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Field Effect Control of Electrokinetic Transport Phenomena in Nanofluidics

Song Xue
Old Dominion University

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FIELD EFFECT CONTROL OF ELECTROKINETIC TRANSPORT

PHENOMENA IN NANOFLUIDICS

by

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ABSTRACT

FIELD EFFECT CONTROL OF ELECTROKINETIC TRANSPORT
PHENOMENA IN NANOFLUIDICS

Song Xue
Old Dominion University, August 2014
Director: Dr. Shizhi Qian

Naturally nanofluidics has applications demanding the samples to be handled in exceedingly small quantities due to the small size of the fluidic channels in nanofluidic devices, such as characterization of single biomolecules. Fluids confined in channels of nanometer characteristic dimensions exhibit physical behaviors not observed in large conduits. Charge properties of the nanochannel wall in contact with an aqueous solution play essential roles in the involved electrokinetic transport phenomena occurring in nanofluidic devices. In addition to tuning the charge properties of the nanofluidic channel wall by adjusting the solution properties such as pH and background salt concentration, field effect transistor (FET) with a gate electrode embedded beneath the nanochannel wall has been demonstrated to rapidly tune the surface charge condition and accordingly the electrokinetic transport phenomena in nanofluidic devices.

The first part of the dissertation develops a mathematical model for the charge properties of the nanofluidic channel and the electroosmotic flow (EOF) in a nanoslit gated by a FET. In contrast to the previous studies, surface chemistry is considered for the first time. The obtained results demonstrated that the surface charge property as well as the direction and magnitude of the EOF can be actively tuned by the FET. The performance of FET control is more sensitive when the pH and/or the bulk electrolyte
concentration is relatively low.

Since the nanofluidics-based biosensing is based on discriminating the ionic current or conductance signal, active control of the surface charge property and accordingly the ionic current/conductance in nanofluidics is investigated in the second part of the dissertation. An analytical model for the surface charge property and the ionic conductance in a FET-gated silica nanochannel is developed considering practical effects of surface chemistry reactions, multiple ionic species, the Stern layer, and the EOF. The results show that the performance of the FET control on ionic conductance is more significant when the background salt concentration and pH are low.

Experimental studies demonstrated that the streaming current in the nanochannel provides a simple and effective scenario for converting hydrodynamics to electrical power. The third part of the dissertation investigated streaming current in a pH-regulated nanochannel gated by FET. Analytical models for the streaming current/conductance with and without considering the electroviscous effects have been derived. The models take into account multiple ionic species, surface chemistry reactions, and the Stern layer effect. Results show the performance of the field effect modulation of the streaming conductance is significant for lower solution pH and salt concentration.

The last part of the dissertation extends the previous studies by considering the overlapping of the EDLs inside the nanochannel. The model takes into account the surface chemistry, Stern layer, multiple ionic species and the EDL overlapping effect. The model is validated by the existing experimental data of the ionic conductance in the silica nanochannel with significant EDL overlapping effect. Results from the model with and without considering EDL overlapping are compared.
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I would like to acknowledge financial contributions from U.S. Army and U.S. Department of Veterans Affairs in support of my graduate education and research at ODU.

Furthermore, I wish to dedicate this dissertation to my wife, my parents, and my children for their unconditional love, inspiration and support.
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CHAPTER 1
INTRODUCTION

1.1 Nanofluidic Technology

Inventions and advances of modern nanofabrication techniques, such as nanolithography techniques [10 - 17], sacrificial layer releasing method [18 - 23], etching and bonding/deposition [24 - 30], and nanomaterial-based techniques [30 - 37], enable the fabrication of nanofluidic devices with characteristic scale of below 100 nm [38 - 47]. The powerful nanofabrication techniques are able to fabricate nanofluidic devices with various nanoscale dimensions ranging from 1-D, 2-D to 3-D, which is based on the number of nanoscale dimensions in the geometry [48 - 53]. In addition, the present nanofabrication techniques can fabricate the nanofluidic devices with a variety of functional materials such as silicon, glass, quartz, polydimethylsiloxane (PDMS), and polymethylmethacrylate (PMMA) [54 - 64]. All these materials in contact with the aqueous solution are charge regulated, and their surface charge density and surface potential depend on the local pH and salt concentration in the vicinity of the surface [65 - 69]. In other words, the charge properties of the nanochannel wall made of the aforementioned materials are not constant, and vary with the local solution properties [70 - 74].

Nanofluidics refers to the study and application of fluid flow confined in a nanochannel or nanopore with at least one characteristic dimension below 100 nm [75 - 79]. Since its dimension is the same order of magnitude as the Debye length and the size of nanoparticles and biomolecules such as DNA and proteins, nanofluidics has very high surface to volume ratio resulted in dominant surface or interfacial forces over the
volumetric body forces [80 - 87]. This unique feature gives rise to the transport of ions, fluids, and (bio)particles in nanofluidics governed by the surface charges of the nanochannel and the nanoparticles, and ions and (bio)particles are selectively transported in charged nanochannels or nanopores [88 - 93]. Due to this feature, the interfacial electrokinetic transport phenomena have been widely used in the control and manipulation of fluids, ions, and (bio)particles in various nanofluidic applications. Nanofluidics has already found many novel applications including single molecule analysis such as the famous nanopore-based DNA sequencing [94 - 99], characterization of nanoparticles and biomolecules [100 - 102], water purification [103 - 105], sample preconcentration and separation [106 - 114], nanofluidic electronics such as nanofluidic transistors and diodes [115 - 123], nanofluidic computing [124], and nanofluidic energy storage and conversion [89, 125 - 130]. Owing to the nanoscale dimension in the nanofluidic devices, obvious advantages of the nanofluidic devices include the use of less reagents and solvents, less power consumption, and fast operation [131 - 138].

Due to the extreme importance of the electrokinetic transport phenomena in various nanofluidic applications, it is no doubt that fundamentally understanding the electrokinetic transport phenomena in nanofluidics is very valuable for the unprecedented development of nanofluidics, which is the main objective of the studies in this dissertation. The following subsection briefly describes the fundamentals of the electrokinetic transport phenomena occurring in nanofluidics.

1.2 Electrokinetic Transport Phenomena In Nanofluidics

Electrokinetic transport phenomena refer to a family of ionic mass transport, fluid/particle momentum transport, and charge transport processes. A common source in
these processes is the net charges accumulated within the electrical double layer (EDL) formed in the vicinity of a charged surface. Under an external electric field applied tangential to a charged surface, the interaction between the net charge within the EDL and the external electric field generates an electrostatic force acting on the fluid within the EDL and accordingly electroosmotic flow (EOF) [139 - 141]. Similarly, the electrostatic force acting on a charged particle under the influence of an external electric field induces electrophoretic motion of the particle relative to the surrounding fluid [139, 142]. The motion of the net charge within the EDL driven by an external pressure-driven flow also induces electrical potential or current, which is called streaming potential or streaming current [139, 143, 144]. Since the dimension of nanofluidics is the same order of magnitude as the EDL thickness, the so-called Debye length, electrokinetic transport phenomena dominate the ionic mass transport, the fluid/particle momentum transport, and charge transport within nanofluidics. The following subsections briefly describe the underlying physics of EDL, EOF, electrophoresis, and streaming current and potential and their applications in nanofluidics.

1.2.1 Electrical Double Layer

Most dielectric material in contact with an aqueous solution becomes charged. The origin of the charge will be discussed in Section 1.4. Due to the electrostatic interaction between the surface charge and ions within the solution, counter-ions will be attracted towards the charged surface, while co-ions will be repelled away from the charged surface. As a result, counter-ions dominate over the co-ions within a screening region in the vicinity of the charged surface, and the screening region is the so-called electrical double layer (EDL). Typically EDL is assumed to contain the Stern layer next to the
solid/liquid interface and the diffusive layer beyond the Stern layer, as shown in Figure 1.1. The Stern layer only contains one layer of immobile counter-ions due to the strong electrostatic interaction between the surface charge and the counter-ions. Within the diffusive layer, counter-ions dominate over the co-ions, and both of them are mobile. The potential at the solid/liquid interface is called surface potential, while the potential at the Stern layer/diffusive layer interface is called zeta potential. Note that the surface potential is different from the zeta potential unless the Stern layer effect is neglected. The electric potential arising from the charged surface first reduces from the surface potential to the zeta potential within the Stern layer, and then exponentially decays within the double layer. Beyond the diffusive layer, the electrostatic effect arising from the charged surface is negligible and the net charge becomes nearly zero [80, 139, 145].

Figure 1.1 Schematics of electric double layer in the vicinity of surface bearing negative surface charges. Reproduced from Ref. [1].
Under equilibrium condition, concentration of the ith ionic species $C_i$, can be described by the Boltzmann equation,

$$C_i = C_{i0} \exp\left(-\frac{z_i F \psi}{RT}\right), \quad (1.1)$$

where $C_{i0}$ and $z_i$ are the bulk concentration and the valence of the ith ionic species, respectively; $F$, $R$ and $T$ are the Faraday constant, universal gas constant and absolute temperature, respectively; and $\psi$ is the electric potential arising from the charged surface, which is governed by the Poisson equation:

$$-\varepsilon_0 \varepsilon_f \nabla^2 \psi = \rho_e. \quad (1.2)$$

In the above, $\varepsilon_0$ and $\varepsilon_f$ are the absolute permittivity in vacuum and the relative permittivity of the aqueous electrolyte solution; and $\rho_e$ is the mobile space charge density,

$$\rho_e = \sum_{i=1}^{N} Fz_i C_i, \quad (1.3)$$

where $N$ is the total number of ionic species present in the solution.

Substituting Equation (1.1) and Equation (1.3) into Equation (1.2), the Poisson-Boltzmann (PB) equation can be obtained to describe the electric potential distribution near a charged surface,

$$-\varepsilon_0 \varepsilon_f \nabla^2 \psi = F \sum_{i=1}^{N} z_i C_{i0} \exp\left(-\frac{z_i F \psi}{RT}\right). \quad (1.4)$$
If the absolute value of the valence of all species is equivalent, i.e. \( z_i = |z_i| \) for \( i = 1 \sim N \), the PB equation can be simplified as

\[
\nabla^2 \psi = \frac{RT \kappa^2}{zF} \sinh \left( \frac{zF \psi}{RT} \right),
\]

(1.5)

With \( \kappa^{-1} = \lambda_D = \sqrt{\varepsilon_0 F_e RT / 2 z^2 F^2 C_0} \) being the Debye length, and \( C_0 \) being the bulk concentration of all counter-ions or co-ions.

If \( |\psi| \ll \frac{RT}{zF} \), \( \sinh \left( \frac{zF \psi}{RT} \right) \approx \frac{zF \psi}{RT} \), Equation (1.5) can be linearized by the Debye-Hückel approximation [139]

\[
\nabla^2 \psi = \kappa^2 \psi
\]

(1.6)

based on which, the electrical potential decays exponentially away from the charged surface.

1.2.2 Electroosmotic Flow

Under an external electric field applied tangential to a negatively (positively) charged surface, the interaction between the external electric field and the net charges accumulated inside the EDL generates an electrostatic force driving the fluid toward the cathode (anode), as shown in Figure 1.2. The resulting fluid motion is called electroosmotic flow (EOF), which has been widely used in nanofluidics for fluid transport and drug delivery [111, 146 - 152].
The EOF of the incompressible electrolyte solution can be described by the Navier-Stokes (NS) equations

$$\nabla \cdot \mathbf{u} = 0 ,$$  \hspace{1cm} (1.7)

and

$$\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho_e \mathbf{E} .$$  \hspace{1cm} (1.8)

In the above, $\mathbf{u}$ is fluid velocity, $t$ is time, $\rho$ is the fluid density, $p$ is the pressure, $\mu$ is the dynamic viscosity of fluid, and $E$ is the applied electric field. The last term in Equation (1.8) represents the electrostatic force for the EOF, which is the interaction between the net charge density and the external electric field.
When the distortion of the EDL by the external electric field and the induced fluid motion is neglected, for a steady, fully developed EOF without external pressure gradient, the z-component EOF velocity $u_z$ can be simplified as

$$\mu \frac{d^2 u_z}{dx^2} = \varepsilon_0 \varepsilon_f \frac{d^2 \psi}{dx^2} E_z,$$

where $E_z$ is the z-component electric field externally applied.

1.2.3 Electrophoresis

Electrophoresis refers to the motion of charged (bio)particles (such as DNA and proteins) suspended in an aqueous solution under an externally applied electric field. For example, negatively (positively) charged particles move toward anode (cathode). EDL also forms in the vicinity of the charged particle, as shown in Figure 1.3.

Figure 1.3 Schematic of a DNA nanoparticle translocation through a nanopore by electrophoresis. Adapted with permission from Ref. [2].
Electrophoresis refers to the motion of charged (bio)particles (such as DNA and proteins) suspended in an aqueous solution under an externally applied electric field. For example, negatively (positively) charged particles move toward anode (cathode). EDL also forms in the vicinity of the charged particle, as shown in Figure 1.3. The net charges within the EDL of the charged particle are opposite to the charge of the particle. Under an external electric field, the direction of the electrostatic force acting the charged particle is opposite to that acting on the fluid within the EDL of the particle. Therefore, the hydrodynamic force acting on the particle, which arises from the fluid motion within the EDL of the particle, is opposite to the electrostatic force acting on the particle. When the two forces are balanced, steady electrophoretic velocity, \( U_p \), results. The electrophoretic mobility of the charged particle is defined as ratio of electrophoretic velocity \( U_p \) to applied electric field \( E \),

\[
\eta = \frac{U_p}{E}
\]  

(1.10)

Electrophoresis has been widely used to separate, pump and characterize biomolecules and colloidal nanoparticles in nanofluidics. For example, in the famous nanopore-based DNA sequencing technology [94 - 99] as schematically shown in Figure 1.3, negatively charged DNA electrophoretically translocates through the nanopore from the cathode reservoir toward the anode reservoir, and alters the ionic current flowing through the nanopore. Typically the nanopore wall is also negatively charged, resulting in EOF toward the cathode reservoir. The steady translocation velocity of the DNA inside the nanopore is determined by balancing the hydrodynamic force arising from the EOF and the electrostatic force exerted on the DNA, which stems from the interaction between the applied electric field and the negative charge on the DNA. In addition,
(bio)nanoparticles can be separated by electrophoresis based on their difference in charges [153 - 156].

1.2.4 Streaming current and potential

When an electrolyte solution is pumped through a charged nanochannel or nanopore by a pressure-driven flow (PDF), the excess counter-ions within the EDLs of the charged nanochannel will move with the pressure-driven flow towards the downstream. Due to the transport of counter-ions from the upstream to downstream of the nanofluidic channel, concentration of counter-ions at the downstream of the nanofluidic channel will be higher than that at the upstream of the nanofluidic channel. The unbalanced concentration of counter-ions at both ends of the nanochannel induces streaming potential, $U_{str}$ [143, 144, 157], as shown in Figure 1.4.

![Pressure Gradient and Streaming Current and Potential](image)

Figure 1.4 Schematic of streaming current and streaming potential of a nanochannel. Adapted with permission from Ref. [3].
The interaction between the induced electric field arising from the induced streaming potential and the net charges within the nanochannel also generates an EOF, the direction of which is opposite to that of the PDF. Therefore, the net flow is reduced, and this phenomenon is called the electroviscous effect because the liquid appears a higher viscosity in the vicinity of the charged nanochannel [158 - 160]. In addition, the motion of the net charges within the nanochannel by PDF generates streaming current, $I_{str}$. The induced streaming potential also generates conductive current, $I_{cond}$, the direction of which is opposite to that of the streaming current. Because of the open circuit, the total current is zero, $I_{str} + I_{cond} = 0$ [139].

Streaming potential/current has been used to determine the surface charge properties such as surface charge density and zeta potential of unknown samples [161]. For example, the streaming current meter becomes a widely adopted instrument to measure the charge of particles suspending in liquid [162, 163]. Studies have demonstrated that the streaming current generated by the PDF in the nanochannel provides a simple and effective means for converting hydrodynamics to electrical power [3, 6, 124, 164, 165]. This clean energy harvesting system using nanofluidics might open a new way for the development of renewable energy resources [124].

1.3 Field Effect Control of Charge Property of Channel Wall

In addition to regulate the surface charge property of a solid/liquid interface by tuning pH and salt concentration, one can actively control it by using the engineering method, field effect transistor (FET), as schematically shown in Figure 1.5. The FET consists an electrode, called a gate electrode, deposit beneath a thin dielectric film in contact with an aqueous solution. Note that the gate electrode and the liquid are
separated by a thin dielectric material typically made of SiO₂. A potential, called gate potential, is applied to the gate electrode. The surface potential at the dielectric solid/liquid interface varies with the applied gate potential. Since the electrokinetic transport phenomena in nanofluidics are highly dependent on the surface potential, one can control the electrokinetic transport within nanofluidics by tuning the gate potential. Figure 1.5a depicts the first nanofluidic FET fabricated by Karnick and his co-workers [4]. In the nanofluidic FET, fluid flows through the nanochannel by either EOF subject to an external electric field parallel to the nanochannel wall or a pressure-driven flow. The surface potential at the oxide/liquid interface is regulated by the imposed gate potential, Vg. In the absence of the FET control, the native surface potential is negative, and the nanochannel is predominated by positive ions. When a positive gate potential is applied, the magnitude of the negative surface potential decreases, resulting in lesser positive ions and more positive ions inside the nanochannel comparing to the case for Vg=0. If the positive Vg is sufficiently high, the surface potential might change to positive, and the nanochannel will be mainly occupied by negative ions. In contrast, when a negative gate potential is applied, the oxide/liquid interface will become more negatively charged, resulting in more positive ions and less negative ions inside the nanochannel. The change of the surface potential yields the change of the net charge and accordingly the conductance and EOF inside the nanochannel. Recently, FET has been used to actively control the EOF [116, 166 - 168], ionic conductance [169 - 171], streaming conductance [172, 173], ionic current rectification [174], and the motion of (bio)particle (such as DNA) inside the nanofluidics.
Figure 1.5 Schematics of a nanofluidic field effect transistor. Modulation of the charge property on the nanopore/liquid interface leads to a redistribution of the ionic concentrations inside the nanopore. Adapted with permission from Ref. [4].

To illustrate the mechanism of the FET control on the surface potential, we consider an aqueous electrolyte solution in contact with a dielectric layer of thickness, \( \delta \), outside of which a gate potential, \( V_g \), is imposed. A Cartesian coordinate system with the origin located at the solid/liquid interface is used, as shown in Figure 1.6a. Assuming that the surface chemistry reaction and effect of the Stern layer are neglected (i.e. the surface potential \( \psi \) equals the zeta potential \( \zeta \)). The electric potential distribution within the dielectric layer and liquid can be described as Laplace equation and Poisson-Boltzmann equation, respectively,

\[
\frac{d^2 \phi}{dx^2} = 0 \quad \text{within the dielectric layer} \quad (-\delta \leq x \leq 0) \quad (1.11)
\]
\[
\frac{d^2\psi}{dx^2} = -\frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\psi}{RT}\right) \text{within the liquid phase (}\ x \geq 0 \text{).}
\] (1.12)

with the following boundary conditions:

\[
\psi = V_g \text{ at } x = -\delta,
\] (1.13)

\[
\psi = \zeta \text{ at } x = 0,
\] (1.14)

\[
\varepsilon_0\varepsilon_r \frac{d\psi}{dx} - \varepsilon_0\varepsilon_d \frac{d\phi}{dx} = -\sigma, \text{ at } x = 0,
\] (1.15)

\[
\psi = 0 \text{ and } \frac{d\psi}{dx} = 0 \text{ as } x \to \infty,
\] (1.16)

Equations (1.11) and (1.12) can be solved subject to Equations (1.13), (1.14) and (1.16),

\[
\psi = (\zeta - V_g) \left(\frac{x}{\delta}\right) + \zeta
\] (1.17)

\[
\psi = \frac{2RT}{Fz} \ln \left[ \frac{1 + \exp(-\kappa x) \tanh\left(\frac{Fz\zeta}{4RT}\right)}{1 - \exp(-\kappa x) \tanh\left(\frac{Fz\zeta}{4RT}\right)} \right].
\] (1.18)

Substituting Equations (1.17) and (1.18) into Equation (1.15), one got

\[
\frac{2\varepsilon_0\varepsilon_r\kappa RT}{zF} \sinh\left(\frac{Fz\zeta}{2RT}\right) + \varepsilon_0\varepsilon_d \left(\frac{\zeta - V_g}{\delta}\right) = \sigma.
\] (1.19)

Assuming the surface charge density is \(\sigma_s = -10^{-4} \text{C/m}^2\) [175], the thickness of the dielectric layer is \(\delta = 30 \text{nm}\), and only \(K^+\) and \(Cl^-\) exist in the KCl background electrolyte solution with \(z = 1\). Equation (1.18) can be easily solved using Matlab function fzero to obtain the zeta potential at different gate potential. When the bulk concentration of KCl aqueous solution is \(C_0 = 0.1\text{mM}\), the effect of gate potential \(V_g\) on zeta potential \(\zeta\) is shown in Figure 1.6b. Obviously, one can tune both sign and magnitude of the zeta
potential by the applied gate potential. Note that this simple analysis used a constant surface charge density at the oxide/liquid interface, and neglect the Stern layer effect and the surface chemistry, which will be considered in the studies of this dissertation.

Figure 1.6 (a) Schematic FET of the ionic distribution near a planar surface. (b) Zeta potential as a function of the applied gate potential. $\varepsilon_f = 80$, $\varepsilon_d = 3.9$, $\delta = 30\text{nm}$, $\alpha = -10^{-4}\text{C/m}^2$, $C_0 = 0.1\text{mM}$.

1.4 Surface Chemistry on the Surface of Channel Wall

When a dielectric material (e.g., SiO$_2$, SiN$_x$, and Al$_2$O$_3$) in contact with an electrolyte aqueous, it becomes charged due to the dissociation/association of the functional groups [66 - 68]. The degree of reaction and thus the surface charge density due to the surface chemistry reactions depend on the site density of the functional groups, local pH and ionic concentrations, and this phenomenon is referred as charge-regulation [65-69].

Assuming the dielectric channel wall bears dissociable functional groups MOH, the following protonation/ deprotonation reactions with equilibrium constants $K_A$ and $K_B$
occur at the oxide/liquid interface:

\[
\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+ \quad (1.20)
\]

\[
\text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}_2^+ \quad (1.21)
\]

Based on the above surface chemical reactions, the equilibrium constants can be described as

\[
K_A = \frac{(\Gamma_{\text{MO}^-}[\text{H}^+])_s}{\Gamma_{\text{MOH}}}
\]

(1.22)

\[
K_B = \frac{\Gamma_{\text{MOH}_2^+}}{(\Gamma_{\text{MOH}}[\text{H}^+])_s}
\]

(1.23)

where \( \Gamma_{\text{MOH}}, \Gamma_{\text{MO}^-}, \) and \( \Gamma_{\text{MOH}_2^+} \) are the surface site densities of MOH, MO\(^-\), and MOH\(^+_2\), respectively, and \([\text{H}^+]_s\) is the molar concentration of H\(^+\) ions at the solid/liquid interface.

If the total number site density of the functional groups MOH on the dielectric channel surface is \( N_{\text{total}} = \Gamma_{\text{MOH}} + \Gamma_{\text{MO}^-} + \Gamma_{\text{MOH}_2^+} \), the surface charge density of at the interface, \( \sigma_s \), can be expressed as [176],

\[
\sigma_s = -F \left( \Gamma_{\text{MO}^-} - \Gamma_{\text{MOH}_2^+} \right) = -FN_{\text{total}} \left\{ \frac{K_A - K_B[H^+]^2}{K_A + [H^+]_s + K_B[H^+]^2} \right\},
\]

(1.24)

where \( pK_j = -\log K_j \) (\( j = A \) and \( B \)). Equation (1.24) shows that the surface charge density is not a constant, and it depends on the total site density of the functional group, \( N_{\text{total}} \), the reaction constants, \( K_A \) and \( K_B \), and the proton’s concentration at the interface. The latter depends on the bulk pH when the proton’s concentration is governed by the Boltzmann distribution.

In contrast to the existing studies on analysis of the FET control of electrokinetic transport in nanofluidics, which neglected the surface chemistry effect and used a
prescribed constant surface charge density on the nanochannel wall regardless of the solution properties, the studies in this dissertation take into account the surface chemistry and the obtained results clearly demonstrate the importance of the surface chemistry on the regulation of the electrokinetic transport phenomena in a nanofluidics gated by FET.

1.5 Objectives and Organization of the Dissertation

Comprehensive understanding the underlying physics of the electrokinetic transport phenomena in nanofluidics is essential to develop and apply the nanofluidic technology for the growing applications. Since the electrokinetic transport phenomena are highly dependent on the surface charge properties of the solid/liquid interface [69, 177, 178], which can be actively controlled by the nanofluidic field effect transistor (FET) [4, 179 - 181], this dissertation will focus on the analysis of the FET control of the electrokinetic transport phenomena in nanofluidics. In contrast to the previous studies in which several limited assumptions were taken, such as without considering the surface chemistry at the channel wall [5, 182-189], only consideration of the background ionic species [5, 176, 182 - 192], and without considering the Stern layer and EOF effects [5, 176, 182 - 189, 191, 192], the objectives of this dissertation are to develop more general analytical models for the electrical double layer, EOF, ionic conductance and streaming conductance in nanofluidics gated by FET with the consideration of the surface chemistry, multiple ionic species, Stern layer, and even overlapping of EDLs. The developed analytical models are verified by experimental data available in the literature. The verified analytical models would be valuable for accurately predicting the electrokinetic transport phenomena in a FET-gated nanofluidics without using the full numerical simulations, and can serve as design tools for the next generation FET-gated
The rest of this dissertation is organized as the following. Chapter 2 proposes and analyzes a floating gate field effect transistor (FGFET) for tuning surface charge property. Chapter 3 investigates the surface charge and electroosmotic flow in a FET-gated nanoslit by taking into account the surface chemistry and multiple ionic species and neglecting the Stern layer effect. Chapter 4 extends the model described in Chapter 3 by further taking into account the Stern layer effect, and investigates the ionic current/conductance under an external electric field. Chapter 5 develops the analytical model for the streaming current/conductance in nanofluidics under a pressure-driven flow without considering the electroviscous effect. However, other factors such as surface chemistry, multiple ionic species, and the Stern layer are considered in this study. Chapter 6 extends the study in Chapter 5 by taking into account the electroviscous effect. The studies from Chapters 3 to 6 do not consider the overlapping of the EDLs. Therefore, Chapter 7 extends the model in Chapter 4 by considering the EDL overlapping. Similar methodology can be used to extend the model in Chapter 6 for streaming current/conductance when the EDLs are significantly overlapped. Chapter 8 concludes the dissertation and provides a list of potential future work based on the studies in this dissertation.
CHAPTER 2
TUNING SURFACE CHARGE PROPERTY BY FLOATING GATE FIELD EFFECT TRANSISTOR

2.1. Introduction

Electrokinetic manipulation of ions, fluids, and particles by the use of electric field has been widely used in various micro/nanofluidic applications [145, 193, 194]. Since the electrokinetic transport phenomena highly depend on the surface charge property of the object in contact with an aqueous solution, one could modulate the zeta potential and accordingly the electrokinetic transport by an ionic field effect transistor (FET) [118, 184, 195 - 199]. In the conventional FET, a gate potential, $V_g$, is applied to a control gate electrode patterned on the outer surface of the dielectric channel wall. However, the floating gate field effect transistor (FGFET) to now has not been used to tune the surface charge property for controlling the electrokinetic transport phenomena in micro/nanofluidics. The structure of the FGFET is similar to the conventional FET except that an electrically isolated floating gate electrode is embedded inside the dielectric material. For the first time, a proposal to tune the surface charge property is made as well as the electrokinetic transport phenomena in micro/nanofluidics by the FGFET, and a theoretical investigation to its feasibility.

2.2. Theoretical Analysis

Figure 2.1 schematically depicts a planar FGFET in contact with a semi-infinite aqueous electrolyte solution of relative permittivity $\varepsilon_r$. The FGFET includes from left to right a control gate; the left dielectric layer of thickness, $\delta_L$, and relative permittivity, $\varepsilon_L$; a floating gate (FG) of thickness, $\delta_{FG}$, and relative permittivity, $\varepsilon_{FG}$; and the right
dielectric layer of thickness, $\delta_R$, and relative permittivity, $\varepsilon_R$. A gate potential, $V_g$, is applied to the control gate electrode. It is assumed that the distributions of the electric potential and the ionic concentrations are uniform along the planar surface. Therefore, the theoretical analysis can be simplified to 1D. The origin of the $x$-axis was chosen at the solid/liquid interface, and the $x$-axis is perpendicular to the planar surface. By neglecting the effect of the stern layer, the electric potential at the solid/liquid interface is the zeta potential of the planar surface, $\zeta$. It is assumed the dielectric material in contact with the aqueous solution bears a uniform surface charge density of $\sigma_w$.

The potentials inside the left dielectric material, FG, and the right dielectric layer, $\phi_j$ ($j=L$, FG, and R), are governed by the Laplace equation. The electric potential within a binary electrolyte solution, $\psi$, is governed by the Poisson-Boltzmann equation [194],

Figure 2.1 Schematics of a FGFET to tune the surface charge property of a planar surface in contact with an aqueous solution. The curve line schematically depicts the potential distribution.
\[
\frac{d^2(zF\psi)}{dx^2} = \kappa^2 \sinh \left( \frac{zF\psi}{RT} \right),
\]

where \( z = |z_i| \); \( \lambda_D = \kappa^{-1} = \sqrt{\varepsilon_0 \varepsilon_f RT / 2z^2 F^2 C_0} \) is the EDL thickness; \( \varepsilon_0 \) is the absolute permittivity of vacuum; \( F \) is the Faraday constant; \( R \) is the universal gas constant; \( T \) is the absolute temperature of the electrolyte solution; \( z_i \) is the valence of the \( i \)th ionic species; and \( C_0 \) is the bulk concentration.

