

Manipulating electrokinetic conductance of nanofluidic channel by varying inlet pH of solution

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Abstract The electrokinetic conductivity of micro-/nanofluidic systems, which strongly depends on the local solution properties (e.g., pH and ionic strength), has wide applications in nanosystems to control the system performance and ion rectification. Accurate and active manipulation of this parameter is proven to be very challenging since, in nanoscale, the ion transport is particularly dominated by the acquired surface charge on the solid–liquid interfaces. In this study, we propose an approach to manipulate the nanochannel electrokinetic conductivity by changing the pH value of the solution at the inlet in order to impose asymmetrical conditions inside nanochannel. The variable surface charge of walls is determined by considering the chemical adsorption on the solid–liquid interface and the electrical double layer interaction. The presented numerical model, which couples Poisson–Nernst–Planck and Navier–Stokes equations, can fully consider the electro-chemo-mechanical transport phenomena and predict the electrokinetic conductivity of nanofluidic channels with good accuracy. Modeling results show that the electrokinetic conductivity of the nanofluidic systems can be regulated by varying the solution pH at the inlet. It is revealed that the stronger electric double layers interaction can enhance the

sensitivity of the nanochannel electrokinetic conductance to the inlet pH. This unique behavior of the nanochannel electrokinetic conductivity could broaden potential applications in biomedical, energy, and environmental systems using nanofluidic devices.

Keywords Manipulating electrokinetic conductance · Nanofluidic channel · Electrical double layer · Lattice Boltzmann · Asymmetrical condition

Abbreviations

ETL	Electrical triple layer
METL	Modified electrical triple layer, EDL, electrical double layer
SCF	Streaming conductance factor
ECF	Electrical conductance factor

1 Introduction

Nanofluidic systems have drawn significant attention in the past decade due to their wide range of applications in different industries such as nanofluidic diodes (Karnik et al. 2007), biosensing (Howorka and Siwy 2009), analysis and separation of biomolecules (Yeh et al. 2012; Li et al. 2013), and energy conversion (Yan et al. 2013; Daiguji et al. 2004; van der Heyden et al. 2006, 2007; Wang and Kang 2010). The advent of well-defined nanoscale fluidic channels (using micro-/nanofabrication techniques) has spurred both speculation and experimentation into their possible applications for high-resolution separation of ionic species (Mao and Han 2005).

From a physical point of view, the ion transport properties of a nanochannel can be controlled by the surface charge density (Schoch and Renaud 2005) or the ionic

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conductivity of the fluid. For the symmetrical scenario, it is assumed that the nanochannel is subjected to reservoirs with symmetrical solution properties where the nanochannel itself is fabricated with a symmetrical geometry and material. To model the unique ion transport behavior under symmetrical conditions, several efforts have been performed. Morgan and Green (2003) proposed a model to obtain the nanochannel conductivity for a binary electrolyte such as KCl. However, this model was suitable just for the high ionic strength conditions. At the low ionic strength conditions, nanochannel conductivity in a log–log scale shows saturation, although further reduction of the ionic strength will not affect the conductivity (Schoch and Renaud 2005; Stein et al. 2004; Karnik et al. 2005). This behavior can be explained by the competition of higher zeta potential and lower surface charge density in the low ionic strength conditions which causes saturated behavior of ionic conductance of nanochannel (Schoch and Renaud 2005; Daiguji et al. 2004; Wang and Revil 2010; Wang et al. 2010). Moreover, modeling the influence of solution pH and ionic strength as important factors in determining the surface charge has been attracted considerable attentions recently (Schoch and Renaud 2005; Stein et al. 2004; Jiang and Stein 2010, 2011; Ma et al. 2014, 2015; Li-Hsien et al. 2015; Taghipoor et al. 2015).

By considering the surface charge dependence on the solution properties, one can control the ionic current/conductance which has a wide range of applications in nanoscale biosensing (Wang et al. 2010; Ma et al. 2014, 2015; Li-Hsien et al. 2015; Wang and Kang 2010) or energy conversion (Yan et al. 2013; Daiguji et al. 2004; van der Heyden et al. 2006, 2007; Stein et al. 2004; Taghipoor et al. 2015). Ma et al. (2015) proposed an analytical model for the ionic conductance in a pH-regulated nanochannel which is gated by a field-effect transistor (FET). Their results revealed that the field-effect control of the ionic conductance would be remarkable in a silica nanochannel when the solution has a low pH. In another study, Chen et al. (2006) fabricated a field-effect pH sensor using silicon nanowires. They measured the conductance of the nanochannel as a function of the pH. Similarly, Li-Hsien et al. (2015) showed that the low pH solution effect on the ionic conductance is significant at a high negative gate voltage. More recently, Jiang and Stein theoretically (Jiang and Stein 2010) and experimentally (Jiang and Stein 2011) investigated the influence of solution pH, ionic strength, and gate voltages on the ionic conductance and electrofluidic gating. van der Heyden et al. (2005) also reported the measurements of the streaming current in different silica nanochannels. They observed that the streaming current depends on both applied pressure gradient and channel height.

The previously mentioned studies are based on the symmetrical nanochannels. However, in nature, there are several examples in which the nanochannel or electrolyte solutions are under asymmetrical conditions. For instance, the asymmetrical nanochannel geometry (Siwy et al. 2002) with conically shaped nanopores shows voltage gating like biological ion channels. The asymmetry in a nanochannel could not solely be obtained by the nanochannel structure. It has been shown that by imposing negative and positive charges on the walls of a structurally symmetrical nanochannel, the ionic current rectification can be achieved (Karnik et al. 2007). The placement of a nanochannel between two different ionic solution reservoirs can also impose asymmetrical ionic rectifying effects (Cheng and Guo 2007). This effect was observed when only a single side of the channel has the electric double layer overlap. Hou et al. (2010) developed a biomimetic asymmetric responsive nanochannel with control over both pH- and temperature-tunable asymmetric ion transport properties. In another work, Guan et al. (2011) designed a field-effect reconfigurable nanofluidic diode with an asymmetrically placed gate on one of the nanochannel walls. They demonstrated that the conduction of ions could be digitally programmed and controlled in situ. Wang et al. (2009) proposed a rectifying nanochannel configuration in which a conical nanochannel is connected to two reservoirs with asymmetrical solution pH. This could help them to make a highly efficient rectifying nanochannel without any chemical modification. All the aforementioned studies elucidated the importance of understanding, manipulating, and controlling the ionic conductance of nanochannels under symmetrical or asymmetrical conditions for development of bioinspired intelligent nanomachines for real-world applications, such as biosensors, molecular filtration, and nanofluidic devices.

This study aims to propose a novel approach to manipulate the electrokinetic conductivity of a nanochannel by varying the solution pH at the inlet. To do this, the whole nanofluidic system is initially filled and modeled for a known solution, i.e., ionic strength and solution pH, which is called the background solution. In order to modify the surface charge density on the nanochannel walls and as a result manipulating the ion transport, we subject the nanochannel to inlet pH variations. Through this and without doing any chemical modification, the nonlinear behavior of the electrokinetic conductivity of the nanochannel can be investigated.

Modeling the local surface charge would be crucial specifically when charge regulation takes place due to the interaction of the electric double layers (EDLs) in a confined environment such a nanochannel (Stumm and Morgan 1996). Numerous efforts have been devoted to study the EDLs interaction and its effects on the zeta

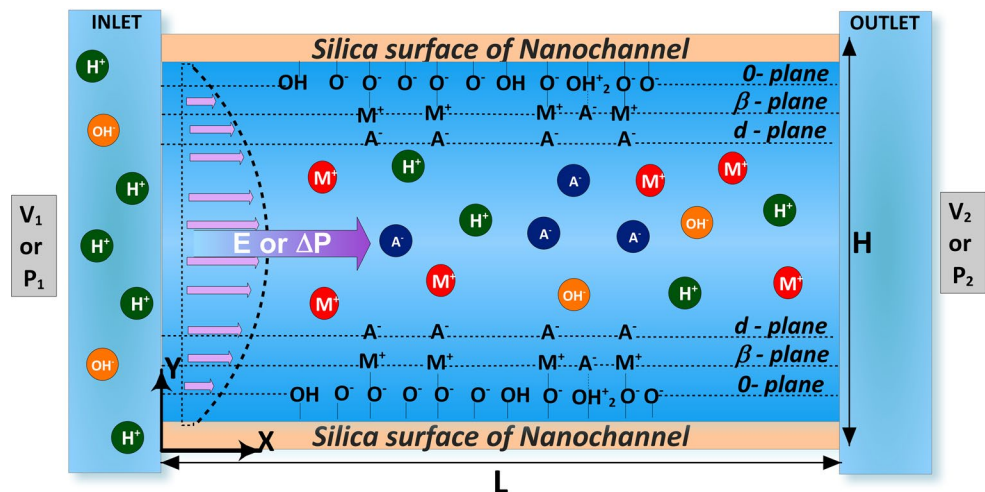
potential at the solid–liquid interface by considering a constant charge density (Daiguji et al. 2004; Thompson 2003; Qiao and Aluru 2004; Wang et al. 2007) or a constant zeta potential (Pennathur and Santiago 2005; Wang and Chen 2007). However, neither the constant zeta potential nor the constant surface charge density could provide accurate predictions at the entire range of ionic strength (i.e., from 10^{-6} to 1.0 [M]) in nanochannels (van der Heyden et al. 2005). Several numerical or analytical schemes have been made to obtain the local surface charge based on the solution properties and EDLs interaction (Wang and Revil 2010; Wang et al. 2010; Ma et al. 2014, 2015; Wang and Kang 2010; Behrens and Grier 2001). Although the basic-Stern (BS) model has been widely used to determine the surface charge density, this model solely considers the silica dissociation with water and ignores the contribution of salt ions in surface chemical reactions. As a result, it is valid only for diluted solutions with monovalent ionic species (Wang and Revil 2010; Behrens and Grier 2001). To address this issue, we developed a modified electrical triple layer (ETL) model by employing the enrichment model as the effective bulk concentration (Wang et al. 2010). This model enables us to take into account the effects of the EDLs interaction, multiple/multivalent ionic species and contribution from the salt–ion adsorption to the surface charge on mineral surfaces. The modified ETL model, generally for the simplest case, has thirteen coupled nonlinear equations. Despite its complexity, it can provide an accurate prediction of surface charge density and zeta potential at a wide range of pH and ionic concentrations. By employing the local surface charges obtained from the proposed modified ETL model, the coupled Nernst–Planck, Poisson and Navier–Stokes equations for multi-species ions can be solved using coupled lattice Boltzmann models (LBM).

