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Role of Surface Chemistry in Nanoscale Electrokinetic Transport

by

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A Dissertation Submitted to the Faculty of Old Dominion University in Partial Fulfillment of the Requirements for the Degree of

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ABSTRACT

ROLE OF SURFACE CHEMISTRY IN NANOSCALE ELECTROKINETIC TRANSPORT

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This dissertation work presents the efforts to study the electrofluidics phenomena, with a focus on surface charge properties in nanoscale systems with the potential applications in imaging, energy conversion, ultrafiltration, DNA analysis/sequencing, DNA and protein transport, drug delivery, biological/chemical agent detection and micro/nano chip sensors.

Since the ion or molecular or particle transport and also liquid confinement in nanostructures are strongly dominated by the surface charge properties, in regards of the fundamental understanding of electrofluidics at nanoscale, we have used surface charge chemistry properties based on 2-pK charging mechanism. Using this mechanism, we theoretically and analytically showed the surface charge properties of silica nanoparticles as a function of their size, pH level and salt ionic strength of aqueous solution. For a fixed particle size, the magnitude of the surface charge typically increases with an increase in pH or background salt concentration. Furthermore, we investigated the surface charge properties of a charged dielectric nanoparticle and flat wall in electrostatic interactions. According to the theoretical results strong interactions cause a non-uniform surface charge density on the nanoparticle and the plate as a result of the enhancement of proton concentration in the gap between the particle and the plate. This effect increases with decreased separation distance (xh). We moreover investigated the ion confinement inside the nanospaces and using a continuum model, we showed the proton enhancement in extended nanochannels. The proton enrichment at the center of the nanochannel is significant when the bulk pH is medium high and the salt concentration is relatively low.

The results gathered are informative for the development of biomimetic nanofluidic apparatuses and the interpretation of relevant experimental data.

Later, we have developed an analytical model for electroosmotic ion transport inside pH-regulated nanoslits and compared the results with the numerical study. We showed the influences of background salt concentration, pH level and the length of nanoslit on EOF velocity. The predictions show that the EOF velocity increases first and then decrease with background salt concentration increasing and the EOF velocity increases with pH level of aqueous solution. To my parents

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Finally, I would like to give my deepest thanks to my family for their endless support and their faith. You are the real MVPs!

NOMENCLATURE

The variables and parameters used in this dissertation

Variables	Description
C ₀	Bulk concentration of cations and anions
$C_{,0}, C_{,}^{*}$	Bulk concentration of the i th ion
C _{KCl}	Bulk Salt Concentration
e	Charge of an electron
Di	Ionic Diffusivity of the i th ion
Ε	Applied Electric Field
F	Faraday Constant
K_{A}, K_{B}	Equilibrium constants of dissociation actions
Ν	Total number of ionic species
N _{Total}	Total number of the site functional groups
p	Pressure of the environments
рН	pH level of aqueous solution
R	Gas Constant
Re	Reynolds Number
Τ	Absolute temperature
и	Fluid velocity
V	Potential bias across the nanochannel
Zi	Valence electron number of the i th ion.
ε_{0}	Absolute permittivity in the vacuum

Variables	Description
\mathcal{E}_{f}	Relative permittivity of the fluid
ρ	Fluid Density
$ ho_f$	Space charge density inside the fluid
ψ, φ	Electric potential distribution
ψ_s	Surface electrical potential
Ψ_d	Zeta potential
ψ_c	Central electrical potential
κ, λ_D	Debye Length parameter
μ	Dynamic Viscosity of the fluid
σ_{s}	Surface charge density
Γ	Surface site density

TABLE OF CONTENTS

CHAPTER	1
1. INTRO	DUCTION
1.1 Ele	ctrokinetic Phenomena in Modern Science1
1.2 Bas	sics of Electrokinetics
1.2.1	Origin of Interfacial Charge
1.3 Ele	ctric Double Layer (EDL)
1.3.1	Helmholtz Model
1.3.2	Gouy-Chapman Model
1.3.3	Gouy-Chapman-Stern Model7
1.4 Pot	ential Distribution of Electric Double Layer for Flat Surfaces
1.4.1	The Boltzmann Distribution9
1.4.2	Debye-Hückel Approximation
1.4.3	Gouy-Chapman Approximation
1.5 Pot	ential for Curved Electric Double Layer
1.6 Fur	ndamental Transport Equations15
1.6.1	Convective-Diffusion-Migration Equation 16
1.6.2	Continuity Equation 17
1.7 Ele	ctrokinetic Phenomena 18
1.7.1	Electroosmosis 18
1.7.2	Streaming Current and Potential 19
1.8 Org	ganization of this Dissertation
CHAPTER	2
2 SIZE NANOPAR	DEPENDENT SURFACE CHARGE PROPERTIES OF SILICA TICLES
2.1 Inti	roduction
2.2 Ma	thematical Model
2.3 Res	sults and Discussion
2.3.1	Size Dependent Surface Charge Properties: pH Effect
2.3.2 Effect	Size Dependent Surface Charge Properties: Background Salt Concentration 35

2.4	Conclusions	40
CHAP	TER 3	
3 AN 41	NALYTICAL MODEL FOR CHARGE PROPERTIES OF SILICA PARTIC	CLES
3.1	Introduction	41
3.2	Mathematical Model	42
3.3	Results and Discussion	46
3.4	Conclusions	53
CHAP	TER 4	
4 SU SUBST	JRFACE CHARGE OF A NANOPARTICLE INTERACTING WITH A I	FLAT 54
4.1	Introduction	54
4.2	Mathematical Model	56
4.3	Numerical Implementation and Code Validation	61
4.4	Results and Discussion	64
4.4	4.1 Salt Concentration Effect	64
4.4	4.2 The Effect of pH level of the aqueous solution	72
4.5	Conclusions	75
CHAP	TER 5	
5 PF	ROTON ENHANCEMENT IN AN EXTENDED NANOCHANNEL	76
5.1	Introduction	76
5.2	Mathematical model	78
5.3	Results and Discussion	82
5	3.1 Verification by experimental data	83
5.:	3.2 Effect of background solution properties	85
5.3	3.3 Effect of nanochannel dimensions	93
5.4	Conclusions	94
CHAP	TER 6	
6 El	LECTROOSMOTIC FLOW IN A pH-REGULATED NANOSLIT	96
6.1	Introduction	96
6.2	Mathematical Model	98

х

6.3	Analytical model of overlapped EOF	
6.4	Results and Discussion	
6.4	1 Model Validation	
6.4	2 The influence of the background solution properties	
6.4	.3 Effect of Nanoslit Length	
6.5	Conclusion	
СНАРТ	`ER 7	
7 CO	NCLUSIONS AND FUTURE RESEARCH	
7.1	Conclusions	
7.2	Future Research	
REFER	ENCES	126

LIST OF FIGURES

.

Figure 1.1. Schematic illustration of free silanol groups, counter and co-ions
Figure 1.2. Ion distribution and corresponding potential profile for Helmholtz model 6
Figure 1.3. Ion distribution and corresponding potential profile for Gouy-Chapman model
within diffuse layer
Figure 1.4. Ion distributions and the corresponding potential profile in Gouy-Chapman-
Stern model
Figure 1.5. Potential distribution near a charged flat surface
Figure 1.6. Normalized potential distribution near a charged flat surface according to the
Debye-Hückel approximation. Curves presents for the three different concentrations. Solid
squares represent the values of κ^{-1} corresponding to each concentration
Figure 1.7. Schematic illustration of diffuse double layer for a nanoparticle with diameter
D _p 14
Figure 1.8. Normalized electric potentials as a function of kr for various diameter
nanoparticles and flat wall surface15
Figure 1.9. Electroosmotic flow in a nanochannel
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a)
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a)
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a) 25 Figure 2.2. (a) The free triangular mesh used in simulation domain is illustrated. (b) A very
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a) 25 Figure 2.2. (a) The free triangular mesh used in simulation domain is illustrated. (b) A very fine mesh is used on the surface of nanoparticle and also within the EDL
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a) 25 Figure 2.2. (a) The free triangular mesh used in simulation domain is illustrated. (b) A very fine mesh is used on the surface of nanoparticle and also within the EDL
Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a) 25 Figure 2.2. (a) The free triangular mesh used in simulation domain is illustrated. (b) A very fine mesh is used on the surface of nanoparticle and also within the EDL

Figure 2.4. Surface charge density of silica nanoparticles of different sizes as a function of
pH in 1 mM (a) and 100mM (b) KCl solutions
Figure 2.5. Normalized surface charge density as a function of pH in 1mM (a) and 100mM
(b) KCl solutions
Figure 2.6. Normalized surface concentration of $[H^+]$ ions as a function of pH at $C_{KCI}=1$
mM. Normalization is done using the surface concentration of $[H^+]$ ions of a flat surface at
a given pH
Figure 2.7. Surface concentrations of H^+ ions (a) and K^+ ions (b) as a function of C_{KCI} for
different particle sizes at a pH=6.5
Figure 2.8. Normalized surface concentration of H ⁺ ions as a function of particle diameter
for various background salt concentrations at pH=6.5
Figure 2.9. Normalized surface charge density as a function of particle diameter for various
background salt concentrations at pH=6.5
Figure 2.10. Normalized surface charge density as a function of the ratio of EDL thickness
to the particle diameter. Different shapes demonstrate different pH values, while different
colors show different salt concentrations. (Blue =1mM, yellow=10mM and red=100mM)
Figure 3.1. Surface charge density of silica particle with radius $R_p=58$ nm as a function of
pH in 1, 10, and 100 mM NaCl solutions. Lines presents the approximation solution results
using $N_{total}=2\times10^{-6}$ mol/m ² , pK _A =6.38, and pK _B =1.87, and filled symbols are the
experimental results [177], and empty ones presents the numerical result where spheres,
triangles and squares present 1, 10 and 100 mM, respectively

Figure 3.2 Surface charge density of a silica nanoparticle with Rp=20 nm as functions of
pH and salt concentration, C _{NaCl}
Figure 3.3. Zeta potential of a silica nanoparticle with Rp=20 nm as functions of pH and
salt concentration, C _{NaCl}
Figure 3.4. Normalized surface charge density of a silica nanoparticle for various radius
size and pH levels when C _{NaCl} =1 mM51
Figure 3.5. Normalized surface charge density of a silica nanoparticle for various radius
size and salt concentration C _{NaCl} at pH=5.5
Figure 4.1. Schematics of a spherical silica nanoparticle interacting with a flat silica plate
immersed in an electrolyte solution containing K^+ , H^+ , Cl^- and OH^- ionic species
Figure 4.2. Free quadratic triangular-type mesh with finer on the charge regulated surfaces
is used on axial-symmetric simulation domain58
Figure 4.3. Surface charge densities of a silica nanoparticle (a) and a planar silica plate as
a function of pH of the electrolyte solution. Circles and line in (a) represent, respectively,
the experimental data from Sonnefeld et al. [177] and the numerical results. Circles and
line in (b) are, respectively, the numerical results and the analytical results derived by Yeh
et al. [209]63
Figure 4.4. Distribution of the electric potential around the nanoparticle interacting with a
flat surface at different kh and pH. Color bars denote the electric potential in Volts 65
Figure 4.5. Surface charge densities along the nanoparticle surface (lines without symbols)
and the flat plate (lines with symbols) at pH=4 (a), 5.5 (b) and 9 (c)67
Figure 4.6. Spatial variation of the normalized surface charge density on nanoparticle (a)
and flat plate (b) for different kh and fixed pH=5.5

Figure 4.7. Spatial distribution of H^+ ion concentration (in mM) near the nanoparticle for
different κh values and pH= 5.568
Figure 4.8. (a) H^+ ion concentration on the particle's top pole (square with dashed line),
and on the particle's bottom pole (circle with solid line). (b) H^+ ion concentration on the
plate at r=0 (solid line with circles) and $r \rightarrow \infty$ (square with dashed line)
Figure 4.9. Ratio of the surface charge density difference at the top and bottom poles of the
particle to the surface charge density at the top pole as a function of kh for different pH
values
Figure 4.10. (a) Surface charge density at the bottom pole of the nanoparticle as a function
of pH for $\kappa h=0.5$, 1.6, and 5. (b) Surface charge density on the bottom pole of the
nanoparticle normalized by that at $\kappa h \rightarrow \infty$ as a function of pH for three different κh values.
Figure 4.11. Concentration of H^+ ions at the bottom pole of the particle normalized by that
at $\kappa h \rightarrow \infty$ as a function of pH for different κh values
Figure 5.1. Schematic illustration of the 3D simulation domain with pH regulated silica
nanochannel
Figure 5.2. The free tetrahedral type mesh used in the simulation with finer near EDL
region
Figure 5.3. Distribution of pH averaged in the height direction, \overline{pH} , at the center of the
extended nanochannel for various $C_{\rm KCl}$. Symbols with error bars: experimental data of
Kazoe et al.[94] at $W = 410$ nm, $H = 405$ nm, $L = 1 \ \mu m$, and $pH = 6.22$; solid lines:

present numerical results at $pK_a = 7$, $pK_b = 1.9$, and $N_i = 6.31 \times 10^{-6} \text{ mol/m}^2$; dotted line:
bulk pH = 6.22
Figure 5.4. The electric potential contour plots in a nanochannel when $z=0$ for different pH
and salt concentration strengths
Figure 5.5. Distribution of surface charge density along the wall of nanochannel with
different pH and salt concentration levels. Straight, dash and dash-dot lines presents pH =
4, 7 and 9, respectively
Figure 5.6. Contour plot of proton distribution in a nanochannel at $z=0$ for different
background solution properties
Figure 5.7. Distribution of the ERP of protons, $\Delta = \left(\left \overline{pH} - pH \right / pH \right) \times 100\%$, for various
$C_{\rm KCl}$ at the bulk pH = 7.5, (a), and for various bulk pH at $C_{\rm KCl}$ = 0.001 M, (b)
Figure 5.8. Variations of the ERP of protons at the center of the extended nanochannel,
$\Delta_{c} = \left(\left \overline{pH}_{c} - pH \right / pH \right) \times 100\%$, with the bulk pH for various C_{KCI} , (a), and with C_{KCI} for various
bulk pH, (b). Other parameters are the same as those in Figure 5.3
Figure 5.9. Variations of the ERP of protons at the center of the extended nanochannel,
$\Delta_c = (\overline{pH}_c - pH /pH) \times 100\%$, with the nanochannel dimension ($H = W$) for various bulk pH
at $C_{\rm KCl} = 0.0001 {\rm M}$
Figure 6.1. Schematic illustration of the EOF within a pH-regulated nanoslit with electric
double layers overlapping, and containing multiple ionic species, Na^+ , Cl^- , H^+ , and
OH ⁻

Figure 6.2. Two dimensional numerical simulations are performed with a flow domain composed of two reservoirs connected with a single nanochannel. The junction of the reservoir and nanochannel is zoomed for detailed look at the mesh type. 109 Figure 6.3. Electroosmotic volume flow rate (Q) varying with nanoslit height H at a constant electric field (0.05V). The length and width of the nanoslit are $L = 3.5 \,\mu m$ and $W = 44 \ \mu m$, and the bulk salt concentration of NaCl is 0.16644 M with pH = 7. Rectangular symbols are experimental data of Zheng et al. [220], and solid line and circles present multi-ion analytical model and numerical results with $pK_a = 7$, $pK_b = 1.9$, and Figure 6.4. EOF velocity profile along height of nanoslit H at various NaCl background salt concentrations $C_{\text{NaCl}}(1, 10, 100, \text{ and } 1000 \text{ mM})$ for pH = 4, pH = 6, and pH = 8 when L/H = 100. The straight line presents 1 and 1000 mM, respectively, and the dash lines presents 10 and 100 mM cases. For numerical results, red squares 1 mM, blue spheres 10 mM, and green triangles 100 mM case, purple diamond symbols presents 1000 mM... 112 Figure 6.5. Average EOF velocity with respect to various concentration and pH levels when Figure 6.6. EOF velocity profile along the height of the nanoslit H at various length height ratios (L/H) with $C_{\text{NaCl}} = 1 \text{ mM}$ and 100 mM for pH = 4 and 7. Spheres, diamonds and triangles presents L/H= 100, 10 and 5, respectively, and the straight line presents the

Figure 6.7. Spatial distribution of the cross-sectional averaged electric field (a) and concentrations of mobile counter ions (b) along the nanoslit length at various L/H values

CHAPTER 1

INTRODUCTION

1.1 Electrokinetic Phenomena in Modern Science

The field of nanofluidics has developed recently as a result of the developments in materials synthesis and nanofabrication techniques [51, 192]. These innovations are leading scientists to create the fluidic systems with a reduced characteristic length scale to the nanometer range. This range of fluidic devices reveals new physics that has never been realized in conventional systems (microfluidic systems) such as non-conventional molecular transport [44], nanocapillarity [194], entropic trapping for DNA [69] and proteins separation [81], ion selectivity [108], and ionic concentration polarization (ICP) [97], and also many unique fluid properties were found such as the viscosity [70, 110, 145, 150], diffusion coefficient of ions [51, 145] and macromolecules [57, 180], dielectric constant [39, 70], enzyme reaction rate [187], dissociation of silanol (SiOH) group [149], vapor pressure [136], electric conductivity [190], the flow rate of water [107], proton mobility [135], and hydrogen ion concentration [94]. These scientific contributions may lead to technological breakthroughs from a fundamental view in the field of nanotechnology, such as nanofluidic transistors [92, 206], single DNA digestion mapping [161], nanoparticle [60] and molecular level separation [73], and water purification [96]. These application areas showed a superior performance compared to bulk-scale operations, such as higher speed, smaller sample, easier operation, higher functionality, and more compact instruments.

Since the dimension of the channel space is about nanometer regime, the behavior of the fluid and ions may be very different than those in bulk due to confinement and surface effects. When the size of the electric double layer (EDL) (1-100 nm) is comparable with the channels 10-100 nm in height, the effects of EDL, i.e., a classical model of solid-liquid interfaces, significantly exerts. The EDL is formed due to the presence of trapped charges as a result of dissociation of ionizable groups or adsorption/reaction of ions at the liquid/solid interface. The surface charges are screened by the accumulation of counterions near the surface, forming a compact and diffuse layer. When the EDL thickness is comparable to the channel height, an overlap of EDLs occurs and thus the local surface, ion, and fluid properties show different behavior than the bulk-scale physics. Even though EDL is a function of surface material, the ionic strength and the pH level of the solution, it is crucial to control EDL properties in order to have a unique and adjustable ionic transportation using nanofluidic devices based on the geometry of the nanochannel, as well as various surface charge densities by changing the nanochannel material. Although the performance of the nanofluidics devices depend on the surface charge properties, many existing studies were assumed to remain constants even the conditions of strong EDL overlaps [3, 44, 72, 89, 124, 175]. The theories (i.e. DLVO theory [48, 84, 141, 198-199]) that developed to predict to surface charge density also assumes a uniform charge distribution of the interaction surfaces [23-24, 26-28, 35, 46, 50, 52, 58, 82, 106, 112, 131, 134, 139, 146, 151, 164, 196, 200, 204, 222-223]. Therefore, the understanding of electrokinetic properties of ion transport and liquid confinement in nanochannel are important aspects, not only from fundamental perspectives but also for the development of next-generation various actuation and sensing tools in the areas of science, analytical chemistry and healthcare.

1.2 Basics of Electrokinetics

1.2.1 Origin of Interfacial Charge

When a solid substrate immerges into an aqueous medium (e.g. KCl in water), spontaneously an electric charge [83] develops on the surface due to several mechanisms. The most relevant ones to electrokinetic fields are ionization of surface groups or adsorption of ions, as shown in Figure 1.1.



Figure 1.1. Schematic illustration of free silanol groups, counter and co-ions.

Ionization of Surface Groups: Many substrate surfaces contain acidic groups, and owing to reactivities of surface groups (oxides, carboxylic acids, and amino groups), their dissociation gives rise to a negatively charged surface. Silica micro/nano devices can be given as a particularly well-studied example. In silica substrate, silanol groups on the surface can be deprotonated in aqueous solutions by leaving a negative surface charge:

$$\text{SiOH} \xleftarrow{k_A} \text{SiO}^- + \text{H}^+$$
 (1.1)

$$\text{SiOH}_{2}^{+} \xleftarrow{K_{B}} \text{SiOH}_{H}^{+}$$
 (1.2)

where K_A and K_B are the equilibrium constants of the reaction. The magnitude of the surface charge depends on the surface chemistry, acidic and basic strength of the surface groups and salt concentration of aqueous solution [6, 77, 180]. Other materials such as SiN_x, Al₂O₃, BN, and the carboxylate-modified surfaces also have surface charges when immersed in solution due to the same physical reasons.

The surface charge density can be basically described as

$$\sigma_s = \sum_{i} z_i e / A \tag{1.3}$$

in which z_i is the valence electron number, e is the charge of an electron, and A is the surface area.

1.3 Electric Double Layer (EDL)

The developed surface charge and the mobile electrolyte ions inside the aqueous solution further interacts with coulomb forces and the counter-ions that have the opposite charge to the substrate surface, approach to the surface in order to neutralize it. However, the thermal Brownian motion of these ions prevents the accumulation of counter ions so that the ions keep their formation on the surface. This structure is called as electric double layer (EDL). The EDL is formed in two layers, one of them is composed of the surface charges and other one is composed of ions attached to the surface charge via the Coulomb force. The sum of the all charges (counter-ion, co-ion and charged surface) within these layers is zero.

There are several theoretical models of EDL:

1.3.1 Helmholtz Model

The earliest EDL model was studied by Helmholtz in 1853. This model considers that the surface charge is fully neutralized by a single layer of counter-ions at a metal-electrolyte interface, as illustrated in Figure 1.2. All the counter-ions are formed within a compact mono-layer on the surface that is limited by a radius of the ion. The potential has a linear drop within this distance. This model cannot explain the real physical behavior of nature.



Figure 1.2. Ion distribution and corresponding potential profile for Helmholtz model.

1.3.2 Gouy-Chapman Model

Gouy and Chapman [34] developed a more sophisticated model by considering the counter and co-ion distribution from the interface, which is called diffuse layer of the EDL, as shown in Figure 1.3. The ion distribution obeys the Boltzmann energy distribution law and the diffusion of point charge ions are given by Fick's law. The Gouy-Chapman model is still not an accurate picture of nature. This model considers that ions behave as a point charge and can approach to the surface indefinitely, meaning that it overestimates the EDL thickness.



Figure 1.3. Ion distribution and corresponding potential profile for Gouy-Chapman model within diffuse layer.

1.3.3 Gouy-Chapman-Stern Model

Neither of these approaches alone predicted exact physical behaviors until Stern did in 1924. Stern introduced an additional layer (immobile layer), which consists of adsorbed and partially absorbed ions, which acts like a capacitor and adsorbs a significant part of potential at the solid/liquid interface. The Stern layer is formed by two inner layers: inner (IHP) and outer (OHP) Helmholtz layers, as shown in Figure 1.4. The ions in the inner Helmholtz layer are non-hydrated positive and negative ions: however, the outer Helmholtz layer is made of only hydrated counter-ions. The thickness of these regions is on the order of one or two hydrated ions.

The interface of OHP and the diffuse layer is referred as the slip plane (or shear plane), and it bears the zeta potential (ζ). In the diffuse layer, Stern used the Gouy–Chapman diffusive theory to describe the counter-ion distribution away from the immobile layer.

Within the Stern layer the potential of IHP becomes higher than OHP; it is due to the fact that the surfactant co-ions are adsorbed to the interface, as shown in Figure 1.4. The potential later decreases by decreasing the total number of ions within OHP, and within the diffuse layer, the Gouy-Chapman model takes places and exponentially approaches to zero voltage.



Figure 1.4. Ion distributions and the corresponding potential profile in Gouy-Chapman-Stern model.

1.4 Potential Distribution of Electric Double Layer for Flat Surfaces

1.4.1 The Boltzmann Distribution

In order to relate the ionic spatial distribution in the diffuse electric double layer to surface potential, the Boltzmann distribution is derived using the thermodynamics probability law, which states that the probability of an isolated system taking a thermodynamic equilibrium state with an energy W is proportional to $\exp(-W/k_BT)$, where T is the absolute temperature and k_B is the Boltzmann constant.