Far away from the charged planar surface (i.e., \( x \to \infty \)), the potential and electric field inside the aqueous solution are zero. The electric potential is continuous at the interface of the right dielectric material and the fluid, and the electric field satisfies Gauss’s law,

\[
\varepsilon_0 \varepsilon_f \frac{d\psi(x = 0)}{dx} - \varepsilon_0 \varepsilon_R \frac{d\phi_R(x = 0)}{dx} = -\sigma_*.
\]

Similarly, the potentials at the interfaces between FG and the adjacent dielectric layers are continuous and satisfy Gauss’s law. At the gate electrode,

\[
\phi_L(x = -\delta_R - \delta_{FG} - \delta_L) = V_g.
\]

When \( \psi \ll RT/zF \), the exponential in Equation (2.1) can be linearized as \( \exp(-zF\psi/RT) \approx 1 - zF\psi/RT \), and the zeta potential of the planar surface is derived as

\[
\zeta = \frac{\sigma_* \left( \frac{\varepsilon_L}{\varepsilon_R} \delta_R + \frac{\varepsilon_L}{\varepsilon_{FG}} \delta_{FG} + \delta_L \right) + \varepsilon_0 \varepsilon_L V_g}{\varepsilon_0 \varepsilon_L + \varepsilon_0 \varepsilon_f \kappa \left( \frac{\varepsilon_L}{\varepsilon_R} \delta_R + \frac{\varepsilon_L}{\varepsilon_{FG}} \delta_{FG} + \delta_L \right)}.
\]

Equation (2.3) clearly shows that the zeta potential is linearly proportional to the externally imposed gate potential, \( V_g \), when \( \zeta \ll RT/zF \). Therefore, one could tune the zeta potential and accordingly the electrokinetic transport phenomena by active control of
the gate potential. The degree of the field effect also depends on the thickness and electrical property of each layer of the FGFET, the Debye length which depends on the ionic bulk concentration, and the intrinsic surface charge density, $\sigma_w$.

When $\psi > RT/zF$, Equation (2.1) can be further derived as the Gouy-Chapman solution [139]. After substituting potential distributions of $\psi$ and $\phi_R$ into Equation (2.2), an implicit equation relating the zeta potential to the applied gate potential is derived as

\[
\varepsilon_0 \varepsilon_f \frac{2RT}{Fz} - \frac{2\kappa \tanh \left( \frac{Fz\zeta}{4RT} \right)}{1 - \tanh^2 \left( \frac{Fz\zeta}{4RT} \right)} \varepsilon_0 \varepsilon_L \frac{\zeta - V_g}{\varepsilon_F \delta_R + \varepsilon_L \delta_{FG} + \delta_L} = -\sigma_w.
\]

(2.4)

One can easily use MATLAB function `fzero` to determine $\zeta$ for given values of other parameters.

Figure 2.2 Zeta potential as a function of the relative permittivity of the FG material.
2.3. Results and Discussion

To demonstrate the advantages of the FGFET over the conventional FET, we consider 10 mM KCl as the bulk ionic solution and the dielectric layers are made of silicon dioxide unless otherwise noted. The relative permittivities of the fluid and the silicon dioxide layers are, respectively, $\varepsilon_f = 80$ and $\varepsilon_L = \varepsilon_R = 3.9$ (silicon dioxide). The FGFET becomes the conventional FET when $\varepsilon_{FG} = \varepsilon_L = \varepsilon_R$. The relative permittivity of the FG, $\varepsilon_{FG} \rightarrow \infty$, if the FG is made of a metal such as gold. Figure 2.2 depicts the zeta potential as a function of the relative permittivity of the FG, $\varepsilon_{FG}$, when $V_g = +2$ V, $\delta_L = \delta_{FG} = \delta_R = 10$ nm, and $\sigma_w = 0$. The zeta potential rapidly increases with $\varepsilon_{FG}$ when the latter is relatively low, and saturates when $\varepsilon_{FG}$ exceeds a certain threshold value. The relative change of the zeta potential is less than 1% when $\varepsilon_{FG} \geq 200$. Therefore, in the following we choose $\varepsilon_{FG} = 200$ for the FG made of a conductive material.
Figure 2.3 Zeta potential as a function of gate potential for the dielectric layers made of silicon dioxide (solid and dashed lines), silicon (solid and dashed lines with circles), and pyrex glass (solid and dashed lines with triangles).

Figure 2.3 depicts the zeta potential as a function of the gate potential for three different dielectric materials, silicon dioxide \((\varepsilon_L = \varepsilon_R = 3.9\), solid and dashed lines without symbols\), silicon \((\varepsilon_L = \varepsilon_R = 4.7\), solid and dashed lines with circles\), and pyrex glass \((\varepsilon_L = \varepsilon_R = 11.7\), solid and dashed lines with triangles\) when \(\sigma_w = 0\) and \(\delta_L = \delta_{FG} = \delta_R = 10\) nm. The solid and dashed lines represent, respectively, the zeta potentials tuned by the FGFET using \(\varepsilon_{FG} = 200\) and the conventional FET (i.e., \(\varepsilon_{FG} = \varepsilon_L = \varepsilon_R\)). When the control gate is also floating, the zeta potential of the uncharged surface is zero. For dielectric layers made of silicon dioxide (solid and dashed lines), the zeta potential can be modulated by the conventional FET from \(-36.69\) mV to \(+36.69\) mV for \(V_g\) varying from \(-8\) V to \(+8\) V. The originally uncharged surface becomes positively charged for \(V_g > 0\) and negatively charged when a negative gate potential is applied. In the presence of a metallic FG, the zeta potential can be modulated from \(-50.61\) mV to \(+50.61\) mV for \(V_g\)
varying from \(-8\) V to \(+8\) V. For \(V_g = \pm 8\) V, the magnitude of the zeta potential regulated by the FGFET is about 38% higher than that by the conventional FET. For both the conventional FET and the FGFET, the field effect is more significant for the dielectric layers with higher permittivity. Under all the other same conditions, the field effect by the FGFET is always more significant than that by the conventional FET.

2.4. Conclusions

Tuning the surface charge property by the FGFET has been proposed and theoretically analyzed. Different from the conventional FET, the FGFET contains a floating gate embedded inside the dielectric layer. Since the relative permittivity of the floating metallic gate is much higher than that of the surrounding dielectric layers, the FGFET is more sensitive than the conventional FET to modulate the surface charge property of a dielectric material in contact with an aqueous solution. An implicit expression relating the zeta potential of a planar surface to the gate potential has been derived.
CHAPTER 3

FET CONTROL OF CHARCAGE AND EOF

3.1. Introduction

With recent advances in nanofabrication techniques [200 - 202] and growing interest in sensing single molecule by nanofluidic-based devices [202 - 205], more clearly understanding how to control the transport of ions, flow and particles through biological and synthetic nanopores has attracted significant attention over the past decade. It is generally accepted that in nanofluidics, ion transport and accordingly the electrokinetic-driven flow depend highly on the surface charge property on the nanochannel, especially when the thickness of double layer is comparable to the nanochannel width [206]. Several attempts have been made on the modulating the surface charge property on nanopores, including, for example, adjusting the pH and chemicals in aqueous solution [207, 208] as well as surface modification via chemically or physically grafting functional groups to the wall [209, 210]. Among these, however, there are no methods flexible and capable of rapidly tuning the surface charge on the nanopore.

Recently, a fluidic field effect transistor (FET) [4, 197], referring to the micro/nanochannel embedded with an electrically controllable gate electrode, has been demonstrated feasibly to simply and rapidly tune the surface charge condition and the direction of electroosmotic flow in micro/nanofluidics [4, 5, 176, 186, 187, 197, 211 - 214]. In the field effect control of surface potential, an electric bias called gate potential is applied perpendicular to the gate electrode surrounding the outer surface of the dielectric channel wall. Note that the gate electrode and the liquid inside the micro/nanochannel are separated by an electrically insulating layer, material of dielectric layer, such as silicon dioxide (SiO$_2$).
The surface of gated dielectric channel wall in contact with an aqueous solution is often assumed bearing a negative surface according to its dissociation/association constant. Depending upon different manufacture process, the point of zero charge (PZC) for SiO2 ranges from 2 to 3.5 [215]. Since the silanol groups (Si–OH) on the SiO2 surface are deprotonated to produce Si–O− when the pH is higher than PZC, the SiO2 surface in contact with an aqueous solution is negatively charged and depends largely on the pH of liquid phase [66]. Previous theoretical studies, however, are almost always based on that the charge condition on the gated solid/liquid interface is constant surface charge density [186, 187] or even uncharged [5, 176, 214]. These assumptions, although they make the mathematical treatment easier, are inaccurate and unrealistic in practice. Therefore, extending the conventional analyses to take the effect of the pH of liquid phase into account that might be significant in practice is highly desirable.

In this study, a charge-regulated model is performed to investigate the surface charge property and electroosmotic flow in a pH-tunable nanofluidic FET by considering the presence of multiple ionic species into account. Approximate expressions are developed including analytical and implicit solutions, to predict the effect of applied gate potential, and the pH and bulk ionic concentration of liquid phase on the zeta potential of the FET surface and the electroosmotic flow velocity. A good agreement between the present charge-regulated model and the available experiment results in the literature is found.

3.2. Theoretical Analysis

Referring to Figure 3.1(a), a steady flow of an aqueous electrolyte solution of relative permittivity $\varepsilon_f$ is considered within a nanofluidic field effect transistor (FET). The FET includes a gate electrode, which is consisted of a dielectric layer of thickness, $\delta$, and
relative permittivity, $\varepsilon_d$. A uniform electric field $E_z$ of strength $E_z$ parallel to the surface of the FET, along the $z$-direction, is applied to drive the steady electroosmotic flow (EOF) of electrolyte solution. A gate potential on the gate electrode, $V_g$, is applied to tune the surface potential of FET, then in turn controlling the EOF and the accordingly electrokinetic transport phenomena.

Figure 3.1. (a) Schematic illustrating the regulation of the electroosmotic flow by a nanofluidic field effect transistor (FET). (b) Schematic representation of the problem under consideration.
The following is assumed: (i) The liquid is incompressible and the flow field is in the creeping flow regime; (ii) The effect of stem layer is neglected so that the electric potential at the solid/liquid interface of the FET is the zeta potential of the planar surface, $\zeta$; (iii) The planar surface of dielectric material in contact with the aqueous solution bears a uniform surface charge density of $\sigma_w$, which exists a charge-regulated nature as will be explained later [216]; and (iv) The effect of double layer overlapping in the nanochannel is insignificant so that the present problem can be simplified to the case of planar FET in contact with a semi-infinite aqueous electrolyte solution, as illustrated in Figure 3.1b. This is reasonable if the Debye length (or the thickness of double layer $\kappa^{-1}$) is much smaller than the half width of the nanochannel, that is, $\lambda_D = \kappa^{-1} << W$, which is not uncommon in practice. For example, the background electrolyte concentration in experiments is typically in the range of 1-1000 mM [5, 186, 208, 217], and therefore, the Debye length ranges from 9.6 to 0.3 nm [206], which is very thin relative to most of $W$. With these considerations, the distributions of the electric potential, the ionic concentrations, and the flow field of the liquid are uniform along the $z$-direction. This implies that the analysis under consideration can be simplified to one-dimensional. A Cartesian Coordinate system $(x, z)$ with the origin located at the solid/liquid interface of the FET.

If the flow of a general electrolyte solution containing $N$ kinds of ionic species is considered, the electric potential inside and outside the dielectric material (region I and II), which are respectively governed by the Laplace equation and the Poisson-Boltzmann equation, and the flow field can be described by

$$\nabla^2 \varphi = 0, \text{ in region I}$$

(2.1)
\( \nabla^2 \psi = -\frac{\rho_e}{\varepsilon_0} = -\frac{1}{\varepsilon_0} \sum_{i=1}^{N} F z_i C_{i0} \exp \left( \frac{z_i F \psi}{R T} \right), \text{ in region II} \)  

(2.2)

\[ \nabla^2 u = -\frac{1}{\mu} \rho_e E, \text{ in region II} \]  

(2.3)

Here, \( \varphi \) is the electric potential inside the dielectric layer, \( \psi \) is that within the liquid phase, and \( u \) is the fluid velocity in the \( z \)-direction; \( \nabla^2 \) is the Laplace operator; \( \varepsilon_0 \) is the absolute permittivity of vacuum; \( \rho_e \) is the net space charge density; \( z_i \) and \( C_{i0} \) are the valence and the bulk concentration of ionic species \( i \), respectively; \( F, R, T, \) and \( \mu \) are the Faraday constant, the universal gas constant, and the absolute temperature and viscosity of the electrolyte solution, respectively.

For a general case of symmetric \( z_1:z_2 \) background electrolyte solutions with \( z_1 \) and \( z_2 \) being the valences of cations and anions, respectively, Equations (3.1) - (3.3) can be rewritten by

\[ \frac{d^2 \varphi}{dx^2} = 0, \text{ in region I} \]  

(3.4)

\[ \frac{d^2 (\frac{z F \psi}{R T})}{dx^2} = \kappa^2 \sinh \left( \frac{z F \psi}{R T} \right), \text{ in region II} \]  

(3.5)

\[ \frac{d^2 u}{dx^2} = \frac{\varepsilon_0 \varepsilon_f E_z}{\mu} \frac{d^2 \psi}{dx^2}, \text{ in region II} \]  

(3.6)

where \( z = z_1 = -z_2 \); \( C_0 = C_{i0} = C_{20} \); \( \lambda_0 = \kappa^{-1} = \sqrt{\frac{\varepsilon_f \varepsilon_0 R T}{2 z^2 F^2 C_0}} \) is the Debye length (or electric double layer thickness).
Suppose that the surface of a gate electrode \((x = -\delta)\) is imposed at a constant gate potential \(V_g\). Then, if the planar surface of the FET in contact with aqueous solution is non-slip, the boundary conditions associated with Equations (3.4) - (3.6) are

\[
\varphi = V_g \text{ at } x = -\delta \tag{3.7}
\]

\[
\varphi = \psi \equiv \zeta \text{ at } x = 0 \tag{3.8}
\]

\[
\varepsilon_0 \varepsilon_f \frac{d\psi}{dx} - \varepsilon_0 \varepsilon_d \frac{d\varphi}{dx} = -\sigma_w \text{ at } x = 0 \tag{3.9}
\]

\[
\psi = 0 \text{ and } \frac{d\psi}{dx} = 0 \text{ as } x \to \infty \tag{3.10}
\]

\[
u = 0 \text{ at } x = 0 \tag{3.11}
\]

\[
\frac{d\nu}{dx} = 0 \text{ as } x \to \infty \tag{3.12}
\]

Equations (3.8) and (3.9) implies that the electric potential is continuous at the solid/liquid interface of the FET, but the electric field is not continuous due to the discontinuity of the electric permittivities at that interface, where the electric field satisfies Gauss’s law.

Solving Equations (3.4) and (3.5) subject to Equations (3.7), (3.8), and (3.10) yields

\[
\varphi = \left(\zeta - V_g\right)\left(\frac{x}{\delta}\right) + \zeta \tag{3.13}
\]

\[
\psi = \frac{2RT}{Fz} \ln \left[\frac{1 + \exp(-\kappa x) \tanh\left(\frac{Fz\zeta}{4RT}\right)}{1 - \exp(-\kappa x) \tanh\left(\frac{Fz\zeta}{4RT}\right)}\right] \tag{3.14}
\]

Note that Equation (3.14) is the well-known Gouy-Chapman solution for the planar surface system.
By substituting Equation (3.14) into Equation (3.6) and solving the resultant equation subject to Equations (3.11) and (3.12), the following relation between the flow velocity $u$ and the zeta potential $\zeta$ is obtained.

$$u = 4u_r \tanh^{-1} \left[ \tanh \left( \frac{Fz\zeta}{4RT} \right) \exp \left( -\kappa x \right) \right] - \frac{\varepsilon_0 \varepsilon_f E_z \zeta}{\mu}$$  \hspace{1cm} (3.15)

where $u_r = (\varepsilon_0 \varepsilon_f E_z / \mu)(RT/Fz)$ is the magnitude of the Smoluchowski electroosmotic velocity.

Typically, due to the protonation/deprotonation surface reactions often occurring on the dissociably functional groups of the solid/liquid interface of the FET, this dielectric layer surface reveals a charge-regulated nature when it is in contact with an aqueous solution. This means surface charge properties of the FET solid/liquid interface depend largely on the solution properties such as its pH and ionic concentration. To simulate this kind of problem, we assume that the following two main dissociation/association reactions occur on that solid/liquid interface:

$$\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+ \hspace{1cm} (3.16)$$

$$\text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}_2^+ \hspace{1cm} (3.17)$$

If we let $K_A$ and $K_B$ be the equilibrium constants associated with these reactions, then

$$K_A = \frac{N_{\text{MO}^-} [\text{H}^+]_s}{N_{\text{MOH}}},$$  \hspace{1cm} (3.18)

$$K_B = \frac{N_{\text{MOH}_2^+}}{N_{\text{MOH}} [\text{H}^+]_s},$$  \hspace{1cm} (3.19)

where $N_{\text{MOH}}, N_{\text{MO}^-},$ and $N_{\text{MOH}_2^+}$ are the surface site densities of MOH, MO$, and MOH_2^+$, respectively; $[\text{H}^+]_s$ is the concentration of H$^+$ on the solid/liquid interface surface of the
If we let \( N_{\text{total}} = N_{\text{MOH}} + N_{\text{MO}^-} + N_{\text{MOH}^2} \) be the total number site density of MOH molecules on the solid/liquid interface surface, then assuming the spatial variation of \( H^+ \) following the Boltzmann distribution and combining Equations (3.18) and (3.19), and the relation of \( \sigma_w = -F(N_{\text{MO}^-} - N_{\text{MOH}^2}) \) gives

\[
\sigma_w = -FN_{\text{total}} \frac{\left( \frac{K_A - K_B \left[ [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) \right]^2}{K_A + [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) + K_B \left[ [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) \right]^2} \right)}{K_A + [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) + K_B \left[ [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) \right]^2} \]

(3.20)

where \([H^+]_0\) is the bulk concentration of \( H^+ \). By substituting Equations (3.13), (3.14), and (3.20) into Equation (3.9) yields the following implicit equation relating the zeta potential, \( \zeta \), to the externally imposed gate potential, \( V_g \), the electric property and thickness of dielectric layer, \( \varepsilon_d \) and \( \delta \), the physicochemical interface properties of dielectric layer, \( K_A \), \( K_B \), and \( N_{\text{total}} \), the Debye-Hückel parameter, \( \kappa \), which depends on the bulk ionic concentration, \( C_0 \), and the pH value of the liquid phase (\( \text{pH} = -\log([H^+]_0) \)).

\[
\frac{2\varepsilon_0 \varepsilon_f \kappa RT}{2F} \sinh \left( \frac{F \zeta}{2RT} \right) + \varepsilon_0 \varepsilon_d \left( \frac{\zeta - V_g}{\delta} \right) = \frac{1}{FN_{\text{total}}} \left( \frac{K_A - K_B \left[ [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) \right]^2}{K_A + [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) + K_B \left[ [H^+]_0 \exp \left( -\frac{F \zeta}{RT} \right) \right]^2} \right) \]

(3.21)

One can easily use, for example, MATLAB function fzero to determine \( \zeta \) for giving appropriate values of other parameters. By substituting \( \zeta \) obtained into Equations (3.14) and (3.15), we obtain the spatial distribution of \( \psi \) and \( u \).
In general, Equation (3.21) needs be solved numerically. However, when considering the case of low surface potential, that is, $\zeta << RT / zF$, then Equations (3.14), (3.15), and (3.21) can be reduced to

$$\psi = \zeta \exp(-\kappa x)$$  \hspace{1cm} (3.22)

$$u = \frac{\varepsilon_0 E_f E_z \zeta}{\mu} \left[ \exp(-\kappa x) - 1 \right]$$ \hspace{1cm} (3.23)

$$\varepsilon_0 \varepsilon_f \kappa \zeta + \varepsilon_0 \varepsilon_d \left( \frac{\zeta - \frac{V_e}{\delta}}{\delta} \right) = -FN_{total} \left\{ \frac{\Phi}{\Omega} + \left( \frac{F \zeta}{RT} \right) \left[ \frac{\Pi}{\Omega} + \frac{\Phi([H^+]_0 + \Pi)}{\Omega^2} \right] \right\}$$ \hspace{1cm} (3.24)

where $\Omega = K_A + [H^+]_0 + K_B [H^+]_0^2$, $\Phi = K_A - K_B [H^+]_0^2$, and $\Pi = 2K_B [H^+]_0^2$. Solving Equation (3.24), results in

$$\zeta = \frac{-\delta FN_{total} \left( \frac{\Phi}{\Omega} \right)}{\varepsilon_0 \varepsilon_f \kappa \delta + \varepsilon_0 \varepsilon_d + \delta FN_{total} \left( \frac{F}{RT} \right) \left[ \frac{\Pi}{\Omega} + \frac{\Phi([H^+]_0 + \Pi)}{\Omega^2} \right]}$$ \hspace{1cm} (3.25)

Under the Debye-Hückel approximation (i.e. $\zeta << RT / zF$), Equation (3.25) clearly shows that, in addition to the behavior that $\zeta$ is linearly proportional to the externally imposed gate potential, $V_e$, it also depends on lots of parameters given such as $\varepsilon_d$, $\delta$, $V_e$, $K_A$, $K_B$, $N_{total}$, and $[H^+]_0$. This implies that the degree of the field effect depends largely on the surface properties and material of the dielectric layer, and the pH and bulk ionic concentration of the liquid phase. Once $\zeta$ is known, $\psi$ and $u$ can be easily evaluated by Equations (3.22) and (3.23), respectively.
3.3. Results and Discussion

3.3.1. Verification of Model by Numerical Solution

To demonstrate the performance of the present charge-regulated models, including zeta potential, Equations (3.21) and (3.25), and the associated electroosmotic velocity profile, Equations (3.15) and (3.23), were examined by comparing the predicted results with the corresponding exact results by solving Equations (3.1) - (3.3) numerically. For illustration, we consider the monovalent background electrolyte solution, such as KCl where $z=1$, and the dielectric layer is made of silicon dioxide where $\varepsilon_d = 3.9$, $N_{total} = 8 \times 10^{-6}$ mol/m$^2$, $pK_A = 6.8$, and $pK_B = 1.9$. [218] Note that $pK = -\log_{10} K$. Also, the relevant physical constants are $\varepsilon_f = 80$, $\varepsilon_0 = 8.854 \times 10^{-12}$ CV$^{-1}$m$^{-1}$, $R = 8.314$ JK$^{-1}$mol$^{-1}$, $T = 298$ K, $\eta = 10^3$ kgm$^{-1}$s$^{-1}$, and $F = 96490$ Cmol$^{-1}$.

Figures 3.2 - 3.5 depict the variations of the zeta potential $\zeta$ at various combinations of the pH value, the bulk ionic concentration $C_0$ and the applied gate potential $V_g$. Both the results based on Equation (3.21) (discrete empty symbols), where only background electrolyte ions, K$^+$ and Cl$^-$, are considered, and the corresponding exact numerical results based on Equations (3.1) and (3.2) (lines), where four major kinds of ions, including K$^+$, Cl$^-$, H$^+$, and OH$^-$, are all considered, are presented. As seen in Figures 3.2-3.5, the present charge-regulated model based on Equation (3.21) agrees very well with the exact numerical solutions except that when $C_0$ is sufficiently small (ca. 1 mM) and pH is sufficiently small (ca. pH < 3.5) or sufficiently large (ca. pH > 10.5), implying that if $C_0$ is large and/or pH is in the middle range (ca. 3.5 < pH < 10.5) the influence of the hydrogen and hydroxyl ions on the zeta potential becomes insignificant. It should be pointed out that even though at low
(high) level of pH the influence of the H⁺ (OH⁻) coming from the dissociation of HCl (KOH) and H₂O becomes significant and should not be ignored compared to C₀, the relative error of the zeta potential between these two results is still less than 5%, showing that the present charge-regulated model is applicable to the entire pH range of 3 to 11 under consideration. Figures 3.2 - 3.5 also reveals that the zeta potential modulated by the FET depends largely on the levels of the pH value and the bulk ionic concentration, two of important modulated parameters in the charge-regulated model. In general, the smaller the C₀ and/or pH the higher magnitude of zeta potential tuned by the FET, as can be seen in Figures 3.4 and 3.5. The former is because the higher the C₀ the thinner the double layer and the greater the amount of counterions confined near the solid/liquid interface of the FET, yielding the harder the FET tuning the zeta potential. Similarly, as pH gets higher, since the greater the amount of hydrogen ions dissociated from the functional groups on the FET surface the higher the surface charge density, and therefore, the larger the amount of counterions gathered on that surface, leading to the same behavior as the case of higher concentration of C₀. This implies that the degree of zeta potential regulated by the FET will also be suppressed when pH is high. It should be noted that although for the present case the point of zero charge (PZC) is approximately at pH=2.45, the PZC will be changed when the gate potential is imposed. As illustrated in Figure 3.3, the PZC increases with increasing V_g, in general.
Figure 3.2. Variations of zeta potential $\zeta$ as a function of pH at various combinations of the bulk ionic concentration $C_0$, for the case of dielectric layer made of SiO$_2$ where $\delta = 10$nm, $\varepsilon_d = 3.9$, $N_{\text{total}} = 8 \times 10^{-6}$ mol/m$^2$, $pK_A = 6.8$, $pK_B = 1.9$ and $V_\varepsilon = 5$V.

Figure 3.3. Variations of zeta potential $\zeta$ as a function of pH at various combinations of applied gate potential $V_\varepsilon$, for the case of dielectric layer made of SiO$_2$ where $\delta = 10$nm, $\varepsilon_d = 3.9$, $N_{\text{total}} = 8 \times 10^{-6}$ mol/m$^2$, $pK_A = 6.8$, $pK_B = 1.9$ and $C_0 = 1$mM.
Figure 3.4. Variations of zeta potential $\zeta$ as a function of $V_g$ at various combinations of the bulk ionic concentration $C_0$, for the case of dielectric layer made of SiO$_2$ where $\delta = 10$nm, $\varepsilon_d = 3.9$, $N_{total} = 8 \times 10^{-6}$ mol/m$^2$. $pK_A = 6.8$, $pK_B = 1.9$ and pH = 3.

Figure 3.5. Variations of zeta potential $\zeta$ as a function of $V_g$ at various combinations of pH, for the case of dielectric layer made of SiO$_2$ where $\delta = 10$nm, $\varepsilon_d = 3.9$, $N_{total} = 8 \times 10^{-6}$ mol/m$^2$. $pK_A = 6.8$, $pK_B = 1.9$ and $C_0 = 1$ mM.
The performance of the approximate analytical expression under the Debye-Hückel approximation, Equation (3.25) (discrete solid symbols), is examined in Figure 3.6, where the corresponding approximate results based on Equation (3.21) (discrete empty symbols) and the exact numerical results based on Equations (3.1) and (3.2) (lines) are also presented. Note that for the present case of SiO2 dielectric layer, since the zeta potential involved exceeds 25.7 mV (one thermal potential $RT/F$) too much as pH gets higher than 8, we only compare these three results in the range of $3 < \text{pH} < 7.5$. Figure 2.6 reveals that if pH is small (ca. pH < 5), the larger the $C_0$ the better the performance of the present approximate analytical results. Otherwise, if pH is large, due to the zeta potential involved is too high the deviation of zeta potential from the exact numerical results gets higher.

Table 3.1. Relative percentage deviation in the zeta potential, $RPD$ (%), the approximate result of implicit equation, Equation (3.21), for the case of Figure 3.6.

<table>
<thead>
<tr>
<th>$C_0$ (mM)</th>
<th>pH=3</th>
<th>pH=5</th>
<th>pH=7</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.39</td>
<td>0.018</td>
<td>0.003</td>
</tr>
<tr>
<td>100</td>
<td>0.53</td>
<td>0.036</td>
<td>0.019</td>
</tr>
<tr>
<td>1000</td>
<td>0.071</td>
<td>0.053</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 3.2. Relative percentage deviation in the zeta potential, $RPD$ (%), for the approximate analytical expression, Equation (3.25), for the case of Figure 3.6.

<table>
<thead>
<tr>
<th>$C_0$ (mM)</th>
<th>pH=3</th>
<th>pH=5</th>
<th>pH=7</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.97</td>
<td>11.08</td>
<td>27.89</td>
</tr>
<tr>
<td>100</td>
<td>1.04</td>
<td>3.65</td>
<td>14.51</td>
</tr>
<tr>
<td>1000</td>
<td>0.24</td>
<td>0.62</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Tables 3.1 and 3.2 summarize the relative percentage deviation in the zeta potential, $RPD$ (%), for the case of Figure 3.6. The $RPD$ is defined by $RPD = 100\% \times (\zeta - \zeta_{\text{exact}}) / \zeta_{\text{exact}}$. 
The excellent agreement between the approximate results based on Equation (3.21) and the exact numerical results is observed except when pH and \( C_0 \) is sufficiently small, which is consistent with the result of Figures 3.2 - 3.5. On the other hand, for the present model of approximate analytical expression, Equation (3.25), the larger the pH and \( C_0 \) the smaller the RPD. Therefore, it should be pointed out that if the zeta potential is not too high, the performance of the present approximate analytical expression, Equation (3.25), is satisfactory, especially when \( C_0 \) is sufficiently large.

Figure 3.6. Variations of zeta potential \( \zeta \) as a function of pH for various values of bulk ionic concentration \( C_0 \) at the applied gate potential \( V_g = 5V \) for the case of dielectric layer made of SiO\(_2\) where \( \delta = 30nm, \varepsilon_d = 3.9, N_{total} = 8\times10^{-6} \text{ mol/m}^2 \), \( pK_a = 6.8, pK_B = 1.9 \).

Figures 3.7 - 3.9 depict the electroosmotic flow velocity profile for various combinations of the pH value, the bulk ionic concentration \( C_0 \) and the applied gate potential \( V_g \). The
lines, discrete empty symbols, and discrete solid symbols, represent the exact numerical results based on Equations (3.1) - (3.3), the approximate results based on Equations (3.15) and (3.21), and the approximate analytical results based on Equations (3.23) and (3.25), respectively. Similar to the results of Figures 3.2 - 3.6, the flow field predicted by the present approximate model based on Equations (3.15) and (3.21) agrees excellently with that by the exact numerical results. However, for the model of the analytical solution based on Equations (3.23) and (3.25), the deviation of the flow profile from that to the exact numerical results becomes obvious when the zeta potential involved gets higher, for example, higher pH in Figure 3.7, lower $C_0$ in Figure 3.8, and higher $V_g$ in Figure 3.9.

Figures 3.7 - 3.9 also indicates that the electroosmotic flow profile can be modulated by adjusting the value of pH, $C_0$, and $V_g$, and even its movement direction can be easily changed by tuning the pH and $V_g$. Note that in addition to the parameters of pH, $C_0$, and $V_g$, one also can regulate the zeta potential, electroosmotic flow profile and the accordingly electrokinetic phenomena (i.e. ionic current) by modulating the other parameters such as $N_{total}$, $pK_A$, and $pK_B$ via choosing various material of the dielectric layer [186, 208] or conducting appropriated surface modification of that layer [207, 210].
Figure 3.7. Spatial variations of the electroosmotic velocity driven by the applied electric field $E_x = 20\text{kV/m}$ at various combinations of pH value, bulk ionic concentration $C_0$, and applied gate potential $V_g$ for the case of dielectric layer made of SiO$_2$ where $\delta = 30\text{nm}$, $\epsilon_d = 3.9$, $N_{\text{total}} = 8\times10^{-6} \text{ mol/m}^2$, $pK_A = 6.8$, $pK_B = 1.9$, $C_0=10\text{mM}$ and $V_g = 5\text{V}$.