2 Problem definition

Our 2D nanochannel configuration for this study is demonstrated in Fig. 1. A long charged silica nanochannel is connected to two big reservoirs at the inlet and outlet. The M^+ and A^- represent the counter- and co-ion, respectively. The three layers near to the silica surface have been demonstrated as 0, β and d planes which represent the layers of the ETL model. The dimensions of the nanochannel are chosen as the one reported by van der Heyden et al. (2005) with length (L) = 4.5 [mm], width (W) = 50 [μ m] and height (H) = 140 [nm]. The fluid flow can be generated by connecting the pressurized chamber or non-zero voltage electrode to the inlet reservoir while the outlet reservoir would be left open to a non-pressurized chamber or grounded (GND).

Both reservoirs are initially filled with electrolyte solution (i.e., background solution) which contains multiple ionic species such as K^+ , Cl^- , H^+ and OH^- . By adding KOH and HCl we can adjust the pH of inlet solution from 3 to 12 gradually. It is known that the background solution properties can also affect the ion transport through the nanochannel (Lanju et al. 2015). So, for our simulation, we chose three backgrounds pH as $pH_{\text{background}} = 4, 7$ and 10, and three background bulk concentrations as $C_{KCl} = 4.5 \times 10^{-6}, 8 \times 10^{-5}$ and 3.6×10^{-3} [M]. The electro-neutrality assumption of the inlet reservoir requires that $C_{K^+} = C_{KCl} + C_{KOH}$, $C_{Cl^-} = C_{KCl} + C_{HCl}$, $C_H^+ = C_{HCl}$, and $C_{OH^-} = C_{KOH}$. It is assumed that the diffusion coefficients of the ions, kinetic viscosity, and solution temperature would be constant everywhere in the solution and equal to: $D_{K^+} = 1.95 \times 10^{-9}$, $D_{Cl^-} = 2.03 \times 10^{-9}$, $D_{H^+} = 9.31 \times 10^{-9}$, $D_{OH^-} = 5.27 \times 10^{-9}$ [$m^2 s^{-1}$] (Samson et al. 2003), $\nu = 8.89 \times 10^{-7}$ [$m^2 s^{-1}$] and $T = 293.15$ [K], respectively. The vacuum electrical permittivity and

Fig. 1 Schematic illustration of a 2D nanochannel containing multi-species ions, A^- , M^+ , H^+ , OH^- . The triple layer illustrated as 0, β and d planes where the zeta potential and surface charge density would be considered as ψ_d and Q_0 , respectively



the ratio of the electrolyte solution permittivity to vacuum permittivity are considered to be $\varepsilon_0 = 8.854 \times 10^{-12}$ [C V⁻¹ m⁻¹] and $\varepsilon_r = 78.54$ (Alizadeh et al. 2014), respectively. For the electrically driven flow scenario (electro-osmotic flow), we applied an external electric field with strength equal to 1800 [V m⁻¹]. Considering the pressure driven case, we applied a pressure gradient equal to 90×10^6 [Pa m⁻¹].

3 Mathematical models

3.1 Governing equations for transports

The electrokinetic transport of multi-species ions is governed by the Nernst–Planck equations coupled with the Poisson and Navier–Stokes equations, which helps taking into account all the electro-chemo-mechanical transport phenomena. For a Newtonian fluid at the nanoscale without any mass source in the laminar regime, the conventional continuity and Navier–Stokes equations are still valid (Alizadeh et al. 2014; Wang et al. 2006):

$$\begin{aligned} \text{(a)} \quad & \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \\ \text{(b)} \quad & \frac{\partial (\rho \mathbf{u})}{\partial t} + \mathbf{u} \cdot \nabla (\rho \mathbf{u}) = -\nabla p + \nabla \cdot [\nu \nabla (\rho \mathbf{u})] + \mathbf{F}, \end{aligned} \quad (1)$$

where ρ [kg m⁻³] is the density of the electrolyte, $\mathbf{u}$ [m s⁻¹] is the flow velocity vector, t [s] is time, p [Pa] is the fluid pressure, ν [m² s⁻¹] is the kinetic viscosity and $\mathbf{F}$ [N m⁻³] is the body force density which may include all the implemented body forces such as electrical body force or pressure gradient. In this study, the pressure gradient and the electrical body force would be employed in streaming and electrical conductance scenario, respectively. Hence, we can define the general term of body force as:

$$\mathbf{F} = \mathbf{F}_e + \mathbf{F}_p = -\rho_e (\nabla \varphi + \nabla \psi) + \nabla P, \quad (2)$$

where $\nabla \varphi$ is the external electric potential field, $-(\nabla \varphi)_x = E_x$ and $(\nabla \varphi)_y = 0$. $\nabla \psi$ represents the internal electric potential field, which is obtained by solving the Poisson equation for free net charge density.

Regarding the ion transport governing equation, the macroscopic mass conservation equation for i th ion species in an electrolyte in nanochannels could be written (Wang et al. 2007; Lichtner 1995)

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0, \quad (3)$$

where C_i demonstrates the i th ionic concentration, $\mathbf{J}_i$ denotes the species flux. The flux of i th ions, $\mathbf{J}_i$, consists of advection, diffusion and dispersion terms. Neglecting the dispersion,

one can define the flux of ions in the form of Wang and Kang (2010)

$$\mathbf{J}_i = - \left(\frac{e Z_i D_i}{K T} \right) C_i \nabla \psi - D_i (\nabla C_i) + C_i \mathbf{u}, \quad (4)$$

where the first term on the right-hand side denotes the electrochemical migration, the second term defines the ions diffusion and the last term represents the advective transport. In Eq. (4), e , Z_i , D_i , K and T denote the absolute charge of electron, valance number for i th ion, diffusion coefficient for i th ion, Boltzmann constant, and the absolute temperature, respectively. Wang and Kang (2010) presented the electrodynamic transport process equation for ions in electrokinetic flows for isothermal incompressible uniform fluids with no polarization, radiation or chemical reactions. Introducing Eq. (4) into Eq. (3) leads to the ions electrodynamic transport equation:

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i = D_i \nabla^2 C_i + \frac{e Z_i D_i}{K T} \nabla \cdot (C_i \nabla \psi). \quad (5)$$

The local internal electric potential field, ψ , which is caused by the ion distribution, is governed by the Poisson equation as follows:

$$\nabla^2 \psi = - \frac{\rho_e}{\varepsilon_r \varepsilon_0}, \quad (6)$$

where ρ_e is defined as $\sum_i e Z_i C_i$ and denotes the local net electric charge density.

It is well known that the accurate and realistic boundary conditions in the electrokinetic transport phenomena would be crucial for modeling the electrokinetic conductance of a nanochannel. For this purpose, we will present the appropriate boundary conditions for the NP and NS equations. For the Poisson equation, the modified ETL model will be presented in next section to solve the Poisson equation based on the local zeta potential on the nanochannel walls.

Boundary conditions governing Navier–Stokes equations for the nanochannel of Fig. 1 are as follows:

For streaming conductance scenario:

$$\begin{aligned} y = 0 & \rightarrow u = v = 0, \quad y = H \rightarrow u = v = 0 \\ x = 0 & \rightarrow \frac{\partial u}{\partial x} = v = 0, \quad p = P_{\text{inlet}} > P_{\text{atm}}, \\ x = L & \rightarrow \frac{\partial u}{\partial x} = \frac{\partial v}{\partial x} = 0, \quad p = P_{\text{atm}}. \end{aligned} \quad (7)$$

For electrical conductance scenario:

$$\begin{aligned} y = 0 & \rightarrow u = v = 0, \quad y = H \rightarrow u = v = 0, \\ x = 0 & \rightarrow \frac{\partial u}{\partial x} = v = 0, \quad p = P_{\text{atm}}, \\ x = L & \rightarrow \frac{\partial u}{\partial x} = \frac{\partial v}{\partial x} = 0, \quad p = P_{\text{atm}}. \end{aligned} \quad (8)$$

The zero normal flux conditions for the ionic species on the solid–liquid interface, S , is applied as

$$(\mathbf{V} \cdot \mathbf{J}_i)_S = 0, \quad (9)$$

where the inlet of the nanochannel is subjected to the inlet solution ionic species concentrations

$$x = 0 \rightarrow C_i = C_{i,\text{inlet}}. \quad (10)$$

In this study, we let the outlet solution properties specified through the numerical solution based on the problem aqueous solution properties. Therefore, one can define the outlet boundary condition for ionic species as:

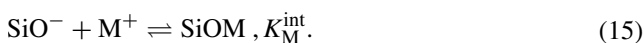
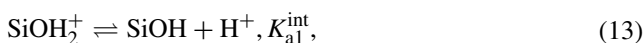
$$x = L \rightarrow \frac{\partial C_i}{\partial x} = 0. \quad (11)$$