Suppose that a charged surface immersed in a liquid contains N type of ionic species with valence number z_i and the bulk concentration C_i^{∞} and based on the electroneutrality condition where $\psi = 0$, one can evaluate:

$$\sum_{i=1}^{N} z_i C_i^{\infty} = 0$$
 (1.4)

The bulk solution is electrically neutral at positions infinitely far away from the charged solid surface. Therefore, the probability density of finding an ion at location x can be written as:

$$C_{i} = C_{i}^{\infty} \exp(-\frac{z_{i} F \psi}{RT})$$
(1.5)

where C_i^{∞} is the ionic number concentration at the neutral state where $\psi = 0$ and C_i is the ionic number concentration of the *i*th ionic species at the state where the electric potential is ψ ; F, R, T are the Faraday constant, universal gas constant and absolute temperature, respectively. The objective here is to obtain an analytical expression for the distribution of potential and ion concentrations due to the presence of a charged surface in a dielectric medium having free charge. The Poisson equation is given by:

$$-\varepsilon_f \varepsilon_0 \nabla^2 \psi = \rho_f \tag{1.6}$$

The space charge density of the mobile ions, ρ_f can be written in terms of the number of concentrations of the ions and the corresponding valences as:

$$\rho_f = \sum_{i=1}^{N} F z_i C_i \tag{1.7}$$

where C_i is the ionic number concentration of the *i*th ionic species, Z_i is the valence of the *i*th ionic species, F is the Faraday constant and N is the number of ionic species in the electrolyte solution. If we substitute the Boltzmann distribution (Eq. (1.5)) into the given Poisson equation (Eq. (1.6)), it leads to the well-known Poisson-Boltzmann equation:

$$-\varepsilon_f \varepsilon_0 \frac{d^2 \psi}{dx^2} = \sum_{i=1}^N F z_i C_i^\infty \exp(-\frac{z_i F \psi}{RT})$$
(1.8)

The Poisson-Boltzmann equation defines the electric potential distribution in the diffuse ionic layer adjacent to a charged surface subject to appropriate boundary conditions: x=0, $\psi = \psi_s$ and $x \to \infty$, $\psi = 0$, where ψ_s is the surface potential at x=0, one can derive the following equation:

$$\psi = 2\ln\left[\frac{1 + \exp(-\kappa x) \tanh(\psi_s / 4)}{1 - \exp(-\kappa x) \tanh(\psi_s / 4)}\right]$$
(1.9)

where $\kappa^{-1} = \lambda_D = \operatorname{sqrt}(\varepsilon_0 \varepsilon_f RT / \sum_{i=1}^{4} F^2 z_i^2 C_i^{\infty})$. The Debye length, κ^{-1} , is a measure of electric double layer thickness and is a property of electrolyte solution. Typically, the Debye length represents a characteristic distance from the charged surface to a point where the electric potential decays to approximately 33% of the surface potential.

Figure 1.5 illustrates the solution of Eq. (1.9) when surface potential equals $\Psi = \Psi_s$. The potential exponentially decreases and reaches its bulk value in the diffuse layer where the counter ion and co-ion numbers are equal to each other.



Figure 1.5. Potential distribution near a charged flat surface.

1.4.2 Debye-Hückel Approximation

Debye-Hückel model is valid when the surface potential is very small, $\psi_s \ll 25 \text{ mV}$, and one can approximate the Poisson-Boltzmann (PB) equation for a planar surface as:

$$\frac{d^2\psi}{dx^2} = \frac{2z^2 e^2 n_{\infty}}{\varepsilon_f \varepsilon_0 k_B T} \psi = \kappa^2 \psi$$
(1.10)

The solution of the linearized PB equation for different salt concentrations is illustrated in Figure 1.6. The figure indicates that the potential decays exponentially as one moves away from the charged surface. Since the each concentration level has a different Debye length, κ^{-1} , the decay length of the potential distribution is longer for low salt ionic concentrations. Solid red squares shows the calculated characteristic length of κ^{-1} where it reaches the 33% percent of surface potential.



Figure 1.6. Normalized potential distribution near a charged flat surface according to the Debye-Hückel approximation. Curves presents for the three different concentrations. Solid squares represent the values of κ^{-1} corresponding to each concentration.

1.4.3 Gouy-Chapman Approximation

Under the assumption of a symmetrical electrolyte where the valence of the co-ion is equal to the valence of the counter-ion $(|z^+| = |z^-| = z)$, the Gouy-Chapman equation is obtained as

$$\tanh\left(\frac{zF\psi(x)}{4RT}\right) = \tanh\left(\frac{zF\psi_s}{4RT}\right)\exp(-\kappa x) \tag{1.11}$$

This approximation reduces to

$$\psi(y) = \psi_s \exp(-\kappa y) \tag{1.12}$$

The Gouy-Chapman potential distribution also exponentially decreases to bulk potential value within the Debye length (κ^{-1}) once the surface potential (Ψ_s) is known.

1.5 Potential for Curved Electric Double Layer

The equations in spherical coordinate for the diffuse double layers near curved surfaces are more difficult to solve comparing to the case of planar diffuse double layers, as shown in Figure 1.7. The presence of electric double layer (EDL) on the nanoparticle surface, in fact, it can be important to investigate curvature effect for nanoparticles. The corresponding Poisson-Boltzmann (PB) equation in spherical coordinates,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{2ezn_{\infty}}{\varepsilon}\sinh(\frac{ze\psi}{k_BT})$$
(1.13)

has analytical solution for low surface potentials (<25mV) and thin EDL thickness.



Figure 1.7. Schematic illustration of diffuse double layer for a nanoparticle with diameter D_{p} .

The results of analytical solutions are shown in Figure 1.8. The normalized electric potential variations away from the surface are plotted for different diameter nanoparticles as a function κr values. The flat wall normalized electric potential and 100 nm diameter particle decay to the bulk potential at $\kappa r = 4.5$. However, as the diameter decreases, the decaying distance to the bulk potential decreases. For the particle with 2 nm diameter, the curvature effect is significant, as there is a large departure from the planar surface. This is attributed to the fact that the surface potential of the nanoparticle gets higher than the flat wall surfaces.



Figure 1.8. Normalized electric potentials as a function of κr for various diameter nanoparticles and flat wall surface.

1.6 Fundamental Transport Equations

When a fluid contains an electrolyte, *i.e.*, ionic species, we are interested in the movement or mass transfer of the anions and the cations as well as the bulk fluid. To this end, mass transfer in an electrolytic solution requires a description of the movement of mobile ionic species, material balances, current flow, electroneutrality, and fluid mechanics.

Although the majority of the analyses of electrokinetic processes are based on the Boltzmann distribution, the situations where the system is not in equilibrium may not be satisfied by using Boltzmann distribution. However, the ion distribution near the solidliquid interface will not significantly deviate from the Boltzmann distribution unless high speed flows are involved (e.g., Re > 10). In the cases of very low speed flows, the applicability of the Boltzmann distribution is still as a good approximation.

1.6.1 Convective-Diffusion-Migration Equation

Consider a differential volume element in a flowing electrolyte solution. At a steady state without chemical reaction, the conservation of ion species requires the divergence of the mass fluxes to be zero.

$$\nabla \cdot \mathbf{j}_i = 0 \tag{1.14}$$

Where \mathbf{j}_i is the flux density of the ith species, which is a vectoral quantity. Using the Nernst-Planck equation, we have

$$\mathbf{j}_i = \mathbf{u}c_i - D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \psi$$
(1.15)

where z_i , c_i , and D_i , are the flux density, valence, molar concentration, and diffusivity of the *i*th ionic species, respectively. The right hand side terms are the fluxes due to bulk convection, the concentration difference and migration in an electric field, respectively. If the flow velocity is very low, the first term can be neglected.

$$\nabla^2 c_i + \nabla \cdot \left(\frac{Fc_i}{RT} \nabla \psi\right) = 0 \tag{1.16}$$

From Eq. (1.16), one can easily derive the Boltzmann distribution using appropriate boundary conditions. This implies that EDL is independent of the flow field if there is no EDL overlap.

1.6.2 Continuity Equation

When the fluid density is independent of time and space, steady incompressible flow the mass conservation equation becomes

$$\nabla \cdot \mathbf{n} = 0 \tag{1.17}$$

which concludes that the divergence of the velocity field is zero everywhere for an incompressible fluid.

The fluid flow of a single-component system under laminar flow conditions with incompressible homogenous Newtonian fluids is governed by the momentum conservation equation and is given by the Stokes equation.

$$-\nabla \mathbf{p} + \mu \nabla^2 \mathbf{u} - \rho_e \nabla \psi = 0 \tag{1.18}$$

In the above, p, μ , u, ϕ are the hydrodynamic pressure, the fluid viscosity, velocity and electric potential inside the electrolyte solution, respectively. For micro/nanosystems, Re <<1 and the fluid flow is said to be Laminar flow. Laminar flow is the fluid flow following streamlines and is free of turbulence. The first term of Eq. (1.18) is pressure gradient, second is viscosity and third is body force due to the applied electric field. Reynold's number (Re) is defined as;

$$\operatorname{Re} = \frac{\rho_f u L}{\mu} \tag{1.19}$$

where ρ_f , u, L, μ are the mass density of the fluid, the velocity of the fluid, the characteristic channel size, and the dynamic viscosity of the fluid, respectively.

1.7 Electrokinetic Phenomena

1.7.1 Electroosmosis

When an electric field is applied to a fluid across the micro/nano channel with an ion distribution described by Eq. (1.6), the counter-ions in the diffuse layer attempt to move in the flow direction and co-ions move in opposite direction, and in result it develops a flow called electroosmotic flow, as illustrated in Figure 1.8. As the ions move, they drag the surrounding molecules inside fluid in the flow direction due to the viscous effects. If the channel is uniformly charged and its dimensions are relatively larger than Debye length, the flow profile is basically uniform and the bulk fluid velocity can be described by Smoluchowski equation,

$$u_{EO} = -\frac{\varepsilon_f \varepsilon_0 \zeta}{\mu} E \tag{1.20}$$

in which ζ is the zeta potential on the surface. To satisfy this equation, a non-slip boundary condition should be applied. In case of the Debye length is comparable to nanochannel dimensions, then due to the strong EDL overlapping, the generated fluid velocity profile cannot be simplified with Eq. (1.8) and the applicability of Eq. (1.5) is no longer valid because the bulk potential at the center of the nanochannel is no longer equal to zero.


Figure 1.9. Electroosmotic flow in a nanochannel.

1.7.2 Streaming Current and Potential

In the absence of an applied electric field across a charged micro/nano nanochannel, by applying a pressure gradient, a flow can be generated in the diffuse layer. The counter-ions are carried toward to the downstream end, and due to migration, an electric current develops in the pressure-driven flow direction. This phenomenon is called *the streaming current*. When the electrolyte concentrations in the two reservoirs are identical, and when there is no net current flowing through the system, the steady-state electric field develops. The potential difference between the upstream and downstream of the channel is called *the streaming potential*. This potential creates a force to migrate counter-ions in the opposite direction of streaming current; this action creates another current in opposite direction, and it is called as *the conduction current*. At a steady-state case, the streaming current will be equal to the conduction current and hence the total current will be zero. This principle is used to desalinate the sea water.

1.8 Organization of this Dissertation

The understanding of electrokinetic properties of ions transport and surface properties is an important feature, not only from fundamental perspectives but also for the development of next-generation nanofluidics devices. This dissertation mainly focuses on a better understanding of the theory on electrostatics, electrokinetic effects, fluid dynamics, and electrochemistry in liquid solutions. The main contribution of this thesis is as follows:

First, we theoretically [17] and analytically [13] investigate the importance of curvature effect of nanoparticles on surface charge properties of silica nanoparticles immersed in an aqueous solution in Chapter 2 and 4, respectively. A multi-ion charge-regulation model is employed for the first time to investigate the surface charge density and surface potential as a function of radius, ionic strength and pH level of aqueous solutions. Later, in Chapter 3 we use the multi-ion charge regulation method to gain further insight into the interactions between two charged surfaces, nanoparticle and a flat wall. We studied theoretically to investigate how the electric double layer overlap influence the surface charge distribution as the separation between the surfaces is decreased.

Second, since nanofluidics channels exhibit unique physical properties, our theoretical study is to reveal ion distribution inside the nanochannel in extended-nanospaces for the first time by using multi-ion 3D model in Chapter 5 [12 14]. The spatial distribution of proton ions for three different salt concentrations is verified with experimental studies for a 400 nm fused silica nanochannel. The potential and surface charge density distribution and enhancement of proton ion concentration are reported as functions of salt ionic concentration, pH level and the height of the nanochannel.

Third, we investigated the electroosmotic flow (EOF) velocity distribution in a silica nanoslit validated with experimental data theoretically and developed an approximation solution for EOF in nanoslits in Chapter 6. For the first time, we comprehensively studied the electroosmotic velocity profile inside nanoslit as a function of aqueous solution properties and the length of the nanoslit by showing the ICP effect.

Finally, Chapter 7 offers a conclusion based on the work presented in the preceding chapters and perspectives for future developments.

CHAPTER 2

SIZE DEPENDENT SURFACE CHARGE PROPERTIES OF SILICA NANOPARTICLES

2.1 Introduction

Recent advances in micro/nano technology attract significant attention on the use of nanoparticles in diverse ranges of applications, including DNA analysis/sequencing systems [37, 85, 95, 101, 109, 128, 132, 184], DNA and protein transport [29, 98, 120, 156, 163], drug delivery [68, 91, 100, 216], biological/chemical agent detection [104-105] and micro/nano chip sensors [47, 78-79]. The performance of these devices relies on precise control and manipulation of various-sized nanoparticles in various ionic solutions. For example, manipulating the cellular uptake of nanoparticles has promised multiple biomedical applications, such as designing nanoparticles according to the dimensional limits for targeting and killing diseased cells [158]. Recent experiments demonstrated that reduced particle size does not necessarily increase the cellular uptake rate. Interestingly, certain sized nanoparticles are internalized faster than the smaller ones by several cell types [40-41, 158, 168, 195], and such unexpected size dependent nanoparticle transport is not yet well understood.

When a particle is immersed in an aqueous medium, it becomes charged due to protonation/deprotonation on the particle surface [83]. The resulting surface charge interacting with dissolved ions forms the electric double layer (EDL) surrounding the charged particle [122]. More counter ions are accumulated, while co-ions are depleted within the EDL. Transport of nanoparticles highly depends on the particle's surface charge

properties. For example, the process of nanoparticle translocation through a nanopore depends on the surface charge densities of the pore and the particle [2, 5, 7]. Due to the curvature effects, the particle's surface charge also depends on its size [1, 20, 66, 99, 140, 201]. However, most existing studies assume that the surface charge density of a particle is a material property independent of the particle size [102, 118, 197]. For example, Kreuter et al. [102] studied nanoparticle-mediated delivery of drugs to the brain and characterized the transport of 20, 40, 60 and 80 nm diameter nanoparticles as a sole function of surfactant coating by ignoring the nanoparticle size effects. Similarly, nanoparticle-cell interactions were characterized based on the particle's surface chemical properties, while the size effects on 14, 30, 50, 74, 100 nm nanoparticles' surface charges were not considered [197]. In addition, Lu et al. [118] studied nanoparticles in the range of 2-100 nm with different surface modifications and assumed constant particle charge in their characterization of particle-water interactions. Many previous studies assumed constant surface charge on particles, regardless of the particle size and solution properties (i.e., solution pH and salt concentration) [5, 7]. For example, electrokinetic transport of charged molecules in nanofluidic channels were studied by assuming a constant surface charge density, even though the background salt concentration and pH levels were varied during the experiments. Similarly, DNA translocation speeds through silica nanopores in different solution environments were directly related with surface charges; however, it is studied without considering the background salt concentration effects on charge densities. The effects of electroosmotic flow on ionic rectification in asymmetric nanopores were also explained by varying the background salt concentration and without taking into account the effect of solution properties on surface charge [5]. Under certain conditions, such

assumptions failed to explain the observed experimental results [20, 99, 177]. These assumptions are inaccurate and unrealistic since the nanoparticle surface charge density strongly depends on the particle size as well as the pH and the background ionic concentration.

The present study theoretically investigates the size-dependent surface charge properties of silica nanoparticles immersed in an aqueous solution. The reason to choose a silica nanoparticle as an example is because it has been widely used for ceramics, chromatography, catalysis, and as a carrier in bio-molecular transport and drug delivery [22, 185]. In contrast to the previous studies neglecting the surface chemistry, we considered the effects of the pH and salt concentration of the aqueous solution, the site number density of the functional groups, and protonation/deprotonation surface reactions on the nanoparticle surface. A multi-ion charge-regulation model is employed for the first time to investigate the size dependent surface charges of silica nanoparticles as functions of salt concentrations and pH. The model is first validated by existing experimental data available from the literature [99].

2.2 Mathematical Model

We considered a spherical nanoparticle of diameter D_p immersed in an infinite electrolyte medium, as shown in Figure 2.1. The background electrolyte contains N types of ionic species. We assume the electrolyte is made of KCl with bulk concentration C_{KCl}, and its pH is adjusted by KOH and HCl solutions. Consequently, there are four ionic species (i.e., N=4), H⁺, OH⁻, K⁺ and Cl⁻ dissolved in the solution. We assume that the silica nanoparticle's suface bears silanol functional groups. The particle becomes charged by the protonation/deprotonation processes. Figure 2.1 schematically shows a negatively charged silica nanoparticle, and ionic distributions in its EDL. The simulation electrolyte domain is discritized using a triangular structured/unstructured mesh, as shown in Figure 2.2, that is able to solve surface chemistry accurately while keeping computational costs within practical limits. A mesh sensitivity analysis is conducted to ensure that the electric double layer and surface charge density near/on the nanoparticle was adequately resolved. Using the presented mesh structure, we are able to carry an effectively mesh-independent results using 85k computational cells, as shown in Figure 2.2.



Figure 2.1. Schematic illustration of the surface charge groups on a silica nanoparticle (a)



Figure 2.2. (a) The free triangular mesh used in simulation domain is illustrated. (b) A very fine mesh is used on the surface of nanoparticle and also within the EDL.

The ionic mass transport within the electrolyte is governed by the Poisson-Nernst-Planck (PNP) equation,

$$-\varepsilon_0 \varepsilon_j \nabla^2 \psi = F \sum_{i=1}^4 z_i c_i, \qquad (2.1)$$

$$\nabla \bullet \mathbf{N} = \nabla \bullet \left(-D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \psi \right) = 0, \ (\mathbf{i} = 1, \dots, 4)$$
(2.2)

where ϕ is the electric potential within the fluid; F is the Faraday constant; c_i, z_i and D_i are the molar concentration, valence, and diffusion coefficient of the *i*th ionic species (i=1 for H⁺; i=2 for K⁺; i=3 for Cl⁻; and i=4 for OH⁻) respectively; R is the universal gas constant; T is the fluid temperature; \mathcal{E}_0 is the permittivity of vacuum; and \mathcal{E}_f is the relative permittivity of the electrolyte solution. Lagrange quadratic elements are used for governing equations. The relative tolerance is set as 1e-6 in all the cases of this chapter.

The set of equations (2.1) and (2.2) are numerically solved with the following boundary conditions. Far away from the particle surface (i.e., $r \rightarrow \infty$), electroneutrality holds and the concentration of each species reach its bulk concentration, $C_{i\infty}$:

$$C_{10} = 10^{-pH+3}$$
 and $C_{40} = 10^{-(14-pH)+3}$, (2.3)

$$C_{20} = C_{KCI} \text{ and } pH \le 7 \quad C_{30} = C_{KCI} + C_{10} - C_{40} \text{ when } pH \le 7,$$
 (2.4)

and

$$C_{20} = C_{KCI} + C_{10} - C_{40} \text{ and } C_{30} = C_{KCI} \text{ when}$$
 (2.5)

Electric potential $\psi = 0$, when $r \to \infty$. On the rigid nanoparticle surface, $\mathbf{n} \cdot \mathbf{N}_i = 0$ (i=1,...,4) and a surface charge density boundary condition, $-\varepsilon_0 \varepsilon_f \mathbf{n} \cdot \nabla \psi = \sigma$, is imposed.

Due to the protonation/deprotonation reactions of the dissociable functional groups at the solid/liquid interface, the nanoparticle surface reveals a charge-regulated nature. The surface charge density of the nanoparticle is modeled by the full multi-ion charge regulation model. To account for the charge regulation, we assume the following two protonation reactions of singly Si-coordinated sites with equilibrium constants K_A and K_B

$$SiOH \leftrightarrow SiO^- + H^+$$
, (2.6)

and

$$SiOH+H^+ \leftrightarrow SiOH_2^+$$
 (2.7)

The equilibrium constants are calculated as

$$K_{A} = \frac{N_{SiO^{-}}[H^{+}]_{s}}{N_{SiOH}} \text{ and } K_{B} = \frac{N_{SiOH_{2}^{+}}}{N_{SiOH}[H^{+}]_{s}},$$
 (2.8)

where N_{SiOH} , $N_{SiO^{-}}$, and $N_{SiOH_{2}^{+}}$ are the surface site densities of SiOH, SiO⁻, and SiOH₂⁺, respectively. [H⁺]_s is the concentration of H⁺ ions at the solid/liquid interface. The total number site density of silanol functional groups on the solid/liquid interface is

$$N_{total} = N_{SiOH} + N_{SiO^{-}} + N_{SiOH_{2}^{+}}.$$
 (2.9)

Based on equations (2.8) and (2.9), the surface charge density of the nanoparticle can be expressed as:

$$\sigma = -FN_{total} \frac{K_A - K_B [H^+]_s^2}{K_A + [H^+]_s + K_B [H^+]_s^2}.$$
(2.10)

The governing equations are normalized with corresponding scale values; the ionic concentration is the bulk ionic concentration (C_{KCl}) , the electric potential scale is RT/F, the length scale is particle radius (R_p) , the diffusivity scale is $\varepsilon_f \varepsilon_0 R^2 F^2/(\mu F)$, the surface charge density scale is $\varepsilon_f \varepsilon_0 RT/(FR_p)$ where R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, μ is the dynamic viscosity. The dimensionless form of the governing equations are

$$-\nabla^{*2}V^{*} = \frac{1}{2}(\kappa R_{p})^{2}(z_{1}c_{1}^{*}+z_{2}c_{2}^{*}+z_{3}c_{3}^{*}+z_{4}c_{4}^{*}), \qquad (2.11)$$

$$\nabla \bullet \mathbf{N}_{i}^{*} = \nabla \bullet (\mathbf{u}^{*} \mathbf{c}_{i}^{*} - \mathbf{D}_{i}^{*} \nabla^{*} \mathbf{c}_{i}^{*} - \mathbf{z}_{i} \mathbf{D}_{i}^{*} \mathbf{c}_{i}^{*} \nabla^{*} \mathbf{V}^{*}) = 0, \ (i=1, ..., 4)$$
(2.12)

where c_i^* , z_i and D_i^* are the dimensionless concentration, valence electron number, and diffusivity of the ith ionic species, respectively.

The dimensionless surface charge density expression is

$$\sigma_{w} = -N_{Total}^{*} \frac{K_{A} - K_{B}[\mathrm{H}^{+}]_{s}^{*2}}{K_{A} + [\mathrm{H}^{+}]_{s}^{*2} + K_{B}[\mathrm{H}^{+}]_{s}^{*2}}$$
(2.13)

where N_{Total}^* and $[\mathrm{H}^+]_s^*$ are the dimensionless scale of N_{Total} which equals to $\varepsilon_f \varepsilon_0 RT/(F^2 \mathrm{R}_p)$ and the dimensionless proton concentration on the nanoparticle surface.

3. Numerical Implementation and Code Validation

The 1D model in a spherical coordinate system is numerically solved using a commercial finite-element package, COMSOL Multiphysics, installed in a high-performance cluster. Since the field variables exponentially decay within the EDL of thickness,

$$\kappa^{-1} = \lambda_{D} = \sqrt{\varepsilon_0 \varepsilon_f RT / \sum_{i=1}^{4} F^2 z_i^2 C_{i\infty}}$$
(2.14)

all simulations used $d=D_p+60\lambda_D$ as the far field boundary. Non-uniform mesh with finer mesh within the EDL was adopted.

Physical parameters used in the simulations are $\varepsilon_0 \varepsilon_f = 7.08 \times 10^{-10}$ F/m, R = 8.31 J/(mol·K), F = 96490 C/mol, T = 300K, N_{total}=8x10⁻⁶sites/m² [10], pK_A =-logK_A=7.6, and pK_B = -logK_B=1.9. The diffusivities of H⁺, K⁺, Cl⁻, and OH⁻ ions are, respectively, 9.31×10^{-9} m²/s, 1.96×10^{-9} m²/s, 2.03×10^{-9} m²/s, and 5.30×10^{-9} m²/s [10].

To validate our numerical procedure, we first modeled a flat silica surface in contact with a semi-infinite electrolyte solution. Analytical solution for the surface charge density of a planar surface has been recently derived by Yeh et al. [209]. Figure 2.3 depicts the surface charge density of a planar surface as a function of pH for bulk C_{KCI} =100 mM. Our numerical results (red squares) are in good agreement with the theoretical results (solid line). Clearly, the surface charge density increases with an increase in pH of the solution.



Figure 2.3. Surface charge densities of a planar silica surface (a) and 80 nm silica nanoparticle (b) as a function of pH. Theoretical result in figure (a) is from [48], while experimental data in figure b is from [34].

To further ensure that the model captures the underlying physics of the origin of interfacial charge, we also compare the model's prediction with the experimental data obtained from the literature [99]. Figure 2.3b depicts the surface charge density of a silica nanoparticle of 80 nm in diameter as a function of pH immersed in 100 mM KCl solution. The model's prediction (solid line) agrees well with the experimental data (red circles),

confirming that the present model successfully captures the essential physics of the origin of the charge of silica nanoparticles. In the following we use the verified model to investigate the side dependent surface charge of silica nanoparticles as functions of pH and background salt concentration, C_{KCI} .