Figure 3.8. Spatial variations of the electroosmotic velocity driven by the applied electric field $E_x = 20\text{kV/m}$ at various combinations of pH value, bulk ionic concentration $C_0$, and applied gate potential $V_g$ for the case of dielectric layer made of SiO$_2$ where $\delta = 30\text{nm}$, $\epsilon_d = 3.9$, $N_{\text{total}} = 8\times10^{-6} \text{ mol/m}^2$, $pK_A = 6.8$, $pK_B = 1.9$, pH=4 and $V_g = 5\text{V}$.
Figure 3.9. Spatial variations of the electroosmotic velocity driven by the applied electric field $E_z = 20\text{kV/m}$ at various combinations of pH value, bulk ionic concentration $C_0$, and applied gate potential $V_g$ for the case of dielectric layer made of SiO$_2$ where $\delta = 30\text{nm}$, $\varepsilon_d = 3.9$, $N_{total} = 8 \times 10^{-6} \text{mol/m}^2$, $pK_A = 6.8$, $pK_B = 1.9$, $C_0 = 10\text{mM}$ and pH=4.

3.3.2. Verification of Model by Experimental Data

The applicability of the present charge-regulated model is examined by fitting it to the experiment data of Gaudin and Fuerstenau at pH=6.5 [219], where the result of zeta potential was conducted for the case of isolated flat silica surface, and to the experiment data of Oh et al. [5] at pH=4, $C_0 = 1 \text{mM}$, and $\delta = 100 \text{nm}$ [5], where the zeta potential versus applied gate potential was conducted in a silica-based nanofluidic FET. In order to verify the model to the result of Gaudin and Fuerstenau [219], let $V_g = 0$ and neglect the permittivity of the dielectric layer of the FET ($\varepsilon_d = 0$) since this permittivity is much smaller than that of the liquid phase.
Therefore, Equation (3.21) can be rewritten as

\[
\frac{2\varepsilon_0 e_i \kappa RT}{zF} \sinh\left(\frac{F_z \zeta}{2RT}\right) = -FN_{total} \left\{ \frac{K_A - K_B [H^+]_0 \exp\left(-\frac{F \zeta}{RT}\right)}{K_A + [H^+]_0 \exp\left(-\frac{F \zeta}{RT}\right) + K_B [H^+]_0 \exp\left(-\frac{F \zeta}{RT}\right)} \right\}^2
\]

(3.26)

One can easily use it to determine the zeta potential of the planar surface of the micro/nanochannel with a charge-regulated nature. Figure 3.10 shows the variation of the zeta potential as a function of bulk ionic concentration. Both the experimental data [219] and the results predicted by Equation (3.26) are presented. The later are based on the values of the parameters, namely, \(N_{total} = 8 \times 10^{-6} \text{ mol/m}^2\), \(pK_B = 1.9\) [218] and \(pK_A = 7.4\). Note that in this case, the value of \(pK_A\) is only modulated to fit the experimental data, and the estimated value of \(pK_A = 7.4\) is in well agreement with the value of silica (\(pK_A = 7.5\)) reported in the literature [220]. The variation of zeta potential as a function of applied gate potential in a silica-based nanofluidic FET is shown in Figure 3.11, where both the experiment data [5] and the approximate result based on Equation (3.21) are presented. In this case, the charge-regulated parameters given in Equation (3.21) are \(N_{total} = 8 \times 10^{-6} \text{ mol/m}^2\), \(pK_B = 1.9\) [218] and \(pK_A = 7.5\) [220], all of which are consistent with the typical values for silica. As seen in Figure 3.11, the present model is capable of describing the general trend of the experimental data. Note that the zeta potential is negative when \(V_g = 0\), which corresponds to the case of silica nanochannel.
Figure 3.10. Zeta potential versus bulk ionic concentration for the case of isolated flat silica surface for the case of a SiO$_2$-based nanochannel embedded with a nanofluidic FET.

Figure 3.11. Versus applied gate potential for the case of a SiO$_2$-based nanochannel embedded with a nanofluidic FET.
3.4. Conclusions

In summary, pH-regulation of the surface charge property and electroosmotic flow velocity by the nanofluidic field effect transistor (FET) with charge-regulated surfaces was proposed and theoretically analyzed. Approximate expressions, including analytical and implicit ones, were derived for the first time to estimate the zeta potential and the electroosmotic velocity tuned by the FET. The applicability of the charge-regulated model derived is verified by the available experimental data in the literature. It was found that the charge property as well as the direction and magnitude of the electroosmotic flow can be tuned by regulating the pH value and bulk concentration of the aqueous electrolyte solution and the applied gate potential of the FET. In addition, its tuning degree of the field effect becomes sensitive when the pH is low and/or the bulk electrolyte concentration is dilute. Finally, it is believed that this study will have a great potential significance in the application of electrokinetics-based micro/nanofluidic devices.
CHAPTER 4

FET CONTROL OF IONIC CONDUCTANCE

4.1. Introduction

Nanofluidics [171, 206, 221, 222], such as nanopores, nanochannels, and nanocapillaries, have recently emerged as powerful platforms for versatile applications such as ionic filters [222, 223], nanofluidic diodes [224, 225], energy conversion [6, 124, 164], and analysis and separation of biomolecules [226 - 230]. The nanopore-based biosensing is based on discriminating the ionic current (or conductance) signals arising from different ion transport phenomena in these nanofluidic devices, which are strongly dependent on their surface charge property [171, 206, 221, 222, 231]. Therefore, actively control the surface charge property and the ionic current/conductance in nanofluidics, and understand mechanisms governing these processes are essential for developing the next-generation nanofluidic devices.

Recently, nanofluidic field effect transistors (FETs) [4, 179, 180, 232], referring to the nanochannels (or nanopores) embedded with electrically controllable gate electrodes, have been developed to actively control the surface charge property and, accordingly, the electrokinetic ion, fluid, and (bio)nanoparticle transport inside the nanochannels. The surface charge property of the nanochannel can be tuned by modulating the gate potential imposed on the gate electrode patterned beneath the dielectric nanochannel wall made of such as silicon dioxide (SiO$_2$) and aluminum oxide (Al$_2$O$_3$). It has been demonstrated that these dielectric materials in contact with aqueous solution reveal a charge-regulated nature [66 - 69], implying that their surface charge properties (e.g., zeta potential), depend upon the local solution properties such as pH and salt concentration. In addition,
the electric double layer (EDL) formed on the nanochannel in contact with aqueous electrolyte solution includes both a Stern layer and a diffusive layer. Because of the attraction of immobile counterions inside the Stern layer, the electric potential at the solid/liquid interface, the so-called surface potential $\psi_s$, is reduced to a lower value called zeta potential $\psi_d$, as illustrated in Figure 4.1. Recently, Hughes et al. [190] confirmed that the Stern layer effect plays a significant role on the surface charge property and electroosmotic flow (EOF) in a gated nanochannel. In that study, analytical expressions for zeta potential and EOF velocity were derived without considering H$^+$ and OH$^-$ ions. The results from the analytical expressions deviate from the full model with the consideration of both H$^+$ and OH$^-$ ions when the solution pH deviates from 7 apparently.
Figure 4.1. Schematic illustration of the field effect modulation of the zeta potential ($\psi_g$) and the ionic current in a pH-regulated nanochannel containing multiple ionic species, $\text{H}^+$, $\text{K}^+$, $\text{Cl}^-$, and $\text{OH}^-$. Four major regions are considered: the dielectric channel layer of thickness $\delta$, the immobile Stern layer with surface capacitance $C_s$, the diffusive layer of Debye length $\lambda_D$, and the bulk state with solution pH and background salt concentration $C_{KCl}$. $V_g$ is the gate potential imposed on the gate electrode and $\psi_s$ is the surface potential resulting from the association and dissociation surface reactions of functional groups on the nanochannel wall.

Many theoretical studies [5, 176, 182 - 192, 233], mainly focused on numerical simulations [5, 183 - 189, 191, 192], have been conducted on the field effect modulation of ion, fluid, and nanoparticle transport in the gated nanofluidic devices. However, these studies possess several limited assumptions, such as a constant surface charge density at the gated dielectric channel wall [5, 182 - 189], consideration of background ionic species only [5, 176, 182 - 192], and without considering Stern layer and EOF effects [5, 176, 182 - 189, 191, 192]. Although these assumptions make mathematical treatment
simpler, developing a more general and realistic model to elaborate experimental observations and design relevant gated devices is highly desirable.

Considering widespread applications using nanofluidics, where the ionic current (or conductance) is the major analysis signal, the surface charge property and ionic current/conductance in a pH-regulated nanochannel gated by FET are investigated with the consideration of multiple ionic species, surface chemistry reactions on the dielectric channel wall, and the Stern layer effect. Moreover, the EOF effect, which was often neglected in previous studies [183, 185 - 189, 191], on the ionic current/conductance modulated by the FET is also considered in this study. Analytical expressions are derived for the first time to predict the zeta potential and surface charge density of the diffusive layer on the channel wall, and the ionic conductance as functions of the solution properties (pH and background salt concentration), applied gate potential, and the surface capacitance of the Stern layer. Since most of the practical effects are taken into account, the analytical results provide better insight into the underlying physics and necessary information for utilizing gated nanochannels in relevant applications.

4.2. Mathematical Model

As schematically shown in Figure 4.1, a steady, electrokinetic transport of an aqueous electrolyte solution of relative permittivity $\varepsilon_f$ in a long pH-regulated nanochannel of height $h$, width $w$, and length $l$ is considered. The nanochannel is equipped with a FET, consisting of a thin dielectric channel layer of thickness $\delta$ and relative permittivity $\varepsilon_d$, and a gate electrode patterned on its outer surface. A gate potential is applied on the gate electrode to tune the surface charge property of the inner nanochannel wall and, in turn, controls the transport of ions and fluid within the
nanochannel. The Cartesian coordinates $x$ and $z$ with the origin located at the solid/liquid interface are adopted, and $E_z = V/l$ is the applied uniform electric field directed in the $z$-direction with $V$ being the potential bias across the nanochannel.

The following is assumed: (i) The liquid phase is an incompressible Newtonian fluid containing $N$ kinds of ionic species, and the resulting electroosmotic flow (EOF) is fully developed and parallel to the channel wall (i.e., $z$-direction); (ii) The wall of the dielectric channel layer (e.g., such as SiO$_2$, Si$_3$N$_4$, and Al$_2$O$_3$) in contact with an aqueous solution is of charge-regulated nature [66 - 68] and bears a uniform surface charge density $\sigma_s$ along the $z$-direction; (iii) The no-slip plane is located at the Stern layer/diffusive layer interface; (iv) No external pressure gradient is applied across the nanochannel; (v) Both width and length of the nanochannel are much larger than its height ($w \gg h$ and $l \gg h$) so that the problem under consideration can be approximated as a nanoslit with two infinite parallel plates; and (vi) The overlapping of the electric double layers (EDLs) of two adjacent nanochannel walls is not significant so that the possible presence of the ion concentration polarization [206, 234, 235], arising from the selective transport of counterions and coions, is neglected. This assumption is valid if the Debye length is much smaller than the half height of the nanochannel (i.e., $\lambda_D = \kappa^{-1} \ll h/2$), and holds for most experimental conditions in nanofluidics. For example, the background salt concentration in experiments varies typically from 1 to 1000 mM, yielding the Debye length ranging from 9.6 to 0.3 nm, which is very thin compared to most of $h$ [5 - 7, 236 - 238]. Based on the above assumptions, the distributions of electric field, ionic concentrations, and the EOF velocity are uniform in the $z$-direction.
4.2.1 Governing Equations and Boundary Conditions

Because ions and fluid inside the Stern layer are immobile, the electric potentials within the dielectric channel layer, Stern layer, and liquid, $\phi$, $\varphi$, and $\psi$, respectively, and the flow field can be described by

$$\frac{d^2 \phi}{dx^2} = 0 \text{ within the dielectric layer } (-\delta \leq x \leq 0),$$  \hspace{1cm} (4.1)

$$\frac{d^2 \varphi}{dx^2} = 0 \text{ within the Stern layer } (0 \leq x \leq \delta_s),$$  \hspace{1cm} (4.2)

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0 \varepsilon_f} = -\frac{1}{\varepsilon_0 \varepsilon_f} \sum_{i=1}^{n} F_i C_{i_0} \exp\left(-\frac{z_i F \psi}{RT}\right) \text{ within the liquid phase } (\delta_s \leq x \leq h/2),$$  \hspace{1cm} (4.3)

$$\frac{d^2 u_z}{dx^2} = -\frac{\rho_e E_z}{\mu} \text{ within the liquid phase } (\delta_s \leq x \leq h/2)$$  \hspace{1cm} (4.4)

In the above, $\rho_e$ is the mobile space charge density; $\varepsilon_0$, $F$, $R$, $T$, and $\mu$ are the absolute permittivity of vacuum, Faraday constant, universal gas constant, absolute temperature, and dynamic fluid viscosity, respectively; $z_i$ and $C_{i_0}$ are the valence and the bulk concentration of the $i$th ionic species, respectively; $u_z$ and $E_z$ are, respectively, the fully developed EOF velocity and the imposed electric field in the $z$-direction.

Because the EDL overlapping inside the nanochannel is neglected, we assume at the center of the nanochannel, the concentration of the $i$th ionic species reaches its bulk value and the electric potential stemming from the charged nanochannel wall vanishes. The following boundary conditions associated with Equations (4.1) - (4.4) are

at the gate electrode $(x = -\delta)$,

$$\phi = V_g,$$  \hspace{1cm} (4.5)
at the dielectric layer/Stern layer interface \( (x = 0) \),

\[
\phi = \varphi = \psi_s, \quad (4.6a)
\]

\[
-\varepsilon_0 \varepsilon_d \frac{d\phi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\varphi}{dx} = -\sigma_s, \quad (4.6b)
\]

at the Stern layer/diffusive layer interface \( (x = \delta_s) \),

\[
\varphi = \psi = \psi_d, \quad (4.7a)
\]

\[
-\varepsilon_0 \varepsilon_f \frac{d\varphi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\psi}{dx} = 0, \quad (4.7b)
\]

\[
u_z = 0, \quad (4.7c)
\]

and at the center of the nanochannel \( (x = h/2) \),

\[
\psi = \frac{d\psi}{dx} = 0, \quad (4.8a)
\]

\[
\frac{d\psi_s}{dx} = 0. \quad (4.8b)
\]

Equations (4.6a) and (4.6b) implies that the electric potential is continuous but the electric field is not at the dielectric channel layer/Stern layer interface due to the discontinuity of the dielectric permittivities \( (\varepsilon_d \text{ and } \varepsilon_f) \), where the electric field satisfies Gauss’s law.

Solving Equations (4.1) and (4.2) subject to Equations (4.5), (4.6a), and (4.7a) yields

\[
\phi = \psi_s + \frac{\psi_s - V_s}{\delta} x, \quad (4.9)
\]

\[
\varphi = \psi_s + \frac{\psi_d - \psi_s}{\delta_s} x. \quad (4.10)
\]
It is worth noting that by substituting Equations (4.9) and (4.10) into Equations (4.6b) and (4.7b), and letting the surface capacitance of the Stern layer, \( C_s = \varepsilon_0 \varepsilon_f / \delta_s \), results in

\[
-\varepsilon_0 \varepsilon_f \frac{\psi_s - V_s}{\delta} + C_s (\psi_d - \psi_s) = -\sigma_s , \tag{4.11}
\]

\[
-C_s (\psi_d - \psi_s) - \sigma_d = 0 . \tag{4.12}
\]

In the above, \( \sigma_d \) is the surface charge density of the diffuse layer and can be expressed as

\[
\sigma_d = -\varepsilon_0 \varepsilon_f d\psi / dx \bigg|_{x=\delta_s} = \text{sign}(\psi_d) \sqrt{2 \varepsilon_0 \varepsilon_f RT \sum_{i=1}^{n} C_{i0} \left[ \exp \left( -\frac{z_i F \psi_d}{RT} \right) - 1 \right]} , \tag{4.13}
\]

where \( \text{sign}(\psi_d) = 1 \) for \( \psi_d > 0 \) and \( \text{sign}(\psi_d) = -1 \) for \( \psi_d < 0 \). In the absence of the FET, the first term of the left hand side of Equation (3.11) is zero and, therefore, Equations (4.11) and (4.12) reduce to

\[
C_s (\psi_s - \psi_d) = \sigma_s = \sigma_d , \tag{4.14}
\]

which is the well-known basic Stern layer model.[66] Apparently, the Stern layer models to describe the relationship between \( \psi_s \) and \( \psi_d \) in the presence (Equations (4.11) and (4.12)) and absence (Equation (4.14)) of FET are different.

4.2.2 Multi-Ion Charge Regulation Model

It is assumed the dielectric channel wall carries dissociable functional groups MOH capable of undergoing the following two main dissociation/association equilibrium reactions:

\[
\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+ \quad \text{and ...} \tag{4.15}
\]
Based on these two surface chemistry reactions, the surface charge density of the
dielectric layer $\sigma_s$ can be described by [190],

$$\sigma_s = -FN_{\text{total}} \left\{ \frac{10^{-pK_A} - 10^{-pK_B}}{10^{-pK_A} + 10^{-pK_B}} \left[ 10^{-pH} \exp \left( -\frac{F\psi_s}{RT} \right) \right]^2 \right\}, \quad (4.16)$$

where $N_{\text{total}} = \Gamma_{\text{MOH}} + \Gamma_{\text{MO}} + \Gamma_{\text{MOH}^2}$ is the total number site density of MOH molecules
on the dielectric layer surface with $\Gamma_k$ being the surface site densities of functional
groups $k$ ($k = \text{MOH, MO}, \text{and MOH}^2$); $pK_j = -\log K_j$ ($j = A$ and $B$) with
$K_A = ([H^+], \Gamma_{\text{MO}^-}) / \Gamma_{\text{MOH}}$ and $K_B = \Gamma_{\text{MOH}^2} / ([H^+], \Gamma_{\text{MOH}})$ being, respectively, the
equilibrium constants of the dissociation and association reactions in Equation 4.15;
$[H^+] = 10^{-pH} \exp(-F\psi_s / RT)$ is the molar concentration of $H^+$ ions at the dielectric
layer/liquid interface, which obeys the Boltzmann distribution since the EDL overlapping
inside the nanochannel is neglected. In contrast to the previous studies assuming a
constant surface charge density on the nanochannel wall [5, 177, 182 - 189, 239, 240],
Equation (4.16) suggests that both $\sigma_s$ and $\psi_s$ are not only functions of the
physicochemical properties of the dielectric channel layer such as $N_{\text{total}}, pK_A$, and $pK_B$, but also the solution properties such as pH and salt concentration. In turn, $\sigma_s$ and $\psi_s$
affect the zeta potential of the nanochannel, $\psi_d$, based on Equations (4.11) and (4.12).

To simulate experimental conditions, we assume that the background salt in aqueous
electrolyte solution is KCl, and the solution pH is adjusted by HCl and KOH. This
implies that four major ionic species (i.e., $N = 4$) including $K^+$, $Cl^-$, $H^+$ and $OH^-$ need
to be considered. If we let \( C_{i0}, i=1, 2, 3, \) and 4 be the bulk concentrations of these ions, respectively, and \( C_{KCl} \) be the background salt concentration, electroneutrality yields the following relations: \[ C_{10} = C_{KCl}, \quad C_{20} = C_{KCl} + 10^{-(-pH+3)} - 10^{-14-pH+3}, \]
\[ C_{30} = 10^{-pH+3}, \quad \text{and} \quad C_{40} = 10^{-14-pH+3} \] for \( pH \leq 7 \); \[ C_{10} = C_{KCl} - 10^{-(-pH+3)} + 10^{-14-pH+3}, \]
\[ C_{20} = C_{KCl}, \quad C_{30} = 10^{-(-pH+3)}, \quad \text{and} \quad C_{40} = 10^{-14-pH+3} \] for \( pH > 7 \).

4.2.3 Analytical Multi-Ion Model (MIM)

Due to electroneutrality, \( C_{0} = C_{10} + C_{30} = C_{20} + C_{40} = C_{NaCl} + 10^{-(-pH+3)} \) for \( pH \leq 7 \) and \( C_{NaCl} + 10^{-14-pH+3} \) for \( pH > 7 \). Therefore, Equations (3.3) and (3.4) can be rewritten as

\[
\frac{d^2\psi}{dx^2} = \frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\psi}{RT}\right) \quad \text{within the liquid phase} \quad \left(\delta_z \leq x \leq h/2\right), \quad (4.17)
\]

\[
\frac{d^2\mu}{dx^2} = \frac{\varepsilon\varepsilon_0E_z d^2\psi}{\mu} \quad \text{within the liquid phase} \quad \left(\delta_z \leq x \leq h/2\right), \quad (4.18)
\]

where \( z = z_1 = -z_2 \) and \( \kappa^{-1} = \lambda_d = \sqrt{\varepsilon_0\varepsilon/RT / 2z^2F^2C_0} \) is the Debye length. Note that if the effect of multiple ionic species is not considered, that is, the presence of \( H^+ \) and \( OH^- \) is neglected, then \( C_0 = C_{NaCl} \), regardless of the level of \( pH \).

Solving Equation (4.17) subject to Equations (4.7a) and (4.8a), yields

\[
\psi = \frac{2RT}{zF} \ln \left[ \frac{1 + \exp(-\kappa x) \tanh \left( \frac{Fz\psi_d}{4RT} \right)}{1 - \exp(-\kappa x) \tanh \left( \frac{Fz\psi_d}{4RT} \right)} \right], \quad (4.19)
\]

and, therefore,

\[
\sigma_d = \frac{2\varepsilon\varepsilon_0\kappa RT}{zF} \sinh \left( \frac{Fz\psi_d}{2RT} \right). \quad (4.20)
\]
By integrating Equation (4.18) subject to Equations (4.7c) and (4.8b), results in the EOF velocity profile

\[ u_z = \frac{\varepsilon_0 \varepsilon_f E_z}{\mu} (\psi - \psi_d). \] (4.21)

Substituting Equations (4.16), (4.19), and (4.20) into Equations (4.11) and (4.12) yields the following implicit expressions connecting the surface potential, \( \psi_s \), and the zeta potential, \( \psi_d \):

\[
-F_{\text{total}} = 0 - V \frac{\psi_s - V}{\delta} + C_s (\psi_d - \psi_s) \\
= \left( 10^{-pK_d} - 10^{-pK_a} \right) \left[ 10^{-pH} \exp\left( -\frac{F \psi_s}{RT} \right) \right]^2, \] (4.22)

and

\[
-C_s (\psi_d - \psi_s) = \frac{2 \varepsilon_0 \varepsilon_f \kappa RT}{zF} \sinh \left( \frac{F \psi_d}{2RT} \right). \] (4.23)

One can easily use Matlab function \texttt{fsolve} to determine \( \psi_s \) and \( \psi_d \) by simultaneously solving above Equations (4.22) and (4.23) for given conditions. Once \( \psi_d \) is obtained, the surface charge density of the diffusive layer (\( \sigma_d \)), and the electric potential (\( \psi \)) and EOF velocity (\( u_z \)) profiles can be probed by Equations (4.19) - (4.21), respectively.

Assuming no concentration gradient is imposed across the nanochannel, the ionic current through the nanochannel, \( I \), can be evaluated by [69]

\[
I = 2w \sum_{j=1}^{h/2} \int_{\delta_j}^{h/2} \left( \rho \right) dx + \frac{2wF^2}{RT} \sum_{i=1}^{\delta_i} \int_{\delta_i}^{h/2} \left( D_iC_{i0} \exp\left( -\frac{z_iF \psi}{RT} \right) \right) dx, \] (4.24)

\[
= I_v + I_c
\]
where $I_v$ and $I_c$ are the ionic currents contributed from the convective (EOF) and the electromigrative (imposed electric field) fluxes, respectively; $D_i$ is the diffusivity of the $i$th ionic species. Substituting Equations (4.3), (4.19) and (4.21) into Equation (4.24) and then integrating the resulted equation yields the following explicit analytical solutions for $I_v$ and $I_c$:

$$I_v = \frac{16w\kappa}{\mu} E_z \left( \frac{\varepsilon_0 \varepsilon_f RT}{F} \right)^2 \left[ \frac{1}{\Omega^2 e^{-x_h} - 1} - \frac{1}{\Omega^2 - 1} \right]$$ (4.25) 

and

$$I_c = \frac{2wF^2}{RT} E_z \left( D_1 C_{10} + D_3 C_{30} \right) \left( h + \kappa \left( \frac{e^{-\frac{x_h}{2}}}{\Omega e^{-\frac{x_h}{2}} + 1} \right) \frac{4\Omega \left( e^{-\frac{x_h}{2}} - 1 \right)}{\kappa \left( \Omega e^{-\frac{x_h}{2}} + 1 \right) (\Omega + 1)} \right),$$ (4.26) 

where $\Omega = \tanh \left( \frac{Fz \psi_d}{4RT} \right)$. The ionic current, $I$, and, accordingly, the conductance, $G = I/V$, of the nanochannel can be exactly evaluated by Equations (4.24), (4.25) and (4.26) based on the obtained $\psi_d$ from Equations (4.22) and (4.23). Note that the present model for the surface charge property and the ionic current/conductance in a FET-gated nanochannel is more general and realistic than most of the previous ones [5, 176, 182 - 192] due to the consideration of multiple ionic species, EOF effect, Stern layer effect, and surface chemistry of the dielectric channel wall. The influence of the presence of $H^+$ and $OH^-$ ions should become significant when the solution pH is sufficiently high and low.
In addition, it has been demonstrated numerically that the influence of EOF on the ionic current in the nanopore is noticeable when its charge density is large [240] (e.g., high solution pH in silica-based nanofluidics [69]).

4.3. Results and Discussion

In the present study, the ionic diffusivities $D_1$ ($K^+$), $D_2$ ($Cl^-$), $D_3$ ($H^+$), and $D_4$ (OH$^-$) are $1.96 \times 10^{-9}$, $2.03 \times 10^{-9}$, $9.31 \times 10^{-9}$, and $5.30 \times 10^{-9}$ m$^2$/s, respectively.[243] Other relevant physical parameters are $F = 96485$ C mol$^{-1}$, $R = 8.314$ JK$^{-1}$mol$^{-1}$, $T = 298$K, $\varepsilon_0 = 8.85 \times 10^{-12}$ CV$^{-1}$m$^{-1}$, $\varepsilon_f = 78.5$, and $\varepsilon_d = 3.9$ (SiO$_2$) [184].

4.3.1 Verification of the Analytical MIM by Experimental Data

The applicability of the analytical results derived in this study is first verified by the experimental data obtained by Oh et al. [5], van der Heyden et al. [6] and Yossifon et al. [7]. The first case has FET, while the other two do not have FET. Figure 4.2 shows the dependence of the zeta potential ($\psi_d$) of the gated silica nanochannel on the gate potential, $V_g$, modulated by the FET at pH = 4 and $C_{KCl} = 1$ mM. Note that, under the considered solution properties, the presence of the $H^+$ ions should be taken into account in the calculation. As shown in Figure 4.2, the present analytical MIM (solid line), with adjustable parameters $C_s = 0.2$ F/m$^2$, $N_{total} = 8$ sites/nm$^2$, $pK_A = 8$, and $pK_B = 1.8$, agrees well with the general trend of the experimental data (symbols). The fitted values of $C_s$, $N_{total}$, $pK_A$, and $pK_B$ are also consistent with those reported in the literatures (e.g., $C_s = 0.15 - 2.9$ F/m$^2$, $N_{total} = 3.8 - 8$ sites/nm$^2$, $pK_A = 6 - 8$, and $pK_B = 0 - 2$ for the dielectric channel layer made of silica [6, 8, 68, 244].
Figure 4.2. Dependence of the zeta potential ($\psi_d$) in the FET-gated silica nanochannel on its applied gate potential $V_g$. Diamonds and Circles denote the experimental data of Oh et al. [5] based on the estimation from Alexa 488 and Rhodamine B, respectively, at pH = 4, $C_{KCl} = 1$ mM, $\delta = 100$ nm, $h = 100$ nm, $w = 500$ nm, and $l=4$ mm. Solid line denotes the result of the present analytical MIM based on Equations (3.22) and (3.23) at $C_s = 0.2$ F/m$^2$, $N_{total} = 8$ sites/nm$^2$, $pK_A = 8$ and $pK_B = 1.8$.

Figure 4.3 and 4.4 depicts the variations of the nanochannel conductance, $G$, as a function of the background salt concentration $C_{KCl}$ for various nanochannel geometries. As shown in Figure 4.3 and 4.4, the predictions from our analytical MIM (solid lines), with the same parameters $C_s = 0.2$ F/m$^2$, $N_{total} = 8$ sites/nm$^2$, $pK_A = 6.3$, and $pK_B = 2$, are in good agreement with the experimental data of van der Heyden et al. [6] (squares and circles in Figure 4.3) and Yossifon et al. [7] (diamonds in Figure 4.4). The fitted values of $C_s$, $N_{total}$, $pK_A$, and $pK_B$ also agree with those reported in the literatures. From Figures 4.2 – 4.4, it is thus confirmed that the present analytical MIM are capable of capturing the essential physics of the field effect modulation of the surface charge property and the ionic current in a gated silica nanochannel. Therefore, the predicted values of $C_s = 0.2$ F/m$^2$, $N_{total} = 8$ sites/nm$^2$, $pK_A = 6.3$, and $pK_B = 2$, are used in the
following discussions. For illustration, a FET-gated nanochannel with height $h = 200\,\text{nm}$, width $w = 50\,\mu\text{m}$, length $l = 4.5\,\text{mm}$ is considered, and the thickness of the dielectric layer is set at $\delta = 30\,\text{nm}$.

Figure 4.3. Dependence of the conductance ($G$) in a silica nanochannel on the background salt concentration $C_{\text{KCl}}$. Squares and spheres denote the experimental data of van der Heyden et al. [6] at $h = 490\,\text{nm}$ and 75 nm, respectively, with $w = 50\,\mu\text{m}$, and $l=4.5\,\text{mm}$, and $p\text{H} = 7.5$. Lines denote the results of the present analytical model at $C_s = 0.2\,\text{F/m}^2$, $N_{\text{total}} = 8\,\text{sites/nm}^2$, $pK_A = 6.3$ and $pK_B = 2$. 
Figure 4.4. Dependence of the conductance (G) in a silica nanochannel on the background salt concentration $C_{KCl}$. Diamonds denote the experimental data of Yossifon et al. [7] at $h = 250$ nm, $w = 2$ mm, and $l = 0.8$ mm, and pH = 8. Lines denote the results of the present analytical model at $C_s = 0.2$ F/m$^2$, $N_{total} = 8$ sites/nm$^2$, $pK_a = 6.3$ and $pK_b = 2$.