The boundary conditions governing the Poisson equation (Eq. 6) would be defined as Baldessari and Santiago (2009)

$$\begin{aligned} x = 0 &\rightarrow \psi = 0, \\ x = L &\rightarrow \frac{\partial \psi}{\partial x} = 0, \\ y = 0 \quad \text{and} \quad y = H &\rightarrow \psi = \psi_d. \end{aligned} \quad (12)$$

3.2 The modified electrical triple layer model

To obtain the ψ_d value based on the local solution properties, we consider an isolated silica surface which is in contact with a binary symmetric aqueous solution such as NaCl or KCl. Naturally, the silica surface will acquire electric charge due to the chemical adsorption of ions in the solution. In the pH range of 3–9, the typical chemical reactions of the surface adsorption at the silica surface can be written as follows (Wang and Revil 2010):



Based on the law of mass action, the reaction equilibrium constants for the chemical adsorptions are written as:

$$K_{a1}^{\text{int}} = \frac{\sigma_{\text{SiOH}}}{\sigma_{\text{SiOH}_2^+}} C_{\text{H}^+,b}^{\text{eff}} \exp\left(-\frac{e\psi_0}{k_b T}\right), \quad (16)$$

$$K_{a2}^{\text{int}} = \frac{\sigma_{\text{SiO}^-}}{\sigma_{\text{SiOH}}} C_{\text{H}^+,b}^{\text{eff}} \exp\left(-\frac{e\psi_0}{k_b T}\right), \quad (17)$$

$$K_M^{\text{int}} = \frac{\sigma_{\text{SiOM}}}{\sigma_{\text{SiO}^-}} \left(\frac{1}{C_{\text{M}^+,b}^{\text{eff}}}\right) \exp\left(\frac{e\psi_\beta}{k_b T}\right), \quad (18)$$

where σ is the surface charge density (in $[\text{C m}^{-2}]$), C^{eff} is the effective bulk concentration (in $[\text{M}]$) which will be determined based on the EDLs interaction, ψ is the electric potential and T is the temperature. Considering the total number of site density as Γ^0 (in $[\text{sites nm}^{-2}]$), one can write the continuity equation for the surface charge density as (Wang and Revil 2010; Kitamura et al. 1999)

$$e\Gamma^0 = \sigma_{\text{SiOH}} + \sigma_{\text{SiO}^-} + \sigma_{\text{SiOH}_2^+} + \sigma_{\text{SiOM}}. \quad (19)$$

The surface charge density at silica surface for three layers of 0, β , d (see Fig. 1) can be written as

$$Q_0 = \sigma_{\text{SiOH}_2^+} - \sigma_{\text{SiO}^-} - \sigma_{\text{SiOM}}, \quad (20)$$

$$Q_\beta = \sigma_{\text{SiOM}}, \quad (21)$$

$$Q_d = -\sqrt{8\varepsilon_r \varepsilon_0 k_b T n_{s,b}^{\text{eff}}} \sinh\left(\frac{e\psi_d}{2k_b T}\right), \quad (22)$$

where $n_{s,b}^{\text{eff}}$ is the effective bulk number density of counter-ions and hydronium (in $[\text{m}^{-3}]$) which is related to the effective bulk ionic molar concentration as:

$$n_{s,b}^{\text{eff}} = 1000 N_A \left(C_{\text{M}^+,b}^{\text{eff}} + C_{\text{H}^+,b}^{\text{eff}}\right), \quad (23)$$

where N_A denotes the Avogadro number.

The global electro-neutrality in the triple layers will lead to:

$$Q_0 + Q_\beta + Q_d = 0. \quad (24)$$

Considering the capacitance concept for two capacitors which is placed between three layers, we can write the correlation between electric potential of three layers with the surface charge density as:

$$\psi_0 - \psi_\beta = \frac{Q_0}{C_1}, \quad (25)$$

$$\psi_\beta - \psi_d = -\frac{Q_d}{C_2}, \quad (26)$$

where C_1 and C_2 (in $[\text{F m}^{-2}]$) are the integral electrical capacities of the inner and outer parts of the stern layer, respectively, which are assumed to be constant in the regions between planes (Charmas et al. 1995). Equations (16)–(26) are formed a set of nonlinear coupled equations for the modified ETL model. In this contribution, the constant parameters for the modified ETL

model are considered as: $C_1 = 1.16$ [F m⁻²], $C_2 = 0.2$ [F m⁻²], $K_{a2}^{\text{int}} = 10^{-6.64}$, $K_M^{\text{int}} = 10^{-2.8}$, $\Gamma^0 = 5$ [sites nm⁻²], $\text{pH}_{\text{PZC}} = 2.5$ and $K_{a1}^{\text{int}} = 2\text{pH}_{\text{PZC}} - \log(K_{a2}^{\text{int}})$ (Wang and Revil 2010) while $Q_0, Q_\beta, Q_d, \psi_0, \psi_\beta, \psi_d$ will be obtained by solving the set of equations numerically. The effective bulk concentration for counter-ion ($C_{M^+,b}^{\text{eff}}$) and Hydronium ($C_{H^+,b}^{\text{eff}}$) should be determined by considering the effects of the EDLs interaction. The conventional ETL model is proposed based on the isolated surface which means that there would not be any interactions between EDLs. In this study, in order to consider the interaction of EDLs, the enrichment effective bulk concentration model has been introduced to the ETL model. Wang et al. (2010) introduced an enrichment coefficient, α , for nanochannels which is defined as:

$$\alpha_i = \frac{C_{i,m}}{C_{i,\text{inlet}}}, \quad (27)$$

where $C_{i,m}$ and $C_{i,\text{inlet}}$ represent the concentration of i th ion at the middle of the nanochannel and the inlet of the nanochannel, respectively. It should be mentioned that if the channel height is much larger than the EDL thickness, the $C_{i,m} = C_{i,\text{inlet}}$ and $\alpha = 1$. However, if the nanochannel height is comparable with the EDL thickness, the EDLs will interact and consequently the concentration of the ions at the middle of the nanochannel will be enriched. As a result, the effective bulk concentration could be calculated as:

$$C_{H^+,b}^{\text{eff}} = \alpha_{i=H^+} C_{i=H^+,\text{inlet}}, \quad (28)$$

$$C_{M^+,b}^{\text{eff}} = \alpha_{i=M^+} C_{i=M^+,\text{inlet}}. \quad (29)$$

By introducing the effective bulk concentrations [Eqs. (28), (29)] to Eqs. (16–18) and (23), the set of equations for modified ETL model would be mathematically solvable.

4 Numerical models and validations

The governing equations in the present work are solved by the coupled lattice Boltzmann methods (Wang and Kang 2010). In this rather new numerical method, for each of the governing equations, one evolution equation is defined as the equivalent governing equation in mesoscopic space. In the supporting information, the evolution equation for each of the governing equations mentioned in the last sections will be presented. It should be noted that we consider the D2Q9 and D2Q5 system of lattice for discretizing the velocities for Navier–Stokes, Poisson, and Nernst–Planck equations, respectively. The directions for both systems are shown in Fig. 2.

To evaluate the accuracy of our numerical results, the modified ETL model coupled with PNP and NS has been validated by the available experimental data for streaming conductance (van der Heyden et al. 2005) (Fig. 3a) and electrical conductance (Karnik et al. 2005) (Fig. 3b). Figure 3a shows the present work streaming conductance predictions, S_{str} , for the nanochannel fabricated by van der Heyden et al. (2005). In this study, the streaming conductance is calculated as:

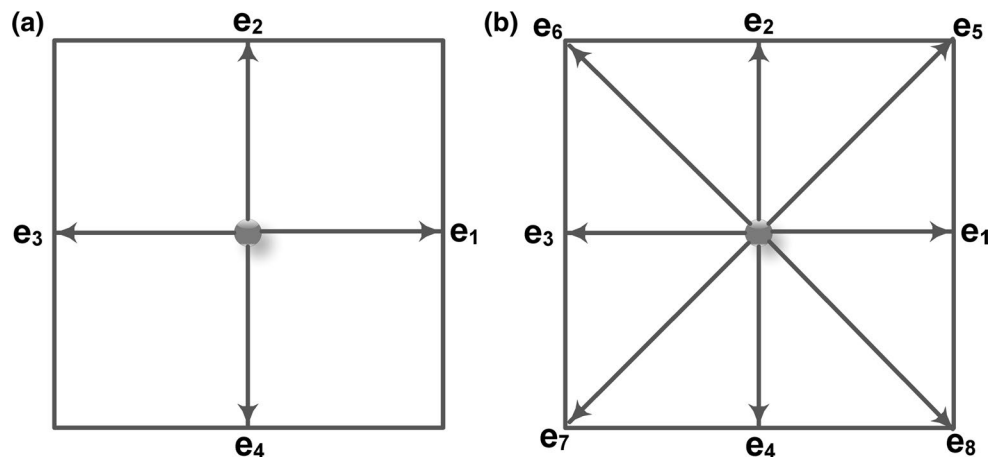
$$S_{\text{str}} = \frac{1}{\Delta PL} \int \int \rho_e(x, y) u(y) dA dx, \quad (30)$$

where ΔP and $u(y)$ denote the applied pressure difference and the pressure driven velocity along the nanochannel cross section.

It can be seen that for a wide range of background KCl concentrations (10^{-6} – 1.0 M) which is equivalent to a background pH of 8.0, the results have good agreements with experimental measurements. Moreover, the present numerical framework could predict more accurate streaming conductance for non-overlapped EDLs ($C_{\text{KCl}} > 10^{-3}$ M) compared to the overlapped EDLs ($C_{\text{KCl}} < 10^{-3}$ M).

