<table>
<thead>
<tr>
<th>Title</th>
<th>pH change in electroosmotic flow hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Lim, Chun Yee; Lim, An Eng; Lam, Yee Cheong</td>
</tr>
<tr>
<td>Date</td>
<td>2017</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/44842">http://hdl.handle.net/10220/44842</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2017 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by Analytical Chemistry, American Chemical Society. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1021/acs.analchem.7b02219">http://dx.doi.org/10.1021/acs.analchem.7b02219</a>].</td>
</tr>
</tbody>
</table>
pH Change in Electroosmotic Flow Hysteresis

Chun Yee Lim, An Eng Lim, and Yee Cheong Lam*

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

AUTHOR INFORMATION

Corresponding Author

*Phone: +65 6790 6874. Fax: +65 6792 4062. E-mail: myclam@ntu.edu.sg.

Author Contributions

All authors contributed equally.

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 (H₃O⁺) 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.

INTRODUCTION

Electroosmotic flow (EOF) or electro-osmosis is the flow of liquid in a micro-/nano-sized channel or a porous medium under an applied electric field. Typically, negative charges are formed spontaneously on a solid surface when it is in contact with water or aqueous solutions. The positive ions in the liquid are then attracted to the charged surface while the negative ions are repelled from it, forming a thin electrical double layer (EDL). When an external electric field is applied parallel to the solid surface, the positively-charged EDL is driven in the direction of the electric field and the momentum is transferred to the bulk of the liquid through viscous force to generate EOF. For a thin EDL in comparison to the size of the channel, the fluid flow velocity \( U \) is given by the Helmholtz-Smoluchowski slip velocity equation:

\[
U = \frac{\varepsilon_0 \varepsilon_r E \eta \zeta}{\mu}
\]

where \( E \) is the applied electric field, \( \varepsilon_0 \) and \( \varepsilon_r \) are the permittivity of free space and the relative permittivity of the liquid respectively, \( \zeta \) is the zeta potential (electric potential developed at the solid surface) and \( \mu \) is the viscosity of the liquid.

EOF has found numerous applications in various fields including manipulation of biomolecules, drug delivery, fuel cell, soil remediation, sludge treatment, biomedical diagnosis, liquid pumping, and mixing in micro-devices. In many practical electrokinetic applications, two or more types of fluids with different conductivities or concentrations are typically involved. For example, electrokinetic instability mixing exploits the high conductivity difference between two electrolytes to enhance the mixing efficiency. Transport and enrichment/stacking of analytes can be achieved with EOF of sample and background solution with large concentration difference.

For EOF involving two solutions with different concentrations, the EOF hysteresis effect, which is manifested by an observable flow velocity difference between two opposing flow directions, has been recently demonstrated in our previous experimental investigations. The EOF hysteresis effect has been reported to induce significant discrepancy in zeta potential values measured with current monitoring method, for two opposing flow directions. This EOF hysteresis could not be described by the existing conventional model. Recently, we have developed a new theoretical model to describe this phenomenon. Through numerical simulations based on this new theoretical framework, we discover that EOF involving two solutions with different concentrations induces accumulation or depletion of minority pH-governing ions at the bulk interface between the two solutions. This effect causes significant pH changes which affect the zeta potential and flow velocity.
The prediction of pH changes in the bulk fluid is rather counterintuitive 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\textsuperscript{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\textsuperscript{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 1800 V (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\textsuperscript{-1} and 147.9µS.cm\textsuperscript{-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 enable the positions of the two-fluid interface along the capillary, x to be determined and nondimensionalized with the capillary length L as p (see Fig. 2A):

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

where $\sigma_1$ and $\sigma_2$ are the 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 1. Experimental setups for (A) current monitoring method and (B) pH quantification of sample collected at different time instances during displacement flow.](image1)

![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.](image2)
**pH measurement.** The EOF was stopped at various interface locations ($p = 0.2, 0.6, 1$) (see Fig. 2) by switching off the voltage. The capillary was immediately detached from the reservoirs to obtain “snapshots” of the pH in the capillary at various time instances, and to prevent any diffusion of solutions into/out of the capillary. The capillary was then connected to a syringe and the liquid was pumped into a white nylon female luer lock coupler (Cole-Parmer), which was capped with a male luer plug at one end to form a small liquid container (see Fig. 1B). Each capillary only contains approximately 7μl of liquid. The experiment was conducted 11 times for each interface position to generate 70 samples in the container. Due to potential fluid loss from the capillary during the execution of this procedure, the exact amount of sample in the container was measured with a chemical balance (A&D GR-200). Subsequently, 2% (based on volume of sample) of pH-sensitive dye, 0.04wt% bromocresol purple (Sigma-Aldrich), was added to the sample collected (2.0μL Microsyringe, Hamilton) and the color change was captured with a color camera (Olympus SC30) attached to a stereo microscope (Olympus SZX7). The entire process was repeated 3 times for each interface position to ensure consistency and reliability of results.