### 4.3.2 Influence of the Background Salt Concentration

Figures 4.5 and 4.6 illustrate the influence of the background salt concentration, $C_{KCl}$, on the field effect modulation of the zeta potential, $\psi_d$, and the conductance, $G$, of a gated silica nanochannel for various applied gate potential, $V_g$. Figure 4.5 clearly shows that, as the applied negative $V_g$ increases, $\psi_d$ becomes more negative (Figure 4.5), thus yielding a larger $G$ (Figure 4.6). Similar phenomena have been experimentally observed in the nanofluidic field effect transistors [4], and can be utilized to control the ion, fluid, and nanoparticle transport [4, 179, 181, 245]. Figure 4.5 also suggests that the magnitude of $\psi_d$ decreases with an increase in $C_{KCl}$. This is because the higher the salt concentration, the thinner the EDL, resulting in more counterions condensed near the nanochannel wall and, thus, reducing its effective charge. Note that the magnitude of the zeta potential modulation by FET becomes insignificant at high $C_{KCl}$, as shown in Figure
4.5. This can be attributed to the combined effects of a thinner EDL (a larger $\kappa$) and a larger surface charge density of the silica nanochannel ($\sigma_s$) [69]. Note that the latter behavior of $\sigma_s$ is different from that of $\psi_d$, and results from the excluded effect of H$^+$ ions by an increase in K$^+$ ions as the background salt concentration increases [69]. Therefore, according to Equations (3.22) and (3.23), a higher gate potential is required to effectively tune the zeta potential of the nanochannel.

![Figure 4.5](image)

Figure 4.5. Zeta potential $\psi_d$, as a function of the background salt concentration $C_{KCl}$ for various levels of the applied gate potential $V_g$ at pH = 5. The blue region highlights where the $V_g$ dependent nanochannel conductance behavior becomes significant.

Figure 4.6 reveals that if $C_{KCl}$ is sufficiently high, $G$ decreases linearly with decreasing $C_{KCl}$ and is nearly independent on the applied gate potential, $V_g$. This behavior is expected because the nanochannel conductance at high ionic strength is dominated primarily by the bulk ionic concentration [69, 206] and very little by the
surface charge of the nanochannel. However, if $C_{kCl}$ is sufficiently low, a nonlinear behavior of $G$ with varying $C_{kCl}$ occurs and the dependence of $G$ on $V_g$ becomes significant at a relatively low salt concentration. The former agrees with the experimental observations in nanofluidics [4, 6, 7, 177, 246, 247], and the latter stems from the fact that at low $C_{kCl}$, the nanochannel conductance depends significantly on the surface charge of the nanochannel. Because the zeta potential varies remarkably at low salt concentration in the presence of the FET (Figure 4.5), the $V_g$-dependent ion transport phenomenon is significant (blue region in Figure 4.6).

![Figure 4.6. Nanochannel conductance $G$ as a function of the background salt concentration $C_{kCl}$ for various $V_g$ at pH = 5. The shaded region highlights where the $V_g$-dependent conductance becomes significant.](image)

It is interesting to note in Figure 4.6 that $G$ shows a local minimum with decreasing $C_{kCl}$ in the low concentration region and the local minimum phenomenon becomes apparent when a negative gate potential is applied (i.e., $V_g < 0$). Recent experimental
results by Guan et al. [179] and Kim et al. [245] showed that the conductance of a silica nanochannel [179] and a triangular polymer nanochannel [245], respectively, first decreases, attains a minimum, and then increases with a decrease in the salt concentration. However, the previous analytical model [177, 239, 248] without considering effects from EOF, multiple ions, and surface chemistry fails to predict the observed experimental results at low salt concentration. The variation of the conductance with the salt concentration is attributed to the significant EOF effect. In general, the conduction current, $I_c$, decreases, but the magnitude of $\psi_d$ increases with decreasing $C_{KCl}$ in the nanochannel. A larger $\psi_d$ also results in a higher EOF velocity [190] and, therefore, a larger convective current, $I_v$. If the EOF effect becomes dominant, the nanochannel conductance increases with decreasing $C_{KCl}$ due to an increase in $I_v$.

Because the zeta potential of the nanochannel is highly tunable by FET at low salt concentration, it becomes more negative and, therefore, a stronger EOF is induced. This explains why the local minimum behavior as $C_{KCl}$ varies at low $C_{KCl}$ shown in Figure 3.6 is remarkable in the presence of FET.

4.3.3 Influence of the Solution pH

Because the performance of the FET control in the gated nanochannel is significant when the salt concentration is low, we examine the influence of the solution pH on the field effect modulation of the zeta potential, $\psi_d$, and the conductance, $G$, at the background salt concentration $C_{KCl} = 0.1$ mM in Figure 4.7 and 4.8. This figure suggests that the degree of the field effect control of $\psi_d$ (Figure 4.7) and $G$ (Figure 4.8) is significant if the solution pH is low, and becomes insignificant if it is sufficiently high.
This is because the lower the proton concentration (higher pH), the more negatively charged functional groups $\text{SiO}^-$ dissociated from the silanol ($\text{SiOH}$) groups on the nanochannel surface, yielding a greater $\sigma_z$. Therefore, a larger number of counterions electrostatically attaches to the channel surface and makes the FET harder to tune its zeta potential and, accordingly, the nanochannel conductance. These phenomena also imply that the tuning efficiency of the FET in nanofluidics is weak at high solution pH, as shown in Figures 4.7 and 4.8.

Figure 4.7. Zeta potential $\psi_{zh}$ as a function of the solution pH for various levels of the applied gate potential $V_g$ at the background salt concentration $C_{\text{KCl}} = 0.1 \text{ mM}$. 
It is interesting to note in Figure 4.7 that regardless of the levels of $V_g$, the magnitude of $\psi_d$ in the gated nanochannel show a local maximum as the solution pH varies. The behavior that $|\psi_d|$ increases with increasing pH at low solution pH results from an increase in $|\sigma_s|$, as described previously. On the other hand, although $|\sigma_s|$ still increases with increasing pH at high solution pH, a higher solution pH deviated apparently from 7 also results in an increase in the ionic strength. This effect becomes significant when $C_{KCl}$ is sufficiently low, leading to a thinner EDL thickness (a larger $\kappa$) and, therefore, lowering $|\psi_d|$ as well. This explains why $|\psi_d|$ decreases with increasing pH when the solution pH is sufficiently high. Figure 4.8 also suggests that $G$ has a local minimum with the solution pH. This behavior has been experimentally observed by Guan et al. [179] in the gated silica nanochannel. Since the ionic strength is high when the solution pH deviates significantly from 7, the resulting nanochannel conductance becomes large.
4.3.4 Influence of the Stern Layer Capacitance

The influences of the surface capacitance of the Stern layer, $C_s$, on the surface charge properties, including the zeta potential, $\psi_d$, and the surface charge density of the diffusive layer, $\sigma_d$, and on the conductance, $G$, of a gated silica nanochannel at two levels of the solution pH are illustrated in Figures 4.9 - 4.14. In general, the larger the value of $C_s$, the smaller difference between the zeta potential ($\psi_d$) and the surface potential ($\psi_s$), yielding a less significant Stern layer effect. Furthermore, as $C_s \to \infty$ the Stern layer effect is neglected, implying that $\psi_d = \psi_s$, which was the typical assumption made in previous theoretical studies with considering the FET control [5, 176, 179, 182 - 189, 191, 192], in order to simplify the problem. Figures 4.9 - 4.14 suggest that the influence of the Stern layer on the field effect of $\psi_d$ and $G$ is quantitatively different from on that behavior of $\sigma_d$. In the latter, if the FET is inactive (i.e., floating gate, $V_g = 0\ V$), the influence of $C_s$ on $\sigma_d$ is insignificant when the background salt concentration, $C_{KCl}$, is low and becomes significant when it is high regardless of the values of the solution pH, as shown in Figures 4.9a and 4.12a. This is expected since the higher the salt concentration the more counterions gathered near the nanochannel surface, leading to a more significant Stern layer effect. On the other hand, if the FET is active (i.e., FET control, $V_g = -20\ V$), the dependence of $\sigma_d$ on $C_s$ is still unremarkable at low $C_{KCl}$ and becomes remarkable at high $C_{KCl}$ when the solution pH is high (Figure 4.12b), but those dependences are reversed when the pH is low (Figure 4.9b). These behaviors can be explained by the fact that for the relatively low solution pH at which the surface charge density of the nanochannel ($\sigma_s$) is very small, the lateral electric field stemming
from the FET is then easy to yield a significant increase in the surface charge density of the diffusive layer ($\sigma_d$). As mentioned previously in Figures 4.5 - 4.8, the performance of the FET control is significant when the solution pH and the salt concentration are low. As a result, more counterions are electrostatically attracted into the nanochannel surface due to the active FET, leading to a more significant Stern layer effect at low solution pH and $C_{KCl}$, as depicted in Figure 4.9b. Since the original $\sigma_s$ in the absence of FET is large when the solution pH is relatively high, implying that most of counterions have been attracted on the nanochannel surface at low $C_{KCl}$, the Stern layer effect on the FET control of $\sigma_d$ is thus unremarkable, as shown in Figure 4.12b.

Figure 4.9. Surface charge density of the diffuse layer $\sigma_{dh}$ (a) and (b), as a function of the background salt concentration $C_{KCl}$ for various surface capacitance of the Stern layer $C_s$ at $V_g=0$ (floating gate), (a), and $V_g=-20$V (FET control), (b), and pH=4.
Figure 4.10. Surface charge density of zeta potential $\psi_{\alpha}$ (a) and (b), as a function of the background salt concentration $C_{\text{KCl}}$ for various surface capacitance of the Stern layer $C_s$ at

- $V_g=0$ (floating gate), (a), and $V_g=-20\text{V}$ (FET control), (b), and pH=4.

Figure 4.11. Surface charge density of nanochannel conductance $G$, (a) and (b), as a function of the background salt concentration $C_{\text{KCl}}$ for various surface capacitance of the Stern layer $C_s$ at

- $V_g=0$ (floating gate), (a), and $V_g=-20\text{V}$ (FET control), (b), and pH=4.
Figure 4.12. Surface charge density of the diffuse layer $\sigma_d$ (a) and (b), as a function of the background salt concentration $C_{KCl}$ for various surface capacitance of the Stern layer $C_s$ at $V_g=0$ (floating gate), (a), and $V_g=-20V$ (FET control), (b), and pH=8.

Figure 4.13. Surface charge density of zeta potential $\psi_d$, (a) and (b), as a function of the background salt concentration $C_{KCl}$ for various surface capacitance of the Stern layer $C_s$ at $V_g=0$ (floating gate), (a), and $V_g=-20V$ (FET control), (b), and pH=8.
It is worth noting in Figure 4.12a that under the considered conditions, the predicted \( \sigma_d \) with significant Stern layer effect (e.g., \( C_s = 0.2 \text{ F/m}^2 \)) at \( \text{pH} = 8 \) varies from -7.9 to -35.3 mC/m\(^2\), in accordance with the typically reported values for the silica-based nanochannels (ca. -2 - 60 mC/m\(^2\)),[4, 6 - 8, 177, 179] for \( C_{\text{KCI}} \) ranging from \( 10^{-2} \) to \( 10^3 \) mM. However, if the Stern layer effect is neglected (e.g., \( C_s \to \infty \)), the predicted \( \sigma_d \) under the same conditions ranges from -13.5 to -505 mC/m\(^2\), which is remarkably larger than the typical values reported in the literature [4, 6 - 8, 177, 179]. This implies that the assumptions of neglecting the Stern layer effect and constant fixed charge density on the nanochannel surface can be inaccurate and unrealistic, and might result in an incorrect estimation in its electrokinetic transport phenomena.

If the FET is floating (\( V_g = 0 \ \text{V} \)), Figures 4.10a and 4.11a reveal that the Stern layer effect on the variations of the zeta potential (\( \psi_d \)) and the conductance (\( G \)) in a silica nanochannel is insignificant at low solution \( \text{pH} = 4 \). This is expected since its surface...
charge density is very small at low solution pH. On the other hand, at relatively high solution pH = 8, the Stern layer effect on the variation of $\psi_d$ is unremarkable when the background salt concentration, $C_{KCl}$, is small, and becomes remarkable when $C_{KCl}$ is relatively high, as shown in Figure 4.13a. This is due to the fact that the surface charge density of the nanochannel is high when the solution pH is high and, therefore, more counterions are electrostatically attracted on its wall surface, thus enhancing the Stern layer effect. However, the dependence of $G$ on the Stern layer effect is reversed, as depicted in Figure 4.14a where the Stern layer effect is significant at low $C_{KCl}$ and insignificant at high $C_{KCl}$. This can be attributed to the strongly (slightly) zeta potential-dependent conductance behavior in the nanochannel at low (high) salt concentration, as verified previously in Figures 4.5 and 4.6.

If the FET is active ($V_g = -20$ V) and the solution pH is low, Figures 4.10b and 4.11b depict that the Stern layer effect on the field effect modulation of the zeta potential ($\psi_d$) and the conductance ($G$) is significant when the background salt solution, $C_{KCl}$, is low and becomes insignificant when it is high. As shown in Figures 4.5 and 4.6, since the conductance of the nanochannel at low $C_{KCl}$ is dominated majorly by its zeta potential, the dependence of $G$ on the Stern layer effect is similar to that on $\psi_d$. One the other hand, if the solution pH is relatively high, Figure 4.13b reveals that the Stern layer effect on the zeta potential is significant when the salt concentration is high and insignificant when it is low. This can be explained by the same reason as employed in Figure 4.12b. At high solution pH, a larger $\sigma_s$ reduces the performance of the FET control and accordingly the Stern layer effect.
4.4. Conclusions

Field effect modulation of the surface charge property and the ionic conductance in a FET-gated silica nanochannel is investigated by considering practical effects of multiple ionic species, surface chemistry reactions, the Stern layer, and the EOF, most of which were often neglected in previous studies. Taking account of these effects, analytical expressions were derived for the first time to estimate the surface charge property and the ionic current/conductance tuned by the FET. The results of the model are validated by comparing their predictions to the existing experimental data of the zeta potential modulated by the FET and the ionic conductance in silica nanochannels. The results clearly show that the performance of the FET control is more significant when the background salt concentration and pH are low. The developed model predicts that the ionic conductance of the nanochannel decreases first and then increases with a decrease in the background salt concentration, in accordance with the experimental observation reported in the literature recently. This phenomenon becomes remarkable if the FET is active and is attributed to a significant EOF effect occurring at low salt concentration and high zeta potential. In addition, the Stern layer effect on the modulated ionic conductance is significant at low salt concentration and becomes insignificant at high salt concentration regardless of the solution pH. However, if the FET is inactive, the Stern layer has nearly no effect on the ionic conductance of the nanochannel when the solution pH is relatively low.
CHAPTER 5

FET CONTROL OF STEAMING CURRENT IN A PH-REGULATED NANOCHANNEL WITHOUT CONSIDERING ELECTROVISCOUS EFFECT

5.1. Introduction

Recent advances in nanofluidics attract considerable attention in using them as promising platforms for diverse applications such as ionic gates [249], ionic diodes [225, 250], energy conversion [3, 6, 124, 164, 165], and single (bio)nanoparticle sensing [205, 228, 230]. All of these nanofluidic-based applications rely on accurately analyzing the resulting ionic current signals, determined by the ion transport phenomena in these nanofluidic devices, in various solution properties [171, 206, 222]. Many experimental results revealed that the ion transport in nanofluidics can be regulated by modulating the surface charge property at the solid/liquid interface of these nanofluidic devices [177, 178, 207]. Therefore, active control of the surface charge property of nanofluidic devices in various solution properties is crucial for the development of next-generation nanofluidics-based apparatus.

To this end, nanofluidic field effect transistors (FETs) [4, 179 - 181, 232, 251], consisting of electrically controllable gate electrodes patterned along the outer wall surface of the dielectric nanochannels (or nanopores) made of such as silicon dioxide (SiO₂), silicon nitride (SiNₓ), and aluminum oxide (Al₂O₃), have been developed to actively modulate their surface charge property. Control of the surface charge property, in turn, controls the transport of ions, fluid, and biomolecules in nanofluidics by modulating the gate potential imposed on the gate electrode. Many theoretical efforts [176, 182 - 189,
have been made to reveal how to regulate the transport of ions, fluid, and biomolecules in the FET-gated nanofluidic devices. However, these studies have several limited assumptions, such as a constant surface charge density at the dielectric nanochannel wall [182-189], consideration of background ionic species only [176, 182-189, 191, 192, 252], and without considering the Stern layer effect [176, 182-189, 191, 192]. Recently, Guan et al. [253] experimentally demonstrated that the field effect modulation of zeta potential and surface charge density at the gated dielectric channel material (e.g., SiO$_2$ and SiNx)/electrolyte interface in various solution pH and ionic strength is distinctly different. They concluded that these intrinsic differences result from the surface chemistry reactions of functional groups with H$^+$ ions at the dielectric/electrolyte interface, thus developing a more general and realistic model to elaborate experimental observations in relevant gated nanofluidic devices is highly desirable.

Recent experimental studies demonstrated that the streaming current, generated by the pressure-driven flow, in the nanochannel provides a simple and effective scenario for converting hydrodynamics to electrical power [3, 6, 124, 164, 165]. This clean energy harvesting system using nanofluidics might open a new way for the development of renewable energy resources [124]. The experimental results show that the streaming current is dependent on the flow of excess counterions, driven by an applied pressure field, in the electric double layer (EDL) in the vicinity of the charged channel wall [8]. This implies that the surface charge property of the nanochannel and net amount of mobile ionic species in various electrolyte solutions can significantly influence the streaming current behavior. Although several theoretical works have been made for the
streaming current in the nanochannel, all of these studies assumed that the liquid phase only contains one kind of cations and anions from the background salt [3, 6, 8, 68, 158, 160, 164, 254 - 256]. This assumption, although it simplifies the mathematical analysis, is unrealistic in practice because other ionic species are usually present. For example, the presence of H\(^+\) and OH\(^-\) ions need to be considered inevitably when the solution pH appreciably deviates from neutral.

In attempt to better understand the aforementioned influences on the streaming current in the nanochannel, an investigation was conducted of the field effect modulation of the surface charge property and the streaming current/conductance in a long pH-regulated nanochannel under various solution properties (pH and background salt concentration). Analytical expressions are derived for the first time to predict the zeta potential and the streaming current/conductance with the consideration of FET, multiple ionic species, surface chemistry reactions on the dielectric channel wall, and the Stern layer effect. In contrast to most of existing studies on the ion transport in nanofluidics, which focused mainly on the numerical simulations [68, 158, 164, 183 - 189, 191, 192, 252, 254, 255], the present analytical results would provide better insight into the underlying physics and present convenient recipes for utilizing gated nanochannels in relevant applications.

5.2. Theoretical Analysis

As schematically shown in Figure 5.1, consider a fully-developed pressure-driven flow of an aqueous electrolyte solution of relative permittivity \( \varepsilon_f \) in a long pH-regulated nanochannel of height \( h \), width \( w \), and length \( l \). A streaming current, \( I_{str} \), is induced by a pressure gradient, \( -\Delta p \), applied across the nanochannel [8]. The nanochannel is
equipped with a FET, including a thin dielectric channel layer of thickness $\delta$ and relativity permittivity $\varepsilon_d$, and a gate electrode patterned on its outer surface. A gate potential, $V_g$, is imposed on the gate electrode to regulate the surface charge property and the streaming current in the nanochannel. The Cartesian coordinates $x$ and $y$ with the origin located at the bottom solid/liquid interface are adopted, and $-\Delta p$ is directed along the $y$-direction.

Figure 5.1. Schematic representation of the field effect regulation of the zeta potential ($\psi_d$) and the streaming current, driven by an applied pressure field ($-\Delta p$), in a pH-regulated nanochannel containing multiple ionic species, $\text{H}^+$, $\text{K}^+$, $\text{Cl}^-$ and $\text{OH}^-$. Four major regions are considered: the dielectric channel of thickness $\delta$, the immobile Stern layer with surface capacitance $C_s$, the diffusive layer of Debye length $\lambda_D$, and the bulk solution state of pH and background salt concentration $C_{\text{KCl}}$. $V_g$ is the gate potential imposed on the gate electrode, and $\psi_s$ is the surface potential stemming from the association and dissociation surface reactions of functional groups on the nanochannel wall.
Assume the following: (i) The liquid phase is an incompressible Newtonian fluid containing $N$ kinds of ionic species, and the $-\Delta p$-driven flow is fully developed and parallel to the nanochannel wall (i.e., $y$-direction); (ii) The Stern layer of a very thin thickness $\delta_s$ is formed on the nanochannel wall, and ions and fluid inside that layer are immobile and do not contribute to streaming current; (iii) The no-slip plane is located at the Stern layer/diffusive layer interface; (iv) The dielectric channel (e.g., SiO$_2$, Si$_3$N$_4$, and Al$_2$O$_3$) wall in contact with an aqueous solution is of charge-regulated nature[66 - 68] and bears a uniform surface charge density $\sigma_y$ along the $y$-direction; (v) The electroviscous effect is neglected, following the treatments of van der Heyden [3, 6, 8] and Chang and Yang [256]; (vi) The nanochannel height is much smaller than both its width and length ($h >> w$ and $h >> l$) so that the present problem can be approximated as a nanoslit with two infinite parallel plates; and (vii) The overlapping of the EDLs of two adjacent nanochannel walls is insignificant, implying that the Debye length is much smaller than the half height of the nanochannel (i.e., $\lambda_D = \kappa^{-1} << h/2$). This assumption holds for most experimental conditions in nanofluidics. For example, the Debye length ranges from 9.6 to 0.3 nm, which is very thin compared to most of $h$.[6, 236 - 238] for the background salt concentration in experiments varying from 1 to 1000 mM. Therefore, the possible presence of the ion concentration polarization [206, 235], arising from the selective transport of counterions and coions, can be neglected. Under above assumptions, the distributions of the electric potential, ionic concentrations, and the fluid velocity are uniform in the $y$-direction.
5.2.1 Governing Equations and Boundary Conditions

Based on the aforementioned assumptions, the electric potentials within the dielectric channel, Stern layer, and liquid, $\phi$, $\varphi$, and $\psi$, respectively, and the flow field can be described by

\[
\frac{d^2 \phi}{dx^2} = 0 \text{ within the dielectric channel } (-\delta \leq x \leq 0),
\]

\[
\frac{d^2 \varphi}{dx^2} = 0 \text{ within the Stern layer } (0 \leq x \leq \delta_s),
\]

\[
\frac{d^2 \psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0 \varepsilon_f} = -\frac{1}{\varepsilon_0 \varepsilon_f} \sum_{i=1}^{N} F_{i} C_{i0} \exp \left( -\frac{z_i F \psi}{RT} \right) \text{ within the liquid phase } (\delta_s \leq x \leq h/2),
\]

\[
\frac{d^2 u_y}{dx^2} = \frac{1}{\mu} \frac{dp}{dy} \text{ within the liquid phase } (\delta_s \leq x \leq h/2).
\]

In the above, $\rho_e$ is the mobile space charge density; $z_i$ and $C_{i0}$ are the valence and the bulk concentration of the $i$th ionic species, respectively; $\varepsilon_0$, $F$, $R$, and $T$ are the absolute permittivity of vacuum, Faraday constant, universal gas constant, and absolute temperature, respectively; $\mu$ and $u_y$ are the dynamic fluid viscosity and the fully developed pressure-driven fluid velocity in the $y$-direction, respectively.

The boundary conditions associated with Equations (5.1) - (5.4) are:

At the gate electrode ($x = -\delta$),

\[
\phi = V_g,
\]

(5.5)
At the dielectric channel/Stem layer interface \( (x = 0) \),

\[
\phi = \phi = \psi, \quad (5.6a)
\]

\[
-\varepsilon_0 \varepsilon_d \frac{d\phi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\phi}{dx} = -\sigma, \quad (5.6b)
\]

At the Stern layer/diffusive layer interface \( (x = \delta) \),

\[
\phi = \psi = \psi_d, \quad (5.7a)
\]

\[
-\varepsilon_0 \varepsilon_f \frac{d\phi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\psi}{dx} = 0, \quad (5.7b)
\]

\[
u_y = 0, \quad (5.7c)
\]

and At the center of the nanochannel \( (x = h/2) \),

\[
\psi = \frac{d\psi}{dx} = 0, \quad (5.8a)
\]

\[
\frac{du_y}{dx} = 0. \quad (5.8b)
\]

Equations (5.6a) and (5.6b) imply that the electric potential is continuous but the electric field, which satisfies Gauss’s law, is not at the dielectric channel/Stern layer interface due to the discontinuity of the dielectric permittivities \( \varepsilon_d \) and \( \varepsilon_f \). Equation 8a depicts that at the center of the nanochannel, the electric potential stemming from the charged nanochannel wall vanishes and the ionic concentrations reach their bulk values due to the neglect of the EDL overlapping inside the nanochannel.
The analytical solutions to Equations (5.1) and (5.2) subject to Equations (5.5), (5.6a), and (5.7a) are

\[ \phi = \psi_s + \frac{\psi_s - V_g}{\delta} x, \quad (5.9) \]

\[ \varphi = \psi_s + \frac{\psi_d - \psi_s}{\delta} x. \quad (5.10) \]

Substituting Equations (5.9) and (5.10) into Equations (5.6b) and (5.7b), and letting the surface capacitance of the Stern layer, \( C_s = \frac{\varepsilon_0 \varepsilon_f}{\delta_s} \), yields

\[ -\varepsilon_0 \varepsilon_d \left( \frac{\psi_s - V_g}{\delta} \right) + C_s (\psi_d - \psi_s) = -\sigma_s, \quad (5.11) \]

\[ -C_s (\psi_d - \psi_s) - \sigma_d = 0. \quad (5.12) \]

Here, \( \sigma_d \) is the surface charge density of the diffuse layer and can be expressed as

\[ \sigma_d = -\varepsilon_0 \varepsilon_f d \psi / dx \bigg|_{\psi_s = \delta_s} = \text{sign}(\psi_d) \sqrt{2\varepsilon_0 \varepsilon_f RT \sum_{i=1}^{N} C_{i0} \left[ \exp \left( \frac{-z_i F \psi_d}{RT} \right) - 1 \right]}, \quad (5.13) \]

where \( \text{sign}(\psi_d) = 1 \) for \( \psi_d > 0 \) and \( \text{sign}(\psi_d) = -1 \) for \( \psi_d < 0 \). It is worth noting that in the absence of the FET, the first term of the left hand side of Equation (5.11) vanishes and, therefore, Equations (5.11) and (5.12) reduce to

\[ \psi_s - \psi_d = \frac{\sigma_s}{C_s} = \frac{\sigma_d}{C_s}, \quad (5.14) \]

which is the well-known basic Stern layer model [66]. In short, the Stern layer models to describe the relationship between the surface potential (\( \psi_s \)) and zeta potential (\( \psi_d \)) of the nanochannel in the absence (Equation (5.14)) and presence (Equations (5.11) and (5.12)) of FET are remarkably different.
Suppose that the dielectric channel wall bears dissociable functional groups $\text{MOH}$, capable of undergoing the following dissociation/association reactions:
$$\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+ \quad \text{and} \quad \text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}_2^+$$
with equilibrium constants $K_A = (\Gamma_{\text{MOH}^-} [\text{H}^+]) / \Gamma_{\text{MOH}}$ and $K_B = \Gamma_{\text{MOH}_2^+} / (\Gamma_{\text{MOH}} [\text{H}^+])$, respectively. Here, $\Gamma_{\text{MOH}}$, $\Gamma_{\text{MO}^-}$, and $\Gamma_{\text{MOH}_2^+}$ denote the surface site densities of MOH, MO$, and MOH_2^+$, respectively; $[\text{H}^+]$ is the molar concentration of H$^+$ ions at the dielectric channel/liquid interface. If we let the total number site density of MOH molecules on the dielectric channel surface $N_{\text{total}} = \Gamma_{\text{MOH}} + \Gamma_{\text{MO}^-} + \Gamma_{\text{MOH}_2^+}$ and assume that the equilibrium distribution of H$^+$ ions follows the Boltzmann distribution, the surface charge density of the dielectric channel $\sigma_s$ can be expressed as,
$$\sigma_s = -FN_{\text{total}} \left\{ \frac{10^{-pK_A} - 10^{-pK_B} \left[ 10^{-p\text{H}^+} \exp \left( \frac{-F\psi_s}{RT} \right) \right]^2}{10^{-pK_A} + 10^{-p\text{H}^+} \exp \left( \frac{-F\psi_s}{RT} \right) + 10^{-pK_B} \left[ 10^{-p\text{H}^+} \exp \left( \frac{-F\psi_s}{RT} \right) \right]^2} \right\}, \quad (5.15)$$
where $pK_j = -\log K_j \ (j = A \text{ and } B)$.

To simulate experimental conditions, it is assumed that the background salt in an aqueous electrolyte solution is KCl of background concentration $C_{\text{KCl}}$, and the solution pH is adjusted by HCl and KOH. This implies that four major kinds of ionic species (i.e., $N = 4$) including $\text{K}^+$, $\text{Cl}^-$, $\text{H}^+$ and $\text{OH}^-$ need to be considered. Let $C_{10}$, $C_{20}$, $C_{30}$, and $C_{40}$ (in mM) be their bulk concentrations, respectively. Electroneutrality yields the following relations: [69, 226] $C_{10} = C_{\text{KCl}}$, $C_{20} = C_{\text{KCl}} + 10^{-p\text{H}^+} - 10^{-(14-p\text{H}^+)}$,
\[ C_{30} = 10^{(-pH+3)}, \text{ and } C_{40} = 10^{-(14-pH)+3} \text{ for } pH \leq 7; \] 
\[ C_{10} = C_{KCl} - 10^{(-pH+3)} + 10^{-(14-pH)+3}, \]
\[ C_{20} = C_{KCl}, C_{30} = 10^{(-pH+3)}, \text{ and } C_{40} = 10^{-(14-pH)+3} \text{ for } pH > 7. \]

### 5.2.2 Analytical Multi-Ion Model (MIM)

The electroneutrality condition results in
\[ C_0 = C_{10} + C_{30} = C_{20} + C_{40} = C_{KCl} + 10^{(-pH+3)} \]
for pH \( \leq 7 \) and \( C_{KCl} + 10^{-(14-pH)+3} \) for pH > 7. Equation 3, therefore, can be rewritten as

\[
\begin{align*}
\frac{d^2 \psi}{dx^2} &= \frac{RT \kappa^2}{zF} \sinh \left( \frac{zF \psi}{RT} \right) \text{ within the liquid phase } (\delta_i \leq x \leq h/2), \\
\end{align*}
\]

where \( z = z_1 = -z_2 \) and \( \kappa^{-1} = \lambda_D = \sqrt{\varepsilon_0 \varepsilon_f RT / 2z^2 F^2 C_0} \) is the Debye length.