Figure 3b demonstrates the present work predictions and experimental measurements performed by Karnik et al.

Fig. 2 Schematic illustration of **a** D2Q5 and **b** D2Q9 lattice systems. e_i represents the discretized lattice velocity



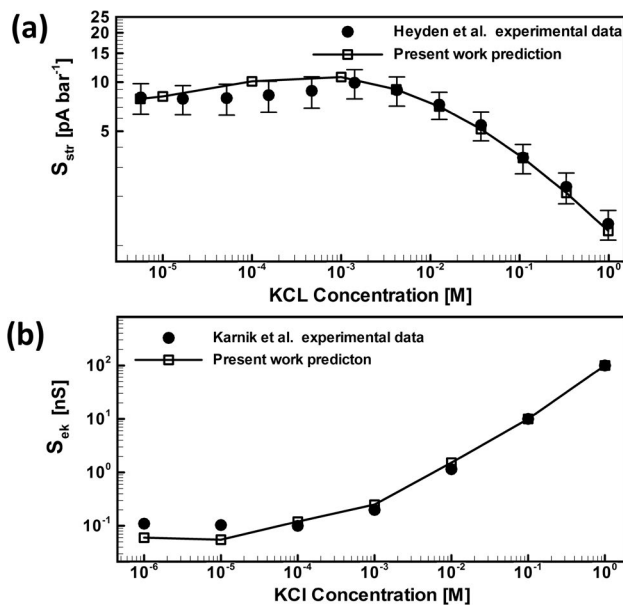


Fig. 3 The present work theoretical framework validation by available experimental data for **a** streaming conductance, S_{str} [pA bar⁻¹], of a silica nanochannel fabricated by Heyden et al. (van der Heyden et al. 2005) under applied pressure gradient $\Delta P = 4$ with background solution pH = 8; **b** electrical conductance, S_{ek} [nS], of a silica nanochannel fabricated by Karnik et al. (2005) under applied external electric field $E = 41,667$ [V m⁻¹] and the deionized background solution with pH = 7, as a function of KCl concentration

(2005) for electrical conductance of a nanochannel. The electrical conductivity in a nanochannel can be defined as:

$$S_{\text{ek}} = \frac{1}{\Delta V L} \left(\sum_i Z_i e \int \int J_i dA dx \right), \quad (31)$$

where ΔV represents the electric potential difference, J_i the ionic flux and A the nanochannel cross section. From Fig. 3a, it is evidence that the presented numerical model can predict more accurate results when the EDLs interactions are relatively weak. As stated earlier, we considered asymmetrical solutions properties for our nanochannel. As a result, we expect to have nonlinear response of surface charge density and zeta potential. Hence, the electrical and streaming conductance should be considered as a variable along the nanochannel. For this reason, we also took into account the changes of electrical conductance along the nanochannel in Eqs. (30) and (31).

5 Results and discussion

5.1 Streaming conductance as a function of inlet pH variations

In order to provide more realistic electrokinetic conductance of the nanochannel, our model will be utilized in

two steps. First, the METL model coupled with PNP and NS equations are solved based on the background solution properties to steady-state. Second, by employing the background macroscopic properties (from the first step), the governing coupled equations (METL model coupled with PNP and NS) are solved because the inlet boundary conditions are subjected to solution properties variations.

Figures 4 and 5 demonstrate the normalized streaming conductance as a function of solution pH at the inlet for different background solution properties. In order to study the influence of the background solution properties on the streaming conductance, three different background KCl concentrations; $C_{\text{KCl}} = 4.5 \times 10^{-6}$, 8.0×10^{-5} and $C_{\text{KCl}} = 3.6 \times 10^{-3}$ [M] and background pH; pH = 4, 7, and 10 are considered. It should be noted that the streaming conductance (Eq. 44) is normalized by the streaming conductance when the pH of the solution at the inlet is kept identical to the background solution pH. For simplicity, in this contribution, hereinafter, the normalized streaming conductance would be represented as $\tilde{S}_{\text{str}}$.

5.1.1 Inlet pH variations effects under different background KCl concentration

Figure 4 depicts the influence of the background KCl concentration on the $\tilde{S}_{\text{str}}$ of nanochannel, while the pH of the solution at the inlet changes. As can be seen, for a defined background pH, by increasing the background C_{KCl} from 4.5×10^{-6} to 8.0×10^{-5} [M], the $\tilde{S}_{\text{str}}$ will be increased. However, this increment would be more significant when $\text{pH}_{\text{background}} = 7$ (see Fig. 4, about 37.9% for $\text{pH}_{\text{background}} = 7$, while this increment is 7.26 and 0.1% for $\text{pH}_{\text{background}} = 4$ and 10, respectively). Moreover, by increasing the C_{KCl} to 3.6×10^{-3} [M] the $\tilde{S}_{\text{str}}$ decreases. Considering the results in Fig. 4b, for neutral background solution ($\text{pH}_{\text{background}} = 7$), it is found that since the inlet solution is also neutral ($\text{pH}_{\text{inlet}} = 7$), the $\tilde{S}_{\text{str}}$ would be minimum. In other words, for a nanofluidic system with neutral background solution, if the inlet solution pH kept neutral, as a result, the streaming current would be minimal. However, this nanofluidic system behavior would not be available anymore for systems with alkaline or acidic background solution. Figure 4a and c indicate that likewise the $\text{pH}_{\text{background}} = 7$ scenario, the S_{str} would be minimum when $\text{pH}_{\text{inlet}} = 7$. As a result, we can say that the behavior of $\tilde{S}_{\text{str}}$ for different background pH and KCl concentration would be parabolic with a minimum value at $\text{pH}_{\text{inlet}} = 7$. This nanochannel conductivity response to inlet pH variations could be interpreted by considering the streaming conductance dependence on ionic strength (Fig. 3a) and the multi-species model which is used in this work. For instance, the electro-neutrality assumption

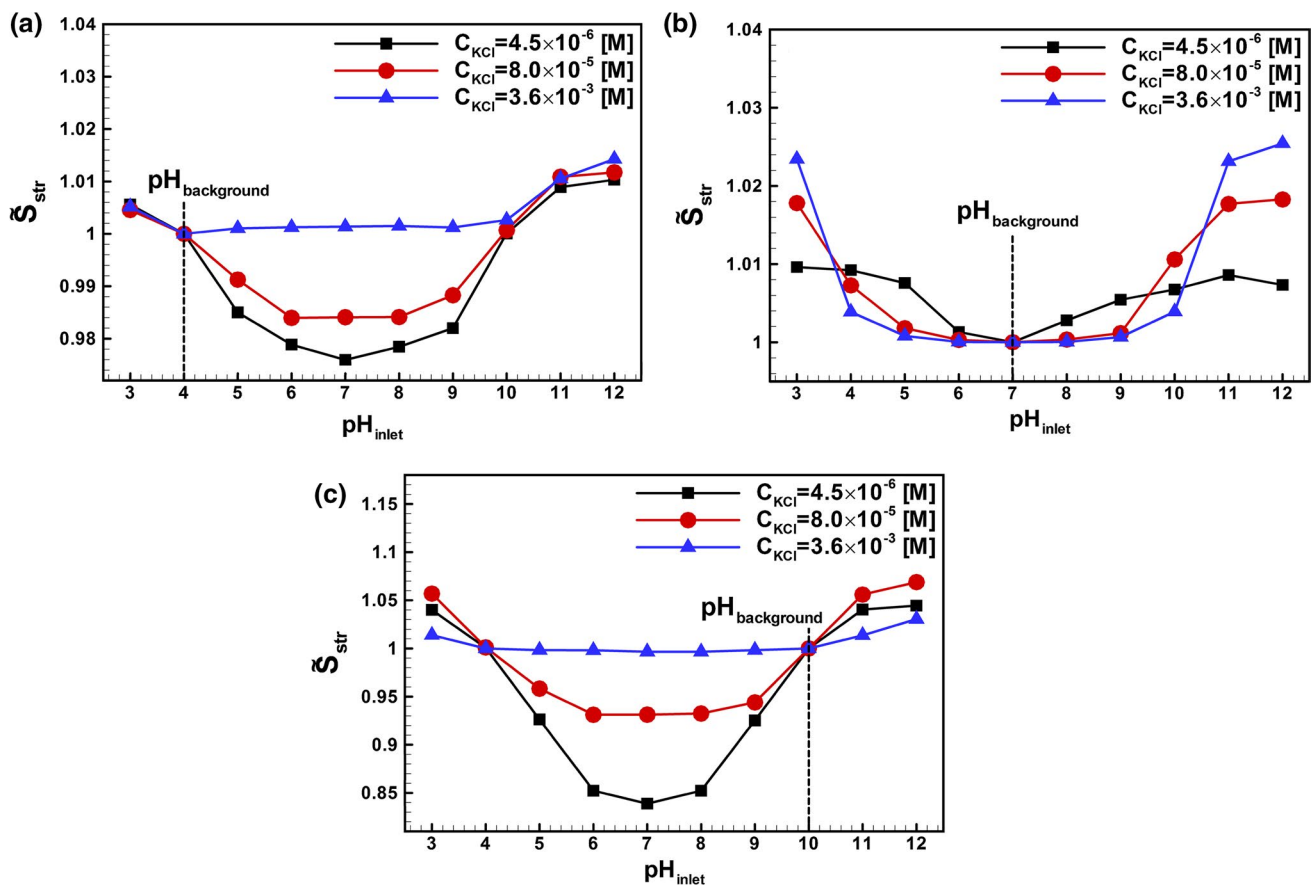


Fig. 4 The nanochannel streaming conductance normalized by the streaming conductance when $pH_{inlet} = pH_{background}$ which defined as $\tilde{S}_{str}(pH_{inlet}, C_{KCl}) = S_{str}(pH_{inlet}, C_{KCl}) / S_{str}(pH_{inlet} = background, C_{KCl})$. The background KCl concentration effects for when; **a** $pH_{background} = 4$ with $S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 0.7113, 0.767 and 0.6049 [pA bar⁻¹], **b** $pH_{background} = 7$ with

$S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 4.7045, 7.5782 and 6.9087 [pA bar⁻¹], **c** $pH_{background} = 10$ with $S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 14.6224, 14.6376 and 12.5245 [pA bar⁻¹] when each of the background solution pH subjected to three background concentrations $C_{KCl} = 4.5 \times 10^{-6}$, 8.0×10^{-5} , and 3.6×10^{-3} [M], respectively

at the inlet solution enforces the lowest ionic strength for when $pH_{inlet} = 7$. However, when the inlet solution pH deviates from 7, the ionic strength would be increased. As a consequence, according to experimental measurements (Fig. 3a), while we are in overlapped EDL region, the streaming conductance would be increased by increasing the ionic strength.

