



Gate manipulation of ionic conductance in a nanochannel with overlapped electric double layers



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ABSTRACT

To improve the development of gated nanofluidic devices for emerging applications, analytical expressions are derived to investigate the gate manipulation of surface charge property and ionic conductance in a pH-regulated nanochannel with overlapped electric double layers (EDLs). Results show that the EDL overlap effect is relatively significant at low pH and salt concentration when a negative gate potential is applied. If pH is low, the EDL overlap effect on the field control of zeta potential of the nanochannel is remarkable at large positive gate voltage, while that effect on ionic conductance is significant at large negative gate voltage.

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1. Introduction

The ability to control the ion transport, which is highly dependent on surface charge properties and ion concentration distributions [1,2], in nanofluidics such as nanochannels and nanopore plays a key role for emerging applications such as energy harvesting [3,4], rectification of ion current [5–7], and sensing and analyzing of (bio)nanoparticles [8–10]. To achieve active control, nanofluidic field effect transistors (FETs) [11,12], referring to gate electrode-embedded nanofluidic devices, have been developed recently. Many experimental results demonstrated that both the surface charge properties [13] and, accordingly, the transport of ions, fluids, and biomolecules [14–23] in the nanochannel can be actively controlled by tuning the gate voltage imposed on the gate electrode.

Thus far, a majority of researches on the numerical modelings of the FET control in nanofluidics have been performed [23–35], while analytical studies [36–40], which are more useful for experimentalists, are still very limited. This is because some limited assumptions, such as assuming a fixed surface charge density on the

dielectric channel wall [36], and neglecting the presence of protons and Stern layer effect [36,37], are typically adopted to derive analytical solutions. Moreover, the existing analytical models assumed the electric double layers (EDLs) of the nanochannel are not overlapped [36–40]. This implies that the ionic concentrations at the center of the nanochannel are assumed to be their bulk value, and the potential at the channel center arising from the charged channel wall vanishes. Although ignoring the EDL overlap effect on the transport phenomena in gated channels makes mathematical models much simpler, it is obviously no longer applicable to the modern FET-gated nanofluidic devices, the characteristic sizes of which are commonly smaller than 30 nm [15–23].

In this study, we analyze the gate manipulation of surface charge property and ionic conductance in a pH-regulated nanochannel with significantly overlapped EDLs under various solution conditions. Analytical expressions are derived for the first time to take into account the effects of EDL overlap, Stern layer, electroosmotic flow (EOF), surface site dissociation/association reactions on the dielectric channel wall, and the presence of multiple ionic species. Note that this is the first attempt to develop an analytical model for the gated nanofluidic system with overlapped EDLs. The developed model is capable of predicting the zeta potential, surface charge density, EOF velocity, and ionic conductance in a gated nanoslit at any levels of pH and salt concentration used in experiments.

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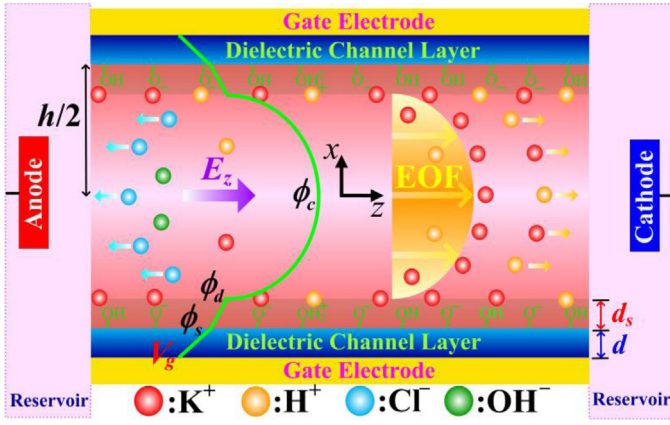


Fig. 1. Schematic of the gate manipulation of the surface potential (ϕ_s), zeta potential (ϕ_d) and ionic current/conductance in a pH-regulated nanochannel filled with electrolyte solution containing K^+ , H^+ , Cl^- , and OH^- . V_g is the gate potential applied to the gate electrode, ϕ_c the central potential in the nanochannel, and d the thickness of the dielectric channel layer.

2. Mathematical model

As schematically depicted in Fig. 1, we consider a nanofluidic FET, including two gate electrodes embedded outside the dielectric layers of the nanochannel walls. The nanochannel of height h , length l , width w , and dielectric layer thickness d , connects two large reservoirs and is filled with an electrolyte solution containing ionic species of valence z_i and concentration C_i , $i = 1, 2, \dots, N$. The Cartesian coordinates, x and z , are adopted with the origin located at the center of the nanochannel. A uniform electric field, $E_z = V/l$, with V being the potential bias applied in the z -direction to drive the transport of ions (ionic current) and fluid (EOF). The surface charge property and, accordingly, the electrokinetic ion and fluid transport in the nanochannel can be manipulated by actively regulating the gate potential V_g imposed on the gate electrodes.

In nanofluidic experiments, the ionic strength of the electrolyte solution is typically adjusted by a background salt KCl (or NaCl) and its pH by HCl and KOH (or NaOH). Therefore, we consider four major ionic species (i.e., $N=4$), namely, K^+ (or Na^+), H^+ , Cl^- , and OH^- . Letting C_{i0} ($i=1, 2, 3$, and 4) be the bulk concentrations of these ions, respectively, and C_b the background salt concentration of KCl (or NaCl), we obtain $C_{10} = C_b$, $C_{20} = 10^{-(pH-3)}$, $C_{30} = C_b + 10^{-(pH-3)} - 10^{-(14-pH-3)}$, and $C_{40} = 10^{-(14-pH-3)}$ for $pH \leq 7$; $C_{10} = C_b - 10^{-(pH-3)} + 10^{-(14-pH-3)}$ and $C_{30} = C_b$ for $pH > 7$ [41,42].

