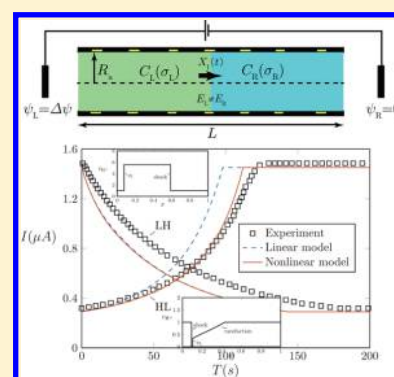


Reactive Transport of Protons in Electro-Osmotic Displacements with Electrolyte Concentration Difference in a Microcapillary

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Supporting Information

ABSTRACT: In this work, we model electro-osmotic displacement with electrolyte concentration difference in a microcapillary by incorporating proton transport coupled with surface complexation reaction and carbonate equilibrium. The hysteretic effect observed in experiments is well-captured by the model. By deriving the semianalytical solution of the nonlinear transport equation using method of characteristics, we elucidate the transport mechanism of protons by classifying their nonlinear transport behavior (shock/rarefaction/discontinuity) into several regimes depending on the concentration ratio and the pH. The model can be used to predict pH variation and characterizes surface property in electro-osmotic experiments.



Electro-osmotic flow (EOF) refers to flow driven by an electrical force exerted on the electrical double layer (EDL) at the solid/liquid interface under an applied electrical field. In microfluidic devices, electro-osmosis has been extensively used as a nonmechanical flow control technique for pumping,^{1,2} analyte separation,³ and mixing of fluids⁴ and offers new methods to characterize the surface potential of composite microchannels⁵ and protein adsorption.⁶ Significant efforts have been exerted toward the understanding of electro-osmotic flow in uniform solutions.^{7–10} However, less attention has been paid to the nonuniform electro-osmotic flow, i.e., displacing one solution by another with different concentration or ionic components.¹¹ This electro-osmotically driven displacement flow is commonly found in the operations of microfluidic devices and has also been used in the current monitoring method to measure the electro-osmotic velocity and ζ -potential.^{12,13}

As the receding solution is displaced by the displacing solution, the solution chemistry in the channel changes gradually. Since surface charge and the electrical field are generally dependent on the solution chemistry, the displacement process will be controlled by a *time-dependent* electro-osmotic velocity. Interestingly, it is experimentally observed that the displacement time by electro-osmosis differs depending on the flow direction. Specifically, the displacement time of a low-concentration solution by a high-concentration solution is longer than vice versa.¹⁴ This is called electro-osmotic flow hysteresis to emphasize the dependence of displacement time on the flow direction.¹⁵

Previous models for displacement flow by EOF^{14,16–18} only focus on the transport of salt ions, ignoring the effect of proton

transport. These models fail to capture the observed hysteretic behavior. Recently, Lim et al.¹⁵ proposed a new model incorporating proton transport with surface complexation and full solution chemistry in the electrolyte solution. The two-dimensional simulation in a miniature system shows good agreement with the experimental results. The authors found that the dependence of proton transport behavior on the flow direction is responsible for the observed hysteretic behavior. In short, due to the change of electrical field across the displacing interface, there is an imbalance of proton flux, leading to a proton accumulation/depletion zone depending on the flow direction. Further evidence of pH variation is provided in Lim et al.¹⁹ using fluorescence imaging. The authors also present a one-dimensional model by replacing the Navier–Stokes equation in the two-dimensional model by an averaged Helmholtz–Smoluchowski (H–S) formula.

In this work, we build a one-dimensional model for proton transport with simple solution chemistry and without dispersion to highlight the fundamental interactions, and then to present a mathematical analysis that gives insight into the root cause of hysteresis in EOF displacement. By comparing with the experimental results, we show that our model well-captures the hysteretic effect. Furthermore, our model allows analysis of the mathematical structure of the physical problem and generalizes the transport behavior of protons under a broader range of conditions.

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MATHEMATICAL FORMULATION AND SEMIANALYTICAL SOLUTION

We model the electro-osmotically driven displacement of two solutions in a negatively charged capillary with radius R_a and potential difference $\psi_L - \psi_R = \Delta\psi$. A solution with concentration C_R and conductivity σ_R is displaced by another solution with concentration C_L and conductivity σ_L as depicted in Figure 1. Two main assumptions are made to simplify

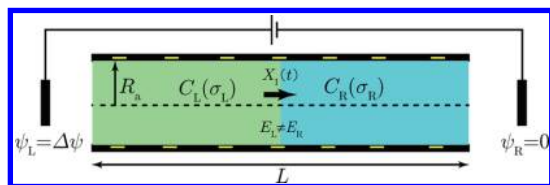


Figure 1. Schematic of electro-osmotic displacement of two solutions with different concentrations in a microcapillary.

the model. First, the thickness of EDL is assumed to be much smaller than the radius of the capillary, i.e., $\lambda_D \ll R_a$, where λ_D is the Debye length. For a typical microcapillary with $R_a \approx 50 \mu\text{m}$ and a concentration of 1 mM, the ratio of λ_D to R_a is about 2×10^{-4} . In this case, if the ζ -potential is not too large, the Dukhin number characterizing the contribution of surface conductivity is small.²⁰ Therefore, only the bulk conductivity needs to be considered in the electric current. Additionally, this thin double layer assumption makes it possible to study EOF in a nonuniformly charged system using an averaged EOF velocity without solving the detailed two-dimensional axisymmetric problem.²¹

The second assumption is that the diffusive flux of ions is much smaller than the advective flux so that a sharp interface between the two solutions persists during the displacement. The Peclet number, Pe , characterizing advective flux over diffusive flux for the electrolyte solution is estimated as $Pe = V_{\text{EOF}} R_a / D = (-e\zeta \Delta\psi R_a) / (\eta DL)$. By taking a typical ion diffusion coefficient $D = 1 \times 10^{-9} \text{ m}^2/\text{s}$ and a typical ζ -potential used in experiment $\zeta = -50 \text{ mV}$ and other parameters in Table 1, Pe is about 20 so that the sharp interface assumption of the electrolyte solution is generally valid. Strong mixing occurs near the interface due to the discontinuity of the wall electro-osmotic velocity, but it is generally confined in a small region for a slender capillary with large aspect ratio considered here. Additionally, a

diffusio-osmotic flow can be induced by concentration difference. It is shown in the Supporting Information that this diffusio-osmotic flow can be generally neglected compared to the electro-osmotic counterpart. Hydrodynamic dispersion owing to variations in wall electro-osmotic velocity may play an important role if the concentration difference becomes larger, but it will not change the general transport behavior determined by hyperbolic analysis.²² In cases that the solution chemistry is complicated, such as for dissimilar anionic solutions in Lim et al.,¹¹ or the concentration difference is very large, which can potentially generate strong dispersion due to variation of electro-osmotic slip velocity, a full simulation in 2D/3D would be necessary and provides detailed insight into the complicated process. On the basis of these two assumptions, a one-dimensional model is established to predict both the movement of the interface X_i and the time-dependent electric current I . In the following, we first revisit a one-dimensional EOF displacement model without proton transport first obtained by Tang et al.¹⁸ and prove that this model cannot capture the hysteretic effect. Then, the reactive transport of protons is considered by incorporating a surface complexation reaction of silica and carbonate equilibrium due to CO_2 dissolution. The nonlinear reactive transport equation for this model is solved semianalytically by constructing the displacing fronts, i.e., shocks, rarefaction, or discontinuity.