Normalizing the streaming conductance as $\tilde{S}_{str} = S_{str} / S_{str}^{pH_{inlet}=pH_{background}}$ helps us to find out that if we increase or decrease the inlet solution pH from $pH_{inlet} = 7$ equally, the streaming conductance of the nanofluidic system would be identical for both alkaline or acidic scenarios. Furthermore, Fig. 4 elucidates the fact that the stronger EDL interaction (lower ionic strength) will cause more conductance dependence on variations of inlet solution properties. In other words, for non-overlapped EDLs, the $\tilde{S}_{str}$ would be less dependent on the inlet solution pH variations. For example, when $C_{KCl} = 3.6 \times 10^{-3}$ [M],

modeling results showed that by changing the inlet pH solution, the $\tilde{S}_{str}$ would not be changed significantly.

5.1.2 Inlet pH variations effects under different background solution pH

Figure 5 demonstrates the influence of the inlet solution pH variations on the $\tilde{S}_{str}$ for different background pH when the KCl concentration has prescribed defined value. It is interesting to note that for $C_{KCl} = 4.5 \times 10^{-6}$ and $C_{KCl} = 8.0 \times 10^{-5}$ [M] (Fig. 5a, b) the solution with $pH_{background} = 10$ has the minimum $\tilde{S}_{str}$ at $pH_{inlet} = 7$. However, for $C_{KCl} = 3.6 \times 10^{-3}$ [M], Fig. 5c indicates that background pH changes will not have a significant influence on the normalized streaming conductance of nanochannel when inlet solution pH changes. In addition, it is shown that how the alkaline background solution ($pH_{background} = 10$) would increase the streaming conductance

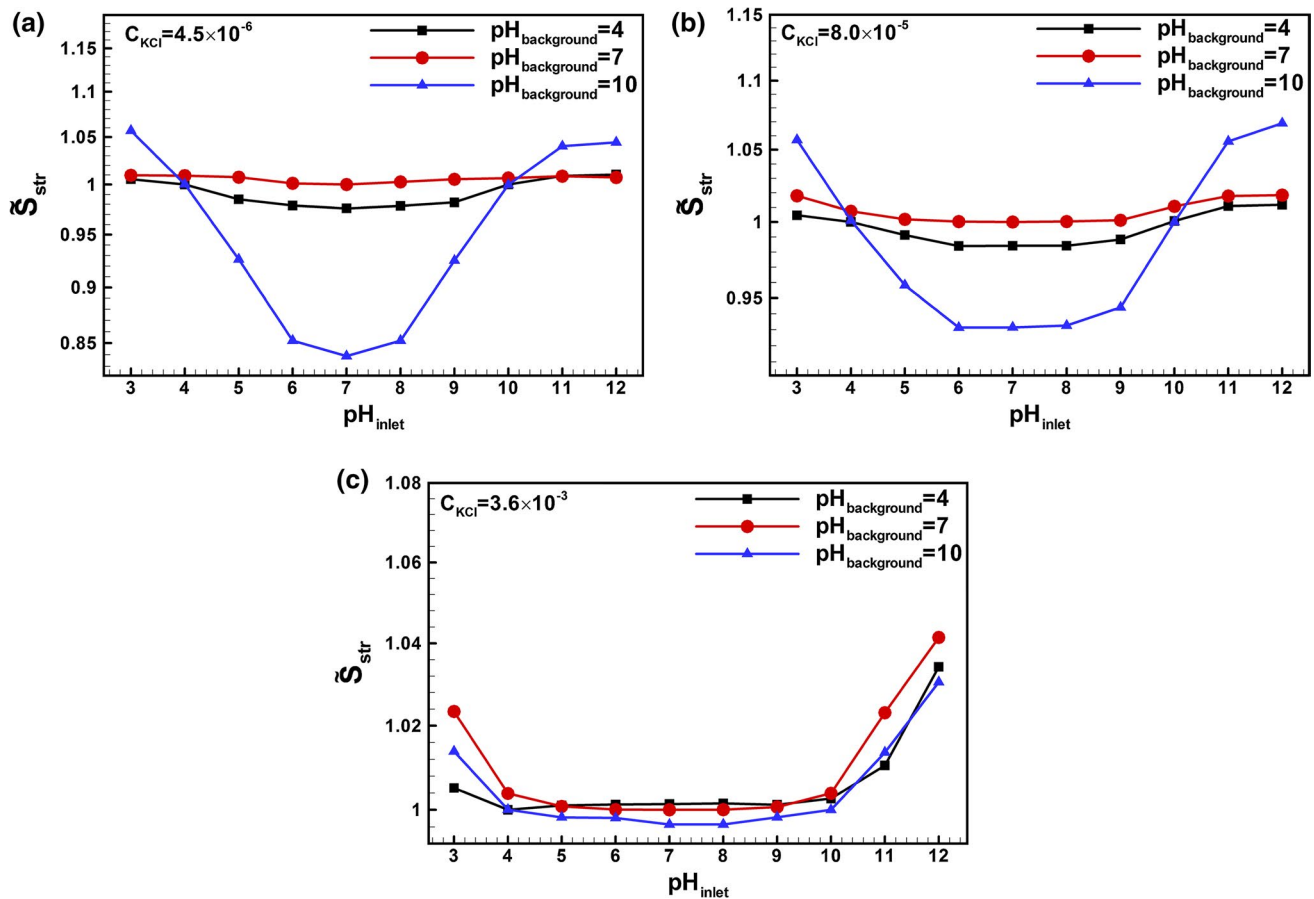


Fig. 5 The normalized streaming conductance, defined similar to what mentioned for Fig. 1, versus the inlet solution pH variations. The background pH solution effects for when; **a** $C_{KCl} = 4.5 \times 10^{-6}$ [M] with $S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 0.7113, 4.7045 and 14.6224 [pA bar⁻¹], **b** $C_{KCl} = 8.0 \times 10^{-5}$ [M] with

$S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 0.767, 7.5782 and 14.6376 [pA bar⁻¹], and **c** $C = 3.6 \times 10^{-3}$ [M] with $S_{str}(pH_{inlet} = background, C_{KCl})$ equal to 0.6049, 6.9087 and 12.5245 [pA bar⁻¹] when each of the background solution subjected to three $pH_{background} = 4.0, 7.0$ and 10.0

dramatically compared with the acidic and neutral background solutions. One reason is that by increasing the pH, the surface charge density would be increased and therefore more counter-ions contribute in forming the electric double layer. Consequently, due to the interaction of the EDLs at the nanoscale, the major ionic current would be carried out by the EDLs.

Considering the behavior of the nanofluidic systems under asymmetrical solution pH conditions (see Figs. 4, 5), one can conclude that the efficiency of the energy conversion systems could be manipulated by the background (more alkaline solution) and inlet solution properties. Our modeling results suggested that the efficiency of the energy conversion system (e.g., battery) would be enhanced when the pH of solution at inlet of system would be less or more acidic or alkaline. In other words, we can say that the energy conversion system

would have a minimum efficiency because the pH of the solution at the inlet is neutral. The main reason in favor of this fact is that the surface charge density in nanofluidic channels has a key role in ionic conductance and depends on the solution acidity and ionic strength. When the inlet solution pH increases, from acidic to neutral, the inlet ionic strength would be decreased. As a result, a competition for increase or decrease of surface charge density due to the elevation of pH and reduction of ionic strength would occur, respectively. This competition would result in minimum ionic conductance at $pH_{inlet} = 7$. However, by increasing the pH of solution at the inlet from neutral to alkaline, the surface charge density would be increased due to elevation of both pH and ionic strength. It is worth noting that this behavior of nanofluidic system would be independent of the background solution ionic strength.

5.1.3 Inlet pH variations effects on surface charge density of nanochannel

As we mentioned before, the transport properties of a nanochannel could be controlled by the acquired surface charges on the solid–liquid interfaces. In the last section, it is shown that the streaming conductance of the nanochannel could be manipulated by imposing inlet pH variations. To shed more lights into the ion transport mechanism, we need to study the surface charge variations as a function of the inlet pH changes. Figure 6 shows the normalized surface charge density as a function of inlet pH for the nanofluidic systems of the last section scenarios. It is found that the surface charge density of the nanochannel could demonstrate different behavior by changing the inlet pH under different background solution pH amounts. Considering the acidic background solution (Fig. 6a), by increasing the inlet pH beyond the background solution pH, the absolute surface charge density should be increased due to the higher inlet pH and decreased due to the lower ionic strength. By increasing the inlet pH from neutral to alkaline solution, the

ionic strength would be increased and as a result the surface charge density increases (Fig. 6a). The surface charge density would be more sensitive to the inlet pH variations when the solution has lower background ionic concentration. When the background solution is neutral (pH = 7), Fig. 6b shows that by reducing the inlet solution pH from neutral to acidic, the surface charge density decreases due to the competition between reduction of the inlet pH and reduction of the ionic strength. However, if the inlet pH increases from neutral to alkaline conditions, the surface charge density would be increased due to elevation of both pH and ionic strength.