2.3 Results and Discussion

2.3.1 Size Dependent Surface Charge Properties: pH Effect

Figure 2.4 depicts the surface charge densities of silica nanoparticles of different sizes as a function of pH for C_{KCI} = 1mM (Figure 2.4a) and 100 mM (Figure 2.4b). For comparison, the surface charge density for a flat silica surface is also plotted. Under the same conditions, the surface charge density magnitude increases as pH increases. This behavior quantitatively agrees with the experimental observations, as shown in Figure 2.3b, and also it qualitatively agrees with the results from Abbas et al. [1], Behrens et al. [20], Kobayashi et al. [99] and Sonnefeld et al. [177]. Variation of the surface charge with pH is expected. As the concentration of H⁺ ions decreases with increased pH, more negatively charged SiO⁻ are dissociated from the functional groups SiOH, resulting in higher negative surface charge density. Overall, Figure 2.4 clearly indicates that the surface charge of silica nanoparticles also depends on their sizes. Under a fixed background salt concentration, the magnitude of the surface charge increases with decreased particle size, which is in qualitative agreement with the previous studies such as Abbas et al. [1], Behrens et al. [20], and Gunnarsson et al. [66]. However, the surface charge density becomes independent of the particle size after a critical diameter. This critical value also depends on the pH and salt concentration of the solution. For example, the critical particle diameter at pH=6 is about 100 nm for $C_{KCl}=1$ mM, while it is about 10 nm for $C_{KCl}=100$ mM.



Figure 2.4. Surface charge density of silica nanoparticles of different sizes as a function of pH in 1 mM (a) and 100mM (b) KCl solutions.

To clearly show the behavior of the surface charge density, the particle's surface charge density is normalized with that of a flat surface at a given pH value. Figure 2.5a and b depict the normalized surface charge density as a function of pH for $C_{KCI}=1$ mM and 100 mM, respectively. The normalized surface charge of particles larger than 100 nm is close to 1, suggesting that the particle size effects on the surface charge becomes insignificant when the particle size is larger than 100 nm under the considered conditions. For particles less than 100 nm, the normalized surface charge first increases with pH, attains a peak

value at a critical pH value, and then decreases with further increases in the pH. The critical pH value also depends on the particle's size. The critical pH value increases with decreased particle size. For example in 1 mM KCl solution, the critical pH for 2 nm particles is 6.5, while this is pH=5.5 for 10 nm particles. In addition, the normalized surface charge density increases significantly with reduced particle size, implying that the surface charge density of the nano particles is significantly higher than that of a flat surface made of the same material.



Figure 2.5. Normalized surface charge density as a function of pH in 1mM (a) and 100mM (b) KCl solutions.

The variation of the normalized surface charge density with pH can be explained by the concentration of H^+ ions on the particle surface. As pH level increases, the bulk concentration of H⁺ ions decreases, resulting in lower concentration of H⁺ ions and accordingly, higher surface charge on the particle surface. Figure 2.6 depicts the surface concentration of H⁺ ions on the particle surface normalized by that on a flat surface at a given pH. The normalized surface concentration of H⁺ ions is less than 1, implying that the concentration of H⁺ ions on small particle's surface is lower than that on a flat surface. At the same pH level and background salt concentration, the surface concentration of H⁺ ions decreases as the particle size decreases, leading to more negatively charged SiOdissociated from the functional groups SiOH and, therefore, higher negative surface charge density, as shown in Figure 2.4. For relatively small particles, the normalized surface concentration of H⁺ ions decreases with increased pH, and obtains a minimum at a certain pH value, above which it increases as the pH is further increased. Since the surface charge of the particle is inversely proportional to the surface concentration of $[H^+]$ ions, the normalized surface charge density increases with pH, attains a maximum, and then declines, as shown in Figure 2.5.



Figure 2.6. Normalized surface concentration of $[H^+]$ ions as a function of pH at $C_{KCI}=1$ mM. Normalization is done using the surface concentration of $[H^+]$ ions of a flat surface at a given pH.

2.3.2 Size Dependent Surface Charge Properties: Background Salt Concentration Effect

Under the same pH and particle size, we found that the particle's surface charge density increases with an increase in the background salt concentration, which is in agreement with the experimental observations [20, 56, 99] and theoretical predictions [1]. Figures 2.7a and b depict, respectively, the surface concentrations of H⁺ and K⁺ ions as a function of the background salt concentration for different particle sizes at pH=6.5. Overall, an increase in salt concentration results in an increase in the concentration of K⁺ ions and a decrease in the concentration of H⁺ ions. For a fixed particle size, more K⁺ ions are attracted to the

negatively charged particle surface with increased background salt concentration. The increased number of K^+ ions exclude H^+ ions, resulting in lower concentrations of H^+ ions on the particle surface, and accordingly higher surface charge density. At a fixed salt concentration, the surface concentration of H^+ ions increases with the particle size and asymptotically reaches the value of the flat plate around a particle diameter of 500 nm. At relatively low background salt concentrations, the surface concentration of H^+ ions surface concentration of H^+ ions increases with the particle size and asymptotically reaches the value of the flat plate around a particle diameter of 500 nm. At relatively low background salt concentrations, the surface concentration of H^+ ions significantly depends on the particle size.



Figure 2.7. Surface concentrations of H^+ ions (a) and K^+ ions (b) as a function of C_{KCI} for different particle sizes at a pH=6.5.

To characterize the background salt concentration effects on the size-dependent surface charge properties, Figure 2.8 depicts the normalized surface concentration of H⁺ ions as a

function of the particle diameter for $C_{KCI}=1$, 10, and 100 mM at pH= 6.5. The normalization was done using the surface concentration of H⁺ ions on a flat plate. For D_p>100 nm, the normalized surface concentrations of H⁺ ions are close to 1 for all salt concentrations. For particles smaller than 100 nm, the concentration of H⁺ ions on smaller particles is lower, yielding a higher negative surface charge. Such size dependence is more significant at lower salt concentrations.



Figure 2.8. Normalized surface concentration of H^+ ions as a function of particle diameter for various background salt concentrations at pH=6.5.

Figure 2.9 shows the particle's surface charge density normalized by that of a flat surface as a function of the particle size. Data is presented for pH=6.5. For all background

salt concentrations, the normalized particle surface charge density decreases as the particle size increases. As explained before, this is attributed to the increase in the normalized surface concentration of the H⁺ ions, as shown in Figure 2.8. For relatively small particles, the normalized surface charge density decreases with an increase in C_{KCl} . This is attributed to the increase in the surface concentration of H⁺ ions with an increase in C_{KCl} , as shown in Figure 2.8.



Figure 2.9. Normalized surface charge density as a function of particle diameter for various background salt concentrations at pH=6.5.

Since both pH and salt concentration affect the bulk concentration of each ionic species, and accordingly the EDL thickness, the combined effects of pH and salt concentration on the size-dependent surface charge density can be described by the ratio of EDL thickness (Eq. 2.14) to the particle diameter, λ_D/D_p . Figure 2.10 shows normalized surface charge density as a function of λ_D/D_p . The normalized surface charge density is close to 1 when λ_D/D_p <0.2, and increases with increased λ_D/D_p . Therefore, regardless of the salt concentration and pH, the surface charge density is independent of the particle size when λ_D/D_p <0.2. In the range of λ_D/D_p >0.2, the surface charge density of the nanoparticle becomes size dependent, and is higher than that of the flat surface made of the same material.



Figure 2.10. Normalized surface charge density as a function of the ratio of EDL thickness to the particle diameter. Different shapes demonstrate different pH values, while different colors show different salt concentrations. (Blue =1mM, yellow=10mM and red=100mM)

2.4 Conclusions

Surface charge densities of spherical silica nanoparticles of different sizes are theoretically investigated as functions of pH and salt concentration. In contrast to most studies in the literature that assume constant surface charge density, the present model takes into account the charge regulation as functions of the solution properties. The results demonstrate increased surface charge density for all particle sizes with an increase of pH and salt concentration [1, 20]. Surface charge density decreases with increased particle size, and asymptotically reaches that of a flat plate. This behavior depends on both pH and salt concentration. Variation of the surface charge with the particle size is attributed to the change in the surface concentration of H⁺ ions. Particle diameter normalized with the EDL thickness is used to combine the effects of pH and salt concentration. In the range of $\lambda_D/D_p < 0.2$, one can neglect the effect of the particle size on its surface charge density, regardless of the pH and salt concentration. However, the surface charge density of silica nanoparticles becomes size dependent when $\lambda_D/D_p>0.2$, and typically the magnitude of surface charge density increases with decreased particle size. These results can be used to explain why certain sized nanoparticles are transported in nanopores faster than the smaller ones made out of the same material [40-41, 158, 168, 195].

CHAPTER 3

ANALYTICAL MODEL FOR CHARGE PROPERTIES OF SILICA PARTICLES

3.1 Introduction

Silica particles have been widely used in biomedical and biochemical sciences as well as material engineering due to their good biocompatibility and wide variety of chemical modification on their surfaces [170-171]. These properties facilitate silica particles with applications for transportation [138], imaging [59, 90], sol-gel science [176], painting [45], coating [123, 166], etc. Its performance in these applications depends on its surface charge properties such as surface charge density and zeta potential [59, 90, 123, 138, 166]. Surface charge properties of silica particles, originating from the protonation/deprotonation of silanol functional groups, depend on the local solution pH, ionic strength [18, 25, 103, 177], and particle size [1]. However, many studies used constant charge properties for silica particles regardless of the particle size and the local solution properties, including pH and salt concentration [62, 143, 189].

In this study, we develop an analytical model for the surface charge density and zeta potential of silica particles with the consideration of multiple ionic species and the protonation/deprotonation surface chemistry. The model is validated by the experimental data available from the literature. The developed analytical model can be used to predict both the surface charge density and the zeta potential of silica particles as functions of pH, background salt concentration, and particle size under the condition of $\kappa R_p \ge 0.5$, where κ^{-1} is the Debye length and R_p is the particle radius.

3.2 Mathematical Model

A spherical silica particle with radius R_P immersed in an infinite electrolyte medium is considered in this analysis. To simulate experimental conditions, we assume that the background salt in the aqueous electrolyte solution is NaCl, and the pH of the solution is adjusted by NaCl and NaOH. Therefore, four major ionic species (i.e. N=4), including Na⁺, Cl⁻, H⁺ and OH⁻, are considered.

Silanol functional groups experience protonation/deprotonation reactions at the solid/liquid interface. Based on the full multi-ion charge-regulation model, the surface charge density of the particle, σ , can be expressed as

$$\sigma = -FN_{total} \left\{ \frac{K_A - K_B \left[10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right) \right]^2}{K_A + 10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right) + K_B \left[10^{-pH} \exp\left(-\frac{F\psi_s}{RT}\right) \right]^2} \right\}$$
(3.1)

where F, R, and T are the Faraday constant, universal gas constant, and absolute temperature, respectively; $N_{total} = N_{SiOH} + N_{SiO^-} + N_{SiOH_2^+}$ is the total site density of silanol functional groups on the particle surface; N_{SiOH} , N_{SiO^-} and $N_{SiOH_2^+}$ are, respectively, surface site densities of SiOH, SiO⁻ and SiOH₂⁺; K_A and K_B are, respectively, the equilibrium constants for the surface reactions, SiOH \leftrightarrow SiO⁻ + H⁺ and SiOH + H⁺ \leftrightarrow SiOH₂⁺; and Ψ_s is the potential on the particle surface. The Stern layer effect is neglected in the current study; therefore, the surface potential is the same as the zeta potential of the particle.

The electric potential in the liquid, ψ , is described by the Poisson-Boltzmann (PB) equation in the spherical coordinate system,

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = -\frac{1}{\varepsilon_0\varepsilon_f}\sum_{i=1}^N Fz_i C_{i0} \exp\left(-\frac{z_iF\psi}{RT}\right) = \frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\psi}{RT}\right)$$
(3.2)

where $\kappa^{-1} = \lambda_D = \sqrt{\varepsilon_0 \varepsilon_f RT / 2z^2 F^2 C_0}$, $C_0 = C_{K^+} + C_{H^+} = C_{CI^-} + C_{OH^-}$, and z=1 for

monovalent ionic species.

The dimensionless form for Eq. (3.2) is

$$\frac{d^2Y}{dr^2} + \frac{2}{r}\frac{dY}{dr} = \kappa^2 \sinh(Y), \qquad (3.3)$$

where $Y = \psi \left/ \frac{RT}{zF} \right|$.

Replacing 2/r by its upper limit occurring at $r = R_p$ and evaluating dY/dr with that for a planar surface, the second term in left-hand-side (LHS) of Eq. (3.3) becomes

$$\frac{2}{r}\frac{dY}{dr} \approx -\frac{4\kappa}{R_p}\sinh\left(\frac{Y}{2}\right)$$
(3.4)

Substituting Eq. (3.4) into Eq. (3.3), one obtains

$$\frac{1}{\kappa^2}\frac{d^2Y}{dr^2} = \sinh\left(Y\right) + \frac{4}{R_p\kappa}\sinh\left(\frac{Y}{2}\right).$$
(3.5)

First multiplying dY/dr on both sides of Eq. (3.5) followed by integrating the resulting equation with respect to r, one can obtain

$$\left(\frac{dY}{dr}\right)^2 = 2\kappa^2 \left[\cosh\left(Y\right) + \frac{8}{R_P\kappa} \cosh\left(\frac{Y}{2}\right)\right] + \text{Constant} .$$
(3.6)

Using the boundary conditions,

$$Y = \frac{dY}{dr} = 0 \text{ for } r \to \infty, \qquad (3.7)$$

and the fact that Y and dY/dr have opposite signs, one can obtain

$$\frac{dY}{dr} = -sign(Y)\sqrt{2\kappa^2 \left[\cosh\left(Y\right) - 1 + \frac{8}{R_P\kappa} \left(\cosh\left(\frac{Y}{2}\right) - 1\right)\right]}$$

$$= -2\kappa \sinh\left(\frac{Y}{2}\right) \left(1 + \frac{2}{R_P\kappa \cosh^2\left(Y/4\right)}\right)^{\frac{1}{2}}$$
 (3.8)

In the above, sign(Y)=1 for Y>=0 and -1 for Y<0.

By expanding the last term in the right-hand-side (RHS) of Eq. (3.8) with respect to $1/R_{p}\kappa$ and retaining up to its first order, Eq. (3.8) becomes

$$\frac{dY}{dr} = -2\kappa \sinh\left(\frac{Y}{2}\right) \left(1 + \frac{1}{R_p \kappa \cosh^2\left(\frac{Y}{4}\right)}\right).$$
(3.9)

Replacing dY/dr in Eq. (3.3) with Eq. (3.9), and 2/r with $2/R_p$, Eq. (3.3) becomes

$$\frac{d^2Y}{dr^2} = \kappa^2 \sinh\left(Y\right) + \frac{4\kappa}{R_p} \sinh\left(\frac{Y}{2}\right) \left(1 + \frac{1}{R_p \kappa \cosh^2\left(Y/4\right)}\right). \tag{3.10}$$

After multiplying dY/dr on both sides of Eq. (3.10), integration of the resulting equation gives,

$$\left(\frac{dY}{dr}\right)^2 = 2\kappa^2 \cosh\left(Y\right) + \frac{16}{R_p}\kappa \cosh\left(\frac{Y}{2}\right) + \frac{64}{R_p^2}\ln\left[\cosh\left(\frac{Y}{4}\right)\right] + C_2$$
(3.11)

Eq. (3.11) subject to the boundary condition Eq. (3.7) can be changed as

$$\frac{dY}{dr} = -sign(Y) \left\{ 2\kappa^{2} \left(\cosh(Y) - 1 \right) + \frac{16}{R_{p}} \kappa \left(\cosh\left(\frac{Y}{2}\right) - 1 \right) + \frac{64}{R_{p}^{2}} \ln \left[\cosh\left(\frac{Y}{4}\right) \right] \right\}^{\frac{1}{2}}$$

$$= -sign(Y) \left\{ 4\kappa^{2} \sinh^{2}\left(\frac{Y}{2}\right) + \frac{32\kappa}{R_{p}} \sinh^{2}\left(\frac{Y}{4}\right) + \frac{64}{R_{p}^{2}} \ln \left[\cosh\left(\frac{Y}{4}\right) \right] \right\}^{\frac{1}{2}}$$
(3.12)
$$= -2\kappa \sinh\left(\frac{Y}{2}\right) \left\{ 1 + \frac{2}{R_{p}\kappa} \left[\cosh\left(\frac{Y}{4}\right) \right]^{-2} + \frac{16}{(R_{p}\kappa)^{2}} \ln \left[\cosh\left(\frac{Y}{4}\right) \right] \left[\sinh\left(\frac{Y}{2}\right) \right]^{-2} \right\}^{\frac{1}{2}}$$

Substituting $Y = \frac{zF\psi}{RT}$ and eq. (3.12) into surface charge density formula, one gets the approximate solution for the surface charge density of the particle [142] with the relative error less than 1% for $\kappa R_p \ge 0.5$:

$$\sigma_{d} = -\varepsilon_{0}\varepsilon_{f} \frac{d\psi}{dr}\Big|_{r=R_{p}}$$

$$= \frac{2\varepsilon_{0}\varepsilon_{f}\kappa RT}{F} \sinh\left(\frac{zF\psi_{s}}{2RT}\right) \begin{cases} 1 + \frac{2}{R_{p}\kappa} \left[\cosh\left(\frac{zF\psi_{s}}{4RT}\right)\right]^{-2} + \frac{16}{(R_{p}\kappa)^{2}} \ln\left[\cosh\left(\frac{zF\psi_{s}}{4RT}\right)\right] \left[\sinh\left(\frac{zF\psi_{s}}{2RT}\right)\right]^{-2} \end{cases}$$
(3.13)

$$\sigma = \frac{2\varepsilon_0\varepsilon_f\kappa RT}{F}\sinh\left(\frac{zF\psi_s}{2RT}\right) \begin{cases} 1 + \frac{2}{R_P\kappa} \left[\cosh\left(\frac{zF\psi_s}{4RT}\right)\right]^{-2} + \frac{16}{\left(R_P\kappa\right)^2}\ln\left[\cosh\left(\frac{zF\psi_s}{4RT}\right)\right] \left[\sinh\left(\frac{zF\psi_s}{2RT}\right)\right]^{-2} \end{cases}$$
(3.14)

For given conditions, one can easily use MATLAB function follow to determine both σ and Ψ_s by simultaneously solving Eqs. (3.1) and (3.14). Note that this analytical model (Eqs. (3.1) and (3.14)) can be used to predict the surface charge properties, including both surface charge density and zeta potential of silica particles as functions of the solution properties (i.e., pH and background salt concentration) and the particle's size (i.e., R_p).

3.3 Results and Discussion

The model is first validated by comparing its predictions with experimental data available from the literature. Figure 3.1 depicts surface charge density of a silica nanoparticle of R_p =58 nm immersed in 1, 10 and 100 mM NaCl solutions as a function of pH. Symbols represent the experimental data obtained by Sonnefeld et al.[177], and lines are predictions from our model using the same parameters N_{total}=1.2sites/nm², pK_A=6.38, and pK_B=1.87 [177]. The predictions are in good agreement with the experimental data. Thus the developed model successfully captures the underlying physics. Figure 3.1 also clearly shows that the surface charge density of the silica particle depends on both pH and background salt concentration, and is not a material property.

1



Figure 3.1. Surface charge density of silica particle with radius $R_p=58$ nm as a function of pH in 1, 10, and 100 mM NaCl solutions. Lines presents the approximation solution results using $N_{total}=2\times10^{-6}$ mol/m², pK_A=6.38, and pK_B=1.87, and filled symbols are the experimental results [177], and empty ones presents the numerical result where spheres, triangles and squares present 1, 10 and 100 mM, respectively.

Using the validated model with the parameters N_{total}=1.2 sites/nm², pK_A=6.38, and pK_B=1.87, one can easily predict the surface charge properties of silica particles as functions of pH, salt concentration and particle size in the range of $\kappa R_p \ge 0.5$. Figure 3.2 depicts the surface charge density of a silica nanoparticle with R_p=20 nm as functions of pH and background salt concentration C_{NaCl}. Under the considered conditions, the particle is negatively charged. For a fixed C_{NaCl}, the magnitude of the surface charge density

increases as pH increases for moderate pH. As pH increases, the concentration of H⁺ ions decreases, leading to more SiO⁻ groups dissociated from the SiOH groups and accordingly higher negative surface charges. The increase in the surface charge density with an increase in pH is also supported by the experimental results shown in Figure 3.1. However, pH effect on surface charge density becomes insignificant when pH significantly deviates from 7, and this is due to the increase in the ionic concentration, C₀, by the contribution of H⁺ and OH⁻ ions. As ionic concentration increases, electrical double layer (EDL) thickness decreases, resulting in a decrease in the surface charge density. Figure 3.2 also shows that the effect of C_{NaCl} on the surface charge density is not as remarkable as that of pH.



Figure 3.2 Surface charge density of a silica nanoparticle with Rp=20 nm as functions of pH and salt concentration, C_{NaCl} .

Since a specific adsorption of charge occurs at the silica surface, counter-ion adsorption usually predominates over co-ion adsorption and this phenomenon creates a potential difference related to the bulk potential, and it is called zeta potential, as shown in Figure 3.3. Under the same condition of Figure 3.2, Figure 3.3 depicts the zeta potential as functions of C_{NaCl} and pH. At relatively low salt concentrations, as pH level increases, zeta potential first increases, attains a maximum at a critical pH, and then decreases as pH further increases. At relatively high salt concentrations, the pH effect on zeta potential is insignificant when pH is relatively low or high, and zeta potential increases as pH increases for a moderate pH. At a fixed pH, the effect of C_{NaCl} on zeta potential is similar to its effect on surface charge density. Typically the magnitudes of zeta potential and surface charge density decrease as the salt concentration increases, which is due to the decrease in the EDL thickness.



Figure 3.3. Zeta potential of a silica nanoparticle with Rp=20 nm as functions of pH and salt concentration, C_{NaCl} .

The surface charge density of nanoparticles is not only a function of the aqueous solution property but also particle size. In order to clearly show the behavior of surface charge density as a function of particle size and pH, the surface charge density is normalized with a flat wall surface charge density. Figure 3.4 demonstrates that the normalized surface charge density larger than 60 nm is close to 1. This result suggests that the simplified PB model can be describe the surface charge density and the radius effect is not significant. However, for particles less than 60 nm, the normalized surface charge increases with increasing pH and reaches a peak value at a critical pH value, which is 5.5, then decreases with increasing of pH. This result can be attributed to the surface charge

density of nanoparticles increasing with a decreasing of particle radius, and the magnitude of surface charge density for a nanoparticle with a 10 nm radius is 1.6 times bigger than a flat wall when pH=5.5.



Figure 3.4. Normalized surface charge density of a silica nanoparticle for various radius size and pH levels when $C_{NaCl}=1$ mM.

Figure 3.5 depicts that the normalized surface charge density as a function of salt ionic concentration and nanoparticle radius. Again, nanoparticles bigger than 60 nm radius are independent of the radius effect, and their surface charge density is almost equal to the corresponding flat wall charge density. For nanoparticles smaller than 60 nm, the surface charge density is nearly 16 times greater when the salt concentration is 0.001 mM. The normalized surface charge density becomes independent of the radius effect for 10 nm radius particles when the salt concentration is higher than 1 mM.



Figure 3.5. Normalized surface charge density of a silica nanoparticle for various radius size and salt concentration C_{NaCl} at pH=5.5.

3.4 Conclusions

An analytical model for the surface charge density and zeta potential of silica particles with the consideration of multiple ionic species and surface chemistry is derived and validated. The model's predictions on the surface charge density agree with the experimental data available from the literature. At relatively low salt concentrations, zeta potential first increases with an increase in pH, attains a maximum at a critical pH, and then decreases as pH further increases. The surface charge density of nanoparticles greater than 60 nm becomes independent of the radius effect and behaves as flat wall surface. The magnitude of the surface charge density increases with decreases in nanoparticle radius, and when salt concentration is higher than 1 mM, the surface charge density of nanoparticle is independent of particle size. The developed model can be used to predict the surface charge density and zeta potential of silica particles as functions of pH, salt concentration, as well as particle size when $\kappa R_p \ge 0.5$.

CHAPTER 4

SURFACE CHARGE OF A NANOPARTICLE INTERACTING WITH A FLAT SUBSTRATE

4.1 Introduction

The Surface charge property of an object in contact with an aqueous solution plays a very important role in the applications of surface science, colloidal science, and electrokinetic transport. For example, electrokinetic transport of ions, fluid, and particles within nanofluidic devices highly depend on the surface charge densities of the channel wall and the nanoparticles [38, 147, 169]. Many (bio)particles such as DNA [19, 33, 86, 153, 188], proteins [36, 55, 133], biological molecules [111, 117], and synthetic particles are separated based on their charge differences. Dispersion stability of colloids depends on the charge properties of the colloids, and typically highly charged colloids are more stable. Cellular uptake of nanoparticles is also affected by the nanoparticle's size and charge. Electrostatic interactions between two objects immersed in an aqueous solution also highly depend on their charge properties.