Solving Equation (5.16) subject to Equations (5.7a) and (5.8a), one gets

\[
\psi = \frac{2RT}{zF} \ln \left[ \frac{1 + \exp(-\kappa x) \tanh \left( \frac{zF \psi_d}{4RT} \right)}{1 - \exp(-\kappa x) \tanh \left( \frac{zF \psi_d}{4RT} \right)} \right],
\]

and, therefore, the charge density of the diffusive layer is

\[
\sigma_y = \frac{2\varepsilon_0 \varepsilon_f \kappa RT}{zF} \sinh \left( \frac{zF \psi_d}{2RT} \right).
\]

By integrating Equation (5.4) twice with the boundary conditions described by Equations (5.7c) and (5.8b), one obtains the pressure-driven flow velocity,

\[
u_y = \frac{1}{2\mu} \frac{dp}{dy} \left( x^2 - hx \right),
\]

where \(-dp/dy = -\Delta p/l\) is the applied pressure gradient across the nanochannel.
Substituting Equations (5.15), (5.17), and (5.18) into Equations (5.11) and (5.12), we have the following implicit expressions relating the surface potential ($\psi_s$) to the zeta potential ($\psi_d$) of the nanochannel:

$$-\varepsilon_0 \varepsilon_d \left( \frac{\psi_s - V_s}{\delta} \right) + C_s (\psi_d - \psi_s)$$

$$= FN_{\text{total}} \left\{ \frac{10^{-pK_s} - 10^{-pK_d}}{10^{-pK_s} + 10^{-pK_d} \exp \left( -\frac{F\psi_s}{RT} \right)} \right\}^2$$

$$+ \frac{10^{-pK_s} - 10^{-pK_d} \exp \left( -\frac{F\psi_s}{RT} \right)}{10^{-pK_s} + 10^{-pK_d} \exp \left( -\frac{F\psi_s}{RT} \right)}$$

and

$$-C_s (\psi_d - \psi_s) = \frac{2\varepsilon_0 \varepsilon f \kappa RT}{zF} \sinh \left( \frac{zF\psi_d}{2RT} \right).$$

For given conditions, one can easily use the Matlab function `fsolve` to determine both $\psi_s$ and $\psi_d$ by simultaneously solving Equations (5.20) and (5.21). Then, the electric potential ($\psi$) and the surface charge density of the diffusive layer ($\sigma_d$) can be probed by Equations (5.17) and (5.18), respectively, based on the resulting $\psi_d$. 
The streaming current \( I_{str} \) through the nanochannel can be exactly evaluated by

\[
I_{str} = 2w \int_{\delta_{i} \to 0}^{h/2} \rho_{e}(x) u_{y}(x) dx = -2w \int_{\delta_{i} \to 0}^{h/2} \varepsilon_{0} \varepsilon_{f} \frac{d^{2}u_{y}(x)}{dx^{2}} u_{y}(x) dx
\]

\[
= -2w \varepsilon_{0} \varepsilon_{f} \int_{\delta_{i} \to 0}^{h/2} u_{y}(x) \frac{dy}{dx} \left[ \frac{d}{dy} \left( x^{2} - hx \right) \right] dx
\]

\[
= 2w \varepsilon_{0} \varepsilon_{f} \int_{\delta_{i} \to 0}^{h/2} \frac{dp}{2 \mu} \left( 2x - h \right) d\psi
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ (2x - h) \psi \int_{\delta_{i} \to 0}^{h/2} \psi dx \right]
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ -2 \int_{\delta_{i} \to 0}^{h/2} \frac{2RT}{zF} \ln \left[ \frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right] dx \right]
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ \ln \left( \frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right) - \ln \left( \frac{2}{1 - A \exp(-\kappa x)} \right) + \ln \left( \frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right) \right]_{\delta_{i} \to 0}^{h/2}
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ \ln \left( \frac{1 + A \exp(-\kappa h/2)}{1 - A \exp(-\kappa h/2)} \right) - \ln \left( \frac{2}{1 - A \exp(-\kappa h/2)} \right) + \ln \left( \frac{1 + A \exp(-\kappa h/2)}{1 - A \exp(-\kappa h/2)} \right) \right]
\]

\[
= \frac{we_{0} \varepsilon_{f} \Delta p}{\mu l} - 4we_{0} \varepsilon_{f} RT \Delta p \frac{\mu zFk}{\mu l}
\]

\[
(5.22)
\]
where \( A = \tanh(zF\psi_d / 4RT) \) and dilog( ) represents the dilogarithm function. Once \( I_{str} \) is obtained, the streaming conductance \( (G_{str}) \) of the nanochannel can be determined by [8]:

\[
G_{str} = \frac{I_{str}}{(-\Delta p)}
\]

\[
= -\frac{w_0 e_f \mu}{\mu d} \frac{4we_0e_fRT}{\mu zFk_l}
\left[\ln\left(\frac{1+A\exp(-\kappa h/2)}{1-A\exp(-\kappa h/2)}\right)\ln\left(\frac{2}{1-A\exp(-\kappa h/2)}\right) + \ln\left(\frac{1+A\exp(-\kappa h/2)}{1-A\exp(-\kappa h/2)}\right) \right] \\
- \ln\left(\frac{1+A}{1-A}\right) \ln\left(\frac{2}{1-A}\right) + \ln\left(\frac{1+A}{1-A}\right) + \ln\left(\frac{2}{1-A}\right)
\]

(5.23)

According to Equations (5.20) - (5.23), \( \psi_d, I_{str} \), and, accordingly, \( G_{str} \) are functions of the gate potential \( (V_g) \), the surface capacitance of the Stern layer \( (C_s) \), the physicochemical properties of the dielectric channel wall \( (\mu d, pK_A, pK_B, \varepsilon_d, \delta) \), and the solution properties \( (\mu d, C_{KC}, \varepsilon_f) \). It is worth noting that the present analytical MIM for the surface charge property and the streaming current and conductance in a gated nanochannel with and without FET control is more realistic and rigorous than most of the previous ones [3, 6, 8, 68, 158, 160, 164, 182 - 189, 191, 192, 254 - 256] due to the consideration of multiple ionic species, the Stern layer effect, and the surface chemistry reactions of the dielectric channel wall. The influence of \( H^+ \) and \( OH^- \) ions becomes significant when the solution pH is sufficiently high and low.
5.2.3 Analytical MIM Solution under the Debye-Hückel Approximation

Under the Debye-Hückel approximation (i.e., $|\psi_s| << RT/zF$), Equations (5.15) and (5.16) can be further approximated, respectively, to

$$
\sigma_s = -FN_{\text{total}} \left[ \Phi \left( \frac{F \psi_s}{RT} \right) \left( \frac{\Pi}{\Omega} + \Lambda \right) \right],
$$

(5.24)

and

$$
\frac{d^2 \psi}{dx^2} = \kappa^2 \psi \quad \text{within the liquid phase (} \delta_s \leq x \leq \bar{h}/2 \text{).}
$$

(5.25)

In the above, $\Omega = 10^{-pK_s} + 10^{-pH} + 10^{-pK_a^{-2pH}}$, $\Phi = 10^{-pK_s} + 10^{-pK_a^{-2pH}}$, $\Pi = 2 \times 10^{-pK_a^{-2pH}}$, and $\Lambda = \Phi(10^{-pH} + \Pi)/\Omega^2$.

Solving Equation (5.25) subject to Equations (5.7a) and (5.8a) gives

$$
\psi = \frac{\psi_d}{\sinh \left( \frac{kh}{2} \right)} \sinh \left( \kappa \left( \frac{\bar{h}}{2} - x \right) \right).
$$

(5.26)

Therefore, the charge density of the diffusive layer $\sigma_d$ can be described by

$$
\sigma_d = \frac{\varepsilon_\delta \varepsilon_f K \psi_d}{\tanh \left( \frac{kh}{2} \right)}.
$$

(5.27)

By substituting Equations (5.24) and (5.27) into Equations (5.11) and (5.12), we obtain

$$
-\varepsilon_0 \varepsilon_f \left( \frac{\psi_s - \psi_e}{\delta} \right) - \frac{\varepsilon_\delta \varepsilon_f K \psi_d}{\tanh \left( \frac{kh}{2} \right)} = FN_{\text{total}} \left\{ \frac{\Phi}{\Omega} \left( \frac{F \psi_s}{RT} \right) \left( \frac{\Pi}{\Omega} + \Lambda \right) \right\},
$$

(5.28)
and

\[-C_s (\psi_d - \psi_s) = \frac{\varepsilon_0 \varepsilon_f \kappa \psi_d}{\tanh\left(\frac{\kappa h}{2}\right)}.\]  \hfill (5.29)

Solving Equations (5.28) and (5.29) yields

\[\psi_s = \frac{\varepsilon_0 \varepsilon_d V_g - \delta F N_{\text{total}} \left(\frac{\Phi}{\Omega}\right)}{\varepsilon_0 \varepsilon_d + \left[\frac{\delta \varepsilon_0 \varepsilon_f \kappa C_s}{C_s \tanh\left(\frac{\kappa h}{2}\right) + \varepsilon_0 \varepsilon_f \kappa} + \frac{\delta F^2 N_{\text{total}}}{RT} \left(\frac{\Pi}{\Omega} + \Lambda\right)\right]},\]  \hfill (5.30)

and

\[\psi_d = \frac{C_s}{C_s + \frac{\varepsilon_0 \varepsilon_f \kappa}{\tanh\left(\frac{\kappa h}{2}\right)}} \left\{ \frac{\varepsilon_0 \varepsilon_d V_g - \delta F N_{\text{total}} \left(\frac{\Phi}{\Omega}\right)}{\varepsilon_0 \varepsilon_d + \left[\frac{\delta \varepsilon_0 \varepsilon_f \kappa C_s}{C_s \tanh\left(\frac{\kappa h}{2}\right) + \varepsilon_0 \varepsilon_f \kappa} + \frac{\delta F^2 N_{\text{total}}}{RT} \left(\frac{\Pi}{\Omega} + \Lambda\right)\right]} \right\}.\]  \hfill (5.31)
\( I_{sr} \) and \( G_{sr} \) can be further approximated, respectively, by

\[
I_{sr} = 2w \int_{\delta_{1}}^{\delta_{2}} \rho_{s}(x) u_{s}(x) \, dx = -2w \int_{\delta_{1}}^{\delta_{2}} \varepsilon_{0} \varepsilon_{f} \frac{d^{2} \psi}{dx^{2}} u_{s}(x) \, dx
\]

\[
= -2we_{0} \varepsilon_{f} \int_{\delta_{1}}^{\delta_{2}} u_{s}(x) \frac{d \psi}{dx} \left( \frac{1}{2} \frac{dp}{dy} (x^{2} - h) \right)
\]

\[
= 2we_{0} \varepsilon_{f} \left( \int_{\delta_{1}}^{\delta_{2}} \frac{1}{2} \frac{dp}{dy} (2x - h) \, dy \right)
\]

\[
= 2we_{0} \varepsilon_{f} \frac{dp}{2 \mu} \left( (2x - h) \psi \bigg|_{\delta_{1}}^{\delta_{2}} - 2 \int_{\delta_{1}}^{\delta_{2}} \psi dx \right)
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ h\psi_{d} - 2 \int_{\delta_{1}}^{\delta_{2}} \frac{\psi_{d}}{\sinh \left( \frac{\kappa h}{2} \right)} \sinh \left( \kappa \left( \frac{h}{2} - x \right) \right) dx \right]
\]

\[
= \frac{we_{0} \varepsilon_{f}}{\mu} \frac{dp}{dy} \left[ h\psi_{d} + \frac{2\psi_{d}}{\kappa \sinh \left( \frac{\kappa h}{2} \right)} \left( 1 - \cosh \left( \frac{\kappa h}{2} \right) \right) \right]
\]

\[
= \frac{we_{0} \varepsilon_{f} \psi_{d}}{\mu l} \left\{ \frac{2 \left[ 1 - \cosh \left( \frac{\kappa h}{2} \right) \right]}{\kappa \sinh \left( \frac{\kappa h}{2} \right)} \right\}
\]

and

\[
G_{sr} = -\frac{we_{0} \varepsilon_{f} \psi_{d}}{\mu l} \left\{ \frac{2 \left[ 1 - \cosh \left( \frac{\kappa h}{2} \right) \right]}{\kappa \sinh \left( \frac{\kappa h}{2} \right)} \right\}.
\]

(5.32) (5.33)
5.3. Results and Discussion

To validate the derived models, Section 5.3.1 compares the predictions of the streaming conductance, $G_{str}$, in the silica nanochannel from the analytical MIM to the existing experimental data available in the literature. The analytical MIM with the fitted parameters (i.e., $N_{total}$, $pK_A$, $pK_B$, and $C_s$) are then used to verify the applicability of that under the Debye-Hückel approximation in Section 5.3.2, and to investigate the field effect regulation of the zeta potential and the streaming conductance in a gated silica nanochannel under various solution properties (pH and salt concentration) in Sections 5.3.3 and 5.3.4. The relevant physical parameters used in the calculations are

$\varepsilon_0 = 8.85 \times 10^{-12} \text{C}^2 \text{V}^{-1} \text{m}^{-1}$, $\mu = 10^{-3} \text{kg} \text{m}^{-1} \text{s}^{-1}$, $F = 96487 \text{C} \text{mol}^{-1}$, $R = 8.31 \text{JK}^{-1} \text{mol}^{-1}$, $T = 298 \text{K}$, $\varepsilon_f = 78.5$, and $\varepsilon_d = 3.9$ (SiO$_2$) [184].

5.3.1. Verification of the Analytical MIM by Experimental Data

The applicability of the present analytical MIM (Equations (5.20) - (5.23) in Section 5.2.2) is first verified by the experimental data of van der Heyden et al. [8], where the streaming conductance, $G_{str}$, in a silica nanochannel of width $w = 50 \mu\text{m}$ and length $l = 4.5 \text{mm}$ was conducted at the applied pressure $\Delta p = -4 \text{bar}$ and $\text{pH} = 8$. Figure 5.2 depicts the dependence of $G_{str}$ on the background salt concentration $C_{KCl}$ for various nanochannel heights $h$ ranging from 140 to 1147 nm. As shown in Figure 5.2, the predictions from the analytical MIM (lines), with the same parameters $C_s = 0.42 \text{F/m}^2$, $N_{total} = 4 \text{nm}^{-2}$, $pK_A = 8$, and $pK_B = 2.5$, agree well with the experimental data of van der Heyden et al. [8] (symbols). The fitted parameters (i.e., $C_s$, $N_{total}$, $pK_A$, and $pK_B$) and the corresponding isoelectric point of the silica nanochannel (e.g., 2.75) are also
consistent with those reported in the literature (e.g., $N_{\text{total}} = 3.8 \sim 8 \text{ nm}^{-2}$, $pK_A = 6 \sim 8$, $pK_B = 0 \sim 3$, and $C_s = 0.15 \sim 2.9 \text{ F/m}^2$ [6, 8, 68], and the isoelectric point is about $2 \sim 3.5$ [257] for the dielectric channel made of silica). It should be pointed out that only one set of the fitted parameters based on our model is used to describe the experimental data of the streaming conductance in a silica nanochannel with various channel heights. This is much better than the model proposed by van der Heyden et al. [8], where they used different fitted parameters to describe the behaviors of the streaming conductance in the silica nanochannels with various heights. Therefore, the predicted values of $C_s = 0.42 \text{ F/m}^2$, $N_{\text{total}} = 4 \text{ nm}^{-2}$, $pK_A = 8$, and $pK_B = 2.5$, are then used in the following discussions. For illustration, consider a FET-gated nanochannel with height $h = 200 \text{ nm}$, width $w = 50 \mu\text{m}$, length $l = 4.5 \text{ mm}$, and the thickness of the dielectric layer $\delta = 30 \text{ nm}$.

Figure 5.2. Dependence of the streaming conductance ($G_{st}$) in a silica nanochannel on the background salt concentration $C_{K\text{Cl}}$ for various nanochannel heights $h$. Symbols: experimental data of van der Heyden et al.[8] at $\Delta \rho = -4 \text{ bar}$, $w = 50 \mu\text{m}$, $l = 4.5 \text{ mm}$, and pH = 8; lines: results of the present analytical MIM at $C_s = 0.42 \text{ F/m}^2$, $N_{\text{total}} = 4 \text{ nm}^{-2}$, $pK_A = 8$, and $pK_B = 2.5$. 

5.3.2. Verification of the Analytical MIM Solution under the Debye-Hückel Approximation

5.3.2.1. The Debye-Hückel Approximation

The applicability of the analytical MIM solutions under the Debye-Hückel approximation (i.e., $|\psi| < 25.7 \text{ mV}$) for the zeta potential, $\psi_d$ (Equation (5.31)), and the streaming conductance, $G_{str}$ (Equation (5.33)), in a gated silica nanochannel is examined in Figure 5.3. In this figure, the variations of $\psi_d$ and $G_{str}$ as a function of the applied gate potential $V_g$ for various background salt concentrations $C_{KCl}$ at $pH = 3$ are plotted in Figures 5.3a and b, respectively. Figure 5.3 clearly shows that the results of $\psi_d$ and $G_{str}$ obtained from the closed-form analytical MIM solutions (Equations (5.31) and (5.33) in Section 5.2.3) match well with those from the implicit solution based on the analytical MIM (Equations (5.20) - (5.23) in Section 5.2.2). An excellent agreement between the results of $\psi_d$ and $G_{str}$ obtained from the above two models is observed when $|\psi_d|$ is below 25.7 mV at small $V_g$ and/or high $C_{KCl}$. Even if $|\psi_d|$ is between 25.7 and 48 mV at large $V_g$ and/or low $C_{KCl}$, a maximum relative error of ca. 10.5 % between the closed-form analytical MIM expressions and the exact implicit solution obtained from the analytical MIM for $\psi_d$ and $G_{str}$ is obtained, as depicted in Figure 5.3. Therefore, it is concluded that the present closed-form analytical MIM solutions are capable of accurately predicting the general trends of $\psi_d$ and $G_{str}$ for $|\psi_d| \leq 48 \text{ mV}$, especially when the salt concentration is sufficiently high, which is the typical condition encountered in FET-gated nanofluidics applications [4, 179, 181, 252]. Figure 5.3b also
suggests that $G_{str}$ is larger for lower $C_{KCl}$. This agrees with the experimental observations for the streaming current (or conductance) [3, 6, 8], and is because both the EDL thickness and the zeta potential (Figure 5.3a) of the nanochannel increase with a decrease in the salt concentration. These two combined effects lead to a greater amount of mobile counterions ($2\int_{h/2}^{h/2} \rho_e(x)dx$) within the EDL experiencing higher pressure-driven flow velocity in the vicinity of the charged channel wall. However, the salt concentration dependence of the streaming current/conductance in the nanochannel is inconsistent with that of the ionic current/conductance, which decreases with a decrease in the salt concentration [179]. This is because the ionic current/conductance in nanofluidics is dominated by the net ionic concentration, $\sum_{i=1}^{N} C_{i0}$, in the bulk electrolyte solution [243] (not mobile counterions $\rho_e$).

Figure 5.3. Zeta potential $\psi_d$ (a), and streaming conductance $G_{str}$ (b), as a function of the gate potential $V_g$ for various background salt concentrations $C_{KCl}$ at pH = 3. Lines denote the results of the analytical MIM, and open symbols in (a) and (b) denote the closed-form results of the analytical MIM under the Debye-Hückel approximation based on Equations (5.31) and (5.33), respectively.
5.3.3. Influence of Solution pH

Figures 5.4 and 5.5 illustrate the influence of the solution pH on the field effect regulation of the zeta potential, $\Psi_d$, and the streaming conductance, $G_{str}$, in a gated silica nanochannel for various applied gate potential, $V_g$, at two levels of the background salt concentration, $C_{KCl}$. This figure clearly shows that the zeta potential, $\Psi_d$, and, accordingly, the streaming conductance, $G_{str}$, of the nanochannel can be actively tuned from negative to positive by the gate potential, $V_g$. Similar behavior has been observed experimentally in the studies of the field effect control of the zeta potential in nanofluidics [4, 253], and can be further utilized to control the transport of ions, fluid, and biomolecules [4, 179, 181, 189, 252, 253]. Figures 5.4 and 5.5 also reveals that the performance of the field effect modulation of $\Psi_d$ (5.4a and b) and $G_{str}$ (5.5a and b) is remarkable at low solution pH, and becomes unremarkable at sufficiently high solution pH. This is because the proton concentration increases with decreasing solution pH, leading to less negatively charged SiO$^-\ $dissociated from the silanol (SiOH) functional groups on the nanochannel surface and, therefore, a smaller $\sigma$, and lesser counterions electrostatically attracted to the channel surface, therefore, makes the FET easiler to tune its zeta potential. According to Equations (5.22) and (5.23), since the streaming current/conductance of the nanochannel strongly depends upon the magnitude of its zeta potential, a superior tuning efficiency of the streaming current by the FET in nanofluidics at low solution pH is observed in Figures 5.5a and 5.5b.
It is interesting to note in Figures 5.4 and 5.5 that the field effect regulation behaviors of $\psi_d$ and $G_{str}$ versus the solution pH depend significantly upon the levels of the applied gate potential $V_g$ and the background salt concentration $C_{KCl}$. If the FET is floating ($V_g = 0 \text{ V}$) and a negative gate potential is applied ($V_g < 0 \text{ V}$), Figures 5.4b and 5.5b reveal that the magnitude of $\psi_d$ and, accordingly, $G_{str}$ increase monotonically with the solution pH at high salt concentration $C_{KCl} = 500 \text{ mM}$. On the other hand, at relatively
low salt concentration $C_{KCl} = 1 \text{ mM}$ (Figures 5.4a and 5.5a), both $|\psi_d|$ and $G_{str}$ increase with the solution pH when it is low, and show a local maximum when the solution pH is sufficiently high. The behavior that $|\psi_d|$ and, accordingly, $G_{str}$, increase with increasing pH is expected due to an increase in $|\sigma_s|$. However, an increase in the solution pH, when it deviates appreciably from 7, also results in an increase in the ionic strength (a decrease in the EDL thickness). If the behavior of $\psi_d$ is dominated by the effect of an increase in the ionic strength, which becomes significant when $C_{KCl}$ is sufficiently low, $|\psi_d|$ decreases accordingly. This explains why $|\psi_d|$ and, accordingly, $G_{str}$ decrease with an increase in the solution pH for pH $> 11$ at $C_{KCl} = 1 \text{ mM}$, as shown in Figures 5.4a and 5.5a.

If a positive gate potential is applied (i.e., $V_g > 0 \text{ V}$), Figures 5.4a and 5.4b show that $\psi_d$ ($G_{str}$) remains negative (positive) at high solution pH and becomes positive (negative) at low solution pH. Note that when the solution pH is low, both $\psi_d$ and $|G_{str}|$ show an apparent local maximum as the solution pH varies at low salt concentration $C_{KCl} = 1 \text{ mM}$ (Figures 5.4a and 5.5a), but decrease monotonically with increasing pH at high salt concentration $C_{KCl} = 500 \text{ mM}$ (Figures 4.4b and 4.5b). The former can be attributed to an increase in the ionic strength when the solution pH declines significantly from 7, thus lowering the modulated zeta potential of the nanochannel. This effect becomes significant when the background salt concentration is sufficiently low, as described previously. From Figures 5.4 and 5.5, it is worth concluding that for a fixed $C_{KCl}$, the behavior of $G_{str}$ as the solution pH varies is consistent with that of $\psi_d$ because
of the significant zeta potential-dependent streaming current (or conductance) behavior in the nanochannel, according to Equations (5.22) and (5.23).

5.3.4. Influence of Background Salt Concentration

Figure 5.6 and 5.7 depicts the influence of the background salt concentration, $C_{\text{KCl}}$, on the field effect regulation of the zeta potential, $\psi_d$, and the streaming conductance, $G_{\text{str}}$, for various gate potentials, $V_g$, at two levels of the solution pH. This figure shows that at low solution pH $= 4$, $\psi_d$ and, accordingly, $G_{\text{str}}$, is modulated from negative to positive as $V_g$ varies; however, only the magnitude of $\psi_d$ and $G_{\text{str}}$ can be tuned for the considered region of $V_g$ ranging from $-10$ to $10$ V at relatively high solution pH $= 8$. These behaviors are consistent with those in Figures 5.4 and 5.5, and can be attributed to a higher surface charge density of the nanochannel, thus making the FET harder to regulate the zeta potential and the corresponding electrokinetic transport phenomena in the nanochannel. Figures 5.6 and 5.7 also suggests that the degree of the field effect regulation of $\psi_d$ (Figures 5.6a and 5.6b) and $G_{\text{str}}$ (Figures 5.7a and 5.7b) is significant if $C_{\text{KCl}}$ is low, and becomes insignificant if $C_{\text{KCl}}$ is sufficiently high. In this case, a higher gate potential is required to effectively tune the zeta potential and streaming current in the nanochannel.
Figures 5.6a and 5.6b reveal that regardless of the levels of pH and $V_g$, the magnitude of $\psi_d$ decreases monotonically with increasing $C_{KCl}$. This is because the EDL thickness decreases with an increase in the salt concentration, resulting in more counterions gathered near the nanochannel wall and, thus, lowering its effective charge. It is interesting to note in Figures 5.7a and 5.7b that for the considered region of $C_{KCl}$, the behaviors of $G_{str}$ with $C_{KCl}$ depend upon the levels of pH and $V_g$. If the solution pH is
low (Figure 5.7a), the magnitude of $G_{str}$ increases with decreasing $C_{KCl}$ in the high salt concentration regime and reaches a nearly saturated value (plateau) in the low salt concentration regime. On the other hand, if the solution pH is high (Figure 5.7b), $G_{str}$ increases first and then attains a plateau as $C_{KCl}$ decreases for the relatively high negative gate potentials (i.e., $V_g = -5$ and $-10$ V), and shows a local maximum for the floating FET (i.e., $V_g = 0$ V) and the positive gate potentials (i.e., $V_g = 5$ and 10 V). The local maximum of $G_{str}$ extends to higher $C_{KCl}$ for larger positive $V_g$. The behavior that $G_{str}$ increases with a decrease in $C_{KCl}$ in the high salt concentration regime can be attributed to the combined effects of a greater $|\psi_d|$ (shown in Figures 5.6a and b) and a thicker EDL. However, if $C_{KCl}$ further declines to a critically low regime, because the major counterions (K$^+$ ions) from the background salt KCl become very dilute, $G_{str}$ shows a decreasing tendency with a decrease in $C_{KCl}$. Note that if the solution pH is sufficiently low, the other counterions (H$^+$ ions) dissociated from HCl and water becomes dominant. Therefore, the aforementioned dilute effect of K$^+$ ions as $C_{KCl}$ decreases becomes relatively insignificant. This is why $G_{str}$ shows a plateau for lower $C_{KCl}$ at the low solution pH, as seen in Figure 5.7a.

5.4. Conclusions

For the first time, an investigation of the field effect control of the surface charge property and the streaming current/conductance, generated by a pressure-driven flow, in a FET-gated silica nanochannel under various solution properties (background pH and salt concentration) was conducted. Taking practical effects such as multiple ionic species,
surface chemistry reactions, and the Stern layer into account, analytical expressions were derived, including implicit and explicit ones, to estimate the surface charge property and the streaming current/conductance tuned by a FET. The implicit analytical multi-ion model (MIM) is validated by comparing its predictions to the existing experimental data of the streaming conductance in the silica nanochannels with various channel heights. The explicit analytical MIM based on the Debye-Hückel approximation is valid especially when the magnitude of the zeta potential is less than the thermal potential, which often holds for relatively high salt concentration, in accordance with typical nanofluidics-based experimental conditions. The results clearly show that the zeta potential as well as the streaming current/direction can be actively tuned by the FET. The performance of the zeta potential and streaming conductance modulation by FET is better when the background salt concentration and pH are low. The developed model predicts that the dependence of the streaming conductance in the gated silica nanochannel on the solution pH is consistent with the dependence of the zeta potential. However, that dependence on the salt concentration might be different from the dependence of the zeta potential, depending on the levels of the solution pH and the gate potential. For example, for relatively high solution pH, the magnitude of the zeta potential of the nanochannel increases with decreasing background salt concentration, but the streaming conductance increases first and then decreases (or exhibits a plateau) with a decrease in the salt concentration.
CHAPTER 6
ELECTROVISCOUS EFFECT ON FET CONTROL OF STEAMING CURRENT IN NANOCHELLE

6.1. Introduction

During the past decade, ionic mass transport in nanofluidic devices, such as nanopores and nanochannels, has drawn growing interests due to their potential applications ranging from regulation of ion transport to single nanoparticle sensing [178, 202, 205, 206, 225, 226, 258 - 261]. The feasibility of these nanofluidics-based applications stems from analyzing their resulting ionic current signals in various aqueous solutions. Therefore, active control of the ionic mass transport in these nanofluidic devices plays a crucial role for the development of the next-generation nanofluidics-based apparatus.

Recently, several experimental works revealed that the transport of ions and nanoparticles in nanofluidics could be controlled by applying a pressure field through them [227, 228, 237, 262 - 264]. The flow of an electrolyte solution driven by an applied pressure gradient through the nanochannel generates both a streaming current and a streaming potential due to an accumulation (a depletion) of excess mobile ions in the downstream (upstream) of the nanochannel [8], as schematically depicted in Figure 6.1. It has also been demonstrated both experimentally and theoretically that the streaming current can provide a simple and effective scenario for converting hydrostatic energy to electrical power [3, 6, 58, 68, 124, 158, 164, 165, 248, 254, 256, 265, 266]. This clean power harvesting system using nanofluidics might open a new avenue in the exploration of new sources for renewable energy [124]. Note that the streaming potential induced by
the pressure-driven flow also generates a streaming electric field, the direction of which is opposite to the flow direction, and, hence, the net flow in the nanochannel is diminished. This phenomenon is typically known as the electroviscous effect because the liquid appears to have a higher viscosity in the vicinity of the charged nanochannel [158 - 160], resulting in a reduction in the streaming current. However, this effect was often neglected in the previous theoretical analysis of the streaming current in the nanochannel [3, 6, 8, 68, 233, 248, 256, 266]. Although this assumption dramatically simplifies the mathematical analysis, results in these studies show that under certain conditions such neglect may yield an incorrect estimation in relevant ion transport phenomena.
Figure 6.1. Schematic illustration of a nanofluidic FET system used to modulate the zeta potential ($\psi_d$) and streaming current, driven by an applied pressure field (-$\Delta p$), in a pH-regulated nanochannel containing multiple ionic species, $H^+$, $K^+$, $Cl^-$, and $OH^-$. Four major regions are considered: the dielectric channel layer of thickness $\delta$, the immobile Stern layer with surface capacitance $C_s$, the diffusive layer of Debye length $\lambda_D$, and the bulk solution. $V_g$ is the gate potential imposed on the gate electrode, and $\psi_s$ is the surface potential stemming from the dissociation and association surface reactions of functional groups on the nanochannel wall. $E_{str}$ is the streaming electric field established by the movement of excess mobile ions through an application of -$\Delta p$ across the nanochannel.