If the background solution be alkaline (pH = 10), Fig. 6c indicates that the nanochannel surface charge density changes with the inlet pH variations in a different way to what we observed before for acidic and neutral conditions. It is found that by decreasing the inlet pH, we have two jumps in surface charge density. The first one occurred when the inlet pH decreases from 10 to 9 where the normalized surface charge decreases from 1 to 0.85. This significant reduction is just happened when the background

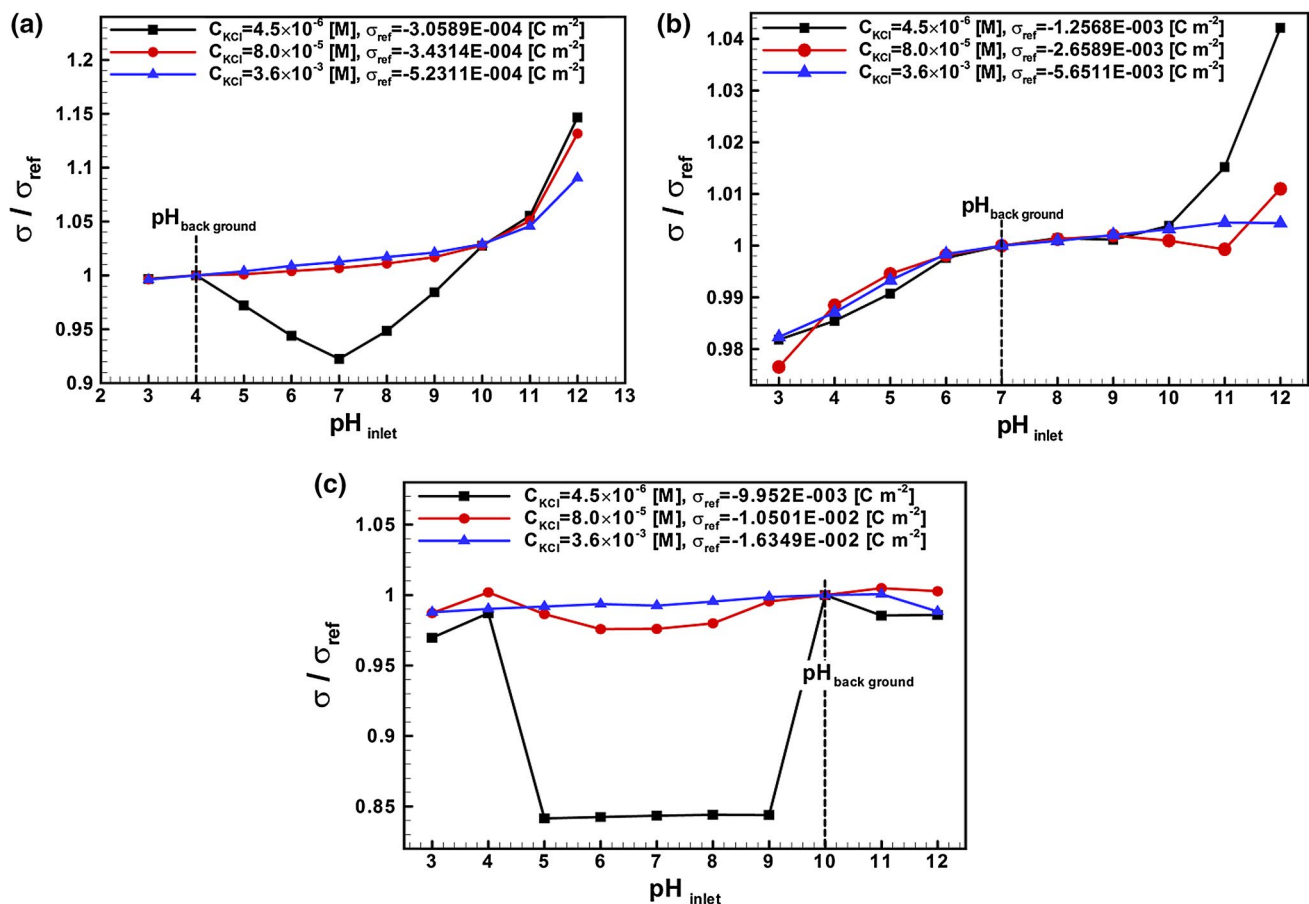


Fig. 6 The normalized surface charge density with the reference surface charge density which the solution pH at inlet and background are identical. The results have been shown for three different background solution pH and KCl concentrations

solution has low ion concentration $C_{\text{KCl}} = 4.5 \times 10^{-6}$ [M]. By further reduction of inlet pH, the surface charge density will stay unchanged up to $\text{pH}_{\text{inlet}} = 5$. Another significant jump occurs when the inlet pH decreases from 5 to 4 where the surface charge density for $C_{\text{KCl}} = 4.5 \times 10^{-6}$ [M] experience a growth.

5.2 Electrical conductance as a function of inlet pH variations

5.2.1 Inlet pH variations effects under different background solution properties

By taking into consideration of the electrical conductance of a nanochannel when the inlet pH varies, a similar nanochannel with streaming conductance scenario has been subjected to an external electric field where the inlet and

outlet reservoirs are depressurized. Figures 7 and 8 indicate the electrical conductance of the nanochannel as a function of the inlet solution pH (Eq. 45). For electrical conductance similar to what we performed for streaming conductance scenario, the influence of the background pH and KCl concentration are taken into account. It should be mention that the $\tilde{S}_{\text{ek}}$ is defined as the normalized electrical conductance with the electrical conductance when pH of the solution at the inlet is kept identical to the background solution pH. Similar to what illustrated for streaming conductance, Fig. 7a–c shows that the $\tilde{S}_{\text{ek}}$ has a parabolic behavior when the inlet solution pH changes. In contrast to the results of $\tilde{S}_{\text{str}}$ for $\text{pH}_{\text{background}} = 7$ (Fig. 4b), Fig. 7b shows that the $\tilde{S}_{\text{ek}}$ changes on the order of 10^{-3} for different pH values. By calculating the $\tilde{S}_{\text{ek}}$ for three different KCl concentrations (Fig. 7a–c), we can see that the EDL interaction has a great influence on the $\tilde{S}_{\text{ek}}$

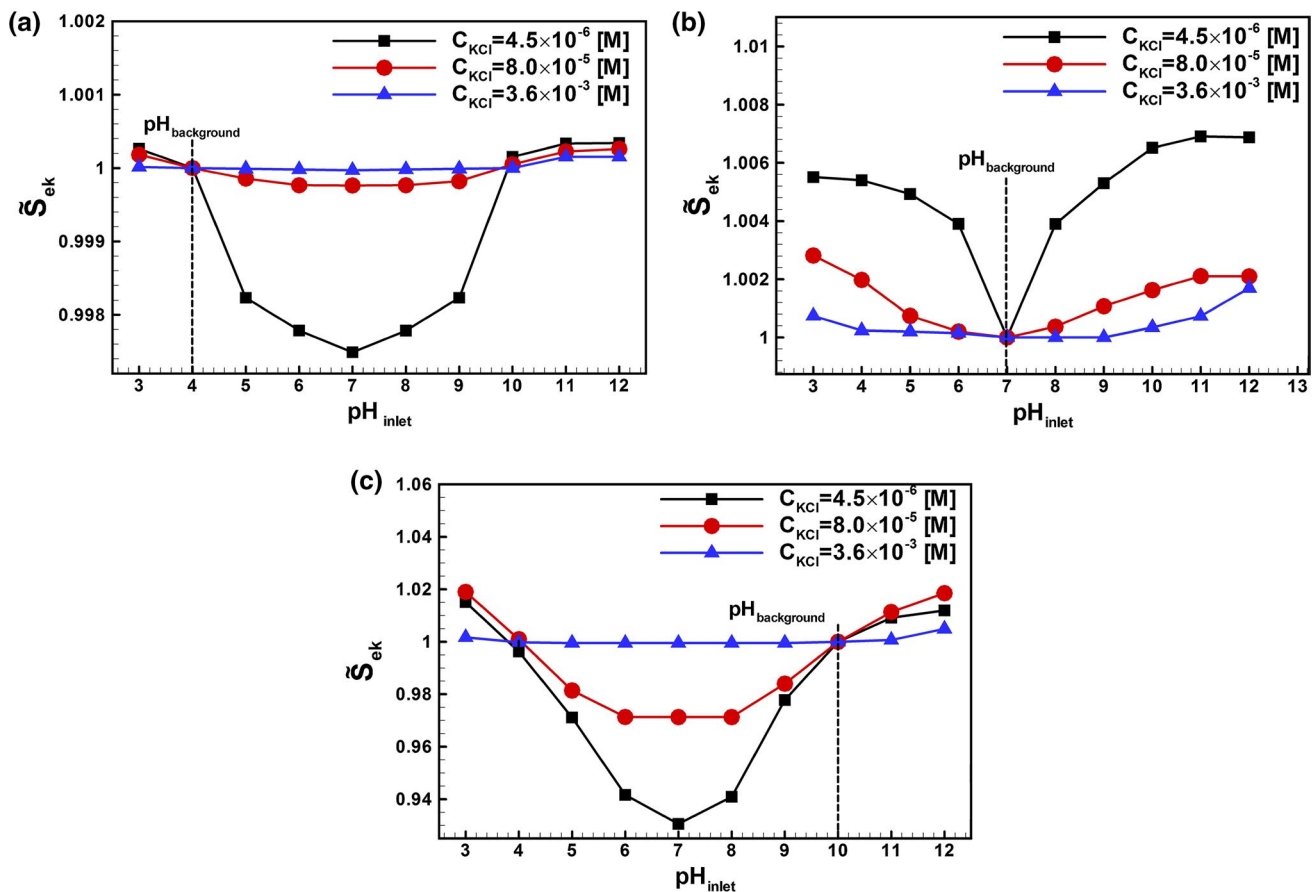


Fig. 7 The nanochannel electrical conductance normalized by the electrical conductance when $\text{pH}_{\text{inlet}} = \text{pH}_{\text{background}}$ which defined as $\tilde{S}_{\text{ek}}(\text{pH}_{\text{inlet}}, C_{\text{KCl}}) = S_{\text{ek}}(\text{pH}_{\text{inlet}}, C_{\text{KCl}}) / S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{pH}_{\text{background}}, C_{\text{KCl}})$. The background KCl concentration effects for when; **a** $\text{pH}_{\text{background}} = 4$ with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{pH}_{\text{background}}, C_{\text{KCl}})$ equal to 8.3848×10^{-3} , 9.7313×10^{-3} and 9.1786×10^{-2} [nS], **b** $\text{pH}_{\text{back-}}$