The pH of the sample can be quantified by performing image analysis on the color images. Similar approaches have been adopted for non-destructive evaluation of chlorophyll content in leaves. The pH calibration curve was produced based on the color images captured under the same optical parameters (exposure time, illumination intensity, magnification etc) when bromocresol purple was added to 7 calibration solutions, which were pH-adjusted with sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH of these calibration solutions were pre-determined by a pH meter (FEP20, Mettler Toledo).

A program was written in MATLAB to extract the RGB (red, green, blue) values from these color images. There was a strong correlation between R, G, and B values of the solutions (see Fig. 3): R and G values are positively correlated to each other (correlation coefficient of 1) while B value is negatively correlated to R and G values (correlation coefficient of -1). This indicates that they are not independent variables; indeed, their combination will represent one independent variable. Therefore, a new variable, C = (R+G-B) was created to represent the RGB values. C is regressed on pH with a cubic curve (see Fig. 3D), which yields a coefficient of determination of 0.97. The calibration curve enables the quantification of the average pH for the sample collected at different time instances during the flow process.

**In situ** measurement of pH change in microchannel with pH-sensitive fluorescent dyes have been reported in the literatures. Due to the effect of electrophoretic movement and stacking/depletion of dye, accurate pH quantification requires the addition of another control dye, which is insensitive to pH change. In our experiments, the pH sensitive dye was not added into the reservoirs or the capillary as it could distort the experimental conditions and variables that we intended to measure. Instead, after the EOF was stopped, the content of the capillary was collected into a separate container, where pH sensitive dye was added. This method allows the average pH measurement of the content in the capillary without the interference of dye concentration stacking/depletion during EOF. Therefore the dye color change observed in our experiment is solely due to pH change, and not related to the dye concentration stacking/depletion.

**Numerical simulations.** To understand the trend and mechanisms of the observed pH change, numerical simulations were performed with finite element method (FEM) software COMSOL Multiphysics. We have reported a 2-D axisymmetric numerical model which captures the fluid dynamics and reversible chemical reactions during EOF in our previous paper. In this study, we simplify the model to a 1-D domain (a straight line) for better understanding of the process and to focus on the pH change.

The calibration curve for pH quantification, where C = (R+G-B) was created to represent RGB values. (A) pH versus (A) R (red), (B) G (green) and (C) B (blue) values curves. (D) Calibration curve for pH quantification, where C = (R+G-B) was created to represent RGB values. (D) Calibration curve for pH quantification, where C = (R+G-B) was created to represent RGB values.
computational efficiency to obtain the pH variation along the axial direction (x-axis) of the capillary. The fluid velocity profile in the radial direction is not simulated by Navier-Stokes and continuity equations in this 1-D model, but it has been replaced by an average velocity which is calculated from the average zeta potential (see Eq. (5)). The applied electric field, the main driving force of EOF, has a negligible radial component as it is parallel to the straight micro-capillary. The governing equations for the model are:

\[
\frac{d}{dx} \left( \sigma \frac{dv}{dx} \right) = 0 ,
\]

(2)

\[
\sigma = 2FC_0u_{m0} ,
\]

(3)

\[
\frac{da}{dt} - D_0 \frac{da}{dx} + U_{ave} \frac{da}{dx} = 0 ,
\]

(4)

\[
U_{ave} = -\frac{e\varepsilon_0k_bT}{\mu} .
\]

(5)

\[
\sqrt{8\varepsilon_0}\varepsilon_0R^2\sinh \left( \frac{F_i}{RT} \right) = \frac{-eN_{total}K_A}{K_A^4[H_2O^+][Cl^+]^2} ,
\]

(6)

\[
\frac{dc_i}{dt} - D_i \frac{dc_i}{dx} = \frac{d}{dx} \left( u_{m0}c_i \frac{dv}{dx} \right) + U_{ave} \frac{dc_i}{dx} = R_i ,
\]