Ionic mass transport in nanofluidics is highly dependent on the surface charge property at the solid/liquid interface of these nanofluidic devices [69, 177, 178]. Control of the surface charge property, therefore, controls the transport of ions, fluid, and (bio)nanoparticles in nanofluidics. To achieve this, a nanofluidic field effect transistor (FET) [4, 179 - 181], referring to a nanochannel (or nanopore) embedded with an electrically controllable gate electrode, have been developed. The surface charge property and, accordingly, the ion transport phenomena in the nanofluidic devices can be actively regulated by modulating the gate potential imposed on the gate electrode. Motivated by
this concept of nanofluidic FET, the field effect control of the surface charge property and the streaming current/conductance in a long pH-regulated nanochannel under various solution properties such as pH and salt concentration is studied. In contrast to previous works on the gated nanofluidic devices mainly focused on full numerical simulations [183 - 186, 188, 189, 191, 192, 252], analytical expressions are derived for the first time to predict the zeta potential and the streaming current/conductance with the consideration of multiple ionic species, surface chemistry reactions on the dielectric nanochannel wall, and the Stern layer effect. Moreover, the electroviscous effect, which was often neglected in previous studies [3, 6, 8, 68, 233, 248, 256, 266], on the streaming current/conductance modulated by the FET is also considered in this study. Since most of the practical effects are taken into account, the analytical results would provide better insight into the underlying physics and convenient recipes for utilizing gated nanochannels in relevant applications.

6.2. Theoretical Analysis

The problem under consideration is depicted in Figure 6.1, where a nanofluidic FET is used to actively modulate the surface charge property and the streaming current \( I_{str} \), induced by an applied pressure field \( -\Delta p \) [8], in a pH-regulated nanochannel of height \( H \), length \( L \), and width \( W \). The FET includes a thin dielectric layer of thickness \( \delta \) and relativity permittivity \( \varepsilon_d \), and a gate electrode patterned on its outer surface. A gate potential, \( V_g \), is imposed on the gate electrode to regulate the surface charge property of the inner channel wall in contact with aqueous solution and, in turn, control the streaming current in the nanochannel. The Cartesian coordinates \( x \) and \( y \) are adopted with the origin located at the bottom solid channel/liquid interface. The pressure-driven flow is
directed in the $y$-direction, and a streaming electric field, $E_{str}$, is established in the opposite flow direction due to the accumulation (depletion) of excess mobile counterions in the downward (upward) of the nanochannel.

The following is assumed: (i) The liquid phase is an incompressible Newtonian fluid containing $N$ kinds of ionic species, and the pressure-driven flow is fully developed along the nanochannel; (ii) The dielectric channel (e.g., SiO$_2$, SiNx, and Al$_2$O$_3$) wall in contact with an aqueous solution is of charge-regulated nature [66, 68] bearing a uniform surface charge density of $\sigma$; (iii) The Stern layer of an extremely thin thickness $\delta_s$ is formed on the charged nanochannel wall, and ions and fluid inside that layer are immobile contributing nothing to streaming current; (iv) The no-slip plane is located at the Stern layer/diffusive layer interface; (v) The nanochannel height is much smaller than its length and width (i.e., $H \ll W$ and $H \ll L$); therefore, the present problem can be viewed as a nanoslit with two infinite parallel plates; and (vi) Electrical double layers (EDLs) of the nanochannel walls in the $x$-direction are not overlapped. This implies that the Debye length is much smaller than the half height of the nanochannel; that is, $\lambda_D = \kappa^{-1} \ll H / 2$, which holds for most experimental conditions in nanofluidics. For example, the background salt concentration in experiments typically varies from 1 to 1000 mM, yielding the corresponding Debye length ranging from 9.6 to 0.3 nm, which is sufficiently thin compared to most of $H$ [6, 237, 238]. Therefore, the effect of ion concentration polarization [206, 235], arising from the selective transport of ions in nanofluidics, can be neglected. Under above assumptions, the distributions of the electric potential arising from the charged channel walls, ionic concentrations, the fluid velocity, and the induced $E_{str}$ are uniform in the $y$-direction.
6.2.1 Governing Equations and Boundary Conditions

Based on the above assumptions, the electric potentials within the dielectric channel layer, Stern layer, and liquid, \( \phi \), \( \varphi \), and \( \psi \), respectively, and the fully developed pressure-driven fluid velocity in the \( y \)-direction, \( u_y \), can be described by

\[
\frac{d^2 \phi}{dx^2} = 0 \text{ within the dielectric channel } (-\delta \leq x \leq 0),
\]

\[
\frac{d^2 \varphi}{dx^2} = 0 \text{ within the Stern layer } (0 \leq x \leq \delta_s),
\]

\[
\frac{d^2 \psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0 \varepsilon_f} - \frac{1}{\varepsilon_0 \varepsilon_f} \sum_{i=1}^{\infty} Fz_i C_{i0} \exp \left( -\frac{z_i F \psi}{RT} \right) \text{ within the liquid phase } (\delta_s \leq x \leq h/2),
\]

\[
\mu \frac{d^2 u_y}{dx^2} = \frac{d\rho_e E_{sr}}{dy} \text{ within the liquid phase } (\delta_s \leq x \leq h/2).
\]

In the above, \( \rho_e \) is the mobile space charge density; \( z_i \) and \( C_{i0} \) are the valence and the bulk concentration of the \( i \)th ionic species, respectively; \( \varepsilon_0 \), \( F \), \( R \), \( T \), and \( \mu \) are the absolute permittivity of vacuum, Faraday constant, universal gas constant, absolute temperature, and dynamic fluid viscosity, respectively. The 2nd term in right-hand-side (RHS) of Equation (6.4) represents the electrostatic force stemming from the interaction between the streaming electric field (\( E_{sr} \)) and the net mobile charge density (\( \rho_e \)), and is dropped without considering the electroviscous effect.

The boundary conditions associated with Equations (6.1) – (6.4) are:

at the gate electrode (\( x = -\delta \)),

\[
\phi = V_g,
\]

\[
(6.5)
\]
at the dielectric channel/Stem layer interface \((x = 0)\),

\[
\phi = \varphi = \psi_s, \quad (6.6a)
\]

\[
-\varepsilon_0 \varepsilon_d \frac{d\phi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\psi}{dx} = -\sigma_s, \quad (6.6b)
\]

at the Stern layer/diffusive layer interface \((x = \delta_s)\),

\[
\varphi = \psi = \psi_d, \quad (6.7a)
\]

\[
-\varepsilon_0 \varepsilon_f \frac{d\varphi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\psi}{dx} = 0, \quad (6.7b)
\]

\[
u_y = 0, \quad (6.7c)
\]

and at the center of the nanochannel \((x = h/2)\),

\[
\psi = \frac{d\psi}{dx} = 0, \quad (6.8a)
\]

\[
\frac{du_y}{dx} = 0. \quad (6.8b)
\]

Equations (6.6a) and (6.6b) imply that the electric potential is continuous but the electric field, which satisfies the Gauss’s law, is discontinuous at the dielectric channel/Stem layer interface due to the discontinuity of the dielectric permittivities \((\varepsilon_d \text{ and } \varepsilon_f)\).

Equation 8a depicts that the electric potential arising from the charged nanochannel wall vanishes and the ionic concentrations reach their bulk values at the center of the nanochannel due to the neglect of the EDL overlapping.

The surface charge density, \(\sigma_s\), of the nanochannel can be determined by the following charge regulation model. To account for the charge regulation, it is assumed that the dielectric channel wall bears dissociable functional groups AOH, capable of
undergoing the following surface chemistry reactions: $\text{AOH} \leftrightarrow \text{AO}^- + \text{H}^+$ and $\text{AOH} + \text{H}^+ \leftrightarrow \text{AOH}_2^+$ with equilibrium constants $K_A = (\Gamma_{\text{AO}^-}[\text{H}^+]) / \Gamma_{\text{AOH}}$ and $K_B = \Gamma_{\text{AOH}_2^+} / (\Gamma_{\text{AOH}}[\text{H}^+])$, respectively. Here, $\Gamma_{\text{AOH}}$, $\Gamma_{\text{AO}^-}$, and $\Gamma_{\text{AOH}_2^+}$ denote the surface site densities of AOH, AO$, and AOH$_2^+$, respectively; $[\text{H}^+]_s$ is the molar concentration of H$^+$ ions at the dielectric channel/liquid interface. The total number site density of AOH molecules on the dielectric channel surface is $N_{\text{total}} = \Gamma_{\text{AOH}} + \Gamma_{\text{AO}^-} + \Gamma_{\text{AOH}_2^+}$. If it is assumed that the equilibrium distribution of H$^+$ ions follows the Boltzmann distribution, the nanochannel surface charge density, $\sigma_s$, can be expressed as [176],

$$\sigma_s = -FN_{\text{total}} \left\{ 10^{-pK_A} - 10^{-pK_B} \left[ 10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right)\right]^2 \right\} \left\{ 10^{-pK_A} + 10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right) + 10^{-pK_B} \left[ 10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right)\right]^2 \right\} , \quad (6.9)$$

where $pK_j = -\log K_j \ (j = A \text{ and } B)$.

### 6.2.2 Analytical Multi-Ion Model (MIM)

Solving Equations (6.1) and (6.2) subject to Equations (6.5), (6.6a) and (6.7a), yields

$$\phi = \psi_s + \frac{\psi_s - V_s}{\delta} x , \quad (6.10)$$

$$\varphi = \psi_s + \frac{\psi_s - \psi_s}{\delta_s} x . \quad (6.11)$$
Substituting Equations (6.10) and (6.11) into Equations (6.6b) and (6.7b), and letting the surface capacitance of the Stern layer, $C_s = \varepsilon_0 \varepsilon_f / \delta_s$, yields the following relations:

$$-\varepsilon_0 \varepsilon_d \left( \frac{\psi_s - V_s}{\delta} \right) + C_s (\psi_d - \psi_s) = -\sigma_s, \quad (6.12)$$

$$-C_s (\psi_d - \psi_s) - \sigma_d = 0. \quad (6.13)$$

Here, $\sigma_d$ is the surface charge density of the diffuse layer and can be expressed as

$$\sigma_d = -\varepsilon_0 \varepsilon_f \left. \frac{d\psi}{dx} \right|_{x=\delta_d \to 0} = \text{sign}(\psi_d) \sqrt{2 \varepsilon_0 \varepsilon_f RT \sum_{i=1}^{N} C_{i0} \left[ \exp \left( -\frac{z_i F \psi_d}{RT} \right) - 1 \right]}, \quad (6.14)$$

where $\text{sign}(\psi_d) = 1$ for $\psi_d > 0$ and $\text{sign}(\psi_d) = -1$ for $\psi_d < 0$. In the absence of the FET, the first term of the left-hand-side (LHS) of Equation (6.12) vanishes and, therefore, Equations (6.12) and (6.13) reduce to

$$C_s (\psi_s - \psi_d) = \sigma_s = \sigma_d, \quad (6.15)$$

which is the well-known basic Stern layer model [66]. Note that the Stern layer models to describe the relationship between the surface potential ($\psi_s$) and zeta potential ($\psi_d$) of the nanochannel in the presence (Equations (6.12) and (6.13)) and absence (Equation (6.15)) of FET are remarkably different.

To simulate experimental conditions with multiple ionic species, we assume that the background salt in the liquid phase comes from KCl and the solution pH is adjusted by HCl and KOH. Therefore, four major kinds of ionic species (i.e., $N = 4$) including $K^+$, $Cl^-$, $H^+$ and $OH^-$ should be considered. Let $C_{i0}$ (in mM), $i = 1, 2, 3, 4$ be the bulk concentrations of these ions, respectively, and $C_{KCl}$ be the background concentration of
KCl. The electroneutrality condition results in the following relations [242]:

\[ C_{10} = C_{KCl}, \]

\[ C_{20} = C_{KCl} + 10^{-pH+3} - 10^{-(14-pH+3)}, \]

\[ C_{30} = 10^{-(pH+3)}, \]

\[ C_{40} = 10^{-(14-pH+3)} \for \ pH \leq 7; \]

\[ C_{10} = C_{KCl} - 10^{-pH+3} + 10^{-(14-pH+3)}, \]

\[ C_{20} = C_{KCl}, \]

\[ C_{30} = 10^{-(pH+3)}, \]

\[ C_{40} = 10^{-(14-pH+3)} \] for pH > 7. Therefore, we obtain

\[ C_0 = C_{10} + C_{30} = C_{20} + C_{40} = C_{KCl} + 10^{-(pH+3)} \] for pH ≤ 7 and

\[ C_{KCl} + 10^{-(14-pH+3)} \] for pH > 7. Based on these relations, Equation 3 can be rewritten as

\[ \frac{d^2 \psi}{dx^2} = \kappa^2 \sinh(\psi) \text{ within the liquid phase (} \delta \leq x \leq h/2), \]

where \( \psi = \psi / \psi_{ref} \) with \( \psi_{ref} = RT / zF \) and \( z = z_1 = -z_2 \), and \( \kappa^{-1} = \sqrt{\varepsilon_0 \varepsilon_f RT / 2z^2 F^2 C_0} \)

is the Debye length.

Solving Equation (6.16) subject to Equation (6.7a) and (6.8a), one obtains

\[ \tilde{\psi} = 2 \ln \left[ \frac{1 + \exp(-\kappa x) \tanh(\frac{\psi_{sd}}{4})}{1 - \exp(-\kappa x) \tanh(\frac{\psi_{sd}}{4})} \right]. \]

(6.17)

The charge density of the diffusive layer is

\[ \sigma_d = 2\varepsilon_0 \varepsilon_f \kappa \psi_{ref} \sinh\left(\frac{\psi_{sd}}{2}\right), \]

(6.18)

where \( \psi_{sd} = \psi / \psi_{ref} \).

By integrating Equation (6.4) twice with the associated boundary Equations (6.7a), (6.7c), (6.8a), and (6.8b), one obtains fluid velocity profile driven by both the imposed pressure gradient and the induced streaming electric field,

\[ u_y = \frac{1}{2\mu} \frac{dp}{dy} \left( \kappa^2 - h^2 \right) + \frac{\varepsilon_0 \varepsilon_f}{\mu} E_{str} (\psi - \psi_d), \]

(6.19)

where \( -dp / dy = -\Delta p / L \) is the applied pressure gradient across the nanochannel.
By substituting Equations (6.9), (6.17) and (6.18) into Equations (6.12) and (6.13), the following implicit expressions relating the surface potential ($\psi_s$) to the zeta potential ($\psi_d$) of the nanochannel are obtained:

$$
-e_0\varepsilon_d\left(\frac{\psi_s - V_s}{\delta}\right) + C_s(\psi_d - \psi_s) = FN_{\text{total}} \left\{ \begin{array}{c}
10^{-p\kappa_s} - 10^{-p\kappa_d} \left[ 10^{-p\psi_d} \exp\left( -\frac{F\psi_s}{RT} \right) \right]^2
+ 10^{-p\psi_s} \left[ 10^{-p\psi_d} \exp\left( -\frac{F\psi_s}{RT} \right) \right]^2
\end{array} \right\},
$$

(6.20)

and

$$
-C_s(\psi_d - \psi_s) = 2\varepsilon_0\varepsilon_f\kappa \psi_{\text{ref}} \sinh\left( \frac{\psi_d}{2} \right)
$$

(6.21)

For given conditions, one can easily use Matlab function $fsolve$ to determine both $\psi_s$ and $\psi_d$ by simultaneously solving Equations (6.20) and (6.21). Once $\psi_d$ is obtained, the electric potential ($\psi$) and the flow velocity ($u_y$) can be evaluated by Equations (6.17) and (6.19), respectively.

The streaming current ($I_{str}$) through the nanochannel can be exactly evaluated by

$$
I_{str} = 2W \int_{H/2}^{H/2} \rho_e(x)u_y(x)dx = -2W \int_{H/2}^{H/2} \varepsilon_0\varepsilon_f \frac{d^2\psi}{dx^2} u_y(x)dx
$$

$$
= -2W \varepsilon_0\varepsilon_f \left[ \frac{d\psi}{dx} \bigg|_{H/2}^{H/2} - \frac{d\psi}{dx} \bigg|_{-H/2}^{-H/2} \right]
$$

$$
= 2W \varepsilon_0\varepsilon_f \left[ \frac{1}{2\mu} \frac{dp}{dy} (x^2 - Hx) + \frac{\varepsilon_0\varepsilon_f E_{str}}{\mu} (\psi - \psi_d) \right]
$$

(6.22)
where $I_{str,p}$ and $I_{str,E}$ denote, respectively, the streaming currents contributed from the imposed pressure gradient and the induced streaming electric field, respectively, and can be expressed by

$$I_{str,p} = 2W\varepsilon_0\varepsilon_f \int_{\delta_s \to 0}^{H/2} \frac{1}{2\mu} \frac{dp}{dy} (2x - H) d\psi$$

$$= \frac{W\varepsilon_0\varepsilon_f}{\mu} \frac{dp}{dy} \left\{ \left[ (2x - H)\psi \right]_{\delta_s \to 0}^{H/2} - 2\int_{\delta_s \to 0}^{H/2} \psi \frac{d\psi}{dx} \right\}$$

$$= \frac{W\varepsilon_0\varepsilon_f}{\mu} \frac{dp}{dy} \left\{ H\psi_a - 2\int_{\delta_s \to 0}^{H/2} \frac{2RT}{ZF} \ln \left[ \frac{1 + \exp(-\kappa x)A}{1 - \exp(-\kappa x)A} \right] dx \right\}$$

$$= \frac{W\varepsilon_0\varepsilon_f}{\mu} \frac{dp}{dy} \left\{ H\psi_a - \frac{4RT}{ZF} + \text{dilog} \left( \frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right) + \text{dilog} \left( \frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right) \right\}$$

$$= \frac{WHE_0\varepsilon_f\psi_a}{\mu} \frac{dp}{dy}$$

$$- \frac{4W\varepsilon_0\varepsilon_f\psi_{ref}}{\mu\kappa} \frac{dp}{dy} \left\{ \ln \left( \frac{1 + A \exp(-\kappa H/2)}{1 - A \exp(-\kappa H/2)} \right) \ln \left( \frac{2}{1 - A \exp(-\kappa H/2)} \right) \right\}$$

$$- \text{dilog} \left( \frac{2}{1 - A \exp(-\kappa H/2)} \right) + \text{dilog} \left( \frac{1 + A \exp(-\kappa H/2)}{1 - A \exp(-\kappa H/2)} \right)$$

$$- \left[ \ln \left( \frac{1 + A}{1 - A} \right) + \text{dilog} \left( \frac{1 + A}{1 - A} \right) + \text{dilog} \left( \frac{2}{1 - A} \right) \right]$$

(6.23)

and

$$I_{str,E} = 2W\varepsilon_0\varepsilon_f \int_{\delta_s \to 0}^{H/2} \frac{1}{\mu} \frac{d\psi}{dy} \frac{d\psi}{dx}$$

$$= 16W\kappa E_{str} \left( \frac{\varepsilon_0\varepsilon_f\psi_{ref}}{\mu} \right)^2 \left[ \frac{1}{A^2 \exp(-\kappa H) - 1} - \frac{1}{A^2 - 1} \right].$$

(6.24)
In the above, \( \frac{dp}{dy} = \Delta p / L \), \( A = \tanh(\psi_d / 4\psi_{\text{ref}}) \), \( \psi_{\text{ref}} = RT / zF \), \( \text{dilog}(\ ) \) represents the dilogarithm function, and

\[
\gamma_1 = \frac{16 W \kappa}{\mu} \left( \varepsilon_0 \varepsilon_f \psi_{\text{ref}} \right)^2 \left[ \frac{1}{A^2 \exp(-\kappa H) - 1} - \frac{1}{A^2 - 1} \right]. \tag{6.25}
\]

At equilibrium, the net ionic current through the nanochannel should be vanish, that is,

\[
I_{\text{str}} + I_{\text{cond}} = 0, \tag{6.26}
\]

where \( I_{\text{cond}} \) is the conductive current arising from the induced streaming potential, and can be estimated by

\[
I_{\text{cond}} = 2WE_{\text{str}} \int_{\delta_x}^{H/2} \left[ \sum_{r=1}^{N} \lambda_{\gamma 0} C_{\gamma 0} \exp \left( -\frac{z_i F \psi}{RT} \right) \right] dx.
\]

The integration in Equation (6.27) for \( i = 1 \) and \( 3 \) with \( z_i = 1 \) is

\[
\int_{\delta_x}^{H/2} \exp \left( -\frac{F \psi}{RT} \right) dx
= \frac{A \exp(-\kappa x) \ln \left[ \exp(-\kappa x) \right] + \ln \left[ \exp(-\kappa x) \right] + 4}{\kappa \left[ 1 + A \exp(-\kappa x) \right]} \bigg|_{0}^{H/2}
= \frac{H}{2} \frac{4}{\kappa \left[ 1 + A \exp(-\kappa H/2) \right]} + \frac{4}{\kappa (1 + A)} \tag{6.28}
\]

The integration in Equation (6.27) for \( i = 2 \) and \( 4 \) with \( z_i = -1 \) is

\[
\int_{\delta_x}^{H/2} \exp \left( \frac{F \psi}{RT} \right) dx
= \frac{A \exp(-\kappa x) \ln \left[ \exp(-\kappa x) \right] - \ln \left[ \exp(-\kappa x) \right] - 4}{\kappa \left[ -1 + A \exp(-\kappa x) \right]} \bigg|_{0}^{H/2}
= \frac{H}{2} + \frac{4}{\kappa \left[ -1 + A \exp(-\kappa H/2) \right]} - \frac{4}{\kappa (-1 + A)} \tag{6.29}
\]
Substituting Equations (6.28) and (6.29) into (6.27), yields

\[ I_{\text{cond}} = 2W E_{\text{str}} \left\{ \left( \lambda_{10} C_{10} + \lambda_{30} C_{30} \right) \left[ \frac{H}{2} - \frac{4}{\kappa(1 + A \exp(-\kappa H/2))} + \frac{4}{\kappa(1 + A)} \right] \\
+ \left( \dot{\lambda}_{20} C_{20} + \dot{\lambda}_{40} C_{40} \right) \left[ \frac{H}{2} + \frac{4}{\kappa(-1 + A \exp(-\kappa H/2))} - \frac{4}{\kappa(-1 + A)} \right] \right\} \]

\[ = \gamma_2 E_{\text{str}} \quad (6.30) \]

where

\[ \gamma_2 = 2W \left\{ \left( \lambda_{10} C_{10} + \lambda_{30} C_{30} \right) \left[ \frac{H}{2} - \frac{4}{\kappa(1 + A \exp(-\kappa H/2))} + \frac{4}{\kappa(1 + A)} \right] \\
+ \left( \dot{\lambda}_{20} C_{20} + \dot{\lambda}_{40} C_{40} \right) \left[ \frac{H}{2} + \frac{4}{\kappa(-1 + A \exp(-\kappa H/2))} - \frac{4}{\kappa(-1 + A)} \right] \right\} \quad (6.31) \]

Based on \( I_{\text{str}} + I_{\text{cond}} = 0 \), the streaming electric field strength \( (E_{\text{str}}) \) through the nanochannel can be evaluated by

\[ E_{\text{str}} = -\frac{I_{\text{str},p}}{\gamma_1 + \gamma_2}, \quad (6.32) \]

where \( \gamma_1 \) and \( \gamma_2 \) can be obtained from Equations (6.25) and (6.31), respectively. Once \( E_{\text{str}} \) is obtained, the streaming current through the nanochannel \( (I_{\text{str}}) \) can be exactly probed by Equations (6.22) - (6.24), and then the streaming conductance \( (G_{\text{str}}) \) can be determined by[8]

\[ G_{\text{str}} = \frac{I_{\text{str},p} + I_{\text{str},b}}{-\Delta p} = -\frac{I_{\text{str},p}}{\Delta p} - \frac{\gamma_1 E_{\text{str}}}{\Delta p} \]

\[ = -\frac{I_{\text{str},p}}{\Delta p} - \frac{\gamma_1}{\gamma_1 + \gamma_2} \left( \frac{I_{\text{str},p}}{\Delta p} \right) = -\frac{I_{\text{str},p}}{\Delta p} \left( \frac{\gamma_2}{\gamma_1 + \gamma_2} \right). \quad (6.33) \]
Note that without considering the electroviscous effect the streaming current arising from the induced $E_{str}$ is zero, yielding $G_{str} = I_{str,p}/-\Delta p$.

From Equations (6.20) - (6.33), $\psi_d$, $I_{str}$, and, accordingly, $G_{str}$ are dependent on the physicochemical properties of the dielectric channel layer (i.e., $N_{total}$, $pK_A$, $pK_B$, $\varepsilon_d$, and $\delta$), the solution properties (i.e., pH, $C_{KCl}$, $\lambda_{\psi_0}$, and $\varepsilon_f$), the applied pressure field ($-\Delta p$), the gate potential ($V_g$) imposed on the gate electrode, and the surface capacitance of the Stern layer ($C_s$). Note that the present analytical MIM for the surface charge property, and/or the streaming electric field strength, current, and conductance in a gated nanochannel with and without FET control is derived taking account of many practical effects such as multiple ionic species, the Stern layer and electroviscous effects, and the surface chemistry reactions of the dielectric channel wall, most of which were often neglected in previous studies [3, 6, 8, 68, 158 - 160, 164, 176, 183 - 186, 188 - 192, 248, 252, 254, 256, 266]. It is thus confirmed that the present model is more realistic and rigorous than most of the previous ones [3, 6, 8, 68, 158 - 160, 164, 176, 183 - 186, 188 - 192, 248, 252, 254, 256, 266].

6.2.3 Analytical MIM Solution under the Debye-Hückel Approximation

Under the Debye-Hückel approximation (i.e., $|\psi_s| < \psi_{ref} = 25.7$ mV), Equations (6.9) and (6.16) can be further simplified, respectively, as

$$\sigma_s = -FN_{total} \left[ \frac{\Phi}{\Omega} + \left( \frac{F\psi_s}{RT} \right) \left( \frac{\Pi}{\Omega} + \Lambda \right) \right], \quad (6.34)$$

and

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi \text{ within the liquid phase (} \delta_s \leq x \leq h/2\text{)}.$$

$$ (6.35)$$
In the above, \( \Phi = 10^{-pK_d} + 10^{-pK_s - 2pH} \), \( \Omega = 10^{-pK_d} + 10^{-pH} + 10^{-pK_s - 2pH} \), \( \Pi = 2 \times 10^{-pK_s - 2pH} \), and \( \Lambda = \Phi(10^{-pH} + \Pi)/\Omega^2 \).