EOF Displacement without Proton Transport. By ignoring the diffusive flux of ions and the diffusion potential induced by the mismatch of ion diffusivities, the transport equation of electrolyte solution reads

$$\frac{\partial C}{\partial T} + \frac{\partial}{\partial X} (V_{\text{EOF}}(T)C) = 0 \quad (1)$$

where C is the concentration of electrolytes, e.g., KCl, and V_{EOF} is the time-dependent electro-osmotic velocity. Together with the inflow boundary condition $C(0, T) = C_L$ and the initial condition $C(X, 0) = C_R$, eq 1 gives a simple traveling wave solution consisting of piecewise constants:

$$C = \begin{cases} C_L & \text{for } 0 \leq X \leq X_i(T) \\ C_R & \text{for } X_i(T) < X \leq L \end{cases} \quad (2a)$$

Accordingly, the conductivity profile is

$$\sigma = \begin{cases} \sigma_L & \text{for } 0 \leq X \leq X_i(T) \\ \sigma_R & \text{for } X_i(T) < X \leq L \end{cases} \quad (2b)$$

Table 1. Parameters Used to Predict the Electric Current Curve in Figure 6

parameter	value ^a
temperature T_K	298 K
dynamic viscosity η	$0.89 \times 10^{-3} \text{ Pa s}$
permittivity of solution ϵ_0	$80 \times 8.854 \times 10^{-12} \text{ C/(V m)}$
diffusion coefficient of H^+	$9.312 \times 10^{-9} \text{ m}^2/\text{s}$
diffusion coefficient of HCO_3^-	$1.105 \times 10^{-9} \text{ m}^2/\text{s}$
equilibrium constant of $\text{H}^+ - \text{HCO}_3^-$ equilibrium K_{eq}	$5.34 \times 10^{-12} (\text{mol/L})^2$
equilibrium constant of silanol deprotonation K_{dep}	$6.31 \times 10^{-8} \text{ mol/L}$
maximum surface sites density Γ_{max}	$8 \times 10^{18} \text{ m}^{-2}$
capillary length L	$8 \times 10^{-2} \text{ m}$
capillary radius R_a	$50 \times 10^{-6} \text{ m}$
potential difference $\Delta\psi$	1000 V
concn of KCl solution	0.2 and 1 mM
pH of KCl solution	5.62 and 5.73

^aDiffusion coefficients of H^+ , HCO_3^- from ref 33; K_{eq} from ref 30; K_{dep} and Γ_{max} from ref 11.

The continuity of electric current gives

$$I = AE_L\sigma_L = AE_R\sigma_R \quad (3a)$$

where $A = \pi R_a^2$ is the cross-sectional area. The total potential drop across the capillary is

$$\Delta\psi = E_L X_I + E_R (L - X_I) \quad (3b)$$

Combining eq 3a and eq 3b, E_L and E_R are solved as

$$E = \begin{cases} E_L = \frac{\Delta\psi}{X_I + \gamma(L - X_I)} & \text{for } 0 \leq X \leq X_I(T) \\ E_R = \gamma E_L & \text{for } X_I(T) < X \leq L \end{cases} \quad (4)$$

where $\gamma = \sigma_L/\sigma_R$ denotes the conductivity ratio. The non-uniform distribution of concentration leads to a nonuniform distribution of surface charge, which will generally induce a two-dimensional flow pattern by external electrical field. A similar heterogeneously charged electrokinetic system has been studied for active control^{23,24} or due to structural surface heterogeneities²⁵ or surface reaction.^{26,27} Although the H-S formula for uniform surface charge cannot be directly applied here, it has been proven that the H-S formula is still valid in the averaged sense to describe the primary flow.^{21,28}

$$V_{\text{EOF}} = -\frac{\epsilon}{\eta} \langle \zeta E \rangle \quad (5)$$

where $\langle \cdot \rangle = \int_0^L \cdot dX/L$ is the longitudinal averaging operator, ϵ is the permittivity, and η is the dynamic viscosity of the solutions. The ζ -potential depends on the local chemistry of the solution, i.e., the electrolyte concentration and pH:

$$\zeta = \begin{cases} \zeta_L(C_L, \text{pH}_L) & \text{for } 0 \leq X \leq X_I(T) \\ \zeta_R(C_R, \text{pH}_R) & \text{for } X_I(T) < X \leq L \end{cases} \quad (6)$$

where pH_L and pH_R are the pH of the left and the right solution. Then, eq 5 can be written as

$$V_{\text{EOF}} = -\frac{\epsilon}{\eta} \left(\zeta_L E_L \frac{X_I}{L} + \zeta_R E_R \frac{L - X_I}{L} \right) \quad (7)$$

The displacing interface moves at the speed of V_{EOF} , i.e., $dX_I/dT = V_{\text{EOF}}$. Substituting eq 7 for V_{EOF} and eq 4 for E_L and E_R leads to an ordinary differential equation of X_I :

$$\frac{dX_I}{dT} = -\frac{\epsilon \Delta\psi}{\eta L} \left(\frac{\zeta_L X_I/L + \zeta_R \gamma (1 - X_I/L)}{X_I/L + \gamma (1 - X_I/L)} \right) \quad (8)$$

Once X_I is obtained by solving eq 8, the electric current is determined by

$$I = \frac{A \Delta\psi \sigma_L}{X_I + \gamma(L - X_I)} \quad (9)$$

Next, we introduce the following characteristic quantities to nondimensionalize the problem:

$$x = X/L, \quad t = T/(L^2 \eta / (-e \zeta_{\text{ref}} \Delta\psi)), \quad v_{\text{EOF}} = V_{\text{EOF}} / (-e \zeta_{\text{ref}} \Delta\psi / \eta L), \quad \mathcal{E} = E / (\Delta\psi / L), \quad i = I / (A \Delta\psi \sigma_{\text{ref}} / L) \quad (10)$$

where $\zeta_{\text{ref}} = -k_B T / e$ and $\sigma_{\text{ref}} = \max(\sigma_L, \sigma_R)$ are the reference ζ -potential and conductivity with k_B , T_K , and e denoting the Boltzmann constant, absolute temperature, and the elementary charge, respectively. The two reference values are chosen to

make the characteristic time and electric current independent of the direction of the displacement. We then rewrite eq 8 and eq 9 in dimensionless forms:

$$\frac{dx_I}{dt} = \frac{\bar{\zeta}_R (\beta - \gamma)x_I + \gamma}{\bar{\zeta}_R (1 - \gamma)x_I + \gamma} \quad (11)$$

$$i = \frac{\gamma}{\max(1, \gamma)((1 - \gamma)x_I + \gamma)} \quad (12)$$

where $\beta = \zeta_L/\zeta_R$, $\bar{\zeta}_R = \zeta_R/\zeta_{\text{ref}}$, and γ are the three dimensionless groups. Equations 11 and 12 are the same as eqs 13 and 5 in Tang et al.¹⁸ with a difference in notation. By integration, eq 11 can be solved as

$$x_I + \frac{\gamma(\beta - 1)}{(1 - \gamma)(\beta - \gamma)} \ln \left(\frac{\beta - \gamma}{\gamma} x_I + 1 \right) = \bar{\zeta}_R \frac{\beta - \gamma}{1 - \gamma} t \quad (13)$$

where t is the displacement time when $x_I = 1$. We denote t' and t'' as the displacement times with opposite flow directions. It follows that $\gamma' = 1/\gamma''$, $\beta' = 1/\beta''$, and $\beta' = \bar{\zeta}_R''/\bar{\zeta}_R'$. Substituting into eq 11 shows that $t' = t''$. Therefore, the displacement time is independent of the flow direction. This means that the hysteretic effect will not be observed in this model even though the ζ -potential dependence on concentration is considered. And it is worth noting that, as no surface chemistry model has been introduced to relate β to γ , this conclusion is valid for any surface chemistry models.

