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Short communication

Buffer effect on the ionic conductance in a pH-regulated nanochannel

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ABSTRACT

An electrical four layer model taking into account surface chemical reactions and adsorption of the metal and Tris buffer cations is developed for the first time to investigate the buffer effect on the ionic conductance in a pH-regulated nanochannel. Predictions from the analytical model agree well with experimental data of the conductance in silica nanochannels. The buffer effect is significant at low salt concentration, and the behaviors of zeta potential, surface charge density, and conductance in a nanochannel with buffer are distinctly different from those without buffer.

1. Introduction

Nanofluidics have received significant attention due to their substantial applications in energy conversion [1–3], ionic diodes [4–6], manipulation of chemical species [7–12], and analysis of (bio)particles [13]. Many of these applications analyze the ionic conductance through the nanochannel, demanding a fundamental understanding of its ionic conductance [14–16]. Many theoretical studies investigated electrokinetic ion transport phenomena and conductance in a nanochannel [15–29], and concluded that they exquisitely depend on the solution properties due to the surface reactions on the nanochannel wall.

In nanofluidic experiments, buffers (e.g., Tris base) are generally incorporated to maintain a stable pH [11,13,16,30–32]. The addition of buffers increases the ionic strength, yielding a decrease in the Debye length due to the simultaneous formation of buffer ions (e.g., TrisH^+). Moreover, the buffer ions may be adsorbed on the channel wall, which in turn affects its surface charge property. All these effects may significantly affect the ionic conductance in a nanochannel. Limited studies, however, have been performed on the buffer effect on the surface charge property and ionic conductance in a nanochannel.

In this study, an electrical four layer (EFL) model is developed to describe the surface charge property of the nanochannel wall. The model considers the surface equilibrium reactions between the functional groups of the channel wall and all counterions (protons, metal cations, and the buffer cations). Analytical expressions based on the EFL model are derived for the first time to predict the ionic current/conductance with the consideration of the electroosmotic flow (EOF) and the presence of buffer cations, H^+, OH^-, and the ions dissociated from the background salt.

2. Mathematical model

As schematically depicted in Fig. 1, we consider the electrokinetic transport of an electrolyte solution of permittivity ε_f in a long nanochannel of length l, height h, and width w subject to a uniform electric field, $E = V/l$, with V being the potential bias applied across the nanochannel. Suppose that the channel height is in nanoscale and both its length and width are in microscale (i.e., $l \gg h$ and $w \gg h$); therefore, the problem can be simplified as a nanoslit with two parallel plates. Cartesian coordinate, (x, y), is adopted with the origin fixed at one of the channel walls, and E is directed in the $y -$ direction.

Buffers are used to maintain the solution pH in the nanofluidic experiments [11,13,16,30–32]. We assume that a buffer cation BH^+ (e.g., TrisH^+, BisTrisH^+, PyridineH^+, and PiperidineH^+), which undergoes the following dissociation reaction $BH^+ \leftrightarrow B + H^+$ with equilibrium reaction constant $K_{Buff} = [B]_0[H^+]_0/[BH^+]_0$, is first introduced to the aqueous solution, followed by adding acid (e.g., HCl) to adjust its pH to the required value. Here, $[B]_0$, $[BH^+]_0$, and $[H^+]_0 = 10^{-\,\text{pH}}$ are the bulk molar concentrations of the buffer (B), buffer cations (BH^+), and H^+ ions, respectively. The initial buffer concentration is $C_{Buff} = 10^3 \times [BH^+]_0(1 + K_{Buff}/[H^+]_0)$. If MA (e.g., KCl or NaCl) is the background salt with the background salt concentration C_{MA}, five major ions, including H^+, BH^+, M^+, OH^-, and A^-, should be considered. Let C_{10}, C_{20}, C_{30}, C_{40}, and C_{50} be the bulk concentrations of these ions, respectively. Electroneutrality of the bulk electrolyte solution yields