Solving Equation (6.35) subject to Equations (6.7a) and (6.8a) gives

\[
\psi = \frac{\psi_d}{\sinh\left(\frac{\kappa H}{2}\right)} \sinh\left[\kappa\left(\frac{H}{2} - x\right)\right].
\] (6.36)

The charge density of the diffusive layer \( \sigma_d \) can then be evaluated by

\[
\sigma_d = \frac{\varepsilon_0 \varepsilon_f \kappa \psi_d}{\tanh\left(\frac{\kappa H}{2}\right)}.
\] (6.37)

By substituting Equations (6.34) and (6.37) into Equations (6.12) and (6.13), yields

\[
\varepsilon_0 \varepsilon_d \left(\frac{\psi - V_g}{\delta}\right) + \frac{\varepsilon_0 \varepsilon_f \kappa \psi_d}{\tanh\left(\frac{\kappa H}{2}\right)} = -FN_{\text{total}} \left\{ \frac{\Phi}{\Omega} + \left(\frac{F \psi_j}{RT}\right)\left(\frac{\Pi}{\Omega} + \Lambda\right) \right\},
\] (6.38)

and

\[
C_s(\psi_d - \psi_j) = -\frac{\varepsilon_0 \varepsilon_f \kappa \psi_d}{\tanh\left(\frac{\kappa H}{2}\right)}.
\] (6.39)

The solutions to Equations (6.38) and (6.39) give

\[
\psi_j = \frac{\varepsilon_0 \varepsilon_d V_g - \delta FN_{\text{total}}\left(\frac{\Phi}{\Omega}\right)}{\varepsilon_0 \varepsilon_d + \left[\frac{\delta \varepsilon_0 \varepsilon_f \kappa C_s}{C_s \tanh\left(\frac{\kappa H}{2}\right) + \varepsilon_0 \varepsilon_f \kappa} + \frac{\delta F N_{\text{total}}}{RT}\left(\frac{\Pi}{\Omega} + \Lambda\right)\right]}.
\] (6.40)
and

\[
\psi_d = \left[ \frac{C_s}{C_s + \frac{\epsilon_0 \epsilon_f \kappa \tanh \left( \frac{\kappa H}{2} \right)}{\tanh \left( \frac{\kappa H}{2} \right)}} \right] \left\{ \frac{\epsilon_0 \epsilon_f V_g - \delta F N_{\text{total}} \left( \frac{\Phi}{\Omega} \right)}{\frac{\delta \epsilon_0 \epsilon_f \kappa C_s}{C_s \tanh \left( \frac{\kappa H}{2} \right) + \epsilon_0 \epsilon_f \kappa} + \left( \frac{\delta F^2 N_{\text{total}}}{RT} \right) \left( \frac{\Pi}{\Omega} + \Lambda \right) \right\}.
\]

(6.41)

By substituting Equation (6.36) into Equation (6.19), \( u_y \) can be rewritten as

\[
u_y = \frac{1}{2 \mu} \frac{dp}{dy} \left( x^2 - Hx \right) + \frac{\epsilon_0 \epsilon_f \epsilon_{\text{str}} \psi_d}{\mu} \left\{ \frac{\sinh \left[ \kappa \left( \frac{H}{2} - x \right) \right]}{\sinh \left( \frac{\kappa H}{2} \right)} - 1 \right\}.
\]

(6.42)

Based on Equation (6.22), \( I_{\text{str},p} \) and \( I_{\text{str},E} \) can be expressed, respectively, by

\[
I_{\text{str},p} = 2 W \epsilon_0 \epsilon_f \int_{\delta_s \rightarrow 0}^{H/2} \frac{dp}{2 \mu} \frac{1}{dy} \left( 2x - H \right) d\psi
\]

\[
= \frac{2 W \epsilon_0 \epsilon_f}{2 \mu} \frac{dp}{dy} \left[ \left( 2x - H \right) \psi \mid_{\delta_s \rightarrow 0}^{H/2} - 2 \int_{\delta_s \rightarrow 0}^{H/2} \psi d\chi \right]
\]

\[
= \frac{W \epsilon_0 \epsilon_f}{\mu} \frac{dp}{dy} \left[ H \psi_d - 2 \int_{\delta_s \rightarrow 0}^{H/2} \frac{\psi_d}{\sinh \left( \frac{\kappa H}{2} \right)} \sinh \left[ \kappa \left( \frac{H}{2} - x \right) \right] d\chi \right]
\]

\[
= \frac{W \epsilon_0 \epsilon_f}{\mu} \frac{dp}{dy} \left\{ H \psi_d + \frac{2 \psi_d}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \left[ 1 - \cosh \left( \frac{\kappa H}{2} \right) \right] \right\}
\]

\[
= \frac{W \epsilon_0 \epsilon_f \psi_d}{\mu} \frac{dp}{dy} \left\{ H + \frac{2 \left[ 1 - \cosh \left( \frac{\kappa H}{2} \right) \right]}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \right\}
\]

(6.43)
and

\[
I_{sr,E} = 2W \varepsilon_o \varepsilon_f \mu \frac{E_{str}}{d\psi} d\psi d\varphi
\]

\[
= \frac{2W(\varepsilon_o \varepsilon_f)^2}{\mu} \int_{\delta}^{\frac{H}{2}} \left\{ \frac{\psi_d}{\sinh \left( \frac{\kappa H}{2} \right)} \cosh \left[ \frac{\kappa}{2} \left( \frac{H}{2} - x \right) \right] \right\}^2 dx
\]

\[
= \frac{2W(\varepsilon_o \varepsilon_f)^2}{\mu} \left[ \frac{\psi}{\sinh \left( \frac{\kappa H}{2} \right)} \right]^2 \int_{\delta}^{H/2} \left\{ \frac{\cosh \left[ \frac{\kappa}{2} \left( \frac{H}{2} - x \right) \right]}{2} \right\}^2 dx
\]

\[
= \frac{2WE_{str}}{\mu} \left[ \frac{-\kappa \varepsilon_o \varepsilon_f \psi_d}{\sinh \left( \frac{\kappa H}{2} \right)} \right] \left[ \frac{H}{4} + \frac{\sinh (\kappa H)}{4\kappa} \right] \quad (6.44)
\]

\[
= \gamma_3 E_{str}
\]

In the above Equation (6.44), \( \gamma_3 \) can be depicted as:

\[
\gamma_3 = \frac{2W}{\mu} \left[ \frac{-\kappa \varepsilon_o \varepsilon_f \psi_d}{\sinh \left( \frac{\kappa H}{2} \right)} \right]^2 \left[ \frac{H}{4} + \frac{\sinh (\kappa H)}{4\kappa} \right] \quad (6.45)
\]
In addition, $I_{\text{cond}}$ can be further approximated by

\[
I_{\text{cond}} = 2WE_{\text{str}} \int_{H/2}^{H} \left[ \left( \lambda_{10} C_{10} + \lambda_{20} C_{20} + \lambda_{30} C_{30} + \lambda_{40} C_{40} \right) \left( \frac{zF\psi}{RT} \left( -\lambda_{10} C_{10} + \lambda_{20} C_{20} - \lambda_{30} C_{30} + \lambda_{40} C_{40} \right) \right) \right] dx
\]

\[
= 2WE_{\text{str}} \int_{H/2}^{H/2} \left\{ \alpha_1 + \alpha_2 \frac{zF\psi_{d}}{\sinh \left( \frac{\kappa H}{2} \right)} \sinh \left[ \kappa \left( \frac{H}{2} - x \right) \right] \right\} dx
\]

\[
= 2WE_{\text{str}} \left\{ \frac{H\alpha_1}{2} + \alpha_2 \frac{\psi_{d}}{\psi_{\text{ref}}} \left[ \frac{\cosh \left( \frac{\kappa H}{2} \right)}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \right] \right\} = \gamma_4 E_{\text{str}}
\]

where $\alpha_1 = \lambda_{10} C_{10} + \lambda_{20} C_{20} + \lambda_{30} C_{30} + \lambda_{40} C_{40}$, $\alpha_2 = -\lambda_{10} C_{10} + \lambda_{20} C_{20} - \lambda_{30} C_{30} + \lambda_{40} C_{40}$, and

\[
\gamma_4 = 2W \left\{ \frac{H\alpha_1}{2} + \alpha_2 \frac{\psi_{d}}{\psi_{\text{ref}}} \left[ \frac{\cosh \left( \frac{\kappa H}{2} \right)}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \right] \right\}.
\]

Based on $I_{\text{str}} + I_{\text{cond}} = 0$, $E_{\text{str}}$ can be expressed by

\[
E_{\text{str}} = -\frac{I_{\text{str}, p}}{\gamma_3 + \gamma_4} = \frac{WE_{\text{str}} \psi_{d}}{\mu (\gamma_3 + \gamma_4)} \left\{ \frac{2 \left[ 1 - \cosh \left( \frac{\kappa H}{2} \right) \right]}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \right\}.
\]
Therefore, $G_{str}$ can then be further approximated by

$$G_{str} = \frac{(I_{str,P} + I_{str,K})}{-\Delta p}$$

$$= -\frac{I_{str,P}}{\Delta p} - \gamma_3 \frac{E_{str}}{\Delta p}$$

$$= -\frac{I_{str,P}}{\Delta p} \left( \frac{\gamma_4}{\gamma_3 + \gamma_4} \right)$$

$$= \left( \frac{\gamma_4}{\gamma_3 + \gamma_4} \right) \left( \frac{W \varepsilon_0 \varepsilon_f \psi_d}{\mu L} \right) \left( \frac{2 \left[ 1 - \cosh \left( \frac{\kappa H}{2} \right) \right]}{\kappa \sinh \left( \frac{\kappa H}{2} \right)} \right)$$

\hspace{1in} (6.49)

### 6.3. Results and Discussion

To validate the derived models, Section 6.3.1 compares the predictions of the streaming conductance in a silica nanochannel from the analytical MIM to the existing experimental data available in the literature. To verify the applicability of our analytical MIM solutions under the Debye-Hückel approximation (i.e., $|\psi| < 25.7 \text{ mV}$), Figure 6.2 depicts the comparison of the results of the explicit analytical MIM expressions for the zeta potential, $\psi_d$ (Equation 6.41), and the streaming conductance, $G_{str}$ (Equation 6.49), described in Section 6.2.3 of the text, and those of the verified implicit ones (Equations 6.20 - 6.33) in Section 6.2.2 of the text. As shown in Figure 6.2, the results of $\psi_d$ and $G_{str}$ obtained from the closed-form analytical MIM solutions (lines) match well with those from the implicit solution based on the analytical MIM (symbols). An excellent agreement between the results of $\psi_d$ and $G_{str}$ based on the above two models is obtained when $|\psi_d| < 25.7 \text{ mV}$ at high $C_{\text{KCl}}$ and/or small applied gate potential $V_g$. Even if $25.7 \text{ mV} \leq |\psi_d| \leq 43.2 \text{ mV}$ at low $C_{\text{KCl}}$ and/or large $V_g$, the relative deviations of $\psi_d$ and...
between the results from the implicit and explicit analytical MIMs are still less than 8%. It is thus confirmed that the closed-form analytical MIM solutions are sufficiently accurate to predict the general trends of $\psi_d$ and $G_{str}$ for the considered $|\psi_d| \leq 43.2$ mV especially when the salt concentration is high, in accordance with the typical experimental condition adopted in FET-gated nanofluidics applications.[4, 179, 181, 252] Investigate the electroviscous effect on the field effect modulation of the streaming conductance in a gated silica nanochannel under various solution properties (pH and salt concentration) in Section 6.3.2.

Figure 6.2. Zeta potential $\psi_d$, (a), and streaming conductance $G_{str}$, (b), as a function of the applied gate potential $V_g$ for various background salt concentrations $C_{KCl}$ at pH=3. Lines in (a) and (b) represent the closed-form results of the analytical MIM under the Debye-Hückel approximation based on Equations 6.41 and 6.49, respectively; symbols represent the results of the analytical MIM.

Figures 6.3 and 6.4 depict the influence of the surface capacitance of the Stern layer, $C_s$, on the zeta potential, $\psi_d$, and the streaming conductance, $G_{str}$, for $V_g = 0$ and $V_g = -15$ V. In general, the smaller the value of $C_s$, the larger difference between the
zeta potential ($\psi_d$) and the surface potential ($\psi_s$), yielding a more significant Stern layer effect. Furthermore, as $C_s \to \infty$ the Stern layer effect is neglected, implying that $\psi_d = \psi_s$. Figures 6.3 and 6.4 reveal that the Stern layer effect on the modulation of $\psi_d$ and, accordingly, $G_{str}$ is remarkable when the background salt concentration, $C_{KCl}$, is high and becomes unremarkable when it is low. That is, the higher the salt concentration the larger the difference of both $\psi_d$ and $G_{str}$ for $C_s$ ranging from 0.15 to $\infty$. This is expected since as $C_{KCl}$ increases, more counterions are confined near the nanochannel surface to reduce its original surface potential, leading to a more significant Stern layer effect. Compared to the case for $V_g = 0$ (Figures 6.3a and 6.4a), the Stern layer effect is less significant in the presence of the FET control (Figures 6.3b and 6.4b) especially when the salt concentration is low. This suggests that when $C_{KCl}$ is relatively low, the dependence of $\psi_d$ and $G_{str}$ on $C_s$ is unremarkable for $V_g = -15 \text{ V}$, and becomes remarkable for $V_g = 0$. For example, the relative percentage deviation (RPD) of $\psi_d$ between $C_s = 0.15$ F/m² and $C_s \to \infty$, calculated by

$$\left| \frac{\psi_d(\text{solid line}) - \psi_d(\text{dash double-dotted line})}{\psi_d(\text{dash double-dotted line})} \right|,$$

is about 13.2 % and 88.9 % (3.4 % and 87.7 %) for $C_{KCl} = 0.01$ mM and $C_{KCl} = 1000$ mM, respectively, without (with) considering the FET control. Similarly, the RPD of $G_{str}$ is about 17.9 % and 88.8 % (4.7 % and 87.6 %) for $C_{KCl} = 0.01$ mM and $C_{KCl} = 1000$ mM, respectively, in the absence (presence) of the FET control. This is because the performance of the FET control in nanofluidics is better when the salt concentration is low, resulting in a significant increase in $|\psi_d|$ and, therefore, a greater
number of counterions are electrostatically attracted on the nanochannel surface, thus enhancing the Stern layer effect.

Figure 6.3. Zeta potential $\psi_{dh}$ as a function of the background salt concentration $C_{KCI}$ for various surface capacitance of the Stern layer at the solution pH = 8 and the applied gate potential $V_g = 0$, (a) and -15V, (b).

Figure 6.4. Streaming conductance $G_{str}$ as a function of the background salt concentration $C_{KCI}$ for various surface capacitance of the Stern layer at the solution pH = 8 and applied gate potential $V_g = 0$, (a) and -15V, (b).
For simplicity, the molar electric conductivities of $\lambda_{10} \ (K^+)$, $\lambda_{20} \ (Cl^-)$, $\lambda_{30} \ (H^+)$, and $\lambda_{40} \ (OH^-)$ are fixed at $7.352 \times 10^{-3}$, $7.634 \times 10^{-3}$, $3.498 \times 10^{-2}$, and $1.976 \times 10^{-2} \ \text{Sm}^2/\text{mol}$, respectively [139]. Other relevant physical parameters used in the calculations are:

$\mu = 10^{-3} \ \text{kgm}^{-1}\text{s}^{-1}$, $F = 96487 \ \text{Cmol}^{-1}$, $R = 8.31 \ \text{JK}^{-1}\text{mol}^{-1}$, $T = 298 K$, $\varepsilon_0 = 8.85 \times 10^{-12} \ \text{CV}^{-1}\text{m}^{-1}$, $\varepsilon_f = 78.5$, and $\varepsilon_d = 3.9 \ (\text{SiO}_2)$ [184].

### 6.3.1 Verification of the Analytical MIM by Experimental Data

The applicability of the present analytical MIM (Equations (6.20) – (6.33) in Section 6.2.2) is first verified by the experimental data of van der Heyden et al. [8] on the streaming conductance, $G_{str}$, in a silica nanochannel with $W = 50 \ \mu m$, $L = 4.5 \ \text{mm}$, $\Delta p = -4 \ \text{bar}$, and $pH = 8$. Figure 6.5 shows the dependence of $G_{str}$ on the background salt concentration $C_{KCl}$ for various nanochannel heights $h$. As depicted in this figure, the predictions from the analytical MIM (lines), with the same fitted parameters $C_s = 0.15 \ \text{F/m}^2$, $N_{total} = 7 \ \text{sites/nm}^2$, $pK_A = 6.6$, and $pK_B = 2$, are in good agreement with the experimental data of van der Heyden et al. [8] (symbols). The fitted parameters of $C_s$, $N_{total}$, $pK_A$, and $pK_B$ for the dielectric channel layer made of silica are also consistent with those reported in the literature (e.g., $C_s = 0.15 \sim 2.9 \ \text{F/m}^2$, $N_{total} = 3.8 \sim 8 \ \text{sites/nm}^2$, $pK_A = 6 \sim 8$, and $pK_B = 0 \sim 3$ [6, 8, 68]). Figure 6.5 suggests that the present analytical MIM is much better than the model proposed by van der Heyden et al. [8], who used different fitted parameters to describe the behaviors of $G_{str}$ in the silica nanochannels of various heights. Therefore, the estimated values of $C_s = 0.15 \ \text{F/m}^2$, $N_{total} = 7 \ \text{sites/nm}^2$, $pK_A = 6.6$, and $pK_B = 2$ are then used in the
following discussions. For illustration, a FET-gated silica nanochannel with $H = 200\,\text{nm}$, $W = 50\,\mu\text{m}$, $L = 4.5\,\text{mm}$, and $\delta = 30\,\text{nm}$ under an application of $\Delta p = -4\,\text{bar}$ was considered.

![Figure 6.5. Streaming conductance $G_{\text{str}}$ in the silica nanochannels of various channel heights as a function of the background salt concentration $C_{\text{KCl}}$ at $\Delta p = -4\,\text{bar}$, pH=8, $W=50\,\mu\text{m}$, and $L=4.5\,\text{mm}$. Symbols: experimental data of van der Heyden et al. [8]; lines: results of the present analytical MIM at $C_s = 0.15\,\text{F/m}^2$, $N_{\text{total}} = 7\,\text{sites/nm}^2$, and $pK_A = 6.6$, and $pK_B = 2$.]

### 6.3.2 Field Effect Control and Electroviscous Effect

The influences of the background solution properties such as pH and salt concentration, $C_{\text{KCl}}$, on the field effect control of the zeta potential, $\psi_d$, and the streaming conductance, $G_{\text{str}}$, for various gate potential, $V_g$, are illustrated in Figures 6.6 – 6.9. In Figures 6.7a, 6.7b, 6.9a, and 6.9b, symbols and lines denote, respectively, the results with and without considering the electroviscous effect arising from the streaming electric field $E_{\text{str}}$. As shown in Figures 6.6 – 6.9, $\psi_d$ and, accordingly, $G_{\text{str}}$ can be regulated from negative to positive by the gate potential, $V_g$, imposed on the FET, and by
the solution pH. The $V_g$-dependent modulation behavior of $\psi_d$ is expected and in accordance with the experimental observation of the field modulation of the zeta potential in gated nanofluidics [4, 5, 253]. Control of the inner wall surface charge property of the nanochannel by the FET, in turn, controls the transport of ions and fluid inside. Recently, the pH-dependent regulation of $\psi_d$ was also observed experimentally by Guan et al. [253] through the direct measurement of the zeta potential at the dielectric SiN$_x$ channel layer/electrolyte interface tuned by the FET under various solution pH. This can be attributed to a higher surface charge density ($\sigma_s$) of the nanochannel due to a greater number of negatively charged SiO$^-$ dissociated from SiOH functional groups at the dielectric channel surface at lower proton concentration (higher pH).

![Figure 6.6. Zeta potential $\psi_d$, as a function of pH for various gate potentials, $V_g$, at the background salt concentration $C_{KCl} = 0.1$ mM, (a), and 100 mM, (b).](image)
Figure 6.7. Streaming conductance $G_{str}$ as a function of pH for various gate potentials, $V_g$, at the background salt concentration $C_{KCl} = 0.1\text{mM}$, (a), and 100 mM, (b). Symbols and lines represent the analytical MIM results with and without considering the electroviscous effect, respectively.

Figure 6.8. Zeta potential $\psi_{dh}$ as a function of the background salt concentration $C_{KCl}$ for various gate potentials, $V_g$, at pH=3, (a), and 8, (b).
Figure 6.9. Streaming conductance $G_{str}$, as a function of the background salt concentration $C_{KCl}$ for various gate potentials, $V_g$, at pH=3, (a), and 8, (b). Symbols and lines represent the analytical MIM results with and without considering the electroviscous effect, respectively.

Figures 6.6 - 6.9 also depict that the efficiency of the field effect control ($V_g$ - dependent) of $\psi_d$ and $G_{str}$ is superior if the background salt concentration $C_{KCl}$ and pH are relatively low, and becomes inferior if they are relatively high. Because the nanochannel surface charge increases with increasing pH, a greater number of counterions electrostatically attracted to the channel surface, making the FET harder to tune its zeta potential and, accordingly, the streaming current (or conductance). On the other hand, the higher the salt concentration the thinner the EDL thickness, resulting in more counterions gathered in the vicinity of the nanochannel wall and, therefore, a stronger lateral equilibrium electric field to reduce the tuning performance of the FET.

Note that regardless of the level of $V_g$, an apparent local maximum of $|\psi_d|$ as pH varies is predicted in the high pH regime at low salt concentration $C_{KCl} = 0.1 \text{ mM}$ (Figure 6.6a), but $|\psi_d|$ increases monotonically with increasing pH at relatively high salt concentration $C_{KCl} = 100 \text{ mM}$ (Figure 6.6b). Similar behaviors of $G_{str}$ can be observed
in Figures 6.7a and 6.7b, implying that the pH dependence of the streaming conductance in the gated silica nanochannel is primarily dominated by its modulated zeta potential behavior. As described previously, an increase in the solution pH results in an increase in $|\sigma_s|$ and, therefore, $|\psi_d|$. However, an increase in the solution pH, when it deviates significantly from 7, also leads to an increase in the ionic strength, yielding a thinner EDL. If the behavior of $\psi_d$ is dominated by the effect of an increase in the ionic strength, which becomes apparent at sufficiently high pH and sufficiently low $C_{KCl}$, $|\psi_d|$ decreases accordingly, as depicted in the high pH regime of Figure 6.6a.

Figures 6.6 - 6.9 depict that the electroviscous effect, as expected, dents the streaming conductance ($G_{str}$) of the gated silica nanochannel and that effect on $G_{str}$ is highly dependent up its modulated zeta potential ($\psi_d$) by the FET. In general, the larger the magnitude of the zeta potential, $|\psi_d|$, the more significant is the electroviscous effect on $G_{str}$. For example, if $V_g < 0$ V, the difference of $G_{str}$ with (symbols) and without (lines) considering the electroviscous effect is larger for lower $C_{KCl}$, moderate pH, and larger $|V_g|$, as shown in Figures 6.7a, 6.7b, 6.9a, and 6.9b. A maximum relative percentage reduction of $G_{str}$ between the results with and without considering the electroviscous effect is about 31 % for the considered conditions in Figures 6.6 - 6.9. Note that if modulated $|\psi_d|$ is sufficiently large, the qualitative behavior of $G_{str}$ with considering the electroviscous effect is different from that without considering the electroviscous effect. For example, if the electroviscous effect is neglected, $G_{str}$ shows a
local maximum as pH varies for $V_g = -5\ \text{V}$ and $-10\ \text{V}$ in Figure 6.7a (dashed and solid lines, respectively), while it has two local maximum if the electroviscous effect is taken into account (spheres and squares). From Figures 6.6 - 6.9, it is worth concluding that for the case where the zeta potential is sufficiently high, neglecting the electroviscous effect on the estimation of the streaming current in nanofluidics, usually assumed in the literatures [3, 6, 8, 68, 248, 256, 266], is inappropriate and might result in an incorrect estimation for relevant ion transport phenomena.

6.4. Conclusion

Regulating the surface charge property and the streaming current/conductance, generated by a pressure-driven flow, in a regulated nanochannel by a field effect transistor (FET) is proposed and analyzed for the first time. To simply, fast, and accurately predict their surface charge property and the streaming current/conductance tuned by a FET, analytical expressions were derived, including implicit and explicit ones, taking into account practical effects such as multiple ionic species, surface chemistry reactions, and the electroviscous and Stern layer effects. Note that the present model neglects the overlapping of the electric double layers in the nanochannel and is only valid for monovalent species. The implicit analytical multi-ion model (MIM) is validated by comparing its predictions to the existing experimental results of the streaming conductance in the silica nanochannels of different channel heights. The closed-form analytical MIM based on the Debye-Hückel approximation is extremely accurate when the magnitude of the zeta potential is less than the thermal potential, which often holds for high salt concentration in accordance with typical nanofluidics-based experimental conditions. The results clearly show that the streaming current/conductance of the gated
silica nanochannel can be effectively controlled by field modulation of its zeta potential. The FET control performance of the zeta potential and the streaming conductance is significant when the solution pH and salt concentration are low. The electroviscous effect, reducing the streaming current/conductance of the gated nanochannel, is remarkable when the salt concentration is low, solution pH is moderate, and the applied gate potential is large because of a larger zeta potential stemmed. Neglecting the electroviscous effect might yield an incorrect estimation of streaming conductance to an order of ca. 31 %.
CHAPTER 7

FET CONTROL OF CHARGE, EOF AND CONDUCTANCE IN NANOCHANNELS WITH OVERLAPPED EDLS

7.1. Introduction

Ion transport in nanofluidics [171, 206, 221, 222] has attracted much attention of scientific researchers due to its widespread applications ranging from biosensing [205, 228, 230] to regulation of ion and molecular transport [225, 249, 250]. This is due to the operation discipline in nanofluidics relying on analyzing the variations of ionic current (or conductance), stemming from different ion transport behaviors in nanofluidics. Many theoretical and experimental results demonstrated that these ion transport phenomena depend strongly on the surface charge property of the nanofluidic devices.

Recent studies revealed that nanofluidic field effect transistors (FETs) [4, 179, 180, 232], including dielectric channel layers such as silicon dioxide (SiO$_2$) and aluminum oxide (Al$_2$O$_3$) and an electrically controllable gate electrode embedded beneath those layers, are able to actively tune the surface charge property of the nanochannel. Controlling the surface charge property of the nanochannel, in turn, controls the ion and fluid transport phenomena by regulating the gate potential imposed on the gate electrode. To improve the development of such gated nanofluidic devices, many theoretical efforts have been made on how to control the transport of ions, fluid, and nanoparticles in these FET-gated nanofluidic devices. However, these studies possesses several limited assumptions, such as a constant surface charge density on the nanochannel wall [182 - 189], neglection of the electric double layer (EDLs) overlapping effects [176, 182, 190, 192, 233], consideration of background ionic species only [176, 182 - 192, 252], and
without considering the Stern layer effect [176, 182 - 189, 191, 192]. The dielectric channel wall of the nanochannel in contact with aqueous solution typically reveals a charge-regulated nature [66 - 69, 253], implying that its surface charge property is highly dependent on the local proton concentration. Moreover, in FET-gated nanofluidic devices, the characteristic size of which is typically smaller than 30 nm [179, 181, 252, 267 - 269], the overlap of EDLs is significant. Neglecting the EDL overlapping effect in the nanochannel might result in an incorrect and unrealistic estimation in its surface charge property and the relevant electrokinetic transport phenomena. Therefore, developing a more general and realistic model to elaborate experimental observations in relevant gated nanofluidic devices is highly desirable.

In this study, field effect control of the surface charge property and ionic current/conductance in a pH-regulated nanochannel are investigated taking into account the EDL overlapping, multiple ionic species, surface chemistry reactions on the dielectric channel wall, the Stern layer, and the electroosmotic flow (EOF) effect, most of which have practical significance and are often neglected in previous relevant gated nanofluidic studies [176, 182 - 192, 233]. Analytical expressions are derived to predict the surface charge property and the ionic conductance in the nanochannel as functions of the applied gate potential and the background salt concentration and pH. Because most of the practical effects are considered, our analytical MIM provides better insight into the underlying physics and necessary information for utilizing gated nanochannels in relevant applications.
7.2. Mathematical Model

As schematically shown in Figure 7.1, a long nanochannel of length $L$, width $W$, and height $H$ connected to two large reservoirs is filled with an electrolyte solution containing $N$ types of multiple ionic species. The nanochannel is made of dielectric material with thickness $d$ and relative permittivity $\varepsilon_d$. Suppose that both $L$ and $W$ are much larger than $H$. Two gate electrodes are embedded on the two outside walls of the nanochannel, and a gate potential $V_g$ perpendicular to the nanoslit surface is applied. Suppose that that nanochannel surface possess dissociable functional groups MOH in contact with aqueous solution. Therefore, the following two main protonation/deprotonation reactions, $\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+$ and $\text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}_2^+$, are considered on the nanochannel surface, and we assume that the surface charge density is homogeneous at the liquid/solid interface. The rectangular coordinates $x$ and $y$ with the origin located at the center of the nanochannel is adopted, and a uniform electric field $E_y = V / L$ is applied across the nanochannel to drive the electroosmotic flow (EOF) in $y$-direction. Assuming the EOF if fully developed within the nanoslit, the ions and liquid within the Stern layer are immobility, and the Stern layer/diffusive layer interface is no-slip. Based on the above, the electrostatic and flow characteristics are identical in $y$-direction, and are central symmetry in $x$-direction.
Figure 7.1. Schematic depiction of the field effect control of the zeta potential ($\psi_s$) and the ionic current in a pH-regulated nanochannel containing multiple ionic species, $H^+$, $K^+$, $Cl^-$, and $OH^-$. $V_g$ is the gate potential imposed on the gate electrode and $\psi_s$ is the surface potential stemming from the surface chemistry reactions of functional groups on the nanochannel wall. Ions inside the Stern layer are immobile and of surface capacitance $C_s$, and $\delta$ is the thickness of the dielectric channel layer.

To simulate experimental conditions, it is assumed that the background salt is KCl and pH is adjusted by HCl and KOH, implying that four kinds of ionic species (i.e., $N = 4$), including $K^+$, $Cl^-$, $H^+$ and $OH^-$, are considered. Let $C_{i0}$ ($i = 1, 2, 3$, and $4$) be the bulk concentrations of these ions. Electroneutrality results in \cite{226, 242} $C_{i0} = C_{KCl}$, $C_{20} = C_{KCl} + 10^{(-pH)} - 10^{-((14-pH))}$, $C_{30} = 10^{(-pH)}$, and $C_{40} = 10^{-((14-pH))}$ for $pH \leq 7$; $C_{10} = C_{KCl} - 10^{(-pH)} + 10^{-((14-pH))}$, $C_{20} = C_{KCl}$, $C_{30} = 10^{(-pH)}$, and $C_{40} = 10^{-((14-pH))}$ for $pH > 7$.

Here $C_{KCl}$ is the background salt concentration of KCl.
The electric potential distributions in the nanochannel can be described by

\[ \frac{d^2 \phi}{dx^2} = 0 \quad \text{within the dielectric layer} \quad \left( \frac{H}{2} < x < \frac{H}{2} + \delta \right), \quad (7.1) \]

\[ \frac{d^2 \varphi}{dx^2} = 0 \quad \text{within the Stern layer of the thickness} \quad \delta \rightarrow 0 \quad \left( \frac{H}{2} - \delta < x < \frac{H}{2} \right), \quad (7.2) \]

\[ \frac{d^2 \psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0 \varepsilon_f} \quad \text{within the liquid phase} \quad \left( 0 < x < \frac{H}{2} - \delta \right), \quad (7.3) \]

where \( \phi, \varphi \) and \( \psi \) are electric potentials distribution within the dielectric layer, Stern layer and diffusive layer, respectively; \( \delta \) and \( \delta_s \) are thicknesses of dielectric and Stern layer, respectively; \( \varepsilon_0 \) and \( \varepsilon_f \) are the permittivity of vacuum and the relative permittivity of the aqueous electrolyte solution, respectively; \( \rho_e \) is mobile space charge density, which can be depicted as

\[ \rho_e = 1000 \sum_{i=1}^{N} F z_i C_{ic} \exp\left( -\frac{z_i F}{RT} (\psi - \psi_c) \right), \quad (7.4a) \]

where \( \psi_c \) is the central electrical potential of the nanochannel; \( F \) is Faraday constant; \( z_i \) is the valence of the \( i \)th ionic species; \( R \) and \( T \) are the universal gas constant and absolute temperature, respectively; \( C_{ic} \) is the center concentration of the \( i \)th ion, and can be expressed by

\[ C_{ic} = C_{i0} \exp\left( -\frac{z_i F}{RT} (\psi_c - \psi_0) \right), \quad (7.4b) \]

where \( \psi_0 = 0 \) is the electrical potential in the reservoirs and \( C_{i0} \) is the \( i \)th ionic concentration in the reservoirs.
Substituting Equations (7.4a) and (7.4b) into Equation (7.3) yields

\[
\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0\varepsilon_f} - \frac{2FC_0}{\varepsilon_0\varepsilon_f} \sinh\left(-\frac{zF}{RT}\psi\right),
\]

(7.4c)

where \( C_0 = C_{10} + C_{30} = C_{20} + C_{40} \) and \( z = z_1 = -z_2 = z_3 = -z_4 = 1 \).

Assuming the flow field is fully developed, the EOF velocity profile can be described by

\[
\frac{d^2u_y}{dx^2} = -\frac{\rho_eE_y}{\mu} \quad \text{within the liquid phase} \ (0 < x < H/2 - \delta),
\]

(7.5)

where \( u_y \) is the EOF velocity, and \( \mu \) is the dynamic fluid viscosity.

Assuming ions inside the Stern layer is immobile, the boundary conditions for Equations (7.1) - (7.3) and (7.5) are

At the outer side surface of the dielectric layer \((x = H/2 + \delta)\),

\[
\phi = V_g.
\]

(7.6)

At the dielectric layer/Stern layer interface \((x = H/2)\),

\[
\phi = \varphi = \psi_s,
\]

(7.7a)

\[
\varepsilon_0\varepsilon_2 \frac{d\phi}{dx} - \varepsilon_0\varepsilon_f \frac{d\varphi}{dx} = -\sigma_s,
\]

(7.7b)
At the Stern layer/diffuse layer interface \((x = H/2 - \delta_s)\),

\[
\varphi = \psi = \psi_d ,
\]  

(7.8a)

\[
-\varepsilon_0\varepsilon_f \frac{d\varphi}{dx} + \varepsilon_0\varepsilon_f \frac{d\psi}{dx} = 0 ,
\]  

(7.8b)

\[
u_y = 0 ,
\]  

(7.8c)

At the center of the nanoslit \((x = 0)\),

\[
\frac{d\psi}{dx} = 0 \text{ and } \psi = \psi_c ,
\]  

(7.9a)

\[
\frac{d\nu_y}{dx} = 0 .
\]  

(7.9b)

In the above, \(\psi_s\) and \(\psi_d\) are the surface and zeta potentials of the nanochannel, respectively.