Proton Transport Model. To account for the hysteresis phenomenon, Lim et al.¹⁵ proposed that the effect of proton transport on the electro-osmotic displacement has to be considered. They argue that the electrical field has a sharp change across the displacing interface (see eq 4) so that the electromigration flux of H^+ is unbalanced at the interface. If $E_L > E_R$, the flux drops across the interface, leading to an accumulation of protons ahead of the interface, whereas if $E_L < E_R$, the flux increases across the interface leading to depletion. This will further change the averaged ζ -potential and the electro-osmotic velocity V_{EOF} . In order to achieve a clear understanding of the proton transport behavior, we establish a reactive transport model for protons to capture the essential physical mechanism in the EOF displacement process. Specifically, the model includes proton exchange on silica surface by surface complexation reaction. Besides, we consider an open system connected to the atmosphere so that carbonate equilibrium between proton and carbonate species due to CO_2 dissolution is included.

First, a diffuse-layer surface complexation model is employed to describe the surface reactions at the silica/solution interface.²⁹ This model assumes that the surface charge density is dominated by the deprotonation reaction of silanol groups:



so that the surface charge density $\Sigma_s = -[>\text{SiO}^-]F$, where $[>\text{SiO}^-]$ is the surface concentration of $>\text{SiO}^-$ groups and F is the Faraday constant. In this model, the equilibrium constant of deprotonation K_{dep} and the maximum surface sites density Γ_{max} need to be characterized by ζ -potential measurements. Further details on the surface complexation model are given in the Supporting Information. Figure 2a shows the dependence of ζ -potential on pH. In general, the magnitude of ζ -potential increases with the increase of pH.

Besides surface complexation, the proton transport model must also consider autoionization of water and carbonate speciation due to CO_2 dissolution:

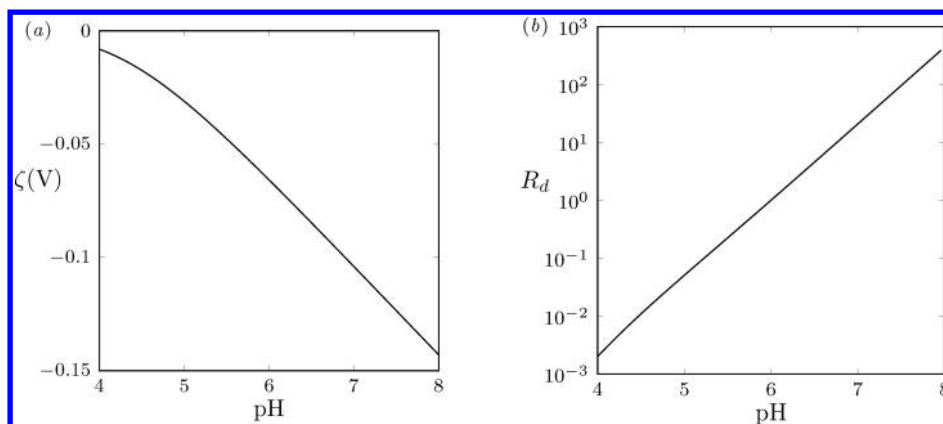
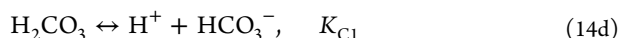
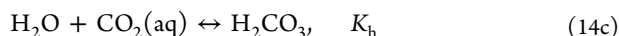
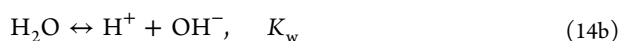


Figure 2. pH dependence of (a) ζ -potential and (b) retardation factor R_d in the diffuse-layer surface complexation model. $R_a = 50 \mu\text{m}$ is used in computing R_d .



where the dissociation of bicarbonate into carbonate is ignored, which is generally valid for pH below 8.5 as the bicarbonate ion is still the dominant species in the carbonate speciation diagram. Reactions in eq 14 involve eight components, and the total concentration of four linearly independent basis components are specified:

$$\Sigma\text{H} = -\{\text{SiO}^-\} + \{\text{H}^+\} - \{\text{HCO}_3^-\} - \{\text{OH}^-\} \quad (15a)$$

$$\Sigma\text{Si} = \{\text{SiOH}\} + \{\text{SiO}^-\} \quad (15b)$$

$$\Sigma\text{C} = \{\text{HCO}_3^-\} + \{\text{CO}_2(\text{aq})\} + \{\text{H}_2\text{CO}_3\} \quad (15c)$$

$$\Sigma\text{H}_2\text{O} = \{\text{HCO}_3^-\} + \{\text{H}_2\text{O}\} + \{\text{H}_2\text{CO}_3\} \quad (15d)$$

where $\{\}$ denotes bulk concentration in the solution, $\{\text{SiOH}\} = \phi[\text{SiOH}]$, and $\{\text{SiO}^-\} = \phi[\text{SiO}^-]$ with $\phi = 2/R_a$ being the surface to volume ratio of the capillary.

Transport of the total proton concentration is described by the conservation equation:

$$\begin{aligned} \frac{\partial}{\partial T}(-\{\text{SiO}^-\} + \{\text{H}^+\} - \{\text{HCO}_3^-\} - \{\text{OH}^-\}) \\ + \frac{\partial}{\partial X}(f(\{\text{H}^+\}) - f(\{\text{HCO}_3^-\}) - f(\{\text{OH}^-\})) = 0 \end{aligned} \quad (16)$$

where f denotes the flux of the component. The effect of surface adsorption is rewritten as a retardation term as $\partial\{\text{SiO}^-\}/\partial T = -\phi\partial S_{\text{H}^+}/\partial T = -R_d \partial C_{\text{H}^+}/\partial T$, where S_{H^+} is the adsorbed concentration of proton due to surface complexation and $R_d = 2/R_a \text{d}S_{\text{H}^+}/\text{d}C_{\text{H}^+}$ is the retardation factor. In the following, we make some simplifications to eq 16. First, we assume that the solution is equilibrated with the atmosphere so that $\{\text{CO}_2(\text{aq})\}$ is a constant and given by Henry's law. Combining eq 14c and eq 14d gives

$$\{\text{H}^+\}\{\text{HCO}_3^-\} = K_h K_{C1} \{\text{CO}_2(\text{aq})\} = K_{\text{eq}} \quad (17)$$

Typically, $K_{\text{eq}} \gg K_w$ (e.g., at room temperature, $K_{\text{eq}} = 5.34 \times 10^{-12} \text{mol}^2/\text{L}^2$ and $K_w = 10^{-14} \text{mol}^2/\text{L}^2$)³⁰ so that $\{\text{HCO}_3^-\} \gg \{\text{OH}^-\}$ and the effect of OH^- is negligible. Then, the diffusive

flux is ignored. With these simplifications, eq 16 can be written as

$$\begin{aligned} R_d \frac{\partial C_{\text{H}^+}}{\partial T} + \frac{\partial}{\partial T} \left(C_{\text{H}^+} - \frac{K_{\text{eq}}}{C_{\text{H}^+}} \right) \\ + \frac{\partial}{\partial X} \left(v_{\text{EOF}} \left(C_{\text{H}^+} - \frac{K_{\text{eq}}}{C_{\text{H}^+}} \right) + E \left(\mu_{\text{H}^+} C_{\text{H}^+} + \mu_{\text{HCO}_3^-} \frac{K_{\text{eq}}}{C_{\text{H}^+}} \right) \right) = 0 \end{aligned} \quad (18)$$