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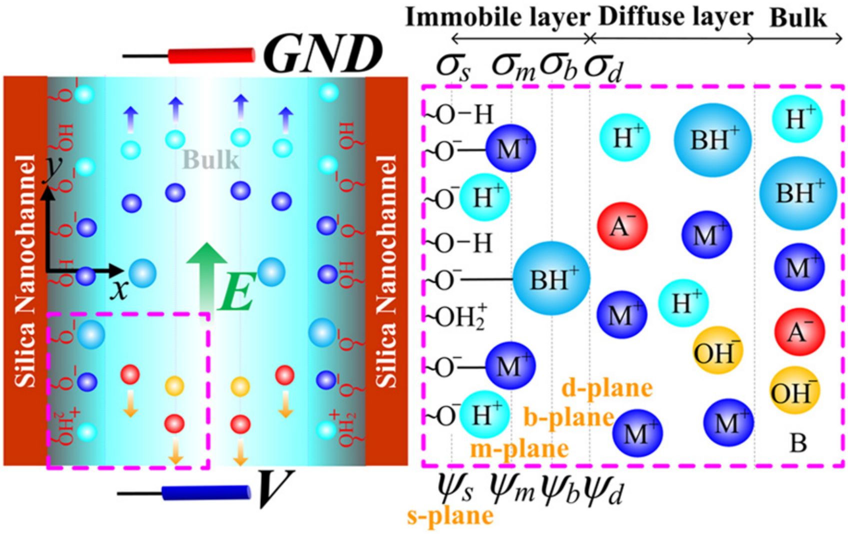

Fig. 1. Schematics of the ion transport in a pH-regulated nanochannel. BH^+ represents buffer cations (e.g., $TrisH^+$), and M^+ and A^- represent metal cations (e.g., K^+ or Na^+) and anions (e.g., Cl^-) from the background salt, respectively. ψ_s, ψ_m, ψ_b, and ψ_d (σ_s, σ_m, σ_b, and σ_d) represent, respectively, the potential (charge density) at the s-, m-, b-, and d-planes. Adsorption of the metal and buffer cations occurs, respectively at the m- and b-planes.

$C_{10} = 10^{-\mathrm{pH}+3}$, $C_{20} = C_{Buff}/\left(1+10^{\mathrm{pH}-\mathrm{p}K_{Buff}}\right)$, $C_{30} = C_{\mathrm{MA}}$, $C_{40} = 10^{-(14-\mathrm{pH})+3}$, and $C_{50} = C_{\mathrm{MA}} + 10^{-\mathrm{pH}+3} + C_{Buff}/\left(1+10^{\mathrm{pH}-\mathrm{p}K_{Buff}}\right) - 10^{-(14-\mathrm{pH})+3}$, where $\mathrm{p}K_{Buff} = -\log(K_{Buff})$. Note that all of the above C_{j0} are based on the SI unit (in mM).

Similar to the treatment of electrical triple layers [26,33], we extend that to the EFL model with consideration of the deprotonation/protonation of dissociable functional groups ($Si-OH$) at the silica nanochannel surface (s-plane), the adsorption reactions between $Si-O^-$ and M^+ at the m-plane, and $Si-O^-$ and BH^+ at the b-plane, as shown in Fig. 1. Based on this model, four major surface equilibrium reactions are considered:

$$Si{-}OH_2^+ \Leftrightarrow Si{-}OH + H^+, \tag{1}$$

$$Si{-}OH \Leftrightarrow Si{-}O^- + H^+, \tag{2}$$

$$Si{-}O^- + M^+ \Leftrightarrow Si{-}OM, \tag{3}$$

$$Si{-}O^- + BH^+ \Leftrightarrow Si{-}OBH, \tag{4}$$

with corresponding equilibrium constants $K_{a1} = \Gamma_{\mathrm{SiOH}}[H^+]_s/\Gamma_{\mathrm{SiOH}_2^+}$, $K_{a2} = \Gamma_{\mathrm{SiO}^-}[H^+]_s/\Gamma_{\mathrm{SiOH}}$, $K_M = \Gamma_{\mathrm{SiOM}}/\Gamma_{\mathrm{SiO}^-}[M^+]_m$, and $K_{BH} = \Gamma_{\mathrm{SiOBH}}/\Gamma_{\mathrm{SiO}^-}[BH^+]_b$, respectively. Here Γ_k is the surface site density of the kth functional group, $k = Si-OH$, $Si-OH_2^+$, $Si-O^-$, $Si-OM$, and $Si-OBH$. $[H^+]_s$, $[M^+]_m$, and $[BH^+]_b$ are the surface molar concentrations of H^+, M^+, and BH^+ in the unit of M, at the s-plane, m-plane, and b-plane, respectively. Assuming that Debye lengths of the nanochannel are not overlapped (i.e., $\lambda_D \ll h/2$), $[H^+]_s$, $[M^+]_m$, and $[BH^+]_b$ can be described by the Boltzmann distribution, $[H^+]_s = 10^{-3} \times C_{10}\exp(-z_1F\psi_s/RT)$, $[M^+]_m = 10^{-3} \times C_{30}\exp(-z_3F\psi_m/RT)$, and $[BH^+]_b = 10^{-3} \times C_{20}\exp(-z_2F\psi_b/RT)$. Here z_i is the valence of the ith ionic species; ψ_s, ψ_m, and ψ_b are the electrical potential at the s-plane, m-plane, and b-plane, respectively; R, T, and F are the gas constant, absolute temperature, and Faraday constant, respectively. Note that the adsorption of anions by the $Si-OH_2^+$ sites is negligible because of rare amount of $Si-OH_2^+$ at the usual solution pH used in experiments, which is typically higher than the isoelectric point (ca. 2–3.5) of the silica nanochannel. Moreover, the reaction rate of $Si-OH_2^+$ and anions is very small at typical pH 3–9 [26] and, therefore, adsorption of anions by the $Si-OH_2^+$ sites can be neglected. If we let $\Gamma_t = \Gamma_{\mathrm{SiOH}} + \Gamma_{\mathrm{SiOH}_2^+} + \Gamma_{\mathrm{SiO}^-} + \Gamma_{\mathrm{SiOM}} + \Gamma_{\mathrm{SiOBH}}$ be the total site density of the functional groups on the nanochannel surface, then

$$\Gamma_t = \Gamma_{\mathrm{SiOH}}\left(1 + \frac{[H^+]_s}{K_{a1}} + \frac{K_{a2}}{[H^+]_s} + \frac{K_M K_{a2}[M^+]_m}{[H^+]_s} + \frac{K_{BH}K_{a2}[BH^+]_b}{[H^+]_s}\right). \tag{5}$$

The EFL model in Fig. 1 yields the charge densities at the s-, m-, b-, and d-planes are, respectively,

$$\sigma_s = e\left(\Gamma_{\mathrm{SiOH}_2^+} - \Gamma_{\mathrm{SiO}^-} - \Gamma_{\mathrm{SiOM}} - \Gamma_{\mathrm{SiOBH}}\right), \tag{6}$$

$$\sigma_m = e\Gamma_{\mathrm{SiOM}}, \tag{7}$$

$$\sigma_b = e\Gamma_{\mathrm{SiOBH}}, \tag{8}$$

and

$$\sigma_d = -\mathrm{sign}(\psi_d)\sqrt{2\varepsilon_f RT\sum_{i=1}^{5} C_{i0}\left[\exp\left(-\frac{z_iF\psi_d}{RT}\right) - 1\right]}, \tag{9}$$

where e is the elementary charge and ψ_d is the zeta potential of the nanochannel. The electroneutrality within the four layers yields

$$\sigma_s + \sigma_m + \sigma_b + \sigma_d = 0. \tag{10}$$

Assuming that ions and fluid inside the immobile Stern layer are stationary, we can obtain the following correlations between the representative electrical potentials and charge densities within the four layers [26,33],

$$\sigma_s = C_{s1}(\psi_s - \psi_m), \tag{11}$$

$$\sigma_s + \sigma_m = C_{s2}(\psi_m - \psi_b), \tag{12}$$

$$\sigma_s + \sigma_m + \sigma_b = C_{s3}(\psi_b - \psi_d). \tag{13}$$

In the above, C_{s1}, C_{s2}, and C_{s3} are the surface capacitance of the inner, middle, and outer layers of the immobile layer, respectively. For the given pH, C_{MA}, C_{Buff}, and values of the parameters C_{s1}, C_{s2}, C_{s3}, K_{a1}, K_{a2}, K_M, K_{BH}, and Γ_t, one can use the MATLAB function *fsolve* to determine the electrical potentials (ψ_s, ψ_m, ψ_b, and ψ_d) and charge densities (σ_s, σ_m, σ_b, and σ_d) by simultaneously solving Eqs. (6)–(13).