Surface charge forms as a result of dissociation of ionizable groups or adsorption/reaction of ions at the interface, when an object is in contact with an electrolyte solution [83]. Since the surface reactions, including adsorption of ions and protonation/deprotonation, depends on the local ionic environment (e.g., local pH and salt concentrations) at the interface, typically the surface charge of an object is not a material property and depends on the local solution properties such as pH, ionic species and their local concentrations [15, 18, 152]. When two charged objects are close to each other, the
electrical double layers (EDLs) of the two interacting objects will overlap. Therefore, the local solution properties such as ionic concentrations in the gap between the two interacting objects are different from those when the two objects are sufficiently away from each other. For example, when two negatively charged objects are very close, their EDLs with dominant cations overlap, resulting in enriched cations, such as H⁺ ions in the interaction region between them. This generates a spatially non-uniform ionic concentration of cations around the interacting objects, yielding non-uniform surface charge properties of the two interacting objects. However, many existing studies assumed that the surface charge properties of two interacting objects remain at their bulk values. For example, the surface charge properties of two interacting objects are assumed to be constants in the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [48, 84, 141, 198-199], which has been widely used to fit the measured interaction forces versus separation distances and estimate the charge properties of two interacting objects [23-24, 26-28, 35, 46, 50, 52, 58, 82, 106, 112, 131, 134, 139, 146, 151, 164, 196, 200, 204, 222-223]. Nanoparticles translocating through charged nanopores are commonly observed in nanopore biosensing applications. Most such investigations assume constant surface charges on the nanoparticle and the nanopore [4, 219]. Since the EDLs are significantly overlapped in the nanopore, local ionic concentration around the bioparticle and the nanopore can be dramatically different than the conditions when the bioparticle is absent.

The objective of this study is to investigate the variation of the surface charge properties of two interacting silica objects as a function of their normalized separation distance (κh) under various pH and salt concentrations. Since the silica nanoparticles have been widely used in colloidal science, bio molecular transport and drug delivery [28, 53-54, 75, 82, 113, 127, 165, 186, 202, 221], and many nanofluidic devices (e.g., nanopores and nanochannels) are made of silica [51], we investigate the charge properties of a silica nanoparticle interacting with a silica flat surface. In contrast to most previous studies which neglected the surface chemistry, we analyze the effects of local pH and salt concentrations on the surface charge using a multi-ion charge regulation model.

4.2 Mathematical Model

We consider a spherical silica nanoparticle of radius R_p located above a flat silica surface which are immersed inside an electrolyte solution containing N type of ionic species, as shown in Figure 4.1. The separation distance between the bottom pole of the particle and the flat surface is h. We assume that the electrolyte solution includes background salt KCI with a bulk concentration of C_{KCI} , and its acidic and basic solution properties are adjusted by HCl and KOH solutions. Therefore, there are four ionic species, K⁺, H⁺, Cl⁻, and OH⁻, in the solution.

Due to the axial symmetry, a symmetric cylindrical coordinate system, (r,z), with the origin fixed at the center of the flat wall surface, is adopted in this study. The electrostatics and ionic mass transport are governed by the Poisson-Nernst-Planck (PNP) equations:

$$-\varepsilon_0 \varepsilon_j \nabla^2 \psi = \rho_e = F \sum_{i=1}^4 z_i c_i, \qquad (4.1)$$

and

$$\nabla \bullet \mathbf{N}_{i} = \nabla \bullet \left(-D_{i} \nabla c_{i} - z_{i} \frac{D_{i}}{RT} F c_{i} \nabla \psi \right) = 0, (i=1,...,4).$$
(4.2)

In the above, ϕ is the electric potential inside the electrolyte solution; $c_{i...z_{i}}$ and D_{i} are, respectively, the molar concentration, valence, and diffusion coefficient of the *i*th ionic species (*i*=1 for H⁺; *i*=2 for K⁺; *i*=3 for Cl⁻; and *i*=4 for OH⁻); *F* is the Faraday constant; *R* is the universal gas constant; *T* is the fluid temperature; ε_{0} is the permittivity of the vacuum; ε_{f} is the relative permittivity of the electrolyte solution; and ρ_{t} represents the space surface charge density inside the electrolyte solution. In contrast to previous studies which used only the Boltzmann equation to evaluate for each ion concentrations on particle and flat wall surface, we directly used PNP equations. Considering only the Boltzmann equation is not right when the electric double layer overlapped. The relaxation times of electrostatic interaction between ions inside the aqueous solution is in the range of 10⁻¹³ to 10⁻¹⁴ seconds [183] so that we neglected the effect of dielectric changes of the material due to the protonation/deportation process [154, 159]. Our all simulation results reached a steady-state equilibrium so that the dynamics of aqueous solutions for different concentrations or temperatures are neglected.



Figure 4.1. Schematics of a spherical silica nanoparticle interacting with a flat silica plate immersed in an electrolyte solution containing K^+ , H^+ , Cl^- and OH^- ionic species.



Figure 4.2. Free quadratic triangular-type mesh with finer on the charge regulated surfaces is used on axial-symmetric simulation domain.

In order to solve the coupled Eqs. (1) and (2), appropriate boundary conditions are required. Along the axis (i.e., r=0), axial symmetry boundary conditions for electric potential and for each ionic concentration are applied. Far away from the charged nanoparticle and plate (e.g., dashed line AB in Figure 4.1), we assume that the ionic concentration of each species maintains its bulk concentration, $c_i = C_{i0}$, for i=1,...,4. Based on the electroneutrality condition, the bulk concentration for each species is

$$C_{10} = 10^{-pH+3}$$
 and $C_{40} = 10^{-(14-pH)+3}$, (4.3)

$$C_{20} = C_{KCl} \text{ and } C_{30} = C_{KCl} + C_{10} - C_{40} \text{ when } \mathbf{pH} \le 7$$
, (4.4)

and

$$C_{20} = C_{KCl} + C_{10} - C_{40} \text{ and } C_{30} = C_{KCl} \text{ when } pH > 7$$
(4.5)

On the rigid surfaces of the nanoparticle and plate, normal ionic flux for each species is zero, $\mathbf{n} \cdot \mathbf{N}_i = 0$ (*i*=1,...,4). For the electrical potential, $\psi = 0$ is imposed far away from the charged surfaces. On the charged surfaces of the nanoparticle and plate, a surface charge density boundary condition, $-\varepsilon_0\varepsilon_f \cdot \mathbf{n} \cdot \nabla \psi = \sigma_w$ is imposed. In contrast to the existing studies that use a constant surface charge density regardless of the separation distance between the particle and the plate, in the present work the surface charge densities of the silica nanoparticle and plate are determined from the protonation/deprotonation surface reactions of silanol functional groups. We assume that the following two protonation reactions of singly Si-coordinated sites with equilibrium constants K_A and K_B occur,

$$SiOH+H^+ \leftrightarrow SiOH_2^+$$
 (4.7)

The equilibrium constants are calculated as

$$K_{A} = \frac{N_{SiO^{-}}[H^{+}]_{s}}{N_{SiOH}} \text{ and } K_{B} = \frac{N_{SiOH_{2}^{+}}}{N_{SiOH}[H^{+}]_{s}}.$$
 (4.8)

In the above, N_{SiOH} , N_{SiO^-} , and $N_{SiOH^{+}_{2}}$ are the surface site densities of SiOH, SiO⁻, and SiOH₂⁺, respectively. [H⁺]_s is the concentration of H⁺ ions at the solid/liquid interface. The effects of the Stern layer on determination of surface charge properties are neglected in the current work. The total number site density of silanol functional groups on the solid/liquid interface is

$$N_{total} = N_{SiOH} + N_{SiO^{-}} + N_{SiOH^{+}}.$$
 (4.9)

Based on equations (4.8) and (4.9), the surface charge density on the nanoparticle and the plate can be expressed as

$$\sigma_{w} = -F N_{total} \frac{K_{A} - K_{B} [H^{+}]_{s}^{2}}{K_{A} + [H^{+}]_{s} + K_{B} [H^{+}]_{s}^{2}}.$$
(4.10)

Note that $[H^+]_s$ in Eq. (4.10) is the proton concentration on the surface of the particle and plate. Although both are made of the same material with the same N_{total} , K_A , and K_B , their surface charge densities might be different if their local proton concentrations are different. Eq. (4.10) also clearly shows that the surface charge density is not a material property due to its dependence on the local proton concentration. The governing equations are normalized with corresponding scale values; the ionic concentration is the bulk ionic concentration (C_{KCI}), the electric potential scale is RT/F, the length scale is particle radius (R_p) , the diffusivity scale is $\varepsilon_f \varepsilon_0 R^2 F^2 / (\mu F)$, the surface charge density scale is $\varepsilon_f \varepsilon_0 RT / (FR_p)$ where R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, and μ is the dynamic viscosity. The dimensionless forms of the governing equations are:

$$-\nabla^{*2} V^{*} = \frac{1}{2} (\kappa R_{p})^{2} (z_{1} c_{1}^{*} + z_{2} c_{2}^{*} + z_{3} c_{3}^{*} + z_{4} c_{4}^{*}), \qquad (4.11)$$

$$\nabla \bullet \mathbf{N}_{i}^{*} = \nabla \bullet (\mathbf{u}^{*} \mathbf{c}_{i}^{*} - \mathbf{D}_{i}^{*} \nabla^{*} \mathbf{c}_{i}^{*} - \mathbf{z}_{i} \mathbf{D}_{i}^{*} \mathbf{c}_{i}^{*} \nabla^{*} \mathbf{V}^{*}) = 0, \ (i=1, ..., 4)$$
(4.12)

$$\nabla^* \bullet \mathbf{u}^* = 0 \tag{4.13}$$

$$-\nabla^* p^* + \nabla^{*2} \mathbf{u}^* - \frac{1}{2} (\kappa R_p)^2 (z_1 c_1^* + z_2 c_2^* + z_3 c_3^* + z_4 c_4^*) \nabla^* V^* = 0$$
(4.14)

where c_i^* , z_i and D_i^* are the dimensionless concentration, valence electron number, and diffusivity of the ith ionic species, respectively.

The dimensionless surface charge density expression is

$$\sigma_{w} = -N_{Total}^{*} \frac{K_{A} - K_{B}[\mathrm{H}^{+}]_{s}^{*2}}{K_{A} + [\mathrm{H}^{+}]_{s}^{*2} + K_{B}[\mathrm{H}^{+}]_{s}^{*2}}$$
(4.15)

where N_{Total}^{*} and $[\mathrm{H}^{+}]_{s}^{*}$ are the dimensionless scale of N_{Total} , which equals to $\varepsilon_{f}\varepsilon_{0}RT/(F^{2}\mathrm{R}_{p})$ and the dimensionless proton concentration on the nanoparticle surface.

4.3 Numerical Implementation and Code Validation

The PNP equations are numerically solved using a commercial finite-element package, COMSOL Multiphysics (<u>www.comsol.com</u>), operating in a high-performance cluster. Finer mesh is used around the surfaces of a charged nanoparticle and plate and in the gap between the particle and the plate. Relatively coarse mesh is used in regions far away from the charged surfaces. In the simulations, the far field boundary (e.g., the dashed line AB in Figure 4.1) is set as R_D =50 R_p , which is sufficiently large and the results do not change as R_D further increases. Through systematic studies of mesh refinements, mesh independent results are established using about 300k elements, as shown in Figure 4.2. Mesh refinement tests have been carried out to ensure that the solutions are convergent and grid independent. Based on the calculated surface charge density by theoretical value using Eq. (4.10), a maximum tolerance of 0.1% is imposed on the relative difference between theoretical and numerical results. Lagrange – Quadratic elements are used for solving PNP equations, while Lagrange – P_2P_1 elements are used for the Stokes equations.

Physical parameters used in the simulations are $\varepsilon_0 \varepsilon_f = 7.08 \times 10^{-10}$ F/m, R = 8.31 J/(K·mol), F = 96490 C/mol, T = 300K, N_{total}=4.816 sites/nm², pK_A=-logK_A=7.0, and pK_B= -logK_B=1.9. The diffusivities of H⁺, K⁺, Cl⁻, and OH⁻ ions are, respectively, 9.31×10^{-9} m²/s, 1.96×10^{-9} m²/s, 2.03×10^{-9} m²/s, and 5.30×10^{-9} m²/s [10]. The particle radius is R_p=10 nm and the separation distance between the particle's bottom pole and the flat surface is kept constant for all simulation cases at *h*=5 nm, and the degree of interaction is adjusted by varying the bulk salt concentration C_{KCI} in the range of 1mM and 100mM.

The EDL thickness is calculated using $\kappa^{-1} = \lambda_{ij} = \sqrt{\varepsilon_0 \varepsilon_f RT / \sum_{i=1}^4 F^2 z_i^2 C_{i\infty}}$ and the results are presented as a function of normalized separation distance κh . The pH of the aqueous solution is adjusted by using H⁺ or OH⁻ ionic species in the range of 4 to 10.

For code validation purposes, we simulated the surface charge density of a spherical silica nanoparticle of $D_p=116$ nm immersed in an infinite electrolyte medium without the plate. The obtained results illustrated in Figure 4.3a shows a good agreement with the experimental data obtained by Sonnefeld et al.[177] for bulk salt concentration $C_{KCI}=100$ mM, $N_{total}=2.1$ sites/nm², $pK_A=6.38$, and $pK_B=1.87$. Therefore, the charge regulation model for the surface charge density captures the underlying physics. We also modeled a flat silica surface in contact with a semi-infinite electrolyte solution. An analytical solution for the surface charge density of a planar surface has been recently derived by Yeh et al. [209] . Figure 4.3b depicts the surface charge density of a planar surface has been recently derived by Yeh et al. [209] . Figure 4.3b depicts the surface charge density of a planar surface has been recently derived by Yeh et al. [209] depicts the surface charge density captures density of a planar surface as a function of pH for bulk salt concentration $C_{KCI}=100$ mM. The numerical results (red circles) are in good agreement with the analytical results (solid line). Clearly, the surface charge density increases with increased pH of the solution.



Figure 4.3. Surface charge densities of a silica nanoparticle (a) and a planar silica plate as a function of pH of the electrolyte solution. Circles and line in (a) represent, respectively,

the experimental data from Sonnefeld et al. [177] and the numerical results. Circles and line in (b) are, respectively, the numerical results and the analytical results derived by Yeh et al. [209].

4.4 **Results and Discussion**

4.4.1 Salt Concentration Effect

When the interaction between the particle and the plate is very weak, which occurs when the separation distance is much larger than the EDL thickness (i.e., $\kappa h >>1$), the surface charge density along the surface of the particle (plate) is spatially uniform. Due to the curvature effect, the surface charge density of the nanoparticle is different from that of the plate. We denote the surface charge densities of the particle and plate under the condition of no interaction as $\sigma_{p\infty}$ and $\sigma_{w\infty}$, respectively.

The electrostatic interaction between the particle and the plate increases as κh decreases. Figure 4.4 depicts the electric potential distribution around the nanoparticle and the interacting plate for different pH and κh values. The EDLs are not overlapped for $\kappa h=5$; therefore, the electric potential along the surface of the particle and the plate are spatially uniform. As κh decreases, the degree of EDL overlap increases. EDLs are slightly overlapped in the gap for $\kappa h=1.6$ and the magnitude of the electrical potential in the gap region between the particle and the plate is higher than that located far away from the interaction region. EDLs are significantly overlapped for $\kappa h=0.5$, resulting in a larger interaction region with an enhanced electric potential. Obviously the electric potential around the particle (plate) becomes significantly non-uniform for $\kappa h\leq 1$ due to serious EDL overlapping. On the particle surface, the highest potential occurs at the bottom pole of the

particle, where the strongest interaction occurs, and the lowest potential occurs at the top pole, which has the weakest interaction with the bottom flat plate. The potential difference between the bottom and top poles of the spherical particle increases as κh decreases for all pH values.



Figure 4.4. Distribution of the electric potential around the nanoparticle interacting with a flat surface at different κ h and pH. Color bars denote the electric potential in Volts.

Figure 4.5 depicts the surface charge densities along arc length of the particle surface starting from the bottom pole to top pole (lines without symbols) and along the flat surface (lines with symbols) under the conditions of Figure 4.4. Under any given condition, the surface charge density of the nanoparticle is typically a little bit higher than that of the plate, and this is attributed to the curvature effect [13 17]. Under the condition of serious EDL overlap (i.e., $\kappa h=0.5$), the surface charge densities of the particle and the plate become spatially non-uniform. The magnitude of the surface charge density in the interacting region is typically lower than that far away from the interaction region. As κh increases, the degree of the non-uniform distribution of the surface charge density decreases. In addition, the surface charge densities of the particle and the plate increase with an increase in κh . To further clearly show the variation of the charge density along the particle and the plate, Figure 4.6 illustrates the spatial distributions of the surface charge densities along arc length of the particle surface (a) and the plate (b) normalized by the corresponding surface charge densities for $\kappa h \rightarrow \infty$. In absence of interaction, the normalized surface charge density is 1. Since the top pole of the spherical particle has very weak interaction with the bottom plate under the considered conditions, the normalized surface charge density at the top pole is 1. However, the normalized surface charge density at the bottom pole significantly deviates from 1, especially when the EDLs are significantly overlapped. For example, at $\kappa h=0.5$ the surface charge density at the bottom pole of the sphere is about 62% of that at the top pole of the nanoparticle. The surface charge density on the plate at r=0 is about 78% of the non-interacting region. Therefore, the assumption of constant surface charge densities of two interacting objects used in previous studies are inappropriate[4, 218]. The normalized surface charge density increases on a particle's surface from the bottom towards the top pole. As κh increases, the interaction region decreases; therefore, the region with normalized surface charge density smaller than 1 shrinks. For $\kappa h=5$, only a small portion of the particle and the plate have a very weak interaction, and their normalized surface charge densities are slightly smaller than 1, as shown in Figure 4.6.



Figure 4.5. Surface charge densities along the nanoparticle surface (lines without symbols) and the flat plate (lines with symbols) at pH=4 (a), 5.5 (b) and 9 (c).



Figure 4.6. Spatial variation of the normalized surface charge density on nanoparticle (a) and flat plate (b) for different κ h and fixed pH=5.5.



Figure 4.7. Spatial distribution of H^+ ion concentration (in mM) near the nanoparticle for different kh values and pH= 5.5.

The significant reduction of the surface charge densities of the particle and the plate is attributed to the significant enrichment of positive ions in the interaction region. Under the considered conditions, both the nanoparticle and the plate are negatively charged. Counterions, (K⁺ and H⁺), are accumulated within each EDL, and co-ions, Cl⁻ and OH⁻, are depleted. Figure 4.7 depicts the spatial distribution of a concentration of H⁺ ions near the nanoparticle for pH=5.5 at different κh values. The variation of κh is achieved by adjusting the bulk concentration of the background salt, C_{KCl}. Figure 4.7 shows that the concentration of H⁺ ions is significantly enhanced as κh decreases. The enriched positive ions decrease the negatively charged SiO^- dissociated from the functional groups SiOH, yielding a lower negative surface charge density in the interaction region [88]. Figure 4.8a depicts ionic concentration of H^+ ions at the bottom (solid line) and top (dashed line) poles of the particle as a function of κh when the pH level is 6.5. Since the increase in κh is achieved by increasing the bulk salt concentration, C_{KCl} , the concentration of K⁺ ions also increases with an increase in κh . The increased K⁺ ions in the EDL of the nanoparticle repels H⁺ ions, resulting in a decrease in the concentration of H⁺ inside the EDL. At the top pole of the nanoparticle, which almost has no interaction with the plate, the concentration of H⁺ ions decreases as κh increases, and this is attributed to the depletion of H⁺ ions by the increased K⁺ ions. When $\kappa h \leq 2$, the concentration of H⁺ ions at the bottom pole is much higher than that at the top pole, which is due to the enriched positive ions in the interaction region by EDL overlap. As κh increases, the degree of EDL overlap decreases, and the difference between the proton concentrations at the bottom and top poles decreases. Figure 4.8b shows the concentration of H^+ ions on the plate at the origin (solid line) and far away from the interaction region (dashed line). Similarly, the proton concentration at the origin where the strongest interaction occurs significantly increases due to the EDLs overlapping. Based on the protonation/deprotonation reactions, the surface charge density is inversely proportional to the local concentration of H^+ ions; the enriched H^+ ions in the interaction region arising from the overlapped EDLs lead to a lower surface charge density in the interaction region, as shown in Figures 4.5 and 4.6.



Figure 4.8. (a) H⁺ ion concentration on the particle's top pole (square with dashed line), and on the particle's bottom pole (circle with solid line). (b)H⁺ ion concentration on the plate at r=0 (solid line with circles) and $r\rightarrow\infty$ (square with dashed line).



Figure 4.9. Ratio of the surface charge density difference at the top and bottom poles of the particle to the surface charge density at the top pole as a function of kh for different pH values.

Figure 4.9 shows the ratio of the surface charge density difference at the top and bottom poles to the surface charge density at the top pole, $(\sigma_{pT} - \sigma_{pb})/\sigma_{pT}$, as a function of κh at pH=4, 5.5, and 9. At each pH, the surface charge density difference at the top and bottom poles of the particle decreases as κh increases. As κh exceeds a certain critical value, the surface charge density difference vanishes, and the surface charge density is uniformly distributed along the particle surface. At the same κh , the relative surface charge difference at pH=5.5 is higher than those at pH=4 and 9, which will be explained in the following section.



Figure 4.10. (a) Surface charge density at the bottom pole of the nanoparticle as a function of pH for $\kappa h=0.5$, 1.6, and 5. (b) Surface charge density on the bottom pole of the nanoparticle normalized by that at $\kappa h \rightarrow \infty$ as a function of pH for three different κh values.

4.4.2 The Effect of pH level of the aqueous solution

Previous results clearly show that the surface charge properties of two interacting objects vary with the degree of their interaction, and the surface charge density in the interaction region is dramatically reduced when the EDLs are significantly overlapped. In this section, the effect of pH on the surface charge density of the particle interacting with the plate is investigated at fixed κh = 0.5, 1.6, and 5, where the corresponding bulk salt concentrations are 1, 10 and 100 mM, respectively.

Figure 4.10a depicts the surface charge density at the bottom pole of the particle as a function of pH at κh =0.5, 1.6 and 5. At fixed κh , the negative surface charge density increases with an increase in pH. This is expected since the bulk concentration of H⁺ ions decreases as pH increases, leading to more SiO⁻ functional groups dissociated from SiOH.

Figure 4.10b depicts the surface charge density at the bottom pole of the particle normalized by that for $\kappa h \rightarrow \infty$. At $\kappa h = 5$, the normalized surface charge density is close to 1, due to very weak interaction. However, for $\kappa h=1.6$ and 0.5, due to strong interaction, the normalized surface charge density is below than 1. The normalized surface charge first decreases as pH increases, attains the minimum at a critical pH, and then increases when pH exceeds the critical value. The variation of the normalized surface charge density with pH can be explained by the variation of the surface concentration of protons under the considered conditions. Figure 4.11 depicts the concentration of H⁺ ions at the bottom pole normalized by that for $\kappa h \rightarrow \infty$ at the same conditions of Figure 4.10. The normalized surface concentration of H^+ ions increases with an increase in pH when the latter is relatively low, attains a maximum at a critical pH, and then decreases as pH further increases. As pH increases, the bulk concentration of H⁺ ions decreases, leading to a decrease in the surface concentration of H⁺ ions. However, the negative surface charge density increases as pH increases, which attracts more H⁺ ions to the negatively charged surface, resulting in an increase in the surface concentration of H⁺ ions. The variation of the surface concentration of H⁺ ions with pH is the net result of the two competitions. When pH is relatively low, since the bulk concentration of H^+ ions is not very low, the increased negative charge attracts a lot of H⁺ ions into the overlapped EDLs, resulting in an increase in the concentration of H⁺ ions in the interaction region. However, at relatively high pH, the bulk concentration of K^+ ions becomes significantly higher than that of H^+ ions, therefore, more K^+ ions than H^+ ions will be accumulated in the overlapped EDLs. The enriched K^+ ions will also deplete H^+ ions, leading to a decrease in H^+ ions inside the EDL. Therefore, the local concentration of H⁺ ions at the bottom pole of the particle increases

with an increase in pH at a relatively low pH, attains the maximum at a critical pH, and then decreases as pH further increases. Since the charge density is inversely proportional to the local concentration of H^+ ions, the surface charge densities of the particle in the interaction region decreases as pH increases, and attains the minimum at the critical pH value, after which they increases as pH further increases.



Figure 4.11. Concentration of H⁺ ions at the bottom pole of the particle normalized by that at $\kappa h \rightarrow \infty$ as a function of pH for different κh values.