(7)

where \(\sigma\) is the conductivity of KCl solution, \(V\) is the applied electric potential, \(F\) is the Faraday constant, \(c_i\) is the bulk concentration of KCl solution, \(u_{m0}\) is the magnitude of ionic mobility for potassium (K+) or chloride (Cl-) ion, \(D_i\) is the diffusion coefficient of K+/Cl- ion, \(U_{ave}\) is the average EOF velocity, \(\zeta\) is the zeta potential, \(N_{total}\) is the total number of surface site density for silanol group (SiOH), \(K_A\) is the equilibrium constant for the deprotonation of SiOH group, \([H_2O^+]\) is the bulk concentration of hydronium ion, \(c_i, D_i, u_{m0}\) and \(R_i\) are the concentration, diffusion coefficient, ionic mobility and total reaction rate respectively, for each ionic species (except for K+ and Cl-). The ionic mobility is related to diffusion coefficient through the Einstein relation, \(D_i = u_{m0}k_BT/\zeta\sigma\), where \(k_B\) is the Boltzmann constant and \(\zeta_i\) is the ionic charge number.

Eq. (2) dictates the applied electrical potential distribution, which is determined by the conductivity of KCl solution. It is assumed that minority ions such as \(H_2O^+\) and bicarbonate ions \((HCO_3^-)\) do not contribute to the conductivity of the solution due to their low concentrations. The conductivity of the solution is related to the concentration of KCl by Eq. (3). Instead of modeling the KCl solution with K+ and Cl- ions separately, a single variable of conductivity \(\sigma\) is adopted because the diffusion coefficient and magnitude of ionic mobility for both ions are almost identical. The evolution of \(\sigma\) due to convection and diffusion is given by Eq. (4). The EOF velocity is provided by the slip velocity equation (Eq. (5)), which is calculated based on the zeta potential averaged along the entire capillary at every time instance. The local zeta potential is related to the bulk KCl concentration and pH through Eq. (6), which is obtained by equating Grahame equation with charge regulation model\(^{18,33}\). A series of Nernst-Planck equations (Eq. (7)) provide the concentration evolution of each minority ionic species under the effect of electromigration, diffusion, convection and reaction. Various chemical equilibrium equations including the auto-ionization of water and equilibria of carbonic acid (carbon dioxide dissolved in water) were also included (see Supporting Information).

The values of all constants employed in the numerical simulations are listed in Table S1 in the Supporting Information.

1. The 1-D simulation domain is a straight line with a length of 1cm. Although the 1-D simulation domain is 1cm, the simulation results can be related to the experimental results (length of 15cm) through the dimensionless interface position \(p\) as defined in Eq. (1). The inlet and outlet boundary conditions along with initial conditions are listed in Table 1. The applied voltage is set to 120V over the 1cm domain to generate similar electric field magnitude (120Vcm\(^{-1}\)) as the experiments. The initial concentrations of minority ions including \(H_2O^+\), \(OH^-\), \(HCO_3^-\), \(H_2CO_3\) and \(CO_3^{2-}\) were calculated based on the respective chemical equilibria (see Supporting Information), and set as the boundary and initial conditions. The initial concentration of \(KCl\) is \(1\text{mM}\). The boundary and initial conditions for each case are given in Table S1.

2. The pH values of 1mM and 0.2mM KCl are identical. The conductivity conditions are set according to the flow scenario based on the experiments. The line was meshed with 2000 elements. Convergence test was performed with higher number of elements and the numerical error was found to be negligible for this mesh selection. The maximum time step and total simulated time was set to 0.005s and 22s respectively.

3. Table 1: Boundary and initial conditions for 1-D numerical simulations for 0.2mM displacing 1mM KCl (HL) and 1mM displacing 0.2mM KCl (HL).

<table>
<thead>
<tr>
<th>Variables</th>
<th>Boundary conditions</th>
<th>Initial conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V)</td>
<td>120V</td>
<td>0</td>
</tr>
<tr>
<td>(c_i)</td>
<td>Initial concentration of minority ions for KCl</td>
<td></td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Conductivity of 0.2mM KCl</td>
<td></td>
</tr>
<tr>
<td>(HL): 0.2mM displacing 1mM KCl</td>
<td>Conductivity of 1mM KCl</td>
<td></td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Conductivity of 1mM KCl</td>
<td>Conductivity of 0.2mM KCl</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

Fig. 4A shows the experimental average pH variations at different interface positions for the two opposing flow directions. When 1mM KCl displaces 0.2mM KCl, the average pH increases from 5.64 (initial pH of KCl solutions) to 6.07 throughout the displacing process. In the reverse flow direction, i.e. 0.2mM KCl displaces 1mM, the average pH decreases from 5.64 to a minimum of 5.24 before increasing to 5.44 at the end of the displacement. Despite the increase from minimum pH, the final pH was still below the initial pH of 5.64.