where $C_{\text{H}^+} = \{\text{H}^+\}$ and μ_{H^+} is the mobility of protons. By choosing the characteristic proton concentration $\tilde{C}_{\text{H}^+} = K_{\text{eq}} \sim 2.31 \times 10^{-6} \text{mol/L}$ such that $c_{\text{H}^+} = C_{\text{H}^+}/\tilde{C}_{\text{H}^+}$, the dimensionless form of eq 18 can be written as

$$\begin{aligned} R_d \frac{\partial c_{\text{H}^+}}{\partial t} + \frac{\partial}{\partial t} \left(c_{\text{H}^+} - \frac{1}{c_{\text{H}^+}} \right) \\ + \frac{\partial}{\partial x} \left(v_{\text{EOF}} \left(c_{\text{H}^+} - \frac{1}{c_{\text{H}^+}} \right) + \bar{\mu}_{\text{H}^+} \mathcal{E} \left(c_{\text{H}^+} + \frac{1}{\theta c_{\text{H}^+}} \right) \right) = 0 \end{aligned} \quad (19)$$

where $\bar{\mu}_{\text{H}^+} = \mu_{\text{H}^+}/(-e\zeta_{\text{ref}}/\eta)$ is the dimensionless mobility of proton and $\theta = \mu_{\text{H}^+}/\mu_{\text{HCO}_3^-}$ (~ 8) is the mobility ratio of proton and bicarbonate ion. Generally, eq 19 is a nonlinear hyperbolic equation with discontinuous coefficient $\mathcal{E}$.

As shown in Figure 2b, the retardation factor increases with pH and has only a minor effect on transport if the pH is lower than 6 for a typical microfluidic capillary with radius $R_a = 50 \mu\text{m}$. On the contrary, the retardation factor becomes larger than unity as pH increases. In this case, however, the chemical equilibrium between H^+ and HCO_3^- will be dominant since the nonlinear term $1/c_{\text{H}^+}$ is much larger than c_{H^+} so that the retardation effect can be ignored. Therefore, we will generally disregard the retardation effect in deriving the semianalytical solution of eq 19. A numerical solution including the retardation term and a detailed discussion about the retardation effect are given in the Supporting Information. It should be noted that, with the decrease of the capillary radius, or more generally, the increase of the surface to volume ratio ϕ (usually large in porous media), the retardation factor becomes large and plays an important role in proton transport. The nonlinearity in the retardation term can generate more complicated transport behaviors depending on the surface chemistry models.³¹

Semianalytical Solution for Proton Transport. In this part, we first present the solution for a reduced linear equation

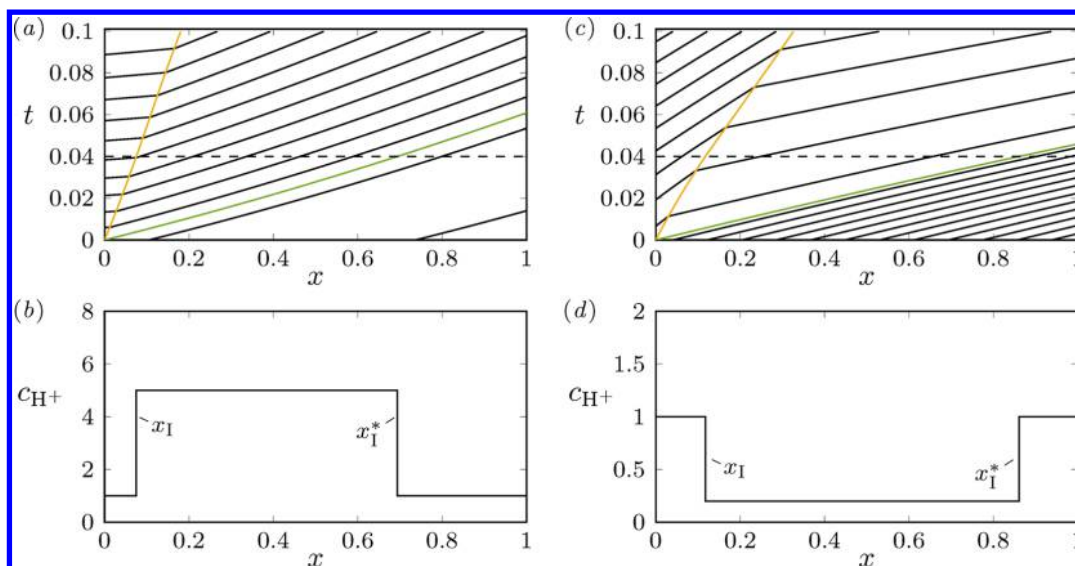


Figure 3. Characteristics and profile of proton concentration at $t = 0.04$ for the linear proton transport model (eq 20). Panels a and b demonstrate the case of a low-concentration solution displacing a high-concentration solution ($\gamma = 0.2$), which leads to a proton accumulation zone. Panels c and d show the case of a high-concentration solution displacing a low-concentration solution ($\gamma = 5$), leading to a proton depletion zone.

of eq 19. This linear model gives rise to the intuitive physical picture of proton accumulation/depletion. Then, we derive a semianalytical solution for the nonlinear equation by method of characteristics, which has been routinely used for chromatographic analysis in chemical engineering.²²

If the concentration of proton is dominant over the concentration of bicarbonate, i.e., $c_{H^+} \gg 1/c_{H^+}$, eq 19 can be simplified to a linear form:

$$\frac{\partial c_{H^+}}{\partial t} + \frac{\partial}{\partial x}((v_{EOF} + \bar{\mu}_{H^+}\mathcal{E})c_{H^+}) = 0 \quad (20)$$

Because of the discontinuity in the electrical field $\mathcal{E}$, the solution of eq 20 is made up of three piecewise constants:

$$c_{H^+} = \begin{cases} c_{H^+,L} & \text{for } 0 \leq x \leq x_I(t) \\ c_{H^+}^* & \text{for } x_I(t) < x \leq x_I^*(t) \\ c_{H^+,R} & \text{for } x_I^*(t) < x \leq 1 \end{cases} \quad (21)$$

where $x_I^* = x_I + \int \bar{\mu}_{H^+}\mathcal{E}_R dt$ is the position of a front interface ahead of the displacing interface and the intermediate concentration of proton $c_{H^+}^*$ is determined from the mass conservation at the displacing interface³² as

$$c_{H^+}^* = \frac{\mathcal{E}_L}{\mathcal{E}_R} c_{H^+,L} = c_{H^+,L}/\gamma \quad (22)$$

Correspondingly, the distribution of ζ -potential is

$$\zeta = \begin{cases} \zeta_L & \text{for } 0 \leq x \leq x_I(t) \\ \zeta^* & \text{for } x_I(t) < x \leq x_I^*(t) \\ \zeta_R & \text{for } x_I^*(t) < x \leq 1 \end{cases} \quad (23)$$

By using eq 5 to calculate the averaged EOF velocity and replace v_{EOF} by dx_I/dt , we obtain an ODE for x_I :

$$\frac{dx_I}{dt} = \frac{(\beta - \gamma)x_I + \gamma + \gamma(\beta^* - 1)\min(1 - x_I, \int_0^t \bar{\mu}_{H^+}\mathcal{E}_R dt)}{(1 - \gamma)x_I + \gamma} \quad (24)$$

where $\beta^* = \zeta^*/\zeta_R$ and the minimum operator accounts for both scenarios when $x_I^* \leq 1$ and $x_I^* > 1$. When $\beta^* = 1$, the intermediate pH is the same with that of the solution on the right, and eq 24 reduces to eq 11 in the constant pH model. However, since $\gamma \neq 1$ in general, $\beta^* \neq 1$. Equation 24 is a nonlinear integro-differential equation and needs to be solved numerically. Figure 3 shows the characteristics and proton concentration profile at $t = 0.04$. In Figure 3, panels a and b, because the characteristic speed goes down (dt/dx increases) across the displacing interface, protons accumulate in the intermediate region. Contrarily, in Figure 3, panels c and d, proton is depleted as the characteristic speed rises up.