4.5 Conclusions

Surface charge properties of interacting a silica nanoparticle and plate are theoretically investigated as functions of pH, background salt concentration, and the degree of their interaction. The model considers multiple ionic species, charge regulation on the interaction objects, and double layer overlap. The Stern layer effects are ignored in the current study. Without interaction, the surface charge density is homogeneous. However, the charge densities become spatially non-uniform, and the magnitude of the surface charge density in the interaction region is significantly reduced when the double layers are overlapped. Under strong interaction, the surface charge density in the interaction region is only about 50% of the bulk value. Since the degree of interaction increases as the ratio of the separation distance to the EDL thickness, κh , decreases, the deviation from constant charge densities for two interacting objects increases as κh decreases. In the interaction region, the normalized surface charge densities of the particle and the plate decrease as pH increases, attain a minimum value at a critical pH value, and then increase with further increase in pH. This arises from the competition of the following two mechanisms: (1) bulk concentration of H⁺ ions decreases as pH increases, yielding to a decrease in the surface concentration of H^+ ions; and (2) the negative surface charge density increases with an increase in pH, which attracts more counter-ions accumulated inside the EDLs. When more K^+ ions are accumulated than the H⁺ ions, the enriched K⁺ ions also deplete H⁺ ions. The results demonstrate that the assumption of constant surface charge density of two interacting objects is invalid under strong EDL interactions between the particle and the surfaces in the range of $\kappa h \leq 1$.

CHAPTER 5

PROTON ENHANCEMENT IN AN EXTENDED NANOCHANNEL

5.1 Introduction

A fundamental understanding of the ion transport in an extended nanospace, in which the thickness of electric double layers (EDLs) is comparable to the characteristic dimension of nanospaces, is substantial for the development of biomimetic nanofluidic devices [67, 125]. Among various ions, protons (H⁺ ions) play an essential role due to their fundamental significance in nanofluidics applications [67, 108, 116, 125, 178, 182, 217]. In addition to the structure and conformation of molecular chains in biological ion channels, the charge properties of nanofluidic devices in contact with an aqueous solution are substantially dependent on the local proton concentration in the vicinity of the nanochannel wall surface [67, 108, 116, 125, 178, 182, 217].

In spite of numerous theoretical and experimental studies on the confined fluid and ion transport in extended nanospaces [30, 93, 160], the relevant analysis focused on proton transport is surprisingly rare. Recently, Kazoe et al.[94] experimentally investigated the proton distribution in an extended silica nanochannel using a super-resolution-laser-induced fluorescence technique and found that the interior proton concentration is apparently enhanced. One set of their experimental data in pure water was then analyzed by Chang et al. [32] based on the 2D Poisson-Boltzmann (PB) equation coupled with a site dissociation model on the nanochannel wall. Their results showed that the PB model matched the experimental data of Kazoe et al. [94] only when the permittivity of the fluid, $\varepsilon_f = 17\varepsilon_0$, with ε_0 being the dielectric constant of vacuum. Note that the general bulk value

of the permittivity of an electrolyte solution is $\varepsilon_f = 78.5\varepsilon_0$ [80]. The results obtained by Chang et al.[32] imply that there is a dramatic reduction of the permittivity of electrolyte solutions confined in extended nanospaces. However, many theoretical studies used the bulk value of the permittivity of an electrolyte solution to investigate various electrokinetic transport phenomena in extended nanochannels, and the models' predictions agree with the experimental data on ionic current/conductance [65, 114-115, 167, 180, 213], streaming conductance [191, 193], and electrophoretic translocation of nanoparticles through a nanopore [61, 148, 214].

Proton distribution and enhancement in an extended is theoretically studied in order to exclude the inconsistent permittivity of electrolyte solution confined in the extended nanospaces by using pH-regulated nanochannel. The theoretical model is created in 3D by including Poisson-Nernst-Planck (PNP) which takes into account multiple ionic species and surface chemistry on the channel wall. Our model extends that of Chang et al. [32], who adopted the 2D PB equation with site dissociation, to a more general case by considering the presence of H^+ and OH^- in addition to the ions dissociated from the background salt solution, site association and dissociation reactions on the channel wall, and 3D nanochannel. The developed model is validated by the existing experimental data of proton distributions using the general bulk value of the permittivity of electrolyte solution, which is also adopted by many theoretical studies on the electrokinetic transport phenomena of an electrolyte solution confined in a nanochannel or nanopore [61, 65, 114-115, 148, 167, 180, 191, 193, 214].

5.2 Mathematical model

We consider a nanofluidic system comprising a straight nanochannel of length L with a rectangular cross section of height H and width W by connected two large, identical reservoirs on either end, as shown in Figure 5.1. To investigate the proton distribution in an extended nanospace, we assume that both the width and height (i.e., W and H) of the nanochannel are in nanoscale and the length of the nanochannel is much larger than the width and height (i.e., $L \gg W$ and $L \gg H$). Both reservoirs and the nanochannel are filled with an aqueous electrolyte solution containing N types of ionic species. The 3D Cartesian coordinate system, (x,y,z), with the origin at the center of the nanochannel is adopted, where x, y, and z are directed along the directions of height, width, and length, respectively.



Figure 5.1. Schematic illustration of the 3D simulation domain with pH regulated silica nanochannel.

To simulate experimental conditions, we assume that the electrolyte solution includes a background salt KCl of background concentration C_{KCl} and the pH level is adjusted by KOH and HCl solutions. Therefore, four ionic species, H⁺, OH⁻, K⁺, and Cl⁻, are considered. Let C_{i0} (*i*=1, 2, 3, and 4) be the bulk molar concentrations of these ions, respectively. Electroneutrality of the bulk solution yields $C_{10} = 10^{-\text{pH}}$, $C_{20} = 10^{-(14-\text{pH})}$, $C_{30} = C_{\text{KCl}}$, and $C_{40} = C_{\text{KCl}} + 10^{-\text{pH}} - 10^{-(14-\text{pH})}$ for pH ≤ 7 ; $C_{30} = C_{\text{KCl}} - 10^{-\text{pH}} + 10^{-(14-\text{pH})}$ and $C_{40} = C_{\text{KCl}}$ for pH > 7 [212, 215].

Since both the width and height of the nanochannel are in nanoscale, EDL overlapping in the extended nanospace is significant. When EDLs are significantly overlapped, the PB model adopted by Chang et al.[32] to describe the distribution of ions in an extended nanochannel is not appropriate. In the present study, the electrostatics and ionic mass transport are governed by the following verified multi-ion Poisson-Nernst-Planck (PNP) equations [213]:

$$-\varepsilon_{f} \nabla^{2} \psi = \rho_{e} = 1000 F \sum_{i=1}^{4} z_{i} c_{i} , \qquad (4.16)$$

$$\nabla \cdot \mathbf{N}_{i} = \nabla \cdot 1000 \left(-D_{i} \nabla c_{i} - z_{i} \frac{D_{i}}{RT} F c_{i} \nabla \psi \right) = 0, \ i = 1, 2, 3, \text{ and } 4.$$

$$(4.17)$$

Here, ϕ is the electrical potential; R, T, and F are the universal gas constant, absolute temperature, and Faraday constant, respectively; N_i , z_i , C_i , and D_i , are the flux density, valence, molar concentration, and diffusivity of the *i*th ionic species, respectively; $\rho_e = 1000F \sum_{i=1}^{4} z_i c_i$ is the mobile space charge density. Note that the factor of 1000 in Eqs. (5.1) and (5.2) arises from the use of molar concentration for the ionic species.

The boundary conditions for Eqs (5.1) and (5.2) are assumed as the following: (i) The ionic concentrations at both ends of the two reservoirs are their bulk values (i.e., $c_i = c_{i\infty}$) and the corresponding electrical potentials are $\psi = 0$. (ii) Insulation boundary condition for the potential ($\mathbf{n} \cdot \nabla \psi = 0$) and zero normal ionic fluxes ($\mathbf{n} \cdot \mathbf{N}_i = 0$) are applied on the side boundaries of the two reservoirs, which are far away from the nanochannel. Here \mathbf{n} is the unit's outer normal vector. (iii) The nanochannel wall is ion-impenetrable and bears a surface charge density, σ_s , yielding $\mathbf{n} \cdot \mathbf{N}_i = 0$ and $-\varepsilon_f \mathbf{n} \cdot \nabla \psi = \sigma_s$, respectively.

The nanochannel wall in contact with aqueous solution is charge-regulated, implying that its surface charge density, σ_s , highly depends on the local solution pH and electrolyte concentration.[64] Suppose that the nanochannel is made of a silica-based material and its charge density stems primarily from the following surface dissociation and association reactions of silanol functional groups, $Si - OH \leftrightarrow Si - O^- + H^+$ and $Si - OH + H^+ \leftrightarrow Si - OH_2^+$, respectively. Let K_a and K_b be the equilibrium constants of these two reactions, respectively. Then it can be shown that [213]

$$\sigma_{s} = -FN_{t} \left\{ \frac{10^{-pK_{u}} - 10^{-pK_{b}} (c_{1s})^{2}}{10^{-pK_{u}} + c_{1s} + 10^{-pK_{b}} (c_{1s})^{2}} \right\}.$$
(4.18)

Here, $pK_a = -\log K_a$, $pK_b = -\log K_b$, N_i is the total number site density of silanol relevant groups (i.e., Si – OH, Si – O⁻, and Si – OH₂⁺) on the nanochannel wall surface, and c_{1s} is the local molar concentration of protons at the nanochannel wall/liquid interface. Eq. (5.3) clearly suggests that σ_s is part of the solution in the current study, and relies on the physicochemical properties of the dielectric channel material (pK_a , pK_b , and N_i), and the local pH (= $-\log c_{1s}$) on its wall surface. For the silica nanochannels, reported values for pK_a , pK_b , and N_i are $pK_a = 6 \sim 8$, $pK_b = 0 \sim 3$, and $N_i = 6.31 \sim 13.3 \times 10^{-6} \text{ mol/m}^2$ [9].

The governing equations are normalized with corresponding scale values; the ionic concentration is the bulk ionic concentration (C_{KCl}), the electric potential scale is RT/F, the length scale is particle radius (R_p), the diffusivity scale is $\varepsilon_f \varepsilon_0 R^2 F^2/(\mu F)$, the surface charge density scale is $\varepsilon_f \varepsilon_0 RT/(FR_p)$ where R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, μ is the dynamic viscosity. The dimensionless form of the governing equations are

$$-\nabla^{*2}V^{*} = \frac{1}{2}(\kappa R_{p})^{2}(z_{1}c_{1}^{*} + z_{2}c_{2}^{*} + z_{3}c_{3}^{*} + z_{4}c_{4}^{*}), \qquad (4.19)$$

$$\nabla \bullet \mathbf{N}_{i}^{*} = \nabla \bullet (\mathbf{u}^{*} \mathbf{c}_{i}^{*} - \mathbf{D}_{i}^{*} \nabla^{*} \mathbf{c}_{i}^{*} - \mathbf{z}_{i} \mathbf{D}_{i}^{*} \mathbf{c}_{i}^{*} \nabla^{*} \mathbf{V}^{*}) = 0, \ (i=1, ..., 4)$$
(4.20)

$$\nabla^* \bullet \mathbf{u}^* = 0 \tag{4.21}$$

$$-\nabla^{*} p^{*} + \nabla^{*2} \mathbf{u}^{*} - \frac{1}{2} (\kappa R_{p})^{2} (z_{1} c_{1}^{*} + z_{2} c_{2}^{*} + z_{3} c_{3}^{*} + z_{4} c_{4}^{*}) \nabla^{*} V^{*} = 0$$
(4.22)

where c_i^* , z_i and D_i^* are the dimensionless concentration, valence electron number, and diffusivity of the ith ionic species, respectively.

The dimensionless surface charge density expression is

$$\sigma_{w} = -N_{Total}^{*} \frac{K_{A} - K_{B}[\mathrm{H}^{+}]_{s}^{*2}}{K_{A} + [\mathrm{H}^{+}]_{s}^{*2} + K_{B}[\mathrm{H}^{+}]_{s}^{*2}}$$
(4.23)

where N_{Total}^* and $[\mathrm{H}^+]_s^*$ are the dimensionless scale of N_{Total} , which equals to $\varepsilon_f \varepsilon_0 RT/(F^2 \mathrm{R}_p)$ and dimensionless proton concentration on the nanoparticle surface.

5.3 Results and Discussion

The present 3D PNP model is numerically solved by a commercial finite element package, COMSOL Multiphysics, operated in a high-performance cluster, which has been applied to solve similar 2D axisymmetric ion transport problems.[214] The computational domain is discretized into quadratic tetrahedral elements and locally used smaller mesh size on the nanochannel surface in order to calculate ionic flux, and the mesh size gradually increases in the region of EDL occurs. The total number of the mesh used is around 300k elements as illustrated in Figure 5.2. The mesh-independent study has been done according the EDL profile for the worst case, where the salt concentration is 100 mM when the pH level of an aqueous solution is 10. Lagrange – Quadratic, weak constraint, conservative form elements are used to solve PNP equations. The following parameters are used in the simulations: $D_1(H^+)=9.31\times10^{-9} \text{ m}^2/\text{s}$, $D_2(OH^-)=5.30\times10^{-9} \text{ m}^2/\text{s}$, $D_3(K^+)=1.96\times10^{-9} \text{ m}^2/\text{s}$, $D_4(Cl^-)=2.03\times10^{-9} \text{ m}^2/\text{s}$, T=298 K, F=96490 C/mol [215]. The dimension of the rectangular reservoir is 800 nm in its width and height and 400 nm in length.

5.3.1 Verification by experimental data

The developed model is first verified by the experimental data of Kazoe et al., [94] who measured the pH distribution along the width (y-) direction of an extended silica nanochannel at W = 410 nm, H = 405 nm, $L = 1 \ \mu m$, with the bulk pH = 6.22. Note that the pH profile reported by Kazoe et al. [94] was based on the averaged pH over the height (x-) direction. To fit this experimental data, we define an x-axis-averaged \overline{pH} on the center cross section of the nanochannel (z = 0),

$$\overline{pH}(y, z=0) = \frac{\int_{0}^{H} pH(x, y, z=0) dx}{H}.$$
(4.24)

Figure 5.3 shows the distribution of \overline{pH} for various background salt concentrations, C_{KCI} . Pure water represents the results of $C_{\text{KCI}} = 0$. This figure clearly shows that the proton concentration inside the nanochannel is remarkably enhanced, yielding a lower \overline{pH} than the bulk pH = 6.22 (dotted line). Figure 5.3 also depicts that predictions from our model (solid lines) with $pK_a = 7$, $pK_b = 1.9$, and $N_r = 6.31 \times 10^{-6} \text{ mol/m}^2$ fit well to the experimental data (symbols with error bars). Different from the previous theoretical study reported by Chang et al. [32], who used a 2D PB model with $\varepsilon_f = 17\varepsilon_0$ to obtain a better agreement with the experimental data and their model only matched the experimental data of \overline{pH} in pure water [94], our multi-ion PNP model with fixed values for ε_f , pK_a , pK_b , and N_r is also able to match the experimental data for $C_{\text{KCI}} = 0.01$ and 0.0001 M, as shown in Figure 5.3. The adopted value of ε_f is also consistent with many existing studies on electrokinetic transport of an electrolyte solution in extended nanochannels or nanopores [13, 19-29]. Moreover, the estimated values of pK_a , pK_b , and N_t are also in accordance with those reported in the existing literatures [9]. Therefore, these values are used in the subsequent discussions. Unless otherwise specified, the nanochannel geometry is fixed at W = H = 20 nm and $L = 1 \ \mu$ m, which is typical for the dimension of nanochannels used in experiments [65, 130].



Figure 5.2. The free tetrahedral type mesh used in the simulation with finer near EDL region.



Figure 5.3. Distribution of pH averaged in the height direction, \overline{pH} , at the center of the extended nanochannel for various C_{KCl} . Symbols with error bars: experimental data of Kazoe et al.[94] at W = 410 nm, H = 405 nm, $L = 1 \ \mu\text{m}$, and pH = 6.22; solid lines: present numerical results at $pK_a = 7$, $pK_b = 1.9$, and $N_i = 6.31 \times 10^{-6} \text{ mol/m}^2$; dotted line: bulk pH = 6.22.

5.3.2 Effect of background solution properties

Figure 5.4 illustrates that the electric potential distribution inside the nanochannel for different pH levels and salt ionic concentrations. The electric potential is a key property which controls the interactions between surfaces and its magnitude is supposed to be

increased with an increasing of salt concentration and also with the pH level of the aqueous solution. However, as demonstrated in Figure 5.4, the magnitude of electric potential on the surface does not increases with increasing salt concentration. To our knowledge, the electrostatic interaction strength develops depending on the EDL thickness, and with increasing of salt concentration, EDL thickness gets thinner and electrostatic interaction strength gets lower because there is no EDL overlap. Moreover, the magnitude of bulk potential increases with decreasing salt ionic concentration and increasing pH levels. This can be attributed to the volume of charged solutions, which is highly located inside the channel and on the surface, and it causes an increase the magnitude of the electric potential for low concentration levels. Since four sides of the nanochannel are pH regulated silica surface, the EDLs are significantly overlapped at the nanochannel corners and this causes a significant increase of electric potential due to the resulting greater amount of counter ions gathered. This phenomenon may cause a reduction of electroosmotic velocity in case of an external applied field existence, and the produced flow within the nanochannel will have a non-uniform pressure distribution along the nanochannel width and height. This phenomenon may significantly affect the trapping performance of nanochannel applications in drug analysis.



Figure 5.4. The electric potential contour plots in a nanochannel when z=0 for different pH and salt concentration strengths.

Figure 5.5 shows the surface charge density variations as a function of the width of the nanochannel for different background pH and ionic properties. As concluded in the previous figure, the variation of the electric potential is not uniform on the charged surfaces. Due to the same reason, the spatial distribution of the surface charge density is also not uniform along nanochannel width. The bulk surface charge density increases by increasing the salt concentration strength and also increasing of pH level of aqueous solution. This result is consistent with previous studies qualitatively [12-13, 206]. The

result of pH=4 is multiplied by 10 for better illustration. The magnitude of the surface charge density decreases very close to the channel surface due to yielding of high counter ions at the corners of nanochannel.



Figure 5.5. Distribution of surface charge density along the wall of nanochannel with different pH and salt concentration levels. Straight, dash and dash-dot lines presents pH = 4, 7 and 9, respectively.

Since the surface charge density is highly dependent on the local H^+ concentration on the silica surface as seen in Eq. (5.3), the demonstration of H^+ concentration inside the nanochannel has great importance to understanding the behavior of the spatial distribution of surface charge density. Since the sign of surface charge density is negative, counter-ions are accumulated on the surface. By decreasing salt ionic concentration and pH level in the bulk, more H⁺ ions are accumulated on the nanochannel surface and significantly enhanced on the corner of nanochannel. The significant reduction of the surface charge densities on the nanochannel wall is attributed to the significant enrichment of H⁺ ions in the interaction region. The enriched H⁺ ions decrease the negatively charged SiO⁻ dissociated from the functional groups SiOH, yielding a lower surface charge density in the EDL interaction region.



Figure 5.6. Contour plot of proton distribution in a nanochannel at z=0 for different background solution properties.

To understand the proton enhancement phenomenon in an extended nanochannel in detail, we define two parameters; one is the enhanced relative percentage (ERP) of protons, $\Delta = (|\overline{pH} - pH|/pH) \times 100\%$, and the other is the ERP of protons at the center of the nanochannel, $\Delta_c = \left(\left| \overline{pH}_c - pH \right| / pH \right) \times 100\%$. Here \overline{pH}_c can be obtained by letting y = 0in Eq. (5.9). In general, larger values of Δ and Δ_c represent more significant enhancement of protons in the nanochannel. Figure 5.7 depicts the influences of the background salt concentration, $C_{\rm KCI}$, and bulk pH on the variation of Δ . Figure 5.7a reveals that at constant bulk pH, Δ increases with a decrease in $C_{\rm KCl}$, implying that the lower the $C_{\rm KCl}$, the more significant enhancement of protons (lower \overline{pH}) within the nanochannel. This is consistent with the experimental observation of Kazoe et al.[94] (see Figure 5.3), and can be attributed to a more significant exclusion effect of protons from the nanochannel surface by an increase in the salt concentration and other counter-ions (K⁺). Figure 5.7a also suggests that, due to a thinner EDL, Δ (or local proton concentration) varies more apparently near the nanochannel surface (y = -10 and 10 nm) as C_{KCl} increases.


Figure 5.7. Distribution of the ERP of protons, $\Delta = (|\vec{pH} - pH|/pH) \times 100\%$, for various C_{KCI} at the bulk pH = 7.5, (a), and for various bulk pH at $C_{\text{KCI}} = 0.001$ M, (b).

Figure 5.7b depicts that at constant C_{KCI} , Δ increases with an increase in the bulk pH near the nanochannel surface (y = -10 and 10 nm), but has a local maximum as pH increases in the interior of the nanochannel. The former arises from the fact that the higher the bulk pH, the larger the negative surface charge density on the channel wall, attracting more protons near its surface and yielding higher Δ . The latter can be explained by the fact that a higher bulk pH also represents a lower bulk concentration of protons. In this case, since a greater proportion of protons are attracted to the negatively charged channel surface, a relatively smaller proportion of residual protons in an extended nanochannel is more significant at higher bulk pH, as shown in Fig 5.7b.



Figure 5.8. Variations of the ERP of protons at the center of the extended nanochannel, $\Delta_c = \left(\left| \overline{pH}_c - pH \right| / pH \right) \times 100\%$, with the bulk pH for various C_{KCI} , (a), and with C_{KCI} for various bulk pH, (b). Other parameters are the same as those in Figure 5.3.

Figure 5.8 summarizes the influence of the background salt concentration, C_{KCI} , and bulk pH on the ERP of protons at the center of the extended nanochannel, Δ_c . This figure suggests that Δ_c shows a local maximum as the bulk pH increases (Figure 5.8a) and decreases monotonically with increasing C_{KCI} (Figure 5.8b). These behaviors can be explained by the same reasoning employed in Figure 5.7. From Figure 5.7 and 5.8, it can be concluded that the degree of enhanced proton concentration in an extended nanochannel is significant if the background salt concentration is low and the bulk pH is medium high (ca. 8). Under considered conditions, the ERP of the pH value can be on the order of ca. 40 %, and that of the corresponding proton concentration, calculated by $(|\overline{C_1} - C_{10}| / C_{10}) \times 100\%$, over 4000 times, where $\overline{C_1} = -\log(\overline{pH})$ and $C_{10} = -\log(pH)$.

5.3.3 Effect of nanochannel dimensions

The influence of the nanochannel dimensions on the ERP of protons at the center of the extended nanochannel, Δ_c , is depicted in Figure 5.9. In this case, the nanochannel height is set to be the same as its width (i.e., H = W). This figure shows that regardless of the levels of the bulk pH, Δ_c decreases with increasing nanochannel dimensions and approaches a steady value at sufficiently large nanochannel. The former is expected because the smaller the nanochannel, the more significant the EDL overlapping effect, leading to more protons (counter-ions) concentrated inside the nanochannel. When the EDL overlapping effect is negligible, the enhancement of protons becomes nearly independent of the nanochannel size.



Figure 5.9. Variations of the ERP of protons at the center of the extended nanochannel, $\Delta_c = \left(\left| \overline{pH}_c - pH \right| / pH \right) \times 100\%, \text{ with the nanochannel dimension } (H = W) \text{ for various}$ bulk pH at $C_{\text{KCl}} = 0.0001 \text{ M}$.

5.4 Conclusions

The proton distribution and enhancement in an extended, pH-regulated, nanochannel are investigated theoretically taking into account the presence of multiple ionic species and the site dissociation/association model on the nanochannel wall. Different from the previous theoretical study using the 2D Poisson-Boltzmann equation and significantly low fluid permittivity, the 3D multi-ion Poisson-Nernst-Planck model with a general bulk value of the fluid permittivity is adopted for the first time to describe the existing experimental data of the proton distributions in a silica nanochannel under various salt concentrations. As expected, the proton concentration is significantly enhanced by the negatively charged

nanochannel, and its distribution depends substantially on the bulk pH and background salt concentration. The variation of protons in an extended nanochannel is considerably remarkable when the bulk pH is relatively high. Moreover, the enhanced relative percentage of protons at the center of the nanochannel is significant at a medium high bulk pH (ca. 8), low salt concentration, and small size of the nanochannel. Our results show that the local pH at the center of the extended nanochannel can be enhanced on the order of ca. 40 %, implying that over 4000 times of the corresponding proton concentration is raised.

CHAPTER 6

ELECTROOSMOTIC FLOW IN A pH-REGULATED NANOSLIT

6.1 Introduction

Electroosmosis flow (EOF) is a common phenomenon particularly observed in various fields of biochemistry and chemistry [129, 137, 144, 157], and with the advances in nanoscale electrokinetic theory and lab-on-a-chip (LOC) devices, EOC have drawn significant attention because it is one of the most exciting nanoscale phenomena that can be utilized in the nanofluidic systems in order to generate flow fields or drive molecules [42, 47, 78-79, 126, 179]. Due to charge and mobility differences between molecules of solutes in electrolyte solutions, EOF can be used in separation and concentration [11, 49, 74, 208] technologies; EOF in porous and fractured media is very import in the engineering problems relating with large-scale porous media, such as gas, oil, groundwater aquifers, and geothermal reservoirs over various length scales [8, 63, 76].

