3^*], \quad (\text{S7})$$

where HCO_3^- represents the bicarbonate ion. The rate of the forward reaction r_{fC2} for carbonate system 2 (Equation S5) is

$$r_{fC2} = K_{fC2} [\text{HCO}_3^-] [\text{H}_2\text{O}], \quad (\text{S8})$$

where K_{fC2} is the apparent specific forward rate constant of carbonate system 2. The equilibrium constant for carbonate system 2 is defined as:

$$K_{C2} = [\text{CO}_3^{2-}] [\text{H}_3\text{O}^+] / [\text{HCO}_3^-], \quad (\text{S9})$$

where CO_3^{2-} represents the carbonate ion.

In order to obtain the equilibrium concentrations for all the species, the concentration of the dissolved carbon dioxide in the form of $[\text{H}_2\text{CO}_3^*]$ must first be calculated from Henry's law:

$$[\text{H}_2\text{CO}_3^*] = PCO_2 / K_H \quad (\text{S10})$$

where PCO_2 is the partial pressure of carbon dioxide and K_H is the Henry's law constant under room temperature T . Equations S3, S7, S9, S10 and the charge neutrality condition (Equation S11):

$$[\text{H}_3\text{O}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] = 0, \quad (\text{S11})$$

are solved simultaneously to calculate the equilibrium concentrations for all species, which are:

$$[\text{H}_3\text{O}^+] = 2.313\mu\text{M},$$

$$[\text{OH}^-] = 4.32\text{nM},$$

$$[\text{H}_2\text{CO}_3^*] = 12\mu\text{M},$$

$$[\text{HCO}_3^-] = 2.309\mu\text{M},$$

$$[\text{CO}_3^{2-}] = 46.8\text{pM}.$$

Control experiments

The control experiment was performed by filling both reservoirs and the capillary with 0.6mM of KCl, which is the average concentration of the two solutions (0.2mM and 1mM) employed in our experiments. The voltage was applied for 5 min, which is the longest displacement time observed in the actual two-fluid displacement flow experiment. Since the contents in the reservoirs and the capillary are the same, the current was observed to be constant throughout the experiment.

After 5 min, the voltage was switched off and the capillary was detached from the reservoirs. The experiment was conducted 11 times to gather 70-80 μ l of solutions for pH measurements, with the method described in the Experimental Section of the paper. The average pH for the solution in the control experiment was measured to be 5.74.

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