$\text{ground} = 7$ with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{pH}_{\text{background}}, C_{\text{KCl}})$ equal to 3.99×10^{-3} , 9.04×10^{-3} and 9.49×10^{-2} [nS], and **c** $\text{pH}_{\text{background}} = 10$ with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{pH}_{\text{background}}, C_{\text{KCl}})$ equal to 2.9013×10^{-2} , 3.13×10^{-2} and 1.1157×10^{-1} [nS] when each of the background solutions pH subjected to three background concentrations $C_{\text{KCl}} = 4.5 \times 10^{-6}$, 8.0×10^{-5} , and 3.6×10^{-3} [M]

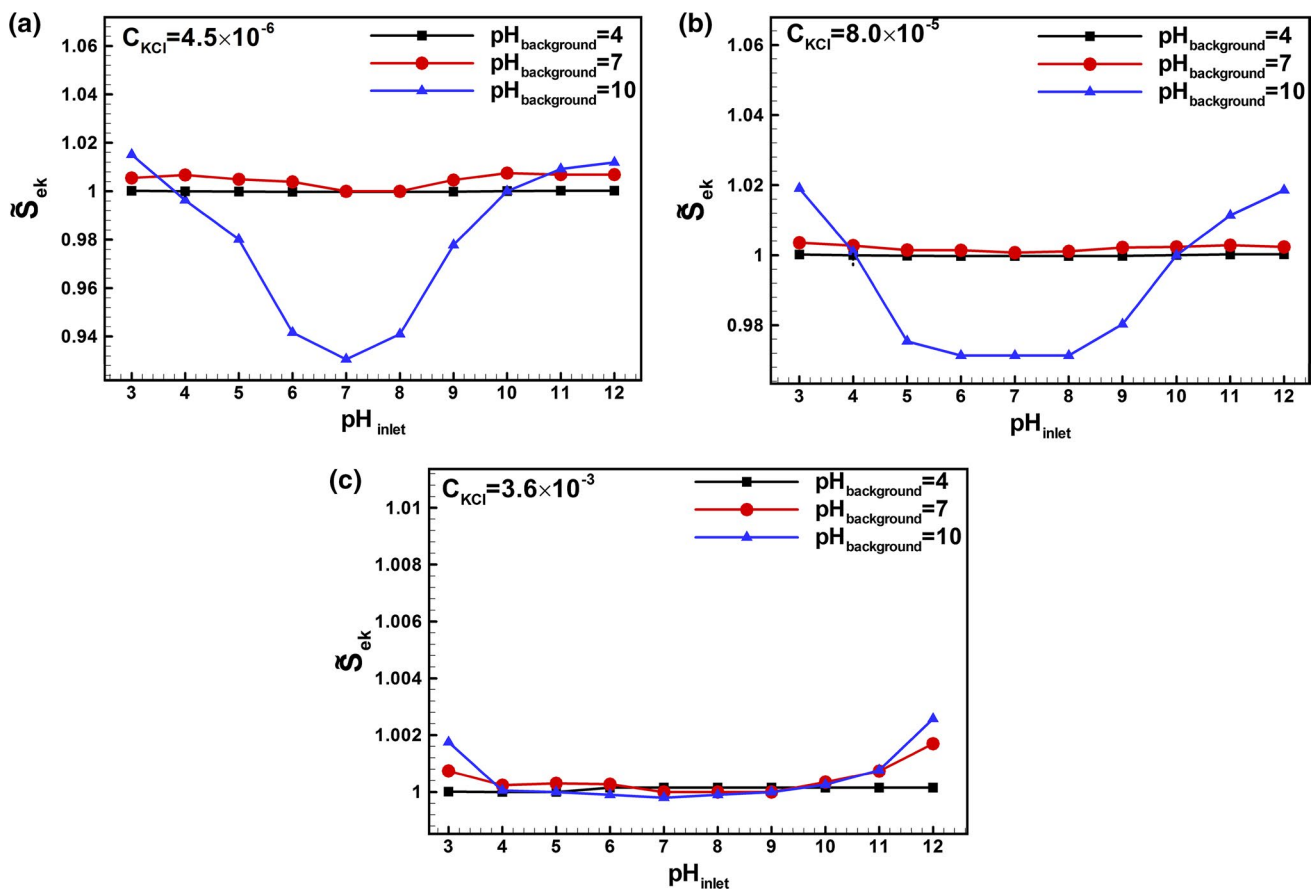


Fig. 8 The normalized electrical conductance defined similarly to what mentioned for Fig. 4, versus the inlet solution pH variations. The background pH effects for when; **a** $C_{\text{KCl}} = 4.5 \times 10^{-6}$ [M] with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{background}, C_{\text{KCl}})$ equal to 8.3848×10^{-3} , 3.99×10^{-3} and 2.9013×10^{-2} [nS], **b** $C_{\text{KCl}} = 8.0 \times 10^{-5}$ with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{background}, C_{\text{KCl}})$ equal to 9.73×10^{-3} , 9.04×10^{-3}

and 3.13×10^{-2} [nS], and **c** $C_{\text{KCl}} = 3.6 \times 10^{-3}$ [M] with $S_{\text{ek}}(\text{pH}_{\text{inlet}} = \text{background}, C_{\text{KCl}})$ equal to 9.17×10^{-2} , 9.49×10^{-2} and 1.1157×10^{-1} [nS] when each of the background solution subjected to three $\text{pH}_{\text{background}} = 4.0, 7.0$, and 10.0

which is changing as a function of pH_{inlet} . On the other hand, Fig. 8 illustrates the influence of the background solution pH on the $\tilde{S}_{\text{ek}}$, while the KCl concentration is kept unchanged. As expected, the electrical conductance of nanochannel behaves similarly to what mentioned for streaming conductance (Fig. 5). For $C_{\text{KCl}} = 3.6 \times 10^{-3}$ [M], similar to what concluded for $\tilde{S}_{\text{str}}$, it is found that the $\tilde{S}_{\text{ek}}$ is independent of the pH changes at the inlet.

Comparing the $\tilde{S}_{\text{ek}}$ with $\tilde{S}_{\text{str}}$ for ionic strength regimes with overlapped EDLs (Figs. 7a, b; 4a, b) revealed that the normalized electrical conductance for $\text{pH}_{\text{background}} = 4$ and 7 is roughly identical; however, the normalized streaming conductance for those background pH values differ significantly. Moreover, as expected, the electrical conductance shows less sensitivity to inlet solution pH variations compared with the streaming conductance.

5.2.2 Inlet pH variations effects on the surface charge density of nanochannel

As we expected, the surface charge density as a function of inlet pH for electrical conductance scenario (Fig. 9) has similar behavior with what presented for streaming conductance (Fig. 6). Our modeling results demonstrated that for the alkaline background solution, if we decrease the KCl concentration, the surface charge would be more sensitive to the variation of pH due to stronger EDLs interactions (Fig. 9c). The two surface charge density jumps are observed similar to what occurred for streaming conductance case. Unlike the alkaline and acidic background solutions, for neutral one, the normalized surface charge density for three background KCl concentrations would have rather identical amounts (Fig. 9b).