The solutions to Equations (7.1) and (7.2) subject to Equations (7.6), (7.7a), and (7.8a) are

\[
\phi = \frac{2\delta \psi_s + h \psi_s - hV_g}{2\delta_s} \frac{\psi_s - V_g}{\delta_s} x ,
\]  

(7.10)

\[
\varphi = \frac{2\delta \psi_d + h \psi_d - hV_s}{2\delta_s} \frac{\psi_d - \psi_s}{\delta_s} x .
\]  

(7.11)

If we let surface capacitance of the Stern layer \(C_s = \varepsilon_0\varepsilon_f / \delta_s\) and the charge density of the diffusive layer \(\sigma_d = -\varepsilon_0\varepsilon_f d\psi / dx \bigg|_{x=H/2-\delta_s} \cdot n = \varepsilon_0\varepsilon_f d\psi / dx \bigg|_{x=H/2-\delta_s} < 0\), then substituting Equations (7.10) and (7.11) into Equations (7.7b) and (7.8b) gets
\[
\varepsilon_0 \varepsilon_r d \frac{V_z - \psi}{\delta} - C_s (\psi_z - \psi_d) = -\sigma_s, \tag{7.12}
\]

\[-C_s (\psi_z - \psi_d) + \sigma_d = 0. \tag{7.13}\]

By integrating Equation (7.3) subject to Equations (7.8a) and (7.9a), we get

\[
\frac{d\psi}{dx} = \text{sign}(\psi_d) \sqrt{\frac{4RTC_0}{\varepsilon_0 \varepsilon_f}} \left[ \cosh \left( \frac{F \psi}{RT} \right) - \cosh \left( \frac{F \psi_c}{RT} \right) \right] \quad (|\psi_c| < |\psi|), \tag{7.14}\]

where \( \text{sign}(\psi_d) = 1 \) for \( \psi_d > 0 \) and \( \text{sign}(\psi_d) = -1 \) for \( \psi_d < 0 \). Solving Equation (7.3) subject to Equations (6.8a) and (6.9a), one yields [177, 270]

\[
\psi = \psi_c + \frac{2RT}{zF} \ln \left( cd \left( l|m \right) \right), \tag{7.15}\]

where \( cd \left( l|m \right) \) is a Jacobian elliptic function of argument \( l \) and parameter \( m \), which are, respectively, defined by

\[
l = \frac{\kappa x}{2 \exp \left( \frac{F \psi_c}{(2RT)} \right)}, \tag{7.16a}\]

\[
m = \exp \left( \frac{2F \psi_c}{(RT)} \right), \tag{7.16b}\]

where \( \kappa^{-1} = \lambda_d = \sqrt{\varepsilon_0 \varepsilon_f RT / 2000 z^2 F^2 C_0} \) is the Debye length. Therefore, the charge density of the diffusive layer can be described by

\[
\sigma_d = \text{sign}(\psi_d) \sqrt{4 \varepsilon_0 \varepsilon_f RTC_0} \left[ \cosh \left( \frac{F \psi_d}{RT} \right) - \cosh \left( \frac{F \psi_c}{RT} \right) \right]. \tag{7.17}\]
From Equations (7.9a) and (7.16), the relationship between \( \psi_d \) and \( \psi_c \) is

\[
\psi_d = \psi \left( \frac{H}{2} - \delta_s \right) = \psi_c + \frac{2RT}{zF} \ln \left( \frac{c_d}{I(x = H/2 - \delta_s)} \right) \tag{7.18}
\]

According to charge-regulated nature of the dielectric layer surface with MOH functional groups, the surface charge density of the nanochannel \( \sigma_s \), can be expressed as [176, 233]

\[
\sigma_s = -FN_{\text{total}} \left\{ \frac{K_A - K_B \left[ C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) \right]^2}{K_A + C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) + K_B \left[ C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) \right]^2} \right\}, \tag{7.19}
\]

where \( N_{\text{total}} \) is the total number site density of the dissociable functional group MOH on the nanoslit surface, and \( K_A \) and \( K_B \) are the equilibrium constants of the protonation/deprotonation reactions, respectively.

Substituting Equations (7.17) and (7.19) into Equations (7.12) and (7.13), one gets

\[
\varepsilon_0 \varepsilon_d \frac{V_g - \psi_s - C_s (\psi_s - \psi_d)}{\delta} = FN_{\text{total}} \left\{ \frac{K_A - K_B \left[ C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) \right]^2}{K_A + C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) + K_B \left[ C_{30} \exp \left( -\frac{F\psi_s}{RT} \right) \right]^2} \right\}, \tag{7.20}
\]

\[
\text{sign}(\psi_s) \sqrt{4000 \varepsilon_0 \varepsilon_f RTC_0 \left[ \cosh \left( \frac{F\psi_d}{RT} \right) - \cosh \left( \frac{F\psi_c}{RT} \right) \right]} = C_s (\psi_s - \psi_d). \tag{7.21}
\]

Equations (7.18), (7.20) and (7.21) are implicit analytical expressions, based on which \( \psi_s \), \( \psi_d \) and \( \psi_c \) can be obtained. Therefore, electric potential distributions, \( \phi \), \( \varphi \),
\( \psi \), \( \sigma_d \), and \( \sigma \) can be obtained by Equations (7.10), (7.11), (7.15), (7.17) and (7.19), respectively.

Based on the obtained \( \psi_d \), the EOF velocity can be by [233]

\[
\mathbf{u}_y = \frac{\varepsilon_0 \mathbf{E}_y (\psi - \psi_d)}{\mu} \tag{7.22}
\]

Assuming there is no pressure and concentration gradients through the nanochannel, the ionic current through the nanochannel can be evaluated by

\[
I = 2000W \int_0^{H/2} \left( \rho_u \mathbf{u}_y \right) dx + \frac{2WF^2}{RT} \mathbf{E}_y \sum_{i=1}^{N} \int_0^{H/2} \left( D_i \mathbf{C}_{i0} \exp \left( -\frac{z_i F \psi}{RT} \right) \right) dx
\]

\[
= I_c + I_c
\]

where \( D_i \) is the diffusivity of the \( i \)th ionic species; \( I_c \) and \( I_e \) are convective current and electromigrative current, respectively, and can be explicitly obtained by

\[
I_c = \frac{8000W \varepsilon_0 \mathbf{E}_y R TC_0}{\mu} \left[ \int_0^{H/2} \cosh \left( \frac{F \psi}{RT} \right) dx - \frac{H}{2} \cosh \left( \frac{F \psi_e}{RT} \right) \right] \tag{7.24}
\]

and

\[
I_e = \frac{2000WF^2}{RT} \mathbf{E}_y \left[ \left( D_1 \mathbf{C}_{10} + D_2 \mathbf{C}_{20} \right) \int_0^{H/2} \exp \left( -\frac{F \psi}{RT} \right) dx 
\right.
\]

\[
+ \left. \left( D_2 \mathbf{C}_{20} + D_4 \mathbf{C}_{40} \right) \int_0^{H/2} \exp \left( \frac{F \psi_e}{RT} \right) dx \right] \tag{7.25}
\]

Based on the obtained \( \psi_c \) from Equations (7.18), (7.20) and (7.21), the total ionic current can be evaluated by Equations (7.23) - (7.25), and then the corresponding ionic conductance \( G = I/V \). Note that in the model, many real physical processes including
surface charge regulation, Stern layer, and pH effects are considered, and the model is suitable for FET nanochannels no matter the EDLs are overlapping or not.

7.3. Results and Discussion

7.3.1. Verification by Experimental Data

Our analytical MIM is first verified by fitting it to the experimental data of Cheng and Guo [9], where the ionic conductance \( G \) in a silica nanochannel of height \( H = 18.7 \) nm, \( W = 12.5 \) \( \mu \)m, and \( L = 60 \) \( \mu \)m was conducted for the background salt concentration \( C_{KCl} \) ranging from \( 10^{-6} \text{ M} \) to \( 1 \text{ M} \). Because the EDL thickness under considered \( C_{KCl} \) is apparently larger than the nanochannel height, the EDL overlapping effect inside the nanochannel is significant and should not be neglected. For comparison, both results with (solid line) and without (dashed line) considering the EDL overlapping effect are presented. The ionic diffusivities \( D_1 (K^+) \), \( D_2 (Cl^-) \), \( D_3 (H^+) \), and \( D_4 (OH^-) \) are \( 1.96 \times 10^{-9} \), \( 2.03 \times 10^{-9} \), \( 9.31 \times 10^{-9} \), and \( 5.30 \times 10^{-9} \) m\(^2\)/s, respectively [243]. Figure 6.2 shows that the analytical MIM with considering the EDL overlapping effect (solid line) is capable of describing the general trend of the experimental data of Cheng and Guo [9]; however, that without considering the EDL overlapping effect (dashed line) is not. Due to the significant overlapping of EDLs in the nanochannel at the low salt concentration, its central electric potential \( \psi_c \) is not zero and, therefore, the results of \( G \) with considering EDL overlapping effect deviate apparently from those without considering EDL overlapping. The fitted values of \( N_{total} = 8 \) sites/nm\(^2\), \( pK_{A}^{-} = 6.1 \), \( pK_{B}^{-} = 1 \), \( C_s = 1.8 \text{ F/m}^2 \), and the resulting isoelectric point (IEP = 2.55) of the nanochannel made of silica are also consistent with those reported in the literatures (e.g.,
$C_s = 0.15 \sim 2.9 \text{ F/m}^2$, $N_{\text{total}} = 3.8 \sim 8 \text{ sites/nm}^2$, $pK_A = 6 \sim 8$, $pK_B = 0 \sim 3$, and $\text{IEP} = 2 \sim 3.5$ [6, 8, 68, 244]. Note that $G$ shows a local minimum as $C_{\text{KCl}}$ varies in the low region of $C_{\text{KCl}}$. Apparently, this interesting behavior can be well described by the analytical MIM, as shown in Figure 6.2. Therefore, the predicted values of $N_{\text{total}} = 8 \text{ sites/nm}^2$, $pK_A = 6.1$, $pK_B = 1$, and $C_s = 1.8 \text{ F/m}^2$ are used in the following discussions. For illustration, the geometry of the gated nanochannel is fixed at $H = 10 \text{ nm}$, $W = 2.5 \mu\text{m}$, $L = 60 \mu\text{m}$, and $\delta = 30 \text{ nm}$.

![Graph](image)

Figure 7.2. Dependence of the conductance ($G$) in a silica nanochannel on the background salt concentration $C_{\text{KCl}}$. Symbols denote the experimental data of Cheng and Guo [9] at $H = 18.7 \text{ nm}$, $W = 12.5 \mu\text{m}$, $L = 60 \mu\text{m}$, and pH = 5. Solid and dashed lines denote the analytical MIM results at $N_{\text{total}} = 8 \text{ sites/nm}^2$, $pK_A = 6.1$, $pK_B = 1$, and $C_s = 1.8 \text{ F/m}^2$ with and without considering the EDL overlapping effect, respectively.
7.3.2. Influence of Solution pH

Figures 7.3 - 7.5 depict the field effect modulation of the zeta potential ($\psi_d$), the surface charge density ($\sigma_s$), and the ionic conductance ($G$) of the nanochannel at various levels of pH. For comparison, both results with (symbols) and without (lines) considering the EDL overlapping effect inside the nanochannel are presented. As expected, Figure 7.3 shows that the zeta potential of the nanochannel can be regulated from negative to positive with the applied gated potential, $V_g$, ranging from -20 to 20 V, exhibiting a field effect control behavior. In addition, $\psi_d$, $\sigma_s$, and $G$ can be modulated by pH, showing a typical pH-regulated nature of the silica nanochannel.

![Figure 7.3. Zeta potential $\psi_d$, as a function of the applied gate potential $V_g$ for various pH at the background salt concentration $C_{KCl} = 10^{-4}$M. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.](image)
It is worth noting in Figure 7.4 that at pH = 4 σᵣ turns from negative to positive at a sufficiently negative value of $V_g$. This is because the surface charge density of the nanochannel at pH = 4 is very small, it is much easier to regulate its zeta potential using a FET. If the gate potential is applied negatively to a certain degree, the negative zeta potential of the nanochannel increases significantly (Figure 7.3) and, therefore, more counterions are condensed on the nanochannel wall. If the surface pH ($= -\log[H^+]_s$) of the nanochannel is lower than its IEP (i.e., 2.55), $\sigma_\ast$, therefore, changes from negative to positive.

![Figure 7.4. Surface charge density as a function of the applied gate potential $V_g$ for various pH at the background salt concentration $C_{KCl} = 10^{-4}M$. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.](image)

It is interesting to note in Figure 7.3 that the difference in $\psi_d$ between the results with and without considering the EDL overlapping effect in the nanochannel is unremarkable when $V_g$ is significantly negatively applied and positively applied at low pH, and at high pH regardless of the values of $V_g$. These behaviors can be explained as a
consequence of the following reasons. If the zeta potential of the nanochannel is significantly larger (e.g., higher pH and/or larger negative $V_g$), a greater number of counterions concentrated on its wall surface, resulting in a thinner EDL thickness and, therefore, a less apparent EDL overlapping effect. Moreover, if the gate potential is imposed positively on the gate electrode, the magnitude of the zeta potential of the nanochannel decreases and, therefore, its central potential decreases accordingly. This results in an insignificant EDL overlapping effect. Similar behaviors of $G$ can be found in Figure 7.5 because the ionic conductance of the nanochannel is primarily dominated by its zeta potential. Figure 7.5 also shows that the results of $G$ with considering the EDL overlapping effect are apparently larger than those without considering. This arises from in the former case a greater number of counterions condensed inside the charged nanochannel, yielding a larger ionic conductance. Note that under the considered conditions taking the EDL overlapping effect into account at pH = 4 and $V_g = -2$ V yields ca. 29% in $\psi_d$ (Figure 7.3) and 114% increase in $G$ (Figure 7.5). These imply that neglecting the EDL overlapping effect might result in an apparent and unrealistic estimation in the ionic conductance in the gated nanochannels and, therefore, wrong design for utilizing gated nanofluidics in relevant nanofluidics applications.
Figure 7.5. Nanochannel conductance $G$ as a function of the applied gate potential $V_g$ for various pH at the background salt concentration $C_{KCl} = 10^{-4}$M. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.

Figure 7.6 shows the variations of the ionic conductance, $G$, of the nanochannel as a function of pH for various levels of the applied gate potential $V_g$. Symbols and lines represent the results with and without considering the EDL overlapping effect, respectively. Figure 7.6 reveals that the difference of $G$ between above two cases is small when the pH is sufficiently low and high, and $|V_g|$ is large. Typically, the surface charges of the silica nanochannel increase as pH increases [69, 176], thus attracting more counterions gathered inside the charged nanochannel. This results in a thinner EDL thickness and, therefore, an insignificant EDL overlapping effect. Note that an increase in $|V_g|$ also leads to the same effect of increasing pH. On the other hand, if pH is sufficiently low, although the surface charges of the silica nanochannel are small, a significant deviation of pH from 7 also results in an decrease in the EDL thickness due to
an increase in the ionic strength from H⁺ ions, thus making the EDL overlapping effect insignificant.

Figure 7.6. Nanochannel conductance G as a function of pH for various applied gate potential $V_g$ for various applied gate potential $V_g$ at the background salt concentration $C_{KCl}=0.1$mM. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.

7.3.3. Influence of Background Salt Concentration

Because the difference in the ionic conductance of the nanochannel between the results with and without considering the EDL overlapping effect is significant when pH is medium low, the solution pH is fixed at 3.5 to investigate the salt concentration effect. Figures 7.7 - 7.9 illustrate the field effect regulation of the zeta potential ($\psi_d$), the surface charge density ($\sigma_s$), and the ionic conductance ($G$) of the nanochannel at various levels of the background salt concentration, $C_{KCl}$. Symbols and lines denote the results with and without considering the EDL overlapping effect inside the nanochannel, respectively. As
expected, the field effect control efficiency is significant when the salt concentration is low. Figures 7.7 - 7.9 show that the differences in $\psi_d$, $\sigma_r$, and $G$ between the above two cases are significant when the salt concentration is low and/or the gate potential is slightly negatively applied. The former is because the lower the salt concentration the thicker the EDL thickness and, therefore, the more significant is the EDL overlapping effect. The latter can be explained by the same reasoning employed in Figures 7.3 - 7.5. Note that the maximum relative percentage differences of $\psi_d$, $\sigma_r$, and $G$ between the results with and without considering the EDL overlapping effect, calculated by $PD = \left| \frac{\Delta(w/o) - \Delta(w/o)}{\Delta(w/o)} \right| \times 100\%$ where $\Delta = \psi_d$, $\sigma_r$, and $G$, are, respectively, ca. 36.7% (Figure 7.7), 202% and 102% (Figure 7.9) at $C_{KCI} = 10^{-4}$ M and $V_g = -2$ V. These imply neglecting the EDL overlapping effect inside the nanochannel is unable to describe the correct ion transport behaviors in gated nanofluidics.

Figure 7.7. Zeta potential as a function of the applied gate potential $V_g$ for various background salt concentrations $C_{KCI}$ at pH = 3.5. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.
Figure 7.8. Surface charge density $\sigma$, as a function of the applied gate potential $V_g$ for various background salt concentrations $C_{KCl}$ at pH = 3.5. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.

Figure 7.9. Nanochannel conductance $G$ as a function of the applied gate potential $V_g$ for various background salt concentrations $C_{KCl}$ at pH = 3.5. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.

Figure 7.10 depicts the variations of the ionic conductance, $G$, of the nanochannel as a function of the background salt concentration, $C_{KCl}$, for various levels of the applied gated potential $V_g$. For comparison, both results with (symbols) and without (lines)
considering the EDL overlapping effect inside the nanochannel are presented. Figure 7.10 clearly shows that the difference of $G$ between above two cases is large when $C_{\text{KCl}}$ is low and $|V_g|$ is large. The former is expected and the latter can be explained by the same reasoning employed in Figure 7.6. It is interesting to note that the nanochannel conductance shows a local minimum in the low regime of $C_{\text{KCl}}$, especially when the FET is active (i.e., $V_g \neq 0$). This can be attributed to a significant EOF effect when the gate potential is negatively applied and the salt concentration is sufficiently low. In this case, the magnitude of the zeta potential of the nanochannel is large, as shown in Figure 7.7, resulting in a higher EOF velocity and, therefore, the ionic conductance.

![Figure 7.10. Nanochannel conductance $G$ as a function of the background salt concentration $C_{\text{KCl}}$ for various applied gate potential $V_g$ at pH = 3.5. Symbols and lines denote the results with and without considering the EDL overlapping effect, respectively.](image)
7.4. Conclusions

For the first time, analytical expressions for predicting the surface charge property and the ionic current/conductance in a pH-regulated gated nanochannel with considering the electric double layer (EDL) overlapping effect have been developed and validated. In addition to the overlap of EDLs in the nanochannel, practical effects of the presence of multiple ionic species, surface chemistry reactions on the nanochannel wall, the Stern layer, and the electroosmotic flow (EOF) effect are also taken into account. The model is validated by comparing its prediction to the existing experimental data of the ionic conductance in a narrow silica nanochannel. An apparent local minimum of the ionic conductance is found at low salt concentration for the case where the EDL overlapping is taken into account. The results gathered show that the difference between the results considering and neglecting the EDL overlapping effects is remarkable when the salt concentration and pH are low, and the applied gate potential is negatively applied and its magnitude is not too high. A maximum difference in the ionic conductance of the nanochannel between the above two cases can be on the order of 114 %, implying that neglecting the EDL overlapping effect inside the nanochannel is unable to describe correct ion transport phenomena in gated nanofluidics.
Chapter 8

CONCLUSIONS AND FUTURE WORK

At least one dimension of the nanofluidic devices ranges from 1 nm to 100 nm, which is the same order of magnitude as the Debye length, the size of biomolecules such as DNA and proteins, and the slip length. Such unique geometry feature provides nanofluidics an ever-growing list of applications for [271 - 274], drug delivery [150, 151, 275], water purification [88, 105, 166, 276], energy harvest [92, 277, 278], public health and welfare [279 - 282]. Electrokinetic transport phenomena play very important roles in the aforementioned applications. For example, in the nanopore-based DNA sequencing technology, a single DNA electrophoretically translocates through a short small nanopore under an external electric field imposed along the axial direction of the nanopore. The translocating DNA perturbs the ionic current flowing through the nanopore. The change in the magnitude of the ionic current through the nanopore depends on the single nucleotides (bases) passing through the nanopore. Therefore, the amount of current passing through the nanopore at any given moment can be used to detect whether the nanopore is blocked by an A, a C, a G or a T or a section of DNA. Electrokinetic transport phenomena including electrical double layer, electroosmosis, and electrophoresis are involved in this process.

This dissertation conducts fundamental studies of various electrokinetic transport phenomena in nanofluidics including electrical double layer, electroosmotic flow, ionic current/conductance under an external electric field, and streaming current and conductance driven by an external pressure field. Special emphasis in this dissertation is afforded to the role of surface chemistry and field effect control of the aforementioned
electrokinetic transport phenomena occurring within the confined nanoscale systems. In contrast to full numerical simulations of the electrokinetic transport phenomena in nanofluidics conducted in most studies available in the literature, this dissertation aims to develop analytical or approximate models which can be easily used for design of the next generation nanofluidic devices. The developed models are validated by comparing their predictions with experimental data available from the literature.

8.1 Conclusions

Main conclusions of the dissertation include

(1) An analytical model for the field effect control of the surface charge properties of pH-regulated nanochannel walls and electroosmotic flow in a nanoslit has been developed for the first time with the consideration of the surface chemistry. The predicted zeta potentials agree with the experimental data available in the literature.

(2) Charge properties of the nanochannel wall can be tuned by pH, background salt concentration, and the gate potential of the FET. The field effect becomes more sensitive when the pH is low and/or the bulk electrolyte concentration is dilute.

(3) Both the magnitude and direction of the electroosmotic flow between two parallel plates can be tuned by the FET. One can use the FET technology to enhance the electroosmotic flow in the applications of electroosmotic pump. In the DNA sequencing technology, one can use the FET to enhance the electroosmotic flow within the nanofluidic devices, and accordingly slows down the translocating DAN within the nanopore to improve the detection resolution.
(4) An analytical model for the ionic current flowing through a nanoslit gated by FET is developed for the first time with considering the practical effects of surface chemistry reactions, multiple ionic species, Stern layer, and the electroosmotic flow. The model is validated by comparing its predictions to the existing experimental data of the ionic conductance in silica nanochannels.

(5) FET control of the ionic current/conductance is more significant when the background salt concentration and pH are low.

(6) As the salt concentration decreases, the ionic conductance first decreases, and attains a minimum at a critical salt concentration. Below the critical salt concentration, ionic conductance increases when the salt concentration further decreases. The predicted results agree with recent experimental observation reported in the literature. The increase in ionic conductance with a decrease in the salt concentration is attributed to a significant electroosmotic flow effect due to high zeta potential at very low salt concentration.

(7) In the absence of FET, the Stern layer effect on the ionic conductance is negligible. However, in the presence of FET, the Stern layer effect on the ionic conductance is significant at low salt concentration and becomes insignificant at high salt concentration regardless of the solution pH.

(8) An analytical model for streaming current/conductance generated by a pressure-driven flow in a nanoslit is developed without considering the electroviscous effect. The model takes into account the surface chemistry reactions, Stern layer, multiple ionic species, and the field effect except the electroviscous effect. The model is validated by comparing its predictions to the existing experimental data
of the streaming conductance in the silica nanochannels with various channel heights.

(9) The dependence of the streaming conductance in the gated silica nanochannel on the solution pH is consistent with the dependence of the zeta potential. However, that dependence on the salt concentration might be different from the dependence of the zeta potential, depending on the levels of the solution pH and the gate potential. For example, for relatively high solution pH, the magnitude of the zeta potential of the nanochannel increases with decreasing background salt concentration, but the streaming conductance increases first and then decreases (or exhibits a plateau) with a decrease in the salt concentration.

(10) Due to the ion concentration polarization induced by the motion of the ions with the pressure-driven flow, concentration of the counterions in the downstream of the nanochannel is higher than that in the upstream of the nanochannel, inducing an electric field, the direction of which is opposite to that of the applied pressure-driven flow. The interaction between the net charge within the nanochannel and the induced electric field generates an electroosmotic flow. The direction of the induced electroosmotic flow is opposite to that of the applied pressure driven flow. The previous model on the streaming current/conductance without electroviscous effect does not consider the induced electric field and the resulting electroosmotic flow and its effect on the current. An analytical model for the streaming current taking into account the electroviscous effect is developed and verified. Under the same conditions, predictions from the models with/without the electroviscous effect are compared. The model with the electroviscous effect is in
better agreement with the experimental data than that without the electroviscous effect.

(11) The electroviscous effect, reducing the streaming current/conductance of the gated nanochannel, is remarkable when the salt concentration is low, solution pH is moderate, and the applied gate potential is large because of a larger zeta potential. Neglecting the electroviscous effect might yield an incorrect estimation of streaming conductance to an order of ca. 31%.

(12) The previous analytical models for charge properties, electroosmotic flow, ionic current/conductance, and streaming current/conductance do not consider the overlapping of the electrical double layers in the vicinity of the parallel channel walls. Double layer overlapping becomes significant when the salt concentration is relatively low. The previous models for charge properties, electroosmotic flow, and ionic current/conductance in a nanoslit are further extended to include the double layer overlapping. The extended model takes into account the most practical effects of multiple ionic species, surface chemistry reactions, Stern layer, electroosmotic flow, and the double layer overlapping effect. The model is validated by the existing experimental data of the ionic conductance in the silica nanochannel with significant double layer overlapping effect.

(13) The difference between the models with and without considering the double layer overlapping effect is significant when the salt concentration and pH are low.

8.2 Future Work

The methodology developed in this dissertation can be extended to the following future works:
(1) This dissertation developed and validated analytical models for charge properties of a planar surface, electroosmotic flow, ionic current/conductance, and streaming current/conductance in a nanoslit. The considered nanochannel geometry is a straight nanochannel with rectangular cross section, and its width is also assumed to be much larger than its height. In many nanofluidic applications, the geometries of the nanofluidic devices are cylindrical nanopores [92, 195, 283, 284] or conical nanopores [170, 283, 285, 286]. Therefore, developing analytical models for the above electrokinetic transport phenomena in cylindrical or conical nanopores is one of the future works to be conducted.

(2) Although multiple ionic species are considered in the studies of the dissertation, only monovalent ions, such as H\(^+\), OH\(^-\), K\(^+\) (or Na\(^+\)), and Cl\(^-\) ions, are considered. Multivalent ions such as Ca\(^{2+}\) and Mg\(^{2+}\) are not considered in the studies. Many existing studies demonstrated that the presence of multivalent ions might even reverse the charge properties of dielectric objects immersed in a multivalent electrolyte [287 - 291]. Extension of the models developed in this dissertation to take into account multivalent ions is another future work.

(3) The studies in this dissertation only considered H\(^+\), OH\(^-\), and ions from the background salt such as K\(^+\) and Cl\(^-\). Buffer solution is not considered in these studies. When pH significantly deviates from 7 at very low salt concentration, usually buffer solution, such as tris(hydroxymethyl)aminomethane, HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), phosphate-buffered saline (PBS)[292 - 295], is added into the solution to maintain the solution pH.
Extension of the developed models to take into account the species from the buffer solution is also part of the future work.

The current models are only valid in the absence of an (bio)particle such as DNA and nanoparticle inside the nanochannel. Sensing and detection of the bioparticle are achieved based on the difference of the currents with and without the bioparticle inside the nanochannel [296 - 300]. Therefore, one future work will be extension of the developed models by including the bioparticle inside the nanochannel, and the new model will be very useful for understanding the underlying physics of the nanopore-based biosensing applications.
## APPENDIX

Table A.1. The variables and parameters used in this dissertation.

<table>
<thead>
<tr>
<th>Variables/Parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>bulk concentration of cations or anions</td>
</tr>
<tr>
<td>$C_{i0}$</td>
<td>bulk concentration of the $i$th ion</td>
</tr>
<tr>
<td>$C_{KCl}$</td>
<td>bulk salt concentration</td>
</tr>
<tr>
<td>$C_s$</td>
<td>surface capacitance of the Stern layer</td>
</tr>
<tr>
<td>$D_i$</td>
<td>ionic diffusivity of the $i$th ion</td>
</tr>
<tr>
<td>$E$</td>
<td>applied electric field</td>
</tr>
<tr>
<td>$E_{str}$</td>
<td>streaming electric field</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$G$</td>
<td>Conductance of the nanochannel</td>
</tr>
<tr>
<td>$G_{str}$</td>
<td>streaming conductance of the nanochannel</td>
</tr>
<tr>
<td>$I_h, K$</td>
<td>ionic currents contributed from the convective and the electromigrative</td>
</tr>
<tr>
<td>$I_{str}$</td>
<td>streaming current through the nanochannel</td>
</tr>
<tr>
<td>$K_A, K_B$</td>
<td>equilibrium constants of dissociation and association reactions</td>
</tr>
<tr>
<td>$l, h, w$</td>
<td>Length, height, and width of nanochannel</td>
</tr>
<tr>
<td>$N$</td>
<td>total number of ionic species present in the solution</td>
</tr>
<tr>
<td>$N_{total}$</td>
<td>total number site density of the functional groups</td>
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<tr>
<td>$p$</td>
<td>pressure</td>
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Table A.I. (continued)

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<th>Symbol</th>
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<td>$\Delta p$</td>
<td>pressure gradient</td>
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<tr>
<td>pH</td>
<td>pH value</td>
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<td>$R$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$U_p$</td>
<td>electrophoretic velocity</td>
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<tr>
<td>$u$</td>
<td>fluid velocity</td>
</tr>
<tr>
<td>$V$</td>
<td>potential bias across the nanochannel</td>
</tr>
<tr>
<td>$V_g$</td>
<td>gate potential</td>
</tr>
<tr>
<td>$z_i$</td>
<td>valence of the $i$th ionic species</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>absolute permittivity in vacuum</td>
</tr>
<tr>
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<td>relative permittivity</td>
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<td>fluid density</td>
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<tr>
<td>$\rho_e$</td>
<td>mobile space charge density</td>
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<tr>
<td>$\psi, \phi, \varphi$</td>
<td>electric potential distribution</td>
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<td>$\kappa$</td>
<td>Debye-Hückel parameter</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity of fluid</td>
</tr>
<tr>
<td>$\eta$</td>
<td>electrophoretic mobility</td>
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<tr>
<td>$\delta$</td>
<td>thickness of dielectric layer</td>
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Table A.1. (continued)

<table>
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<th>Symbol</th>
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<tbody>
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<td>( \delta_s )</td>
<td>thickness of the Stern layer</td>
</tr>
<tr>
<td>( \sigma_s )</td>
<td>surface charge density</td>
</tr>
<tr>
<td>( \sigma_d )</td>
<td>surface charge density of the diffuse layer</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>surface site densities</td>
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</table>
REFERENCES


VITA

EDUCATION

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