Much theoretical and experimental research has been carried out to study EOF characteristics [11, 173, 203]. As a reliable method, molecular dynamics (MD) method, which deals with atoms explicitly [162, 207], has been used to simulate EOF inside the nanochannel with different geometry and surface boundary conditions [43, 155]. The numerical method (e.g. finite element method and finite volume method) is also widely used by solving coupled Poisson-Nernst-Planck (PNP) equations and the Stokes equations to simulate kinds of EOF [121, 137, 203]. But both the molecular dynamics method and the numerical method are computing resource consuming, and cannot efficiently guide the

design of nanofluidic devices or elaborate experimental observations. To overcome this drawback, some analytical models are developed with some limited assumptions, such as neglecting the electric double layers (EDLs) overlapping [11], constant surface charge density or surface electric potential on the nanoslit walls without surface chemical reactions [11, 16, 121, 172], and only considering background ionic species [205]. But these assumptions restrict the application of analytical models because EOF is caused by the excess counter-ions inside the EDLs, with regard to the dielectric wall with dissociable functional groups, EOF is significantly influenced by local ionic concentrations and pH value, site density of the functional groups; and surface charge density [9, 21, 31, 87]. Neglecting the EDL's overlapping phenomena within the nanoslit would introduce unrealistic deviation on nanofluidics properties, finally resulting in miscalculation of EOF velocity.

In this study; with consideration of EDLs overlapping, pH effects (multiple ionic species including background ionic species, H⁺ and OH⁻), and surface protonation/deprotonation reactions, an analytical model of EOF velocity calculation is proposed first time. Simultaneously, the EOF processes within a 2-D nanofluidic device composed of a pH-regulated silica nanoslit connected with two big fluid reservoirs on both ends are taken into account, and simulations of coupled multiphysics are performed numerically based on continuum-based models including the Nernst-Planck (NP) equation, the Poisson-Boltzmann (PB) equation, the Stokes equation, and surface reactions. Both the analytical model and the numerical simulation are validated by comparing their predictions with the experimental data from flow rate measurements of electroosmotic driven flow for the silica nanoslit [71, 220]. Subsequently, the influences of background salt concentration,

pH value and length of nanoslit on EOF velocity are investigated comparatively, and the scope of application of the proposed analytical model is given by comparing the predictions with numerically simulation results.

6.2 Mathematical Model

As shown in Figure 6.1, we study a nanoslit with a length (L) and height (H) connecting two large reservoirs filled with an electrolyte solution (i.e., *NaCl solution*) containing Ntypes of ionic species. The height of the nanochannel is significantly less than the width of the channel, W (H << W) so that this study is considered 2D symmetric. The reservoir dimensions are chosen to be large enough in order to avoid high potential drop inside the reservoirs. Since we model to describe steady-state flow distribution and the ion transport in nanochannel, three coupled steady-state partial differential equations are needed to reveal the physics correctly. They are defined for all domains. The Nernst-Planck (NP) equation describes the ionic mass flux densities and the flux of species is the sum of the advection, diffusion and conduction terms and the Poisson-Boltzmann (PB) equation defines the electric potential distribution inside the whole domain, and they are given by:

$$\nabla \bullet \mathbf{N}_{i} = \nabla \bullet \left(\mathbf{u}c_{i} - D_{i}\nabla c_{i} - z_{i}\frac{D_{i}}{RT}Fc_{i}\nabla \psi \right) = 0, \ (\mathbf{i}=1,\dots,4).$$
(5.1)

$$-\varepsilon_0 \varepsilon_t \nabla^2 \psi = \rho_e = F \sum_{i=1}^4 z_i c_i$$
(5.2)

to \mathcal{E}_0 and \mathcal{E}_f are the dielectric constant of a vacuum and the relative dielectric constant of the electrolyte solution, respectively. **u**, N_i , D_i , c_i , z_i are the fluid velocity, flux density, ionic diffusivity, ionic concentration, valence electron number of i^{th} ionic species, respectively. The volume charge density can be expressed as the total sum of the all ion densities multiplied by their respective charge: $\rho_e = F \sum_{i=1}^{4} z_i c_i$, where F is the Faraday constant.

The Stokes equation, which consists of the electric body force term due to the electrostatic force applied for an incompressible Newtonian flow in a low Reynolds limit describes the fluid flow that is given by

$$-\nabla \mathbf{p} + \mu \nabla^2 \mathbf{u} - \rho_e \nabla \psi = 0 \tag{5.3}$$

$$\nabla \cdot \mathbf{u} = 0 \tag{5.4}$$

In the above, p, μ , u, ψ are the hydrodynamic pressure, the dynamic fluid viscosity, velocity and electric potential inside the electrolyte solution, respectively.



Figure 6.1. Schematic illustration of the EOF within a pH-regulated nanoslit with electric double layers overlapping, and containing multiple ionic species, Na⁺, Cl⁻, H⁺, and OH⁻

In contrast to many existing studies, those uses prescribed constant surface charge [refs], our model considers the chemical reactions at the oxide surface to describe the protonation/deprotonation functional groups. Here, the effects of the Stern layer on determination of surface charge property are neglected. On the oxide electrolyte interface the following reactions take place:

$$\mathrm{SiOH} \xleftarrow{\kappa_{*}} \mathrm{SiO}^{-} \mathrm{H}_{\mathrm{s}}^{+} \tag{5.5}$$

$$\text{SiOH}_2^+ \xleftarrow{K_h} \text{SiOH}_H^+$$
 (5.6)

The equilibrium constants of the two dissociation reactions are $K_a = \Gamma_{\text{SiO}^-}[\text{H}_s^+]/\Gamma_{\text{SiOH}}$ and $K_b = \Gamma_{\text{SiOH}_2^+}/\Gamma_{\text{SiOH}}[\text{H}_s^+]$. The total number of silica site density can be expressed as $\Gamma_{\text{Total}} = \Gamma_{\text{SiOH}} + \Gamma_{\text{SiO}} + \Gamma_{\text{SiOH}_2^+}$ and the surface charge density based on the site-dissociation model for silicon dioxide is given as

$$\sigma_{w} = -F\Gamma_{total} \frac{K_{A} - K_{B}[H_{s}^{+}]^{2}}{K_{A} + [H_{s}^{+}] + K_{B}[H_{s}^{+}]^{2}}.$$
(5.7)

The chemical reaction constants used in this study are $pK_A=7$, $pK_B=1.9$ and $\Gamma_{Total}=3.8 \text{ sites/nm}^2$, and those parameters are consistent with reported values for silicon dioxide surfaces and $[H_s^+]$, which represents the molar concentration of protons on the wall/liquid interface. Here, it can be concluded that the surface charge propetry does not only depend on N_{total} , K_A , and K_B , it is also depends on the pH and salt concentration density of electrolyte solution. The salt concentration is defined as C_{NaCl} and the pH value is adjusted by adding HCl or NaOH. In general, a multi-ion model is used in order to satisfy the correct chemical reactions on silica material; those ions are H⁺, Na⁺, Cl⁻, and OH⁻, and their bulk concentrations are, respectively, $C_{10} = 10^{-pH+3}$, $C_{20} = C_{NaCl}$, $C_{30} = C_{NaCl} + 10^{-pH+3} - 10^{-(14-pH)+3}$, and $C_{40} = 10^{-(14-pH)+3}$ for, $pH \le 7$ and for pH > 7 they are as following; $C_{10} = 10^{-pH+3}$, $C_{20} = C_{NaCl} - 10^{-pH+3} + 10^{-(14-pH)+3}$. $C_{30} = C_{NaCl}$, and $C_{40} = 10^{-(14-pH)+3}$ [209].

The solution of these governing equations requires the appropriate boundary conditions in order to calculate for a correct description of the phenomena. (i) At the both ends of the reservoir, ionic concentrations are maintained at their bulk values (i.e., $c_i = C_{ix}$), the corresponding electric potentials are $V_{Anode}=V_0$ and $V_{Cathode}=0$, and normal flow with no external pressure gradient ($\Delta p = 0$), or concentration gradient, is specified for flow field. (ii) For the nanochannel wall, nonslip, ion impenetrable and surface charge density (σ_x) boundary conditions are assigned and they are $\mathbf{u} = 0$, $\mathbf{n} \cdot \mathbf{N}_i = 0$, and $-\mathbf{n} \cdot \nabla \Psi = \sigma_x / \varepsilon_f$, respectively. (iii) For the side boundaries of the two reservoirs, slip, zero normal ionic flux ($\mathbf{n} \cdot \mathbf{N}_i = 0$), and insulation ($\mathbf{n} \cdot \nabla \Psi = 0$) boundary conditions are applied, respectively. (iv) And finally along the axis of the nanoslit, the symmetric boundary condition is applied in order to keep the computational costs within practical limits.

We assume that the diffusivities for H⁺, Na⁺, Cl⁻, and OH⁻ are 9.31e-9, 1.96e-9, 2.03e-9 and 5.3e-9 m²/sec, respectively, and assume the diffusivities of ions does not change from their bulk values when the nanoslit height is 10 nm [51]. We also assume that the dielectric permittivity and viscosity of the electrolyte solution as the bulk values $\varepsilon_f = 80$ and $\mu = 1 \times 10^{-3}$ Pa·s and they have a uniform distributions. The fluid temperature is kept constant as T = 298 K The nanoslit used in simulations has H = 10 nm, L = 1 μ m, and W = 0.5 μ m. The EDL thickness is calculated using $\kappa^{-1} = \lambda_{ij} = \text{sqrt}(\varepsilon_0 \varepsilon_f RT / \sum_{i=1}^4 F^2 z_i^2 C_{ix})$.

The applied electric field is kept constant at 50 kV/m for all simulations and approximation simulation cases except for the model validation part. The governing equations are normalized with corresponding scale values; the ionic concentration is the bulk ionic

concentration ($C_{\kappa ct}$), the electric potential scale is RT/F, the length scale is particle radius (R_p), the diffusivity scale is $\varepsilon_f \varepsilon_0 R^2 F^2/(\mu F)$, the surface charge density scale is $\varepsilon_f \varepsilon_0 RT/(FR_p)$ where R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, μ is the dynamic viscosity. The dimensionless form of the governing equations are

$$-\nabla^{*2}V^{*} = \frac{1}{2}(\kappa R_{p})^{2}(z_{1}c_{1}^{*} + z_{2}c_{2}^{*} + z_{3}c_{3}^{*} + z_{4}c_{4}^{*}), \qquad (5.8)$$

$$\nabla \bullet \mathbf{N}_{i}^{*} = \nabla \bullet (\mathbf{u}^{*} \mathbf{c}_{i}^{*} - \mathbf{D}_{i}^{*} \nabla^{*} \mathbf{c}_{i}^{*} - \mathbf{z}_{i} \mathbf{D}_{i}^{*} \mathbf{c}_{i}^{*} \nabla^{*} \mathbf{V}^{*}) = 0, \ (i=1, ..., 4)$$
(5.9)

$$\nabla^* \bullet \mathbf{u}^* = \mathbf{0} \tag{5.10}$$

$$-\nabla p^{*} p^{*} + \nabla^{*2} \mathbf{u}^{*} - \frac{1}{2} (\kappa R_{\rho})^{2} (z_{1}c_{1}^{*} + z_{2}c_{2}^{*} + z_{3}c_{3}^{*} + z_{4}c_{4}^{*}) \nabla^{*} V^{*} = 0$$
 (5.11)

where c_i^* , z_i and D_i^* are the dimensionless concentration, valence electron number, and diffusivity of the ith ionic species, respectively.

The dimensionless surface charge density expression is

$$\sigma_{w} = -N_{Total}^{*} \frac{K_{A} - K_{B}[\mathrm{H}^{+}]_{s}^{*2}}{K_{A} + [\mathrm{H}^{+}]_{s}^{*2} + K_{B}[\mathrm{H}^{+}]_{s}^{*2}}$$
(5.12)

where N_{Total}^{*} and $[\mathrm{H}^{+}]_{s}^{*}$ are the dimensionless scale of N_{Total} , which equals to $\varepsilon_{f}\varepsilon_{0}RT/(F^{2}\mathrm{R}_{p})$ and the dimensionless proton concentration on the nanoparticle surface.

6.3 Analytical model of overlapped EOF

In order to get the analytical solution, based on the above mathematical model, the following hypotheses are used to simplify the derivation: (1) the length of nanoslit is long enough so that the electric field within the nanoslit is identical $(E_x^a = \psi_{Anode}/L)$, and the electroosmotic flow is fully developed and parallel to the channel wall; (2) the surface charge density distribution of the nanoslit walls are uniform; (3) the electric potentials are continuous on the interfaces between the dielectric layer and the liquid layer; (4) the thickness of dielectric material layer is very large and the gradient of electric potential within the dielectric layer is negligible. From the above hypotheses, the EOF in the x-axis direction is uniform and only varies in y-axis direction.

The electrostatics governing equations within the dielectric layer (y > H/2) can be written as

$$\frac{d\varphi}{dy} = 0 \tag{5.13}$$

and Eq. (6.2) can be reduced as

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon_0\varepsilon_f}$$
(5.14)

in which ϕ and ψ are y-axis direction electric potentials distribution within the dielectric layer and diffusive layer, respectively. According to the Boltzmann distribution, concentration of the ith ion at the center line of the nanoslit and within the nanoslit can be depicted respectively as

$$C_{ic} = C_{i0} \exp\left(-\frac{z_i F}{RT}(\psi_c - \psi_0)\right)$$
(5.15)

$$C_i = C_{ic} \exp\left[-\frac{z_i F}{RT}(\psi - \psi_c)\right], \qquad (5.16)$$

where Ψ_c is the central electrical potential of the nanochannel in the y-axis direction. As the nanochannel is connected with two much bigger reservoirs, in which the reference electrical potential is defined as $\Psi_0 = 0$, then the charge density can be written as

$$\rho_e = \sum_{i=1}^{N} F z_i C_{i\infty} \exp\left(-\frac{z_i F}{RT}\psi\right) = 2FC_{\infty} \sinh\left(-\frac{F}{RT}\psi\right), \qquad (5.17)$$

in which $C_{\infty} = C_{10} + C_{20} = C_{30} + C_{40}$ is the cation or anion concentration of bulk solution in the reservoirs, and the valence electron number of ith ionic species are $z = z_1 = z_2 = -z_3 = -z_4 = 1$.

Because no pressure bias is imposed across the nanoslit, the electroosmotic flow field along the y-axis direction can be simplified from eqn. (6.3) and described as

$$\frac{d^2 u_x}{dy^2} = -\frac{\rho_e E_x^a}{\mu},\tag{5.18}$$

in which u_x is the EOF velocity along the nanoslit.

The boundary conditions for eqs (6.13), (6.14) and (6.18) are as follows:

At the dielectric layer/liquid interface (y = H/2),

$$\varphi = \psi = \psi_d \,, \tag{5.19}$$

$$\varepsilon_0 \varepsilon_d \frac{d\varphi}{dy} - \varepsilon_0 \varepsilon_f \frac{d\psi}{dy} = -\sigma_w, \qquad (5.20)$$

$$u_x = 0. \tag{5.21}$$

The symmetric boundary conditions are used at the center of the nanochannel (y = 0),

$$\frac{d\psi}{dy} = 0 \quad \text{and} \quad \psi = \psi_c \,, \tag{5.22}$$

$$\frac{du_x}{dy} = 0. (5.23)$$

In the above, ψ_a is the electric potential at the solid/liquid interface, and σ_w is the surface charge density of the nanoslit shown in eqn. (6.7).

Based on eqns. (6.15) and (6.16), the surface proton concentration can be written as

$$[H_s^+] = [H_0^+] \exp\left(-\frac{F\psi_d}{RT}\right), \qquad (5.24)$$

in which $[H_0^+]$ is the H⁺ concentration in the reservoirs, and can be found from the pH value defined as $pH = -\log([H_0^+])$. Then the surface charge density can be depicted as

$$\sigma_{w} = -F\Gamma_{total} \left\{ \frac{K_{A} - K_{B} \left[[H_{0}^{+}] \exp\left(-\frac{F\psi_{d}}{RT}\right) \right]^{2}}{K_{A} + [H_{0}^{+}] \exp\left(-\frac{F\psi_{d}}{RT}\right) + K_{B} \left[[H_{0}^{+}] \exp\left(-\frac{F\psi_{d}}{RT}\right) \right]^{2}} \right\}.$$
(5.25)

Subject to eqs (6.17), (6.20) and (6.22), Eq. (6.14) can be solved as;

$$\psi = \psi_c + \frac{2RT}{zF} \ln\left(cd\left(l|m\right)\right), \tag{5.26}$$

where cd(l|m) is a Jacobian elliptic function of argument l and m, which are defined as

$$l = \frac{\kappa x}{2 \exp(F \psi_c / (2RT))}$$
(5.27)

$$m = \exp(2F\psi_c/(RT))$$
(5.28)

and the charge density within the EDL can be defined as

$$\sigma_{d} = -\varepsilon_{0}\varepsilon_{f}d\psi/dy\Big|_{x=H/2} \cdot \vec{n} = \varepsilon_{0}\varepsilon_{f}d\psi/dy\Big|_{x=H/2}$$

= $sign(\psi_{d})\sqrt{4\varepsilon_{0}\varepsilon_{f}RTC_{0}\left[\cosh\left(\frac{F\psi_{d}}{RT}\right) - \cosh\left(\frac{F\psi_{c}}{RT}\right)\right]}.$ (5.29)

From Eqs. (6.19) and (6.26), the relationship between surface potential Ψ_d and central electrical potential Ψ_c can be obtained as

$$\psi_d = \psi(H/2) = \psi_c + \frac{2RT}{zF} \ln\left(cd\left[l(y=H/2)|m\right]\right)$$
(5.30)

And based on Eqs. (6.13), (6.25) and (6.29), Eq. (6.20) can be transformed as

$$sign(\psi_{d})\sqrt{4\varepsilon_{0}\varepsilon_{f}RTC_{0}\left[\cosh\left(\frac{F\psi_{d}}{RT}\right) - \cosh\left(\frac{F\psi_{c}}{RT}\right)\right]}$$
$$= -F\Gamma_{total}\left\{\frac{K_{A} - K_{B}\left[\left[H^{+}\right]_{0}\exp\left(-\frac{F\psi_{d}}{RT}\right)\right]^{2}}{K_{A} + \left[H^{+}\right]_{0}\exp\left(-\frac{F\psi_{d}}{RT}\right) + K_{B}\left[\left[H^{+}\right]_{0}\exp\left(-\frac{F\psi_{d}}{RT}\right)\right]^{2}}\right\}.$$
(5.31)

Eqs. (6.30) and (6.31) are implicit expressions about the surface potential Ψ_d and central potential Ψ_c , which can be solved by Matlab function *fsolve*. Then the electric potential distribution along y-axis direction can be derived from eq. (6.26), and the EOF velocity can be solved from Eqs. (6.18), (6.21) and (6.23)

$$u_{x} = \frac{\varepsilon_{0}\varepsilon_{f}E_{x}^{a}}{\mu}(\psi - \psi_{d})$$
(5.32)

6.4 Results and Discussion

The fully coupled equations of (6.1), (6.2), (6.3), and (6.4) and the associated boundary conditions are solved numerically by COMSOL Multiphysics, a finite element method-based software which has been validated to be sufficiently efficient and accurate for solving similar electrokinetic ion transport problems [210-211] and ionic flux determination for the charge regulated nanoparticles. The simulation domain is discretized using a hybrid structured/unstructured mesh that can solve the real physics in lost cost of computational ranges. In order to calculate the electrokinetic flow of a binary electrolyte through a nanochannel, very fine structured mesh is used inside the nanochannel and in the transition of the nanochannel and reservoir, the mesh size is gradually increased through reservoirs as shown in Figure 6.2. Again to reduce the computational time, a symmetric boundary condition is used along the channel half-plane.

6.4.1 Model Validation

The applicability of the numerical results are first verified by the experimental data carried out by Zheng et al. [220] on flow rate measurements of electroosmotic driven flow for silica nanoslit with 3.5 µm length, 44 µm width and for various height ranges when the applied electric field is ~14 kV/m and the salt concentration is 0.16664 M NaCI solution with pH=7. As illustrated in Figure 6.3, the prediction of our model with the parameters of p $K_a = 7$, p $K_b = 1.9$, and $N_{total} = 3.8$ sites/nm², have excellent agreement. Our model is much better than the model proposed by Zheng et al. [220] where they did not consider a charge regulated model to determine the surface charge density.



Figure 6.2. Two dimensional numerical simulations are performed with a flow domain composed of two reservoirs connected with a single nanochannel. The junction of the reservoir and nanochannel is zoomed for detailed look at the mesh type.



Figure 6.3. Electroosmotic volume flow rate (Q) varying with nanoslit height H at a constant electric field (0.05V). The length and width of the nanoslit are $L = 3.5 \,\mu\text{m}$ and $W = 44 \,\mu\text{m}$, and the bulk salt concentration of NaCl is 0.16644 M with pH = 7. Rectangular symbols are experimental data of Zheng et al. [220], and solid line and circles present multi-ion analytical model and numerical results with $pK_a = 7$, $pK_b = 1.9$, and $N_{und} = 3.8 \,\text{sites/nm}^2$.

6.4.2 The influence of the background solution properties

Figure 6.4 illustrates that the influence of the solution properties, background salt concentration, C_{KCl} , and pH level on the EOF velocity distribution (*u*) as a function of the height-wise position x obtained at the cross-section line in the middle of nanoslit with $L = 1 \ \mu m$. The velocity profiles are plotted for different salt concentrations 1, 10, 100, and

1000 mM and pH levels are 4, 6, and 8. The straight and dash lines in Figure 6.4 represents the approximation solution (lines) based on the continuum flow theory and the numerical results (symbols) for comparison. Due to the decrease of electric double layer (EDL) thickness by increasing of salt concentration strength within the nanoslit, the EOF velocity increases. However, the space charge density gradually decreases for very high salt concentration levels. Because the counter-ions are compressed in the region very close to the charged surface. In the centerline of the nanochannel the amount of counter-ion becomes negligible and causes a reduction on the EOF velocity. Since the nanoslit wall is negatively charged, increasing pH level may lead to an increase of the net charge density inside the nanoslit, and accordingly an increase in EOF velocity. Our approximation solutions (Eqs. (6.31) and (6.32)) are capable of predicting the general trends quantitatively and qualitatively of EOF velocity in a nanoslit when pH is either sufficiently low or high and C_{KCI} is sufficiently high. The relative errors of approximation solution and numerical results are less than 1%. However, we determined that the approximation solution overestimates the EOF velocity for lower concentration levels (1 and 10 mM) and the deviation increases remarkably when the concentration of bulk ionic concentration is 1 and 10 mM and/or OH[•] is higher in the bulk. This is because the approximation solution fails to take into account the ionic concentration polarization (ICP) that occurs at the both ends of the nanoslit. As has been reported earlier [[97], ICP reduces the fluid velocity as the counter ions K^+ and H^+ are enriched (depleted) near the cathode (anode) side of the negatively charged nanoslit. Here, it is revealed that ICP becomes significant by increasing of the EDL overlap strength or increasing of the pH level. ICP reduces the EOF flow inside nanoslit.



Figure 6.4. EOF velocity profile along height of nanoslit H at various NaCl background salt concentrations $C_{\text{NaCl}}(1, 10, 100, \text{ and } 1000 \text{ mM})$ for pH = 4, pH = 6, and pH = 8 when L/H = 100. The straight line presents 1 and 1000 mM, respectively, and the dash lines presents 10 and 100 mM cases. For numerical results, red squares 1 mM, blue spheres 10 mM, and green triangles 100 mM case, purple diamond symbols presents 1000 mM.

Figure 6.5 depicts that the averaged EOF velocity, $\langle u \rangle$, in the middle of the nanoslit is plotted as a function of both aqueous solution pH level and salt concentration strength when L/H=100. The $\langle u \rangle$ increases with increasing bulk ionic salt concentration till 100 mM, for high salt concentration levels it gradually decreases, as explained in the previous figure, and also increases with an increasing pH level of the aqueous solution. For low pH levels 3 - 4, the $\langle u \rangle$ difference between different salt concentrations is not significant and it is very low as ~0.005 mm/sec. The reason is that the surface charge density of the nanoslit is very low at low pH levels, resulting in counter-ions gathered near the nanoslit surface and accordingly, less co-ions repelled out of the nanoslit. And by increasing the pH level, the surface charge density increases and accordingly, the ionic flux of cations inside the nanoslit becomes significantly larger. It is worth noting that the surface charge density of silica surfaces increase with increasing the pH levels and also ionic salt concentrations of aqueous solutions.



Figure 6.5. Average EOF velocity with respect to various concentration and pH levels when L/H = 100.

6.4.3 Effect of Nanoslit Length

The EOF velocity profiles as a function of height of the nanoslit are plotted for different L/H values, when salt concentrations are 1, 100 mM and the pH level is 4 and 7, as illustrated in Figure 6.6. The general trend of the plots confirms that the EOF velocity decreases by decreasing the L/H ratio for all ionic concentrations and pH levels, and for high pH values when bulk ionic salt concentration is low, the EOF velocity is remarkably reduced compared to low pH levels. Even though the aqueous solution has the same

properties, their EOF velocity is different, which is is due to the concentration polarization occurred at the both ends of the nanoslit, which are schematically shown in Figure 6.1.



Figure 6.6. EOF velocity profile along the height of the nanoslit H at various length height ratios (L/H) with $C_{\text{NaCl}} = 1 \text{ mM}$ and 100 mM for pH=4 and 7. Spheres, diamonds and triangles presents L/H= 100, 10 and 5, respectively, and the straight line presents the approximation solution of Eq. (6.32).