A control experiment was conducted by filling both reservoirs with a solution of 0.6mM KCl (average of 1mM and 0.2mM). The control experiment only demonstrated a low pH increase of 0.1 (see Supporting Information) in comparison to the ±0.4 pH changes in the displacement flow of 1mM and 0.2mM KCl. The slight pH increase is potentially due to electrolytic reactions of water at the electrodes. Precautionary measures such as employing low solution concentration and large reservoirs (4ml) have been adopted to minimize the pH variation in micro-capillary due to electrolysis\(^{34}\). In conclusion, the experimental results demonstrate the definite dichotomic pH changes in micro-capillary depending on the flow directions, i.e. pH increases when a high conductivity solution displaces a low conductivity solution while pH decreases when a low conductivity solution displaces a high conductivity solution.

The numerical simulation reveals the mechanism for the pH change during the displacement flow of two solutions with different concentrations. The electric field distribution across the two solutions is determined by the conductance ratio between the two segments of fluid. The pH-governing minority ions are forced to
The simulated pH is averaged along the capillary and compared with the experimental results (see Fig. 4A). The diffusion coefficient of hydrogen ion in water is typically cited as $9.3 \times 10^{-9}$ m$^2$/s$^1$. With this value, it is found that the curves from numerical simulation have large discrepancies with the experimental data points, beyond the limit of experimental error.

**CONCLUSION**

In conclusion, we have presented conclusive evidence for the pH change during EOF involving two solutions with different concentrations. The average pH in micro-capillary was quantified with a pH-sensitive dye through color image processing. When a higher concentration solution displaced a lower concentration solution, a pH increase was observed, while the flow in the reverse direction caused a decrease in pH. pH-governing minority ions such as H$_2$O$^+$ and HCO$_3^-$ are depleted or accumulated at the interface between two solutions due to electromigrative flux imbalance, causing significant pH changes. The experimental results agree well with 1-D numerical simulations. The understanding of pH changes during EOF is important for accurate flow manipula-

![Figure 4](image)

**Figure 4.** (A) Experimental and numerical average pH variations at different dimensionless interface positions $p$ for 1mM KCl displaces 0.2mM KCl (HL), and 0.2mM KCl displaces 1mM KCl (LH). $D_{H_3O^+}$ is the diffusion coefficient of hydronium ion. (B) Simulated local pH distribution along the micro-capillary at various interface positions, which are marked with short vertical line.
tion in microfluidic channels and maintaining of constant pH in biological and chemical systems under an electric field.

3 ASSOCIATED CONTENT

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

6 ACKNOWLEDGMENTS

7 The authors would like to gratefully acknowledge Agency for Science, Technology and Research (A*STAR) for its financial support (SERC grant no. 122-PSF-0019). An Eng Lim thanks Nanyang Technological University (NTU) for awarding him a Ph.D. scholarship.

12 REFERENCES

31 (19) Lim, C. Y.; Lam, Y. C. Biomicrofluidics 2012, 6, 012816.
36 (24) Rodríguez, I.; Chandrasekhar, N. Electrophoresis 2005, 26, 1114-1121.
41 (29) Yadav, S. P.; Ibaraki, Y.; Dutta Gupta, S. Plant Cell, Tissue Organ Cult. 2010, 100, 183-188.
42 (30) Ng, W. Y.; Lam, Y. C.; Rodríguez, I. Biomicrofluidics 2009, 3, 022405.
Supporting Information

pH change in Electroosmotic Flow Hysteresis

Chun Yee Lim, An Eng Lim & Yee Cheong Lam*
School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

Corresponding Author
*Phone: +65 6790 6874. Fax: +65 6792 4062. E-mail: myclam@ntu.edu.sg.

Author Contributions
All authors contributed equally.

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 µS.cm⁻¹ and 147.9 µS.cm⁻¹ for 0.2 mM and 1 mM KCl respectively) to ensure that the effect of Joule heating is negligible. A conservative estimate of Joule heating can be calculated from the energy balance between the energy generation and the energy storage in the liquid. For the worst case scenario in our experiments (applied electric field = 120 V.cm⁻¹, solution conductivity of 1mM KCl = 147.9 µS.cm⁻¹, capillary diameter = 250 µm 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 (H₃O⁺) and hydroxide (OH⁻) ions from the undesirable electrolytic reactions at the electrodes. The reservoirs (4 ml) were designed to be significantly larger than the volume of the capillary (7.4 µL) to dilute the concentrations of H₃O⁺ and OH⁻ ions produced at the electrodes. 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 microchannel. More importantly, the current across the capillary was maintained at low values (1.8 - 8.6 µA) to minimize electron transfer at the electrodes, thus reducing the production of H₃O⁺ and OH⁻ ions at the electrodes. This was achieved by employing solutions with low conductivities (30.8 – 147.9 µS.cm⁻¹) and a long capillary (15 cm) with a small diameter (250 µm).
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>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permittivity of free space</td>
<td>$\varepsilon_0$ (C.V$^{-1}$.m$^{-1}$)</td>
<td>8.85 x 10$^{-12}$</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>$\varepsilon_r$</td>
<td>80</td>
</tr>
<tr>
<td>Viscosity of water</td>
<td>$\mu$ (kg.m$^{-1}$.s$^{-1}$)</td>
<td>8.90 x 10$^{-4}$</td>
</tr>
<tr>
<td>Density of water</td>
<td>$\rho$ (kg.m$^{-3}$)</td>
<td>1000</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>$F$ (C.mol$^{-1}$)</td>
<td>96485</td>
</tr>
<tr>
<td>Gas constant</td>
<td>$R$ (J.mol$^{-1}$K$^{-1}$)</td>
<td>8.314</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$k_B$ (J.K$^{-1}$)</td>
<td>1.38 x 10$^{-23}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$ (K)</td>
<td>298</td>
</tr>
<tr>
<td>Electron charge</td>
<td>$e$ (C)</td>
<td>1.602 x 10$^{-19}$</td>
</tr>
<tr>
<td>Diffusion coefficient of K$^+$/Cl$^-$ ion$^a$</td>
<td>$D_0$ (m$^2$.s$^{-1}$)</td>
<td>1.957 x 10$^{-9}$</td>
</tr>
<tr>
<td>Diffusion coefficient of H$_3$O$^+$ ion</td>
<td>$D_{H3O}^+$ (m$^2$.s$^{-1}$)</td>
<td>9.3 x 10$^{-9}$/2.3 x 10$^{-9}$</td>
</tr>
<tr>
<td>Diffusion coefficient of OH$^-$ ion</td>
<td>$D_{OH}^-$ (m$^2$.s$^{-1}$)</td>
<td>5.26 x 10$^{-9}$</td>
</tr>
<tr>
<td>Diffusion coefficient of H$_2$CO$_3$</td>
<td>$D_{H2CO3}$ (m$^2$.s$^{-1}$)</td>
<td>1.3 x 10$^{-9}$</td>
</tr>
<tr>
<td>Diffusion coefficient of HCO$_3$$^-$ ion</td>
<td>$D_{HCO3}$ (m$^2$.s$^{-1}$)</td>
<td>1.105 x 10$^{-9}$</td>
</tr>
<tr>
<td>Diffusion coefficient of CO$_3$$_2^-$ ion</td>
<td>$D_{CO3}^{2-}$ (m$^2$.s$^{-1}$)</td>
<td>9.2 x 10$^{-10}$</td>
</tr>
<tr>
<td>Magnitude of ionic mobility$^b$ of K$^+$/Cl$^-$ ion</td>
<td>$u_m0$ (m$^2$.V$^{-1}$.s$^{-1}$)</td>
<td>7.621 x 10$^{-8}$</td>
</tr>
<tr>
<td>Ionic mobility of H$_3$O$^+$ ion</td>
<td>$u_m(H3O^+)$ (m$^2$.V$^{-1}$.s$^{-1}$)</td>
<td>3.622 x 10$^{-7}$/8.957 x 10$^{-8}$</td>
</tr>
<tr>
<td>Ionic mobility of OH$^-$ ion</td>
<td>$u_m(OH^-)$ (m$^2$.V$^{-1}$.s$^{-1}$)</td>
<td>-2.048 x 10$^{-7}$</td>
</tr>
<tr>
<td>Ionic mobility of HCO$_3$$^-$ ion</td>
<td>$u_m(HCO3^-)$ (m$^2$.V$^{-1}$.s$^{-1}$)</td>
<td>-4.303 x 10$^{-8}$</td>
</tr>
<tr>
<td>Ionic mobility of CO$_3$$_2^-$ ion</td>
<td>$u_m(CO3^{2-})$ (m$^2$.V$^{-1}$.s$^{-1}$)</td>
<td>-7.166 x 10$^{-8}$</td>
</tr>
<tr>
<td>Ionic charge number of K$^+$/Cl$^-$ ion</td>
<td>$z_K^+/z_{Cl^-}$</td>
<td>+1/-1</td>
</tr>
</tbody>
</table>
### Ionic Charge Numbers

<table>
<thead>
<tr>
<th>Ion</th>
<th>Charge</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_3\text{O}^+)</td>
<td></td>
<td>+1</td>
</tr>
<tr>
<td>(\text{OH}^-)</td>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>(\text{HCO}_3^-)</td>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>(\text{CO}_3^{2-})</td>
<td></td>
<td>-2</td>
</tr>
</tbody>
</table>

### Equilibrium Constant of SiOH Deprotonation Reaction

\[ K_A = 6.310 \times 10^{-8} \]

### Total Number Site Density of SiOH

\[ N_{\text{Total}} = 8 \times 10^{18} \text{ m}^{-2} \]

### Partial Pressure of Carbon Dioxide

\[ P_{\text{CO}_2} = 3.5 \times 10^{-4} \text{ atm} \]

### Henry’s Law Constant

\[ K_H = (\text{L.atm.mol}^{-1}) = 29.76 \]

### Apparent Specific Forward Rate Constant of Water

\[ K_{fw} = (\text{mol.dm}^{-3}.\text{s}^{-1}) = 1 \times 10^{-4} \]

### Water Ionization Constant

\[ K_w = (\text{mol}^2.\text{dm}^{-6}) = 1 \times 10^{-14} \]

### Apparent Specific Forward Rate Constant of Carbonate System 1

\[ K_{fC1} = (\text{s}^{-1}) = 4.45 \]

### Equilibrium Constant of Carbonate System 1

\[ K_{C1} = (\text{mol.dm}^{-3}) = 4.45 \times 10^{-7} \]

### Apparent Specific Forward Rate Constant of Carbonate System 2

\[ K_{fC2} = (\text{s}^{-1}) = 0.469 \]

### Equilibrium Constant of Carbonate System 2

\[ K_{C2} = (\text{mol.dm}^{-3}) = 4.69 \times 10^{-11} \]

---

\(^a\)Diffusion coefficient of \(K^+\) is used to model a single variable of conductivity \((\sigma = 2Fc_0\mu_0)\), where \(c_0\) is the bulk concentration of KCl) as the diffusion coefficient and magnitude of ionic mobility for both \(K^+\) and \(\text{Cl}^-\) ions are almost identical.

\(^b\)Ionic mobility is related to diffusion coefficient through the Einstein relation, \(D_i = (\mu_im_kT)/(z_ie)\).
Reversible acid-base equilibria included in numerical simulations

The auto-ionization of water (H$_2$O):

$$2\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+,$$

where OH$^-$ and H$_3$O$^+$ represent the hydroxide and hydronium ions. The rate of the forward reaction $r_{fw}$ is

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

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

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

for which the value of [H$_2$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$_2$CO$_3^*$, undergoes deprotonations through the following acid-base equilibria:

$$\text{H}_2\text{CO}_3^* + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+,$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+. $$

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

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

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

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

where HCO$_3^-$ represents the bicarbonate ion. The rate of the forward reaction $r_{fC2}$ for carbonate system 2 (Equation S5) is

$$r_{fC2} = K_{fC2} [\text{HCO}_3^-] [\text{H}_2\text{O}],$$
where $K_{fC2}$ is the apparent specific forward rate constant of carbonate system 2. The equilibrium constant for carbonate system 2 is defined as:

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

where $\text{CO}_3^{2-}$ 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 $[\text{H}_2\text{CO}_3^\ast]$ must first be calculated from Henry’s law:

$$[\text{H}_2\text{CO}_3^\ast] = \frac{\text{PCO}_2}{K_H} \quad (S10)$$

where $\text{PCO}_2$ 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):

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

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

$$[\text{H}_3\text{O}^+] = 2.313 \mu\text{M},$$
$$[\text{OH}^-] = 4.32 \text{nM},$$
$$[\text{H}_2\text{CO}_3^\ast] = 12 \mu\text{M},$$
$$[\text{HCO}_3^-] = 2.309 \mu\text{M},$$
$$[\text{CO}_3^{2-}] = 46.8 \text{pM}.$$
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 µl 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.

Reference:

(3) Rodríguez, I.; Chandrasekhar, N. Electrophoresis 2005, 26, 1114-1121.