To deal with the nonlinear eq 19, we introduce the following accumulation function $\mathcal{A}(c_{H^+})$ and flux function $\mathcal{F}(c_{H^+})$:

$$\mathcal{A}(c_{H^+}) = c_{H^+} - \frac{1}{c_{H^+}} \quad (25a)$$

$$\begin{aligned} \mathcal{F}(c_{H^+}) &= v_{EOF}\left(c_{H^+} - \frac{1}{c_{H^+}}\right) + \bar{\mu}_{H^+}\mathcal{E}\left(c_{H^+} + \frac{1}{\theta c_{H^+}}\right) \\ &= v_{EOF}\mathcal{A} + \bar{\mu}_{H^+}\mathcal{E}\left(\frac{\theta - 1}{2\theta}\mathcal{A} + \frac{\theta + 1}{2\theta}\sqrt{\mathcal{A}^2 + 4}\right) \end{aligned} \quad (25b)$$

to write eq 19 in a hyperbolic form

$$\frac{\partial \mathcal{A}}{\partial t} + \frac{\partial \mathcal{F}}{\partial x} = 0 \quad (26)$$

The characteristics of eq 26 are

$$\frac{dx}{dt} = \frac{d\mathcal{F}}{d\mathcal{A}} = v_{EOF} + \frac{c_{H^+}^2 - 1/\theta}{c_{H^+}^2 + 1}\bar{\mu}_{H^+}\mathcal{E} \quad (27)$$

When $c_{H^+} \gg 1$, eq 27 reduces to the characteristics of the linear proton transport eq 20:

$$\frac{dx}{dt} = v_{EOF} + \bar{\mu}_{H^+}\mathcal{E} \quad (28)$$

Note that the characteristics have two different branches due to the difference between $\mathcal{E}_L$ and $\mathcal{E}_R$. It can be proven that the

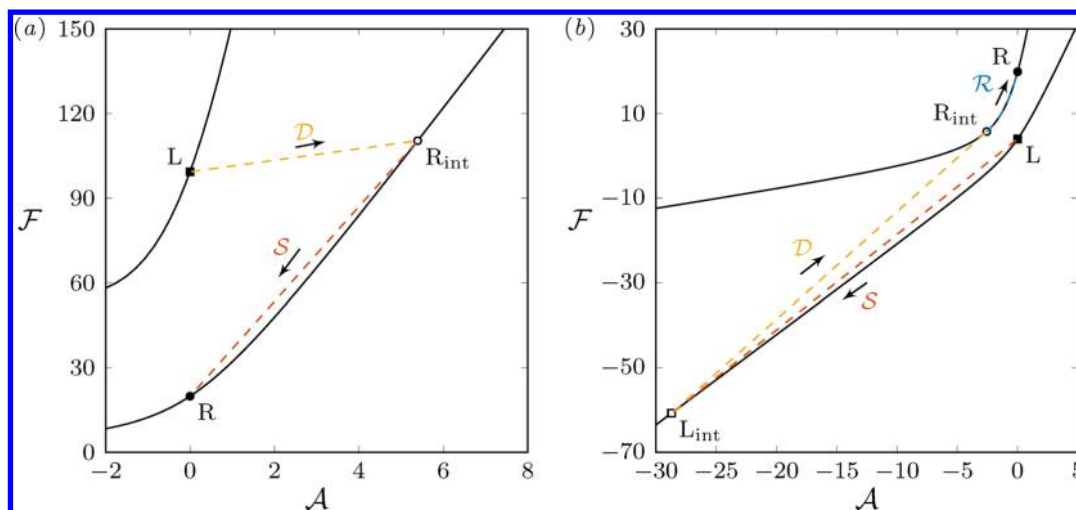


Figure 4. Construction of the waves for (a) low concentration displacing high concentration and (b) high concentration displacing low concentration at $t = 0$. S , R , and D denote the shock, rarefaction, and discontinuity path, respectively. In this case, the initial and injected proton concentration $c_{H^+,L}$ and $c_{H^+,R}$ are set to unity.

characteristic speed dx/dt increases monotonically with c_{H^+} in eq 27. Therefore, instead of a proton accumulation/depletion zone, there will be a shock/rarefaction wave ahead of the displacing interface. The wave structures are constructed in an $\mathcal{F} - \mathcal{A}$ diagram shown in Figure 4 for a case with $c_{H^+,L} = c_{H^+,R} = 1$ ($\mathcal{A} = 0$). The two solid curves represent the two branches of the flux function with $\mathcal{E}_L$ and $\mathcal{E}_R$. L and R denote the state of the left solution (displacing solution) and the right solution (receding solution). D , S , and R denote a discontinuity path across x_i , a shock path, and a rarefaction path, respectively. For the case of a low-concentration solution displacing a high-concentration one, the state first jumps from L on the left branch to an intermediate state R_{int} on the right branch, and then connects R_{int} to R by a shock path. For the reverse case under the specified conditions, a direct jump from L to the right branch is not possible. Hence, there must be a shock path S from L to L_{int} first and jumps from L_{int} to another intermediate state R_{int} tangential to the right branch by the discontinuity path D . Finally, the state follows a rarefaction path to the state of the right solution R . It can be proven that these are the only admissible paths for each case. Details about determining the intermediate states and a comparison with numerical simulations are given in the Supporting Information. Note that although the shape of the flux function changes with time due to the change in $\mathcal{E}$, the intermediate states are proven to be independent of time. The shock speed is determined by the jump condition

$$\mathcal{V} = \frac{[\mathcal{F}]}{[\mathcal{A}]} \quad (29)$$

where $\mathcal{V}$ is the velocity and $[\cdot]$ is the jump across the shock. As to the rarefaction wave, an implicit problem has to be solved. To obtain the analytical solution is intractable for this coupled process, so we solve it numerically. After constructing the wave structures and determining the intermediate states, the profile of proton concentration can be constructed. Then, the electro-osmotic velocity is obtained by eq 5. This procedure is repeated for every time step. Note that the proton transport behavior generally depends on the initial and the final state and a thorough discussion on this topic will be given in the results.

Figure 5 shows the characteristics and concentration profile of the nonlinear model (eq 19) at $t = 0.04$. Compared with the linear model, the shock wave in Figure 5b moves slower than the front interface x_i^* in Figure 3b, but the intermediate value is slightly larger than that in Figure 3b. The formation of the rarefaction wave greatly smooths the depletion zone in Figure 3d and will have an impact on the electro-osmotic velocity.

RESULTS AND DISCUSSION

In this section, we first show that the model presented above captures the hysteretic effect by comparing with the experimental results. Then, we extend the previous semianalytical solution to general initial and injected proton concentrations by presenting a regime diagram of proton transport behaviors. Due to the discontinuity and nonlinearity in the system, the intermediate pH may be out of the range of the initial and injected pH. We will discuss when this “unexpected” pH occurs and the effect of concentration ratio on the intermediate pH.