In order to explain the reason that fluid velocity decreases for different L/H values in figure 6.6, Figure 6.7 plots the axial variation of the cross-sectional averaged (a) electric field, (b) pressure, and (c) counter-ion concentration. The applied electric field is kept constant for all different L/H values. The x-position is also normalized by the nanochannel length (L) and $x^* = x/L$ in Figure 6.7. Since the voltage bias was applied on the left side, the magnitude of the electric field, $E_x = -\partial \phi / \partial x$, is higher on left side. By decreasing of the L/H, the magnitude of electric field gets higher as a result of significant ion depletion in that region, which causes a reduction of osmotic pressure in this region. Figure 6.7b shown the cross-sectional averaged pressure distribution along the length direction. The osmotic pressure increases by increasing of L/H and in the region of enrichment, the magnitude of the osmotic pressure gets higher. The EOF is dominant on the depletion region and when counter-ions accumulated intensively at the right end of nanoslit, the accumulation of the ions increases the osmotic pressure and decreases the EOF flow. As Figure 6.7c shows, the generated ion concentration for L/H=5 has less counter-ions inside the nanoslit and thus, reduces the ionic flux inside the nanoslit, and accordingly, the EOF velocity inside the nanoslit and the amount of counter-ions inside nanoslit increases with increasing L/H, meanly the EOF flow rate inside the nanoslit.



Figure 6.7. Spatial distribution of the cross-sectional averaged electric field (a) and concentrations of mobile counter ions (b) along the nanoslit length at various L/H values when the background salt concentration $C_{\text{NaCl}}=1$ mM and pH=4. Straight, dash and dash dot lines presents L/H = 5, 10 and 100, respectively.

Figure 6.8 and 6.9 depict, respectively, the averaged EOF velocity, $\langle u \rangle$, as a function of the L/H for different salt concentration and various pH levels, and Figure 6.8 also includes the numerical results comparison with corresponding approximation solutions for each case. The symbols and lines represent the numerical results and approximation solutions, respectively. Figure 6.8 reveals that $\langle u \rangle$ increases with increasing salt ionic concentration and L/H and asymptotically reaches to a value at L/H=100. This behavior can be attributed to the ICP, which becomes significant at low ionic concentrations and/or high pH levels. While the ICP is not significant, the numerical results have a good agreement with approximation solution.



Figure 6.8. Average EOF velocity varies with length height ratio ($L/H = 1 \sim 100$) at various background salt concentration (1, 10, and 100 mM) with pH = 6.



Figure 6.9. Average EOF velocity varies with length height ratio ($L/H = 1 \sim 100$) at various pH values 4, 6, 8 when bulk ionic salt concentration $C_{\text{NaCl}} = 10 \text{ mM}$.

6.5 Conclusion

Electroosmosis flow velocity inside the long pH-regulated nanoslits are investigated by considering the effects of electric double layers overlapping, surface chemistry reactions, and multiple ionic species. With taking account these effects, the analytical model for EOF velocity calculations is derived for the first time, and the corresponding EOF process in a realistic 2-D nanofluidic device is numerically simulated. Both the analytical model and the numerical simulation results are validated by comparing the existing experiment data of EOF velocity in long pH-regulated nanoslits. The influences of pH value and

background salt concentration on EOF velocity are studied by comparing the analytical results with numerically simulation results. The predictions show that the EOF velocity increases first and then decreases with background salt concentrations increasing because of the combined effects of counter ions concentrations and EDL thickness; the EOF velocity increases with the pH level of the aqueous solution because more counter ions are attracted at higher pH values. The comparisons between the analytical and numerical results also provide the scope of application of the analytical model, which is only suitable for lower pH levels, higher background salt concentrations and long enough nanoslits, in what situations the ionic concentration polarization effects at the ends of the nanoslits are not obvious.

CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH

Electrokinetic properties of ion transport and liquid confined in nanochannel is an important aspect not only from fundamental perspectives but also the development of next-generation emerging fields, such as lab-on-a-chip devices (LOC) and bioNEMS. These state-of-the-art fluidic devices have showed unique physical properties different than usual conventional systems. There are a lot of undiscovered behaviors in nanoscale that may profoundly affect the field of fluid and chemical engineering, such as surface charge properties of nanoparticles, viscosity of the fluides, diffusion coefficients of ions, the dielectric constant of fluid, dissociation of silanol groups, vapor pressure, proton mobility, and hydrogen ion concentration. Understanding these physical and chemical phenomena will lead to new applications which have not been possible before in the areas of biological systems, separation science, geoscience, single molecular detection, fuel cells and batteries.

This dissertation presents the understanding of electrokinetic ion behavior on both nanoparticles and nanofluidics systems while accounting for the role of surface charge chemistry in which the surface groups are determined by the multiple ionic species and the site dissociation/associations so that the surface groups are responding to their local environment.

This dissertation has two main parts related to electrokinetic phenomena which correspond to two main aspects that are presented in this dissertation: (1) theoretical and analytical study of surface charge properties of nanoparticles, and (2) theoretical and approximation solution of ionic concentration distribution and its transportation in nanochannels.

7.1 Conclusions

The main contributions of this dissertation are

(1) The experimentally validated theoretical model is to present the size of the nanoparticle, the pH level of aqueous solution and the salt concentration strength dependence of surface charge properties of silica nanoparticle. The results demonstrate that the surface charge density increases with increasing pH and salt concentrations [1, 20]. Surface charge density decreases with increased particle size, and asymptotically reaches a flat plate approximation. In the range of $\lambda_D/D_p < 0.2$, one can neglect the effect of the particle size on its surface charge density, regardless of the pH and salt concentration. These results are attributed to why certain sized nanoparticles are transported in nanochannels faster than the smaller ones made out of the same material.

(2) An analytical solution validated with existing experimental data available in the literature is developed for particles. The charge properties of the particles can be easily predicted using the developed model as functions of pH, salt concentration, as well as particle size when $\kappa R_p \ge 0.5$.

(3) A finite element method is used to accurately reproduce surface charge densities to gain insights into the interaction between a nanoparticle and a flat wall charged surface. The results show that the surface charge density is spatially non-uniform based on the separation distance, and the magnitude of the surface charge density in the interaction region is significantly reduced related to strength of electric double layer overlap in contrast to theoretical solution (i.e DLVO theory). The results demonstrate that the assumption of a constant surface charge density of two interacting objects is invalid under strong EDL interactions between the particle and the surfaces in the range of $\kappa h \leq 1$.

(4) The surface charge properties, electric potential and proton distribution is investigated for an extended nanochannel using a finite element. As expected, due to EDL overlaps on the corner of the nanochannel, a significant charge density drop occurs due to enrichment of the counter-ions. Moreover, the proton concentration is significantly enhanced by the negatively charged nanochannel, and its distribution depends substantially on the bulk pH and background salt concentrations. The variation of protons in an extended nanochannel is considerably remarkable when the bulk pH is relatively high. Moreover, the enhanced relative percentage of protons at the center of the nanochannel is significant at medium high bulk pH (ca. 8), low salt concentration, and in a small size of the nanochannel. These results will illuminate the unique fluid properties inside nanochannels and allow us to measure dielectric and viscosity properties of fluid inside the nanochannel.

(5) Using theoretical and approximation solution methods, electroosmosis flow (EOF) velocity inside the long pH-regulated nanoslits is investigated by considering the effects of electric double layers overlapping. Both the analytical model and the numerical simulation results are validated by comparing with the existing experimental data of EOF velocity in long pH-regulated nanoslits. The influences of pH value and background salt concentration on EOF velocity are studied by comparing the analytical results with numerical simulation results. The predictions show that the EOF velocity increases first and then decreases with background salt concentration increasing because of the combined effects of counter ion concentrations and EDL thickness; the EOF velocity increases with the pH level of the aqueous solution because more counter ions are attracted at higher pH values. The

comparisons between the analytical and numerical results also provide the scope of application of the analytical model, which is only suitable for lower pH levels, higher background salt concentrations and long enough nanoslits, in which situations the ionic concentration polarization effects at the ends of the nanoslits are not obvious.

7.2 Future Research

Based on the research study in this dissertation, for future research, several important aspects can be addressed in the following.

We used the chemistry of the oxides to describe the charge properties on the pHregulated surface. Although the model used in our studies only included the activity of hydrogen (H⁺) and hydroxyl (OH⁻) ions to determine the surface charge in terms of the 2pK charging mechanisms, in order to get more realistic results, the absorption of CO_2 and also metal absorption need to be considered in aqueous solutions. When the accumulation metal cations (i.e. K⁺ or Na⁺) of ions next to the negatively charged surface have a considerably high concentration comparing to the bulk, the metal anions and cations may absorbed or partially absorbed at the interface of the oxide surface and liquid, and forms a compact layer called the Stern Layer (described in Introduction). Since the surface charging mechanism and forming of EDL also depend on the metal adsorption, the Stern Layer model needs to be included in the model.

In the existence of multivalent ions, such as Ca^{2+} and Mg^{2+} in the electrolyte solution, many existing studies verified that the charge properties of dielectric objects may be reversed so that the considering of multivalent ions is highly important while calculating the correct surface charge properties. In order to maintain a constant pH level in an aqueous solution or indicate a specific type of ion in the solution during experimental studies, the scientist uses a buffer solution (i.e. citric acid or disodium phosphate or sodium dihydrogenphospate or Tris) which consists of a mixture of a weak acid and its conjugate base. Since the dissociation of silanol groups on the oxide surface in the existence of the buffer solution in electrolyte solution are dependent upon the concentration of buffer solution, in order to get better validation or determining the correct N_{total}, pK_a, pK_b values with experimental data, the buffer solution needs to be take into account.

Although in most cases the viscosity and density of the fluid is considered as a constant, in the existence of high ion accumulations on the pH-regulated surfaces, indeed, the viscosity is affected by the temperature of the fluid [174], the electric field [119] and electrolyte concentration of the aqueous solution (change due to the crowding) [181]. The prediction of the correct viscosity of the fluid may give us a better result of fluid behavior inside the nanochannel and also correct conductance across the nanochannel.

For better understanding of the electrokinetic flow behavior inside the nanochannel, the effects of geometrical field on concentration polarization needs to be investigated further by comparing the 1-D, 2-D and 3-D models. Electroconvection effects can affect the electrodiffusive solution to yield concentration polarization at the interface of nanochannel and reservoirs.

REFERENCES

 Abbas, Z.; Labbez, C.; Nordholm, S.; Ahlberg, E. Size-Dependent Surface Charging Of Nanoparticles. The Journal of Physical Chemistry C, 112 (15), 5715-5723, 2008.

Actis, P.; Vilozny, B.; Seger, R. A.; Li, X.; Jejelowo, O.; Rinaudo, M.; Pourmand,
 N. Voltage-Controlled Metal Binding On Polyelectrolyte-Functionalized Nanopores.
 Langmuir, 27 (10), 6528-6533, 2011.

3. Ai, Y.; Liu, J.; Zhang, B. K.; Qian, S. Field Effect Regulation Of DNA Trans Location Through A Nanopore. Analytical Chemistry, 82 (19), 8217-8225, 2010.

4. Ai, Y.; Qian, S. Electrokinetic Particle Translocation Through A Nanopore. Physical Chemistry Chemical Physics, 13 (9), 4060-4071, 2011.

5. Ai, Y.; Zhang, M.; Joo, S. W.; Cheney, M. A.; Qian, S. Effects Of Electroosmotic Flow On Ionic Current Rectification In Conical Nanopores. The Journal Of Physical Chemistry C, 114 (9), 3883-3890, 2010.

6. Ali, M.; Ramirez, P.; Mafé, S.; Neumann, R.; Ensinger, W. A Ph-Tunable Nanofluidic Diode With A Broad Range Of Rectifying Properties. ACS Nano, 3 (3), 603-608, 2009.

 Ali, M.; Yameen, B.; Cervera, J.; Ramírez, P.; Neumann, R.; Ensinger, W.; Knoll,
 W.; Azzaroni, O. Layer-By-Layer Assembly Of Polyelectrolytes Into Ionic Current Rectifying Solid-State Nanopores: Insights From Theory And Experiment. Journal Of The American Chemical Society, 132 (24), 8338-8348, 2010.

8. Allaire, G.; Brizzi, R.; Dufreche, J. F.; Mikelic, A.; Piatnitski, A. Ion Transport In Porous Media: Derivation Of The Macroscopic Equations Using Upscaling And
Properties Of The Effective Coefficients. Computational Geosciences, 17 (3), 479-495, 2013.

9. Andersen, M. B.; Bruus, H.; Bardhan, J. P.; Pennathur, S. Streaming Current And Wall Dissolution Over 48 H In Silica Nanochannels. Journal of Colloid and Interface Science, 360 (1), 262-271, 2011.

10. Andersen, M. B.; Frey, J.; Pennathur, S.; Bruus, H. Surface-Dependent Chemical Equilibrium Constants And Capacitances For Bare And 3-Cyanopropyldimethylchlorosilane Coated Silica Nanochannels. Journal of Colloid And Interface Science, 353 (1), 301-310, 2011.

11. Anthony L. Garcia, L. K. I., Dimiter N. Petsev, Michael J. O'Brien, Paul Bisong, Andrea A. Mammoli, Steven R. J. Brueckc, Gabriel P. Lo'Pez. *Electrokinetic Molecular Separation In Nanoscale Fluidic Channels*. Lab Chip, 5, 6, 2005.

12. Atalay, S.; Barisik, M.; Beskok, A.; Qian, S. Surface Charge Of A Nanoparticle Interacting With A Flat Substrate. The Journal Of Physical Chemistry C, 2014.

13. Atalay, S.; Ma, Y.; Qian, S. Analytical Model For Charge Properties Of Silica Particles. Journal Of Colloid And Interface Science, 425, 128-130, 2014.

Atalay, S.; Yeh, L.-H.; Qian, S. Proton Enhancement In An Extended Nanochannel.
 Langmuir, 2014.

15. Baldessari, F. Electrokinetics In Nanochannels - Part II. Mobility Dependence On Ion Density And Ionic Current Measurements. Journal of Colloid and Interface Science, 325 (2), 539-546, 2008.

16. Bandopadhyay, A.; Chakraborty, S. Ionic Size Dependent Electroosmosis In Ion-Selective Microchannels And Nanochannels. Electrophoresis, 34 (15), 2193-2198, 2013. Barisik, M.; Atalay, S.; Beskok, A.; Qian, S. Z. Size Dependent Surface Charge Properties Of Silica Nanoparticles. Journal Of Physical Chemistry C, 118 (4), 1836-1842, 2014.

18. Barr, S. A.; Panagiotopoulos, A. Z. Interactions Between Charged Surfaces With Ionizable Sites. Langmuir, 27 (14), 8761-8766, 2011.

 Baumgartner, S.; Vasicek, M.; Bulyha, A.; Heitzinger, C. Optimization Of Nanowire DNA Sensor Sensitivity Using Self-Consistent Simulation. Nanotechnology, 22 (42), 2011.

20. Behrens, S. H.; Christl, D. I.; Emmerzael, R.; Schurtenberger, P.; Borkovec, M. Charging And Aggregation Properties Of Carboxyl Latex Particles: Experiments Versus DLVO Theory. Langmuir, 16 (6), 2566-2575, 2000.

21. Behrens, S. H.; Grier, D. G. The Charge Of Glass And Silica Surfaces. Journal of Chemical Physics, 115 (14), 6716-6721, 2001.

22. Bharti, B.; Meissner, J.; Findenegg, G. H. Aggregation Of Silica Nanoparticles Directed By Adsorption Of Lysozyme. Langmuir, 27 (16), 9823-9833, 2011.

23. Bowen, W. R.; Doneva, T. A.; Stoton, J. A. G. *The Use Of Atomic Force Microscopy To Quantify Membrane Surface Electrical Properties*. Colloids And Surfaces A-Physicochemical And Engineering Aspects, 201 (1-3), 73-83, 2002.

24. Briscoe, W. H.; Horn, R. G. Direct Measurement Of Surface Forces Due To Charging Of Solids Immersed In A Nonpolar Liquid. Langmuir, 18 (10), 3945-3956, 2002.

25. Brown, M. A.; Beloqui Redondo, A.; Sterrer, M.; Winter, B.; Pacchioni, G.; Abbas, Z.; Van Bokhoven, J. A. Measure Of Surface Potential At The Aqueous-Oxide

Nanoparticle Interface By XPS From A Liquid Microjet. Nano Letters, 13 (11), 5403-5407, 2013.

26. Butt, H.-J. Measuring Local Surface Charge Densities In Electrolyte Solutions With A Scanning Force Microscope. Biophysical Journal, 63 (2), 578-582, 1992.

27. Butt, H.-J.; Cappella, B.; Kappl, M. Force Measurements With The Atomic Force Microscope: Technique, Interpretation And Applications. Surface Science Reports, 59 (1), 1-152, 2005.

28. Butt, H. J. Measuring Electrostatic, Vanderwaals, And Hydration Forces In Electrolyte-Solutions With An Atomic Force Microscope. Biophysical Journal, 60 (6), 1438-1444, 1991.

29. Calvo, P.; Remunan-Lopez, C.; Vila-Jato, J.; Alonso, M. Novel Hydrophilic Chitosan-Polyethylene Oxide Nanoparticles As Protein Carriers. Journal Of Applied Polymer Science, 63 (1), 125-132, 1997.

 Cazade, P. A.; Hartkamp, R.; Coasne, B. Structure And Dynamics Of An Electrolyte Confined In Charged Nanopores. Journal Of Physical Chemistry C, 118 (10), 5061-5072, 2014.

31. Chan, D.; Perram, J. W.; White, L. R.; Healy, T. W. Regulation Of Surface Potential At Amphoteric Surfaces During Particle-Particle Interaction. Journal Of The Chemical Society, Faraday Transactions 1: Physical Chemistry In Condensed Phases, 71 (0), 1046-1057, 1975.

32. Chang, C. C.; Kazoe, Y.; Morikawa, K.; Mawatari, K.; Yang, R. J.; Kitamori, T. Numerical Simulation Of Proton Distribution With Electric Double Layer In Extended Nanospaces. Analytical Chemistry, 85 (9), 4468-4474, 2013.

33. Chang, H.; Kosari, F.; Andreadakis, G.; Alam, M. A.; Vasmatzis, G.; Bashir, R. DNA-Mediated Fluctuations In Ionic Current Through Silicon Oxide Nanopore Channels. Nano Letters, 4 (8), 1551-1556, 2004.

34. Chapman, D. L. LI. A Contribution To The Theory Of Electrocapillarity. The London, Edinburgh, And Dublin Philosophical Magazine And Journal Of Science, 25 (148), 475-481, 1913.

35. Chen, L.; Conlisk, A. T. *DNA Nanowire Translocation Phenomena In Nanopores*. Biomedical Microdevices, *12* (2), 235-245, 2010.

36. Chen, M. Y.; Sailor, M. J. Charge-Gated Transport Of Proteins In Nanostructured Optical Films Of Mesoporous Silica. Anal Chem, 83 (18), 7186-7193, 2011.

37. Chen, P.; Gu, J.; Brandin, E.; Kim, Y.-R.; Wang, Q.; Branton, D. Probing Single
DNA Molecule Transport Using Fabricated Nanopores. Nano Letters, 4 (11), 2293-2298,
2004.

38. Cheng, L. J.; Guo, L. J. Ionic Current Rectification, Breakdown, And Switching In Heterogeneous Oxide Nanofluidic Devices. ACS Nano, 3 (3), 575-584, 2009.

39. Chinen, H.; Mawatari, K.; Pihosh, Y.; Morikawa, K.; Kazoe, Y.; Tsukahara, T.; Kitamori, T. *Enhancement Of Proton Mobility In Extended-Nanospace Channels*. Angewandte Chemie International Edition, *51* (15), 3573-3577, 2012.

40. Chithrani, B. D.; Chan, W. C. Elucidating The Mechanism Of Cellular Uptake And Removal Of Protein-Coated Gold Nanoparticles Of Different Sizes And Shapes. Nano Letters, 7 (6), 1542-1550, 2007. 41. Chithrani, B. D.; Ghazani, A. A.; Chan, W. C. Determining The Size And Shape Dependence Of Gold Nanoparticle Uptake Into Mammalian Cells. Nano Letters, 6 (4), 662-668, 2006.

42. Craighead, H. Future Lab-On-A-Chip Technologies For Interrogating Individual Molecules. Nature, 442 (7101), 387-393, 2006.

43. Daejoong Kim, E. D. Molecular Dynamics Simulation Of Electro-Osmotic Flows In Rough Wall Nanochannels. Physical Review E, 73 (051203), 12, 2006.

44. Daiguji, H.; Yang, P.; Majumdar, A. *Ion Transport In Nanofluidic Channels*. Nano Letters, *4* (1), 137-142, 2004.

45. Dal Bianco, B.; Bertoncello, R. The Development Of Growth Rings On Ancient Glass Surfaces: Description And Simulation Of The Weathering. Journal Of Non-Crystalline Solids, 354 (2-9), 773-779, 2008.

46. Das, S.; Dubsky, P.; Van Den Berg, A.; Eijkel, J. C. Concentration Polarization In Translocation Of DNA Through Nanopores And Nanochannels. Physical Review Letters, 108 (13), 138101, 2012.

47. Dekker, C. Solid-State Nanopores. Nature Nanotechnology, 2 (4), 209-215, 2007.

48. Derjaguin, B.; Landau, L. The Theory Of Stability Of Highly Charged Lyophobic Sols And Coalescence Of Highly Charged Particles In Electrolyte Solutions. Zh. Eksp. Teor. Fiz, 11 (2), 802-821, 1941.

49. Dirk Gillespie, S. P. Separation Of Ions In Nanofluidic Channels With Combined Pressure-Driven And Electro-Osmotic Flow. Analytical Chemistry, 85, 8, 2013. 50. Drelich, J.; Long, J.; Yeung, A. Determining Surface Potential Of The Bitumen-Water Interface At Nanoscale Resolution Using Atomic Force Microscopy. Canadian Journal Of Chemical Engineering, 85 (5), 625-634, 2007.

51. Duan, C. H.; Majumdar, A. Anomalous Ion Transport In 2-Nm Hydrophilic Nanochannels. Nature Nanotechnology, 5 (12), 848-852, 2010.

52. Duan, J. M. Interfacial Forces Between Silica Surfaces Measured By Atomic Force Microscopy. Journal Of Environmental Sciences-China, 21 (1), 30-34, 2009.

53. Ducker, W. A.; Senden, T. J.; Pashley, R. M. Direct Measurement Of Colloidal Forces Using An Atomic Force Microscope. Nature, 353 (6341), 239-241, 1991.

54. Ducker, W. A.; Senden, T. J.; Pashley, R. M. Measurement Of Forces In Liquids Using A Force Microscope. Langmuir, 8 (7), 1831-1836, 1992.

55. Duffy, C. F.; Gafoor, S.; Richards, D. P.; Admadzadeh, H.; O'Kennedy, R.; Arriaga,

E. A. Determination Of Properties Of Individual Liposomes By Capillary Electrophoresis With Postcolumn Laser-Induced Fluorescence Detection. Analytical Chemistry, 73 (8), 1855-1861, 2001.

56. Dunér, G.; Iruthayaraj, J.; Daasbjerg, K.; Pedersen, S. U.; Thormann, E.; Dédinaité, A. Attractive Double-Layer Forces And Charge Regulation Upon Interaction Between Electrografted Amine Layers And Silica. Journal Of Colloid And Interface Science, 2012.

57. Durand, N. F.; Bertsch, A.; Todorova, M.; Renaud, P. Direct Measurement Of Effective Diffusion Coefficients In Nanochannels Using Steady-State Dispersion Effects. Applied Physics Letters, 91 (20), 203106, 2007.

58. Elmahdy, M. M.; Drechsler, A.; Gutsche, C.; Synytska, A.; Uhlmann, P.; Kremer, F.; Stamm, M. Forces Between Blank Surfaces As Measured By The Colloidal Probe

Technique And By Optical Tweezers - A Comparison. Langmuir, 25 (22), 12894-12898, 2009.

59. Fielding, L. A.; Mykhaylyk, O. O.; Schmid, A.; Pontoni, D.; Armes, S. P.; Fowler,
P. W. Visible Mie Scattering From Hollow Silica Particles With Particulate Shells.
Chemistry Of Materials, 26, 1270-1277, 2014.

60. Gaborski, T. R.; Snyder, J. L.; Striemer, C. C.; Fang, D. Z.; Hoffman, M.; Fauchet, P. M.; Mcgrath, J. L. High-Performance Separation Of Nanoparticles With Ultrathin Porous Nanocrystalline Silicon Membranes. ACS Nano, 4 (11), 6973-6981, 2010.

61. German, S. R.; Luo, L.; White, H. S.; Mega, T. L. Controlling Nanoparticle Dynamics In Conical Nanopores. The Journal Of Physical Chemistry C, 117 (1), 703-711, 2013.

62. Getfert, S.; Tows, T.; Reimann, P. Reluctance Of A Neutral Nanoparticle To Enter A Charged Pore. Physical Review E, 88 (5), 052710, 2013.