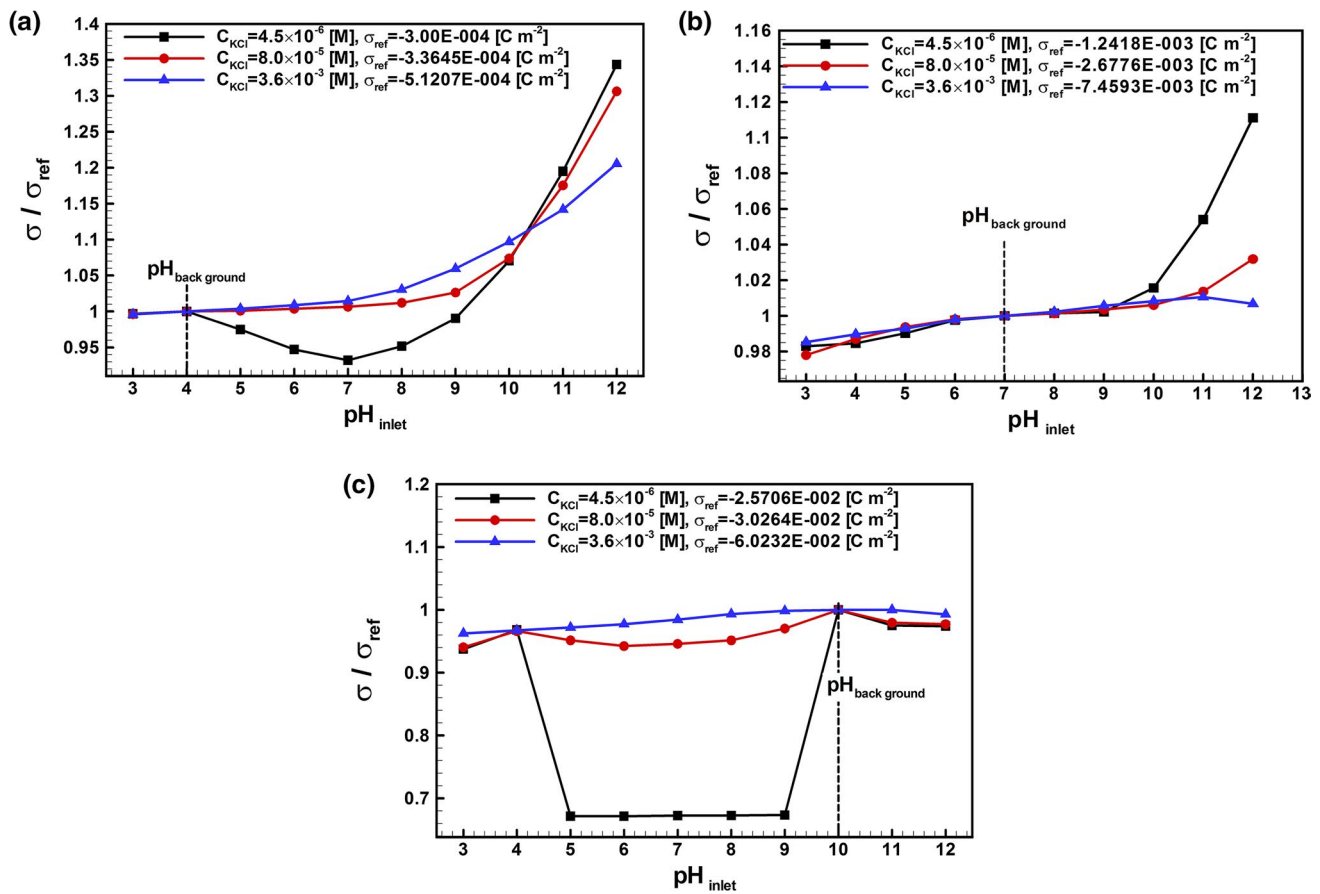


Fig. 9 The normalized surface charge density with the reference amounts which the solution pH at inlet and background are identical. The results have been shown for three different background solution pH and KCl concentrations

5.3 Electrokinetic conductance manipulation factors of the nanochannel

By evaluating the modeling results presented in Figs. 4, 5, 6, 7, 8 and 9, we can conclude that the normalized streaming and electrical conductance of nanochannel are depend on three main factors; (a) the background solution pH (b) the background solution KCl concentration, and (c) the pH of the solution at the inlet. Therefore, in this work, in order to characterize the nanochannel behavior for the aforementioned scenarios, two conductance factors are defined as follows:

$$SCF = \left| \frac{S_{str} - S_{str}^{pH_{inlet}=pH_{background}}}{S_{str}^{pH_{inlet}=pH_{background}}} \right| \times 100\%, \quad (32)$$

$$ECF = \left| \frac{S_{ek} - S_{ek}^{pH_{inlet}=pH_{background}}}{S_{ek}^{pH_{inlet}=pH_{background}}} \right| \times 100\%, \quad (33)$$

where the SCF and ECF represent the streaming conductance factor and electrical conductance factor of

nanochannel, respectively. These factors are defined to demonstrate how the electrical conductance of a nanochannel can be manipulated by the inlet and background solution properties.

Figure 10 illustrates the (a) SCF and (b) ECF as a function of inlet pH for different background solution scenarios. As shown in Fig. 10a, b, the conductance behavior of the nanochannel can be studied in three different pH regions ($pH_{inlet} < 4$, $pH_{inlet} > 10$ and $4 < pH_{inlet} < 10$). When $4 < pH_{inlet} < 10$, Fig. 10a, b indicates that for the alkaline background solution ($pH_{background} = 10$) and $C_{KCl} = 4.5 \times 10^{-6}$ [M] both streaming and electrical conductance factors (SCF and ECF) of the nanochannel are higher compared with other background solutions. It is interesting that for $4 < pH_{inlet} < 10$, the nanochannel has the highest conductance factor for the pH value of 7 due to overlapped EDLs and the acidic (or alkaline) environment. For this pH range, the solution with $C_{KCl} = 3.6 \times 10^{-3}$ [M], independent of the background solution pH, would not have a significant amount of SCF or ECF. For condition where $pH_{inlet} < 4$, Fig. 10a, b demonstrates that both SCF and ECF would be maximum when the background solution

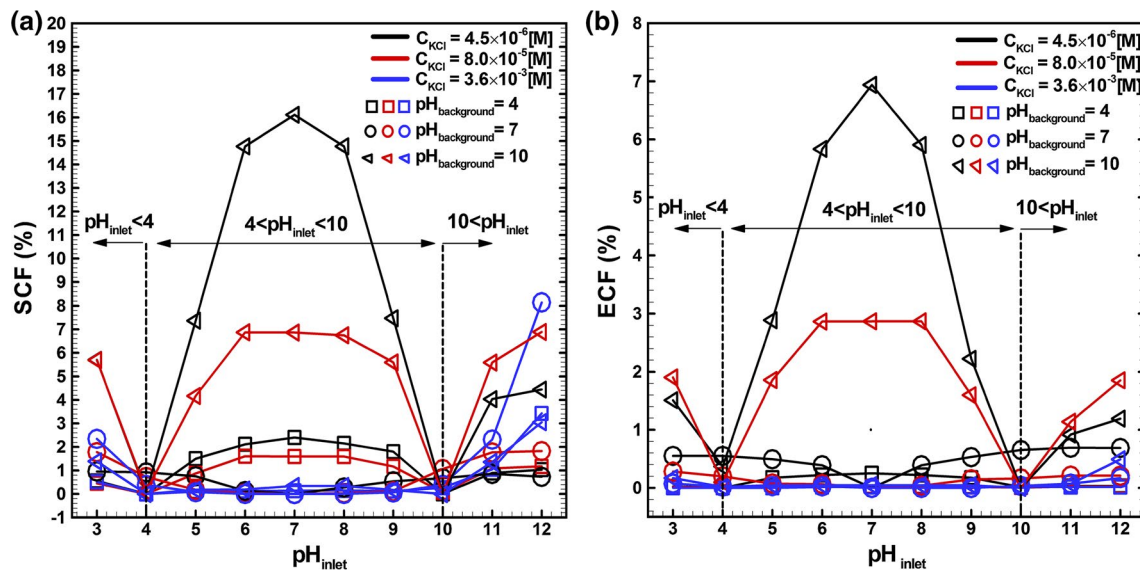


Fig. 10 **a** Streaming conductance factor (SCF) and **b** electrical conductance factor (ECF) of the nanochannel as a function of the inlet solution pH for three background solution properties. The black, red, and blue lines represent the background KCl concentration as

$C_{\text{KCl}} = 4.5 \times 10^{-6}$, 8.0×10^{-5} , and 3.6×10^{-3} [M], respectively. The square, circle, and left triangle symbols, regardless of their color, represent the background pH as $\text{pH}_{\text{background}} = 4$, 7, and 10, respectively (color figure online)

properties are $\text{pH}_{\text{background}} = 10$ and $C_{\text{KCl}} = 8.0 \times 10^{-5}$ [M]. As seen in Fig. 10, the SCF and ECF would be higher for $\text{pH}_{\text{background}} = 7$ compared with the acidic solution ($\text{pH}_{\text{background}} = 4$). For $\text{pH}_{\text{inlet}} > 10$, Fig. 10 shows a similar behavior with $\text{pH}_{\text{inlet}} < 4$ for both SCF and ECF.

6 Conclusions

We have demonstrated that by varying the pH of the solution at the inlet of a nanochannel, one can manipulate the electrokinetic conductance of a nanofluidic channel without any surface chemical modifications. The asymmetrical solution properties, which are imposed by different inlet solution pH, provide nonlinear responses of the nanochannel surface charge density and, as a result, of the nanochannel electrokinetic conductivity. However, the degree of nanochannel surface charge dependency to the inlet pH and as a result the electrokinetic conductivity is considerably influenced by the background solution properties. It is found that the neutral inlet solution ($\text{pH}_{\text{inlet}} = 7$) imposed the minimum electrokinetic conductance among the acidic or alkaline conditions. In addition, the minimum amount of the electrokinetic conductance for neutral inlet solution depends on the background solution acidity. By defining a conductance factor which characterized the manipulation of the electrokinetic conductivity of the nanochannel by inlet pH variations, it is revealed that a solution with alkaline background property, strong EDL interaction, and inlet pH range of

4–10 has the maximum ability of electrokinetic conductance manipulation. Our modeling results elucidate that the EDLs interaction plays a key role on the manipulation of the electrokinetic conductance of the nanochannel under asymmetrical solution conditions. In other words, one can implies that the strong EDLs interaction causes enhanced sensitivity of nanochannel electrokinetic conductance to the inlet pH. Our theoretical results propose that the solution pH variations at the inlet of nanofluidic devices could manipulate the nonlinear electrokinetic conductance of nanochannels, which may broaden potential applications in biomedical, energy and environmental systems.

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