As stated previously, the electrical properties of the fluid are a function of solution chemistry. Therefore, the electric current can be used to monitor the EOF displacement process. Figure 6 shows the measurement of electric current in a microfluidic experiment¹⁵ and the corresponding model predictions using parameters in Table 1. It is worth mentioning that we use a value of $9.312 \times 10^{-9} \text{ m}^2/\text{s}$ for proton diffusion coefficient instead of $7 \times 10^{-10} \text{ m}^2/\text{s}$ used in Lim et al.¹⁵ as the former one is more commonly used in classical literature.³³ Because the diffusion coefficient of proton is larger compared with that of the electrolyte solution, the corresponding Peclet number drops to around 2. This will smear any variation of the proton concentration and reduce the hysteresis effect, but will not change the basic transport behavior determined by the hyperbolic analysis.²²

As shown in Figure 5, the asymmetric proton transport behavior for $\gamma < 1$ and $\gamma > 1$ will give rise to the hysteretic effect. In the LH case, i.e., a low-concentration solution displacing a high-concentration one, because of the accumulation of proton in the intermediate state, the magnitude of the averaged ζ -potential in the channel is reduced so that the displacement time measured by the electric current increases. On the contrary, the shorter displacement time in the HL case

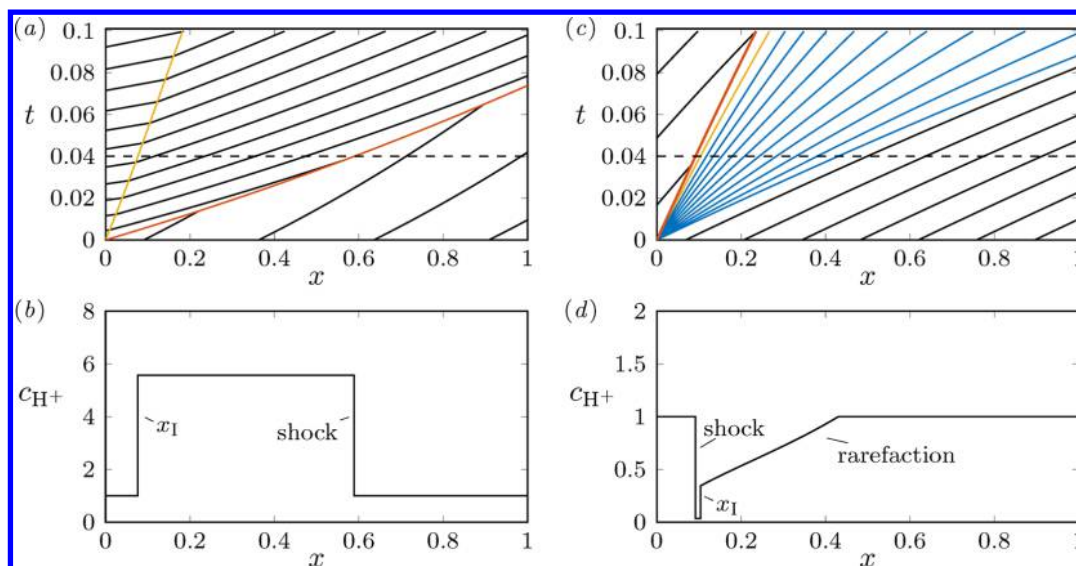


Figure 5. Characteristics and profile of proton concentration at $t = 0.04$ for nonlinear proton transport model. Panels a and b demonstrate the case of a low-concentration solution displacing high-concentration one ($\gamma = 0.2$). A shock wave ahead of the displacing interface is formed where the characteristics collide. Panels c and d show the case of a high-concentration solution displacing low-concentration one ($\gamma = 5$). There is a rarefaction wave ahead of and a shock wave behind the displacing interface. In this case, the initial and injected proton concentration $c_{H^+,L}$ and $c_{H^+,R}$ are set to unity.

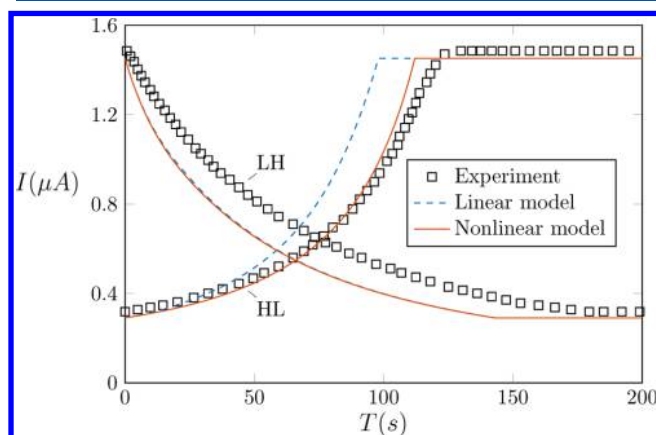


Figure 6. Comparison of electric current curves between experimental results (ref 15) (squares) and model predictions using parameters in Table 1 (dashed, linear model; solid, nonlinear model). LH denotes a low-concentration displacing high-concentration case with $\gamma = 0.2$, and HL denotes a high-concentration displacing low-concentration case with $\gamma = 5$.

is attributed to the fact that the induced depletion zone increases the averaged ζ -potential. This hysteretic behavior can be captured by both the linear and nonlinear proton transport model, but the nonlinear model has a better quantitative agreement with the experimental data for the HL case. As to the LH case, the two predictions are similar because the shock wave in the nonlinear model moves with a slower speed and larger intermediate proton concentration than the front interface x_i^* in the linear model, as shown by the proton concentration profiles in Figure 5, panels a and b. Therefore, the average ζ -potential is similar in both models. Although the electric current in this case is generally smaller than the experimental data, the predictability of the current model is still acceptable considering no tunable parameters are introduced. The equilibrium constant of deprotonation, K_{dep} , and the maximum surface sites density, Γ_{max} , in the surface

chemistry model are the same as that in Lim et al.,¹⁵ determined by fitting model with ζ -potential measurements. The displacement times are sensitive to the values of K_{dep} and Γ_{max} , which suggests that the present model can be used to characterize the surface property by monitoring the electric current, similar to the idea in Kuo et al.⁵ although the authors use a model without proton transport. The other possible reason for the discrepancy may be that, in the LH case, the sharp shock front is smoothed by dispersion effect and thus the shock speed is reduced. This will compress the accumulation region and increase the average ζ -potential in the system so that the displacement time is decreased.

Next, the semianalytical solution constructed in the previous section for the case $c_{H^+,L} = c_{H^+,R} = 1$ is extended to general initial and injected proton concentration of the corresponding solution. The proton transport behaviors can be categorized into several regimes in a $c_{H^+,L}$ – $c_{H^+,R}$ diagram. For the LH case with $\gamma < 1$, there are three regimes of the transport behavior shown in Figure 7a, where c_{H^+,R_{crt}^-} and c_{H^+,R_{crt}^+} are two critical final states, determined by intersecting the discontinuity path from L with the flux function of the right branch. Specifically, if $c_{H^+,R} < c_{H^+,R_{\text{crt}}^-}$, the initial state on the left branch will first connect to an intermediate state by a slow-moving or even left-moving shock, and then jump to the final state (regime ①). If $c_{H^+,R} > c_{H^+,R_{\text{crt}}^+}$, the initial state on the left branch will first connect to c_{H^+,R_{crt}^+} through the discontinuity, and then connect to the final state by a shock (regime ②) or rarefaction (regime ③) depending on the relative position of $c_{H^+,R}$ to c_{H^+,R_{crt}^+} .