Assuming that both l and w are remarkably larger than h , and ions confined inside the Stern layer of thickness d_s are immobile [1], without considering the ion concentration polarization effect [43,44] the electric potential arising from the charged channel wall can be described by

$$\frac{d^2\varphi}{dx^2} = 0 \quad \left(\frac{h}{2} < x < \frac{h}{2} + d \right), \quad (1)$$

$$\frac{d^2\varphi}{dx^2} = 0 \quad \left(\frac{h}{2} - d_s < x < \frac{h}{2} \right), \quad (2)$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0\varepsilon_f} = -\frac{2FC_{t0}}{\varepsilon_0\varepsilon_f} \sinh\left(-\frac{zF\psi}{RT}\right) \quad \left(0 < x < \frac{h}{2} - d_s \right) \quad (3)$$

In the above, φ , ϕ , and ψ are the electric potentials within the dielectric channel layer, Stern layer, and liquid, respectively; ε_0 and ε_f are the permittivity of vacuum and the relative permittivity of electrolyte solution, respectively; $\rho_e = \sum_{i=1}^4 Fz_i C_{i0} \exp(-z_i F\psi/RT)$ is the mobile space charge density; R , F , and T are the universal gas constant, Faraday constant, and absolute fluid temperature,

respectively; $z = |z_i| = 1$ and $C_{t0} = C_{10} + C_{20} = C_{30} + C_{40} = C_b + 10^{-(pH-3)}$ for $pH \leq 7$ and $C_b + 10^{-(14-pH-3)}$ for $pH > 7$. Note that because H^+ and OH^- ions are taken into account, the present model is applicable to any levels of pH in nanofluidic experiments.

The boundary conditions associated with Eqs. (1)–(3) can be expressed as

$$\varphi = V_g \text{ at } x = \frac{h}{2} + d, \quad (4)$$

$$\varphi = \phi = \phi_s \text{ at } x = \frac{h}{2}, \quad (5a)$$

$$\varepsilon_0\varepsilon_d \frac{d\varphi}{dx} - \varepsilon_0\varepsilon_f \frac{d\phi}{dx} = -\sigma_s \text{ at } x = \frac{h}{2}, \quad (5b)$$

$$\phi = \psi = \phi_d \text{ at } x = \frac{h}{2} - d_s, \quad (6a)$$

$$\varepsilon_0\varepsilon_f \frac{d\phi}{dx} = \varepsilon_0\varepsilon_f \frac{d\psi}{dx} \text{ at } x = \frac{h}{2} - d_s \quad (6b)$$

$$\psi = \phi_c \text{ and } \frac{d\psi}{dx} = 0 \text{ at } x = 0 \quad (7)$$

In the above, ε_d is the relative permittivity of the dielectric channel layer; σ_s , ϕ_s , and ϕ_d are the surface charge density, surface potential, and zeta potential of the nanochannel, respectively; ϕ_c is the electrical potential at the center of the nanochannel (central potential). Note that if the EDL overlap effect is neglected, ϕ_c vanishes (i.e., $\phi_c = 0$), which is often assumed for nanochannels in the previous literatures for simplicity [36–39,45].

Many experimental results show that the wall of dielectric channels (e.g., SiO_2 , Al_2O_3 , Si_3N_4) in contact with aqueous solution reveals a charge regulation behavior. This implies that σ_s depends substantially on the solution properties such as pH and ionic strength. To account for this effect, we assume that the following two major surface reactions, $AOH \leftrightarrow AO^- + H^+$ and $AOH_2^+ \leftrightarrow AOH + H^+$, occur on the dielectric channel wall. The surface charge density of the nanochannel can be expressed as [46]

$$\sigma_s = (eN_t \times 10^{18}) \left[\frac{[H^+]_s^2 - K_{a1}K_{a2}}{[H^+]_s^2 + [H^+]_sK_{a2} + K_{a1}K_{a2}} \right], \quad (8)$$

where e is the elementary charge; N_t (in sites/nm²) is the total number site density of functional groups, including AOH , AO^- , and AOH_2^+ , on the dielectric channel surface; K_{a1} and K_{a2} are the equilibrium constants for the aforementioned dissociation reactions of AOH and AOH_2^+ , respectively; $[H^+]_s = 10^{-3} \times C_{20} \exp(-F\phi_s/RT)$ is the molar concentration of H^+ at the dielectric channel surface.

If we let the surface capacitance of the Stern layer $\chi_s = \varepsilon_0\varepsilon_f d_s$, based on the solutions to Eqs. (1) and (2) the interface boundary conditions Eqs. (5b) and (6b) yield the following two equations (detailed derivations can be found in the supplementary data)

$$\begin{aligned} \varepsilon_0\varepsilon_d \left(\frac{V_g - \phi_s}{d} \right) - \chi_s(\phi_s - \phi_d) \\ = -(eN_t \times 10^{18}) \left[\frac{[H^+]_s^2 - K_{a1}K_{a2}}{[H^+]_s^2 + [H^+]_sK_{a2} + K_{a1}K_{a2}} \right], \end{aligned} \quad (9)$$

$$\begin{aligned} \chi_s(\phi_s - \phi_d) \\ = \text{sign}(\phi_d) \sqrt{4RT\varepsilon_0\varepsilon_f C_{t0} \left[\cosh\left(\frac{F\psi}{RT}\right) - \cosh\left(\frac{F\phi_c}{RT}\right) \right]}. \end{aligned} \quad (10)$$

The exact solution to Eq. (3) subject to Eqs. (6a) and (7) is [47]

$$\psi = \phi_c + \frac{2RT}{F} \ln[CD(l|m)], \quad (11)$$

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