63. Gopmandal, P. P.; Bhattacharyya, S. *Electrokinetics Of A Charged Permeable Porous Aggregate In An Aqueous Medium*. Colloids And Surfaces A-Physicochemical And Engineering Aspects, 433, 64-76, 2013.

64. Guan, W. H.; Rajan, N. K.; Duan, X. X.; Reed, M. A. Quantitative Probing Of Surface Charges At Dielectric-Electrolyte Interfaces. Lab On A Chip, 13 (7), 1431-1436, 2013.

65. Guan, W. J.; Reed, M. A. Electric Field Modulation Of The Membrane Potential In Solid-State Ion Channels. Nano Letters, 12 (12), 6441-6447, 2012. 66. Gunnarsson, M.; Abbas, Z.; Ahlberg, E.; Nordholm, S. Corrected Debye-Hückel Analysis Of Surface Complexation: III. Spherical Particle Charging Including Ion Condensation. Journal Of Colloid And Interface Science, 274 (2), 563-578, 2004.

67. Guo, W.; Tian, Y.; Jiang, L. Asymmetric Ion Transport Through Ion-Channel-Mimetic Solid-State Nanopores. Accounts Of Chemical Research, 46, 2834-2846, 2013.

68. Han, A.; Creus, M.; SchüRmann, G.; Linder, V.; Ward, T. R.; De Rooij, N. F.; Staufer, U. Label-Free Detection Of Single Protein Molecules And Protein- Protein Interactions Using Synthetic Nanopores. Analytical Chemistry, 80 (12), 4651-4658, 2008.

69. Han, J.; Craighead, H. Separation Of Long DNA Molecules In A Microfabricated Entropic Trap Array. Science, 288 (5468), 1026-1029, 2000.

70. Haneveld, J.; Tas, N. R.; Brunets, N.; Jansen, H. V.; Elwenspoek, M. *Capillary Filling Of Sub-10nm Nanochannels*. Journal Of Applied Physics, *104* (1), 014309, 2008.

71. Haywood, D. G.; Harms, Z. D.; Jacobson, S. C. *Electroosmotic Flow In Nanofluidic Channels*. Analytical Chemistry, 2014.

72. He, Y. H.; Tsutsui, M.; Fan, C.; Taniguchi, M.; Kawai, T. Gate Manipulation Of DNA Capture Into Nanopores. ACS Nano, 5 (10), 8391-8397, 2011.

73. He, Z. J.; Zhou, J.; Lu, X. H.; Corry, B. Bioinspired Graphene Nanopores With Voltage-Tunable Ion Selectivity For Na⁺ And K⁺. ACS Nano, 7 (11), 10148-10157, 2013.

74. Hoettges, K. F.; Mcdonnell, M. B.; Hughes, M. P. Continuous Flow Nanoparticle Concentration Using Alternating Current-Electroosmotic Flow. Electrophoresis, 35 (4), 467-473, 2014. 75. Hoh, J. H.; Revel, J.-P.; Hansma, P. K. *Tip-Sample Interactions In Atomic Force Microscopy: I. Modulating Adhesion Between Silicon Nitride And Glass.* Nanotechnology, 2 (3), 119, 1991.

76. Hossein Hamzehpour, A. A., Alok Kumar Gupta, Muhammad Sahimi. *Electro-Osmotic Flow In Disordered Porous And Fractured Media*. Physical Review E, 89 (033007), 11, 2014.

77. Hou, X.; Yang, F.; Li, L.; Song, Y.; Jiang, L.; Zhu, D. *A Biomimetic Asymmetric Responsive Single Nanochannel*. Journal Of The American Chemical Society, *132* (33), 11736-11742, 2010.

78. Howorka, S.; Cheley, S.; Bayley, H. Sequence-Specific Detection Of Individual DNA Strands Using Engineered Nanopores. Nature Biotechnology, 19 (7), 636-639, 2001.

79. Howorka, S.; Siwy, Z. Nanopore Analytics: Sensing Of Single Molecules. Chemical Society Reviews, 38 (8), 2360-2384, 2009.

80. Hsu, C.; Lo, T. W.; Lee, D. J.; Hsu, J. P. Electrophoresis Of A Charge-Regulated Zwitterionic Particle: Influence Of Temperature And Bulk Salt Concentration. Langmuir, 29 (7), 2427-2433, 2013.

81. Hsu, W. L.; Inglis, D. W.; Jeong, H.; Dunstan, D. E.; Davidson, M. R.; Goldys, E.
M.; Harvie, D. J. E. Stationary Chemical Gradients For Concentration Gradient-Based
Separation And Focusing In Nanofluidic Channels. Langmuir, 30 (18), 5337-5348, 2014.

82. Huettl, G.; Beyer, D.; Müller, E. Investigation Of Electrical Double Layers On Sio2 Surfaces By Means Of Force Vs. Distance Measurements. Surface And Interface Analysis, 25 (7-8), 543-547, 1997. Hunter, R. J. Zeta Potential In Colloid Science: Principles And Applications.
 Academic Press London: Vol. 125, 1981.

84. Israelachvili, J. N. Intermolecular And Surface Forces: Revised Third Edition. Academic Press, 2011.

85. J. J. Kasianowicz, E. B., D. Branton And D.W. Deamer. Proc. National Academic Science U.S.A., 93, 13370-13773, 1996.

86. Jenison, R.; Yang, S.; Haeberli, A.; Polisky, B. Interference-Based Detection Of Nucleic Acid Targets On Optically Coated Silicon. Nature Biotechnology, 19 (1), 62-65, 2001.

87. Jiang, Z. J.; Stein, D. Electrofluidic Gating Of A Chemically Reactive Surface. Langmuir, 26 (11), 8161-8173, 2010.

 Jiménez-Ángeles, F. Effects Of Mixed Discrete Surface Charges On The Electrical Double Layer. Physical Review E, 86 (2), 021601, 2012.

89. Jin, X. Z.; Aluru, N. R. *Gated Transport In Nanofluidic Devices*. Microfluidics And Nanofluidics, 11 (3), 297-306, 2011.

90. Johnson, P. M.; Van Kats, C. M.; Van Blaaderen, A. Synthesis Of Colloidal Silica Dumbbells. Langmuir, 21 (24), 11510-11517, 2005.

91. Kaasalainen, M.; Mäkilä, E.; Riikonen, J.; Kovalainen, M.; Järvinen, K.; Herzig, K.-H.; Lehto, V.-P.; Salonen, J. *Effect Of Isotonic Solutions And Peptide Adsorption On Zeta Potential Of Porous Silicon Nanoparticle Drug Delivery Formulations*. International Journal Of Pharmaceutics, 431 (1), 230-236, 2012.

92. Karnik, R.; Fan, R.; Yue, M.; Li, D. Y.; Yang, P. D.; Majumdar, A. Electrostatic Control Of Ions And Molecules In Nanofluidic Transistors. Nano Letters, 5 (5), 943-948, 2005.

93. Kato, M.; Inaba, M.; Tsukahara, T.; Mawatari, K.; Hibara, A.; Kitamori, T. Femto Liquid Chromatography With Attoliter Sample Separation In The Extended Nanospace Channel. Analytical Chemistry, 82 (2), 543-547, 2010.

94. Kazoe, Y.; Mawatari, K.; Sugii, Y.; Kitamori, T. Development Of A Measurement Technique For Ion Distribution In An Extended Nanochannel By Super-Resolution-Laser-Induced Fluorescence. Analytical Chemistry, 83 (21), 8152-8157, 2011.

95. Keyser, U. F.; Koeleman, B. N.; Van Dorp, S.; Krapf, D.; Smeets, R. M.; Lemay, S. G.; Dekker, N. H.; Dekker, C. Direct Force Measurements On DNA In A Solid-State Nanopore. Nature Physics, 2 (7), 473-477, 2006.

96. Kim, S. J.; Ko, S. H.; Kang, K. H.; Han, J. Direct Seawater Desalination By Ion Concentration Polarization. Nature Nanotechnology, 5 (4), 297-301, 2010.

97. Kim, S. J.; Wang, Y. C.; Lee, J. H.; Jang, H.; Han, J. Concentration Polarization And Nonlinear Electrokinetic Flow Near A Nanofluidic Channel. Physical Review Letters, 99 (4), 2007.

98. Kneuer, C.; Sameti, M.; Haltner, E. G.; Schiestel, T.; Schirra, H.; Schmidt, H.; Lehr, C.-M. Silica Nanoparticles Modified With Aminosilanes As Carriers For Plasmid DNA. International Journal Of Pharmaceutics, 196 (2), 257-261, 2000.

99. Kobayashi, M.; Juillerat, F.; Galletto, P.; Bowen, P.; Borkovec, M. Aggregation And Charging Of Colloidal Silica Particles: Effect Of Particle Size. Langmuir, 21 (13), 5761-5769, 2005. 100. Kowalczyk, S. W.; Hall, A. R.; Dekker, C. Detection Of Local Protein Structures Along DNA Using Solid-State Nanopores. Nano Letters, 10 (1), 324-328, 2009.

101. Kowalczyk, S. W.; Wells, D. B.; Aksimentiev, A.; Dekker, C. Slowing Down DNA Translocation Through A Nanopore In Lithium Chloride. Nano Letters, 12 (2), 1038-1044,
2012.

102. Kreuter, J. Influence Of The Surface Properties On Nanoparticle-Mediated Transport Of Drugs To The Brain. Journal Of Nanoscience And Nanotechnology, 4 (5), 484-488, 2004.

103. Labbez, C.; Jonsson, B.; Skarba, M.; Borkovec, M. Ion-Ion Correlation And Charge Reversal At Titrating Solid Interfaces. Langmuir, 25 (13), 7209-7213, 2009.

104. Lan, W.-J.; Holden, D. A.; Liu, J.; White, H. S. Pressure-Driven Nanoparticle Transport Across Glass Membranes Containing A Conical-Shaped Nanopore. The Journal Of Physical Chemistry C, 115 (38), 18445-18452, 2011.

105. Lan, W.-J.; Holden, D. A.; Zhang, B.; White, H. S. Nanoparticle Transport In Conical-Shaped Nanopores. Analytical Chemistry, 83 (10), 3840-3847, 2011.

106. Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. Direct Force Measurements Between Dissimilar Metal-Oxides. Journal Of Physical Chemistry, 99 (7), 2114-2118, 1995.

107. Lee, C.; Joly, L.; Siria, A.; Biance, A.-L.; Fulcrand, R. M.; Bocquet, L. R. Large Apparent Electric Size Of Solid-State Nanopores Due To Spatially Extended Surface Conduction. Nano Letters, 12 (8), 4037-4044, 2012.

108. Li, C. Y.; Ma, F. X.; Wu, Z. Q.; Gao, H. L.; Shao, W. T.; Wang, K.; Xia, X. H. Solution-Ph-Modulated Rectification Of Ionic Current In Highly Ordered Nanochannel

Arrays Patterned With Chemical Functional Groups At Designed Positions. Advanced Functional Materials, 23 (31), 3836-3844, 2013.

109. Li, J.; Gershow, M.; Stein, D.; Brandin, E.; Golovchenko, J. DNA Molecules And Configurations In A Solid-State Nanopore Microscope. Nature Materials, 2 (9), 611-615,
2003.

110. Li, L.; Kazoe, Y.; Mawatari, K.; Sugii, Y.; Kitamori, T. Viscosity And Wetting Property Of Water Confined In Extended Nanospace Simultaneously Measured From Highly-Pressurized Meniscus Motion. The Journal Of Physical Chemistry Letters, 3 (17), 2447-2452, 2012.

111. Liang, L.; Rulis, P.; Ching, W. Y. Mechanical Properties, Electronic Structure And Bonding Of Alpha- And Beta-Tricalcium Phosphates With Surface Characterization. Acta Biomaterialia, 6 (9), 3763-3771, 2010.

Lima, E. R.; Bostrom, M.; Schwierz, N.; Sernelius, B. E.; Tavares, F. W. Attractive Double-Layer Forces Between Neutral Hydrophobic And Neutral Hydrophilic Surfaces.
Phys Rev E Stat Nonlin Soft Matter Phys, 84 (6 Pt 1), 061903, 2011.

113. Lin, X. Y.; Creuzet, F.; Arribart, H. Atomic Force Microscopy For Local Characterization Of Surface Acid-Base Properties. The Journal Of Physical Chemistry, 97
(28), 7272-7276, 1993.

114. Liu, J.; Kvetny, M.; Feng, J. Y.; Wang, D. C.; Wu, B. H.; Brown, W.; Wang, G. L. Surface Charge Density Determination Of Single Conical Nanopores Based On Normalized Ion Current Rectification. Langmuir, 28 (2), 1588-1595, 2012. 115. Liu, J.; Wang, D. C.; Kvetny, M.; Brown, W.; Li, Y.; Wang, G. L. Quantification Of Steady-State Ion Transport Through Single Conical Nanopores And A Nonuniform Distribution Of Surface Charges. Langmuir, 29 (27), 8743-8752, 2013.

116. Liu, S. R.; Pu, Q. S.; Gao, L.; Korzeniewski, C.; Matzke, C. From Nanochannel-Induced Proton Conduction Enhancement To A Nanochannel-Based Fuel Cell. Nano Letters, 5 (7), 1389-1393, 2005.

117. Lopes, M.; Candini, A.; Urdampilleta, M.; Reserbat-Plantey, A.; Bellini, V.; Klyatskaya, S.; Marty, L.; Ruben, M.; Affronte, M.; Wernsdorfer, W.; Bendiab, N. Surface-Enhanced Raman Signal For Terbium Single-Molecule Magnets Grafted On Graphene. ACS Nano, 4 (12), 7531-7537, 2010.

118. Lu, Y.; Yin, Y.; Mayers, B. T.; Xia, Y. Modifying The Surface Properties Of Superparamagnetic Iron Oxide Nanoparticles Through A Sol-Gel Approach. Nano Letters, 2 (3), 183-186, 2002.

119. Lyklema, J.; Overbeek, J. T. G. On The Interpretation Of Electrokinetic Potentials.Journal Of Colloid Science, 16 (5), 501-512, 1961.

Mao, H.-Q.; Roy, K.; Troung-Le, V. L.; Janes, K. A.; Lin, K. Y.; Wang, Y.; August,
J. T.; Leong, K. W. Chitosan-DNA Nanoparticles As Gene Carriers: Synthesis,
Characterization And Transfection Efficiency. Journal Of Controlled Release, 70 (3), 399421, 2001.

121. Mao, M.; Sherwood, J. D.; Ghosal, S. *Electro-Osmotic Flow Through A Nanopore*. Journal Of Fluid Mechanics, 749, 167-183, 2014.

122. Masliyah, J. H.; Bhattacharjee, S. Electrokinetic And Colloid Transport Phenomena. John Wiley & Sons, 2006. 123. Matijevic, E. Preparation And Properties Of Uniform Size Colloids. Chemistry Of Materials, 5 (4), 412-426, 1993.

124. Matovic, J.; Adamovic, N.; Radovanovic, F.; Jaksic, Z.; Schmid, U. Field Effect Transistor Based On Ions As Charge Carriers. Sensors And Actuators B-Chemical, 170, 137-142, 2012.

125. Mawatari, K.; Kazoe, Y.; Shimizu, H.; Pihosh, Y.; Kitamori, T. Extended-Nanofluidics: Fundamental Technologies, Unique Liquid Properties, And Application In Chemical And Bio Analysis Methods And Devices. Analytical Chemistry, 86 (9), 4068-4077, 2014.

Maynes, D.; Webb, B. W. Fully Developed Electro-Osmotic Heat Transfer In Microchannels. International Journal Of Heat And Mass Transfer, 46 (8), 1359-1369, 2003.

127. Meagher, L. Direct Measurement Of Forces Between Silica Surfaces In Aqueous
Cacl₂ Solutions Using An Atomic Force Microscope. J Colloid Interface Sci, 152 (1), 293295, 1992.

128. Meller, A.; Nivon, L.; Branton, D. Voltage-Driven DNA Translocations Through A Nanopore. Physical Review Letters, 86 (15), 3435-3438, 2001.

129. Melvin, E. M.; Moore, B. R.; Gilchrist, K. H.; Grego, S.; Velev, O. D. On-Chip Collection Of Particles And Cells By AC Electroosmotic Pumping And Dielectrophoresis Using Asymmetric Microelectrodes. Biomicrofluidics, 5 (3), 2011.

130. Menard, L. D.; Ramsey, J. M. Electrokinetically-Driven Transport Of DNA Through Focused Ion Beam Milled Nanofluidic Channels. Analytical Chemistry, 85 (2), 1146-1153, 2013. Miklavic, S.; Chan, D. Y.; White, L.; Healy, T. W. Double Layer Forces Between Heterogeneous Charged Surfaces. The Journal Of Physical Chemistry, 98 (36), 9022-9032, 1994.

132. Min, S. K.; Kim, W. Y.; Cho, Y.; Kim, K. S. Fast DNA Sequencing With A Graphene-Based Nanochannel Device. Nature Nanotechnology, 6 (3), 162-165, 2011.

133. Miura, A.; Tanaka, R.; Uraoka, Y.; Matsukawa, N.; Yamashita, I.; Fuyuki, T. The Characterization Of A Single Discrete Bionanodot For Memory Device Applications. Nanotechnology, 20 (12), 2009.

134. Montes Ruiz-Cabello, F. J.; Maroni, P.; Borkovec, M. Direct Measurements Of Forces Between Different Charged Colloidal Particles And Their Prediction By The Theory Of Derjaguin, Landau, Verwey, And Overbeek (DLVO). Journal Of Chemical Physics, 138 (23), 234705, 2013.

135. Morikawa, K.; Mawatari, K.; Kazoe, Y.; Tsukahara, T.; Kitamori, T. Shift Of Isoelectric Point In Extended Nanospace Investigated By Streaming Current Measurement.
Applied Physics Letters, 99 (12), 123115, 2011.

136. Mortensen, N. A.; Kristensen, A. Electroviscous Effects In Capillary Filling Of Nanochannels. Applied Physics Letters, 92 (6), 063110, 2008.

137. Nayak, A. K. Analysis Of Mixing For Electroosmotic Flow In Micro/Nano Channels With Heterogeneous Surface Potential. International Journal Of Heat And Mass Transfer, 75 10, 2014.

138. Nordström, J.; Matic, A.; Sun, J.; Forsyth, M.; Macfarlane, D. R. Aggregation, Ageing And Transport Properties Of Surface Modified Fumed Silica Dispersions. Soft Matter, 6 (10), 2293-2299, 2010. 139. Notley, S. M.; Norgren, M. Measurement Of Interaction Forces Between Lignin And Cellulose As A Function Of Aqueous Electrolyte Solution Conditions. Langmuir, 22
(26), 11199-11204, 2006.

140. Ohshima, H. Surface Charge Density/Surface Potential Relationship For A Spherical Colloidal Particle In A Salt-Free Medium. Journal Of Colloid And Interface Science, 247 (1), 18-23, 2002.

141. Öhshima, H.; Furusawa, K. Electrical Phenomena And Interfaces: Fundamentals, Measurements, And Applications. CRC Press, 1998.

142. Ohshima, H.; Healy, T. W.; White, L. R. Accurate Analytic Expressions For The Surface-Charge Density Surface-Potential Relationship And Double-Layer Potential Distribution For A Spherical Colloidal Particle. Journal Of Colloid And Interface Science, 90 (1), 17-26, 1982.

Paillusson, F.; Dahirel, V.; Jardat, M.; Victor, J. M.; Barbi, M. Effective Interaction Between Charged Nanoparticles And DNA. Physical Chemistry Chemical Physics, 13 (27), 12603-12613, 2011.

144. Pamukcu, S.; Weeks, A.; Wittle, J. K. Enhanced Reduction Of Cr(VI) By Direct Electric Current In A Contaminated Clay. Environmental Science & Technology, 38 (4), 1236-1241, 2004.

145. Pappaert, K.; Biesemans, J.; Clicq, D.; Vankrunkelsven, S.; Desmet, G. Measurements Of Diffusion Coefficients In 1-D Micro-And Nanochannels Using Shear-Driven Flows. Lab On A Chip, 5 (10), 1104-1110, 2005. Pelto, J. M.; Haimi, S. P.; Siljander, A. S.; Miettinen, S. S.; Tappura, K.; Higgins,
M. J.; Wallace, G. G. Surface Properties And Interaction Forces Of Biopolymer Doped
Conductive Polypyrrole Surfaces By Atomic Force Microscopy. Langmuir, 2013.

147. Perry, J. M.; Zhou, K. M.; Harms, Z. D.; Jacobson, S. C. Ion Transport In Nanofluidic Funnels. ACS Nano, 4 (7), 3897-3902, 2010.

Pevarnik, M.; Schiel, M.; Yoshimatsu, K.; Vlassiouk, I. V.; Kwon, J. S.; Shea, K.
J.; Siwy, Z. S. Particle Deformation And Concentration Polarization In Electroosmotic Transport Of Hydrogels Through Pores. ACS Nano, 7 (4), 3720-3728, 2013.

149. Phan, V.-N.; Yang, C.; Nguyen, N.-T. Analysis Of Capillary Filling In Nanochannels With Electroviscous Effects. Microfluidics And Nanofluidics, 7 (4), 519-530, 2009.

150. Plecis, A.; Schoch, R. B.; Renaud, P. Ionic Transport Phenomena In Nanofluidics: Experimental And Theoretical Study Of The Exclusion-Enrichment Effect On A Chip. Nano Letters, 5 (6), 1147-1155, 2005.

151. Popa, I.; Sinha, P.; Finessi, M.; Maroni, P.; Papastavrou, G.; Borkovec, M. Importance Of Charge Regulation In Attractive Double-Layer Forces Between Dissimilar Surfaces. Physical Review Letters, 104 (22), 2010.

152. Prieve, D. C.; Ruckenstein, E. The Surface Potential Of And Double-Layer Interaction Force Between Surfaces Characterized By Multiple Ionizable Groups. Journal Of Theoretical Biology, 56 (1), 205-228, 1976.

153. Pu, Q. S.; Oyesanya, O.; Thompson, B.; Liu, S. T.; Alvarez, J. C. On-Chip Micropatterning Of Plastic (Cylic Olefin Copolymer, COC) Microfluidic Channels For The Fabrication Of Biomolecule Microarrays Using Photografting Methods. Langmuir, 23 (3), 1577-1583, 2007.

154. Qiao, W. C.; Yang, K. J.; Thoma, A.; Dekorsy, T. Dielectric Relaxation Of Hcl And Nacl Solutions Investigated By Terahertz Time-Domain Spectroscopy. Journal Of Infrared Millimeter And Terahertz Waves, 33 (10), 1029-1038, 2012.

155. R. Qiao, N. R. A. Ion Concentrations And Velocity Profiles In Nanochannel Electroosmotic Flows. Journal Of Chemical Physics, 118 (10), 10, 2003.

156. Ravi Kumar, M.; Bakowsky, U.; Lehr, C. Preparation And Characterization Of Cationic PLGA Nanospheres As DNA Carriers. Biomaterials, 25 (10), 1771-1777, 2004.

157. Reddy, K. R.; Saichek, R. E. Enhanced Electrokinetic Removal Of Phenanthrene From Clay Soil By Periodic Electric Potential Application. Journal Of Environmental Science And Health Part A-Toxic/Hazardous Substances & Environmental Engineering, 39 (5), 1189-1212, 2004.

158. Redhead, H.; Davis, S.; Illum, L. Drug Delivery In Poly (Lactide-Co-Glycolide) Nanoparticles Surface Modified With Poloxamer 407 And Poloxamine 908: In Vitro Characterisation And In Vivo Evaluation. Journal Of Controlled Release, 70 (3), 353-363, 2001.

159. Renou, R.; Ding, M.; Zhu, H.; Szymczyk, A.; Malfreyt, P.; Ghoufi, A. Concentration Dependence Of The Dielectric Permittivity, Structure And Dynamics Of Aqueous Nacl Solutions: Comparison Between The Drude Oscillator And Electronic Continuum Models. The Journal Of Physical Chemistry B, 2014. 160. Renou, R.; Ghoufi, A.; Szymczyk, A.; Zhu, H.; Neyt, J. C.; Malfreyt, P. Nanoconfined Electrolyte Solutions In Porous Hydrophilic Silica Membranes. Journal Of Physical Chemistry C, 117 (21), 11017-11027, 2013.

161. Riehn, R.; Lu, M.; Wang, Y.-M.; Lim, S. F.; Cox, E. C.; Austin, R. H. *Restriction Mapping In Nanofluidic Devices*. Proceedings Of The National Academy Of Sciences Of The United States Of America, *102* (29), 10012-10016, 2005.

162. Rotenberg, B.; Pagonabarraga, I. Electrokinetics: Insights From Simulation On The Microscopic Scale. Molecular Physics, 111 (7), 827-842, 2013.

163. Roy, K.; Mao, H.-Q.; Huang, S.-K.; Leong, K. W. Oral Gene Delivery With Chitosan–DNA Nanoparticles Generates Immunologic Protection In A Murine Model Of Peanut Allergy. Nature Medicine, 5 (4), 387-391, 1999.

164. Ruiz-Cabello, F. J. M.