As regard to the HL case with $\gamma > 1$, the transport diagram is divided into four regimes in Figure 7b, where $c_{H^+,L_{\text{crt}}}$ and $c_{H^+,R_{\text{crt}}}$ are the critical initial and final state, respectively. The critical final state $c_{H^+,R_{\text{crt}}}$ is the one on the right branch with a slope of v_{EOF} and tangential to the discontinuity path. It can be analytically determined as

$$\mathcal{A}_{R_{\text{int}}} = \frac{1 - \theta}{\sqrt{\theta}} \quad (30a)$$

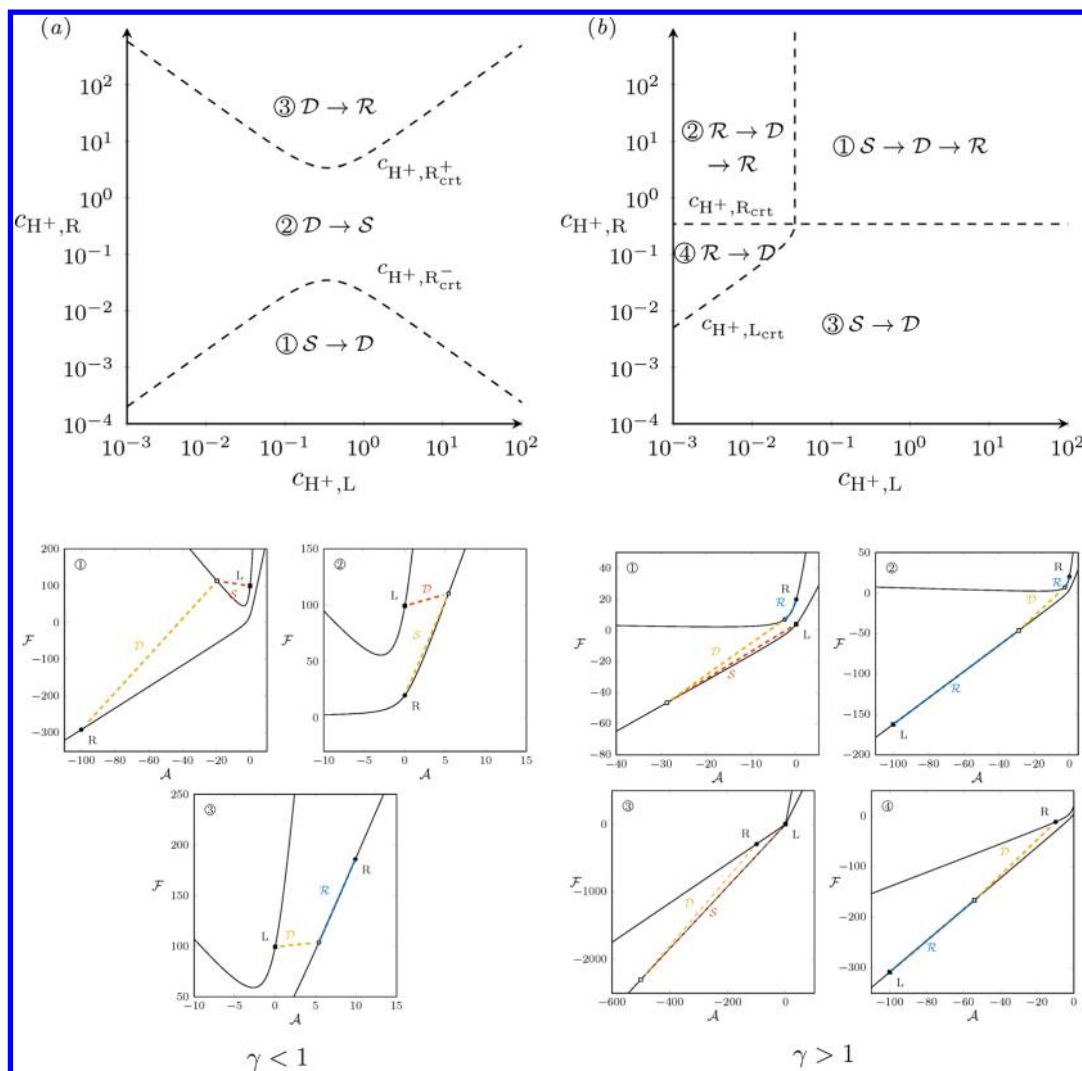


Figure 7. Diagram of proton transport behaviors for (a) $\gamma < 1$ and (b) $\gamma > 1$ and examples of the regimes. $\mathcal{D}$, $\mathcal{S}$, and $\mathcal{R}$ refer to the discontinuity path across x_i , shock path, and rarefaction path, respectively. In panel a, $c_{H^+,R}^{+}$ and $c_{H^+,R}^{-}$ are the critical states determined as the two intersections of the discontinuity path and the flux curve of the right branch. In panel b, $c_{H^+,L}^{crt}$ and $c_{H^+,R}^{crt}$ are the critical initial and final state.

which is only a function of θ . If $c_{H^+,R} > c_{H^+,R}^{crt}$ the corresponding critical state on the left branch is

$$\mathcal{A}_{L_{int}} = \frac{1 - \theta}{\sqrt{\theta}} \gamma - \frac{1 + \theta}{\sqrt{\theta}} \sqrt{\gamma^2 - 1} \quad (30b)$$

The critical discontinuity jump is necessary to connect $c_{H^+,L}^{crt}$ and $c_{H^+,R}^{crt}$ followed by a rarefaction wave. Depending on the state of the left solution, there will be a shock (①) or rarefaction (②) wave. If $c_{H^+,R} < c_{H^+,R}^{crt}$ the critical left state $c_{H^+,L}^{crt}$ is a function of the final state $c_{H^+,R}$. The discontinuity jump connects the intermediate state on the left branch directly to the final state on the right branch. Similarly, the initial shock (③) or rarefaction (④) wave is determined by the relative position between the initial state L and the intermediate state L_{int} on the left branch. If $\gamma = 1$, the two branches of the flux function collapse into one, and a simple shock or rarefaction wave will form depending on whether $c_{H^+,L}$ is larger or smaller than $c_{H^+,R}$.

In the linear proton transport model, the intermediate proton concentration is proportional to the inverse of the concentration ratio $1/\gamma$. If $\gamma \ll 1$ or $\gamma \gg 1$, this can be substantially above/below the injected proton concentration

because of accumulation/depletion. Similarly, the intermediate concentration in the nonlinear model can be out of the range between the initial and the injected proton concentration. This case is more complicated as the intermediate concentration in the nonlinear model may depend on both the initial and the injected solution, whereas in the linear model it only depends on the injected solution. This can be seen in Figure 7 as the proton concentration varies monotonically with the accumulation flux function $\mathcal{A}$. The intermediate proton concentration will be larger than both the initial (R) and the injected proton concentration (L) in regime ② when $\gamma < 1$ and smaller than R and L in regimes ① and ③ when $\gamma > 1$. Figure 8 shows the intermediate proton concentration for different γ with $c_{H^+,L} = c_{H^+,R} = 1$. When $\gamma \gg 1$ or $\gamma \ll 1$, the scaling of the nonlinear model is asymptotic to 1, being the same as the linear model. However, for $\gamma > 1$, due to the shock wave behind the displacing interface in regime ①, the nonlinear model will induce a proton concentration about 10 times lower than that of the linear model, i.e., one unit of pH larger. These unexpected pH changes should be carefully taken into account for some pH-sensitive devices or biological systems.

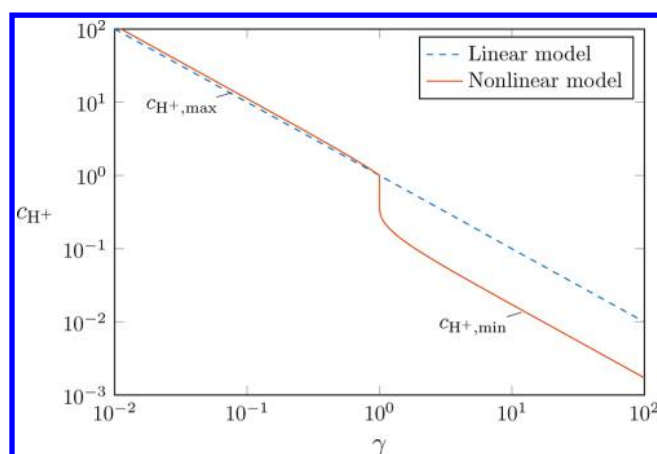


Figure 8. Amplified ($\gamma < 1$) or reduced ($\gamma > 1$) intermediate proton concentration. Dashed lines are results of the linear proton transport model $c_{H^+}^* = c_{H^+,L}^*/\gamma$, and solid lines are results of the nonlinear proton transport model. $c_{H^+,L}^* = c_{H^+,R}^* = 1$ in this case.

CONCLUSION

This paper presents a one-dimensional model for displacement by EOF with electrolyte concentration difference in a microcapillary. The current model is derived with the assumptions that (I) the double layer thickness is much smaller than the radius of the capillary channel, (II) diffusive flux can be neglected, and (III) the equilibrium between proton and bicarbonate is the dominant reaction in the solution. If the radius of the microcapillary reduces, more complex transport behaviors will be observed because the retardation factor will play a critical role as would be the case in the nanochannel and most reactive porous media. There have been some efforts to understand the pH effect on the transport property in the nanochannels at steady state,^{34,35} but the transient behavior considered in this work has not been well-studied. Also, with the decrease of the radius, the contribution of surface conductivity may not be negligible and should be carefully tested. Another difficulty in dealing with porous media comes from the effect of complex geometry on the transport in a heterogeneously charged system, as shown by pore-scale modeling.³⁶ The effect of diffusion generally smears the displacement fronts and weakens the hysteretic effect. Sometimes, the microfluidic systems have buffers to maintain the solution pH, and it has been shown in Lim et al.¹⁵ that buffers can depress the hysteresis effect. The buffering system poses more mathematical complexity in chromatographic analysis, and a further discussion on the buffering system will be given in the future work. Lastly, when finalizing this work, the authors find that the nonlinear proton transport eq 19 here is mathematically similar to a nonlinear traffic flow problem shown in LeVeque.³²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.8b00349.

Description of the diffuse-layer surface complexation model, analytical solution procedure for the nonlinear model, description of the numerical method, and discussion on retardation effect and diffusio-osmosis effect (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Yao, S.; Santiago, J. G. *J. Colloid Interface Sci.* **2003**, *268*, 133–142.
- (2) Wang, X.; Cheng, C.; Wang, S.; Liu, S. *Microfluid. Nanofluid.* **2009**, *6*, 145–162.
- (3) Jorgenson, J. W.; Lukacs, K. D. *Journal of Chromatography A* **1981**, *218*, 209–216.
- (4) Chang, C.-C.; Yang, R.-J. *Microfluid. Nanofluid.* **2007**, *3*, 501–525.
- (5) Kuo, A.-T.; Chang, C.-H.; Wei, H.-H. *Appl. Phys. Lett.* **2008**, *92*, 244102.
- (6) Tang, S.-W.; Chang, C.-H.; Wei, H.-H. *Appl. Phys. Lett.* **2010**, *97*, 043704.
- (7) Li, D. *Electrokinetics in Microfluidics*; Academic Press: Oxford, U.K., 2004.
- (8) Kirby, B. J. *Micro- and Nanoscale Fluid Mechanics*; Cambridge University Press: Cambridge, U.K., 2010.
- (9) Cummings, E. B.; Griffiths, S. K.; Nilson, R. H.; Paul, P. H. *Anal. Chem.* **2000**, *72*, 2526–2532.
- (10) Wang, M.; Kang, Q. *Anal. Chem.* **2009**, *81*, 2953–2961.
- (11) Lim, A. E.; Lim, C. Y.; Lam, Y. C. *Anal. Chem.* **2016**, *88*, 8064–8073.
- (12) Ren, L.; Escobedo-Canseco, C.; Li, D. *J. Colloid Interface Sci.* **2002**, *250*, 238–242.
- (13) Peng, R.; Li, D. *Nanoscale* **2016**, *8*, 12237–12246.
- (14) Gan, H. Y.; Yang, C.; Wan, S. Y. M.; Lim, G. C.; Lam, Y. C. *J. Phys.: Conf. Ser.* **2006**, *34*, 283–290.
- (15) Lim, C. Y.; Lim, A. E.; Lam, Y. C. *Sci. Rep.* **2016**, *6*, 22329.
- (16) Ren, L.; Escobedo, C.; Li, D. *J. Colloid Interface Sci.* **2001**, *242*, 264–271.
- (17) Ren, L.; Masliyah, J.; Li, D. *J. Colloid Interface Sci.* **2003**, *257*, 85–92.
- (18) Tang, S.-W.; Chang, C.-H.; Wei, H.-H. *Microfluid. Nanofluid.* **2011**, *10*, 337–353.
- (19) Lim, C. Y.; Lim, A. E.; Lam, Y. C. *Anal. Chem.* **2017**, *89*, 9394–9399.
- (20) Lyklema, J. *Fundamentals of Interface and Colloid Science: Solid–Liquid Interface*; Academic Press: London, 1995; Vol. 2.
- (21) Anderson, J. L.; Idol, K. W. *Chem. Eng. Commun.* **1985**, *38*, 93–106.
- (22) Rhee, H.-K.; Aris, R.; Amundson, N. R. *Theory and Application of Hyperbolic Systems of Quasilinear Equations*; Dover Publications, Inc.: Mineola, NY, 2001.
- (23) Ajdari, A. *Phys. Rev. Lett.* **1995**, *75*, 755–758.
- (24) Stroock, A. D.; Weck, M.; Chiu, D. T.; Huck, W. T. S.; Kenis, P. J. A.; Ismagilov, R. F.; Whitesides, G. M. *Phys. Rev. Lett.* **2000**, *84*, 3314–3317.
- (25) Kim, Y. W. C. F.; Netz, R. R. *J. Chem. Phys.* **2006**, *124*, 114709.
- (26) Ren, L.; Li, D. *J. Colloid Interface Sci.* **2001**, *243*, 255–261.
- (27) Zhang, L.; Wang, M. *J. Eng. Thermophys.* **2015**, *36*, 154–157.
- (28) Ghosal, S. *J. Fluid Mech.* **2002**, *459*, 103–128.

- (29) Behrens, S. H.; Grier, D. G. *J. Chem. Phys.* **2001**, *115*, 6716–6721.
- (30) Möller, D. M. *Chemistry for Environmental Scientists*; De Gruyter: Berlin, Germany, 2015; Chapter 4.6.2, pp 206–208.
- (31) McNeece, C. J.; Hesse, M. A. *Adv. Water Resour.* **2016**, *97*, 314–325.
- (32) LeVeque, R. J. *Finite Volume Methods for Hyperbolic Problems*; *Cambridge Texts in Applied Mathematics*; Cambridge University Press: Cambridge, U.K., 2002; Vol. 31.
- (33) Newman, J.; Thomas-Alyea, K. E. *Electrochemical Systems*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, 2004.
- (34) Ma, Y.; Yeh, L. H.; Lin, C. Y.; Mei, L.; Qian, S. *Anal. Chem.* **2015**, *87*, 4508–4514.
- (35) Yeh, L. H.; Chen, F.; Chiou, Y. T.; Su, Y. S. *Small* **2017**, *13*, 1770253.
- (36) Zhang, L.; Wang, M. *J. Colloid Interface Sci.* **2017**, *486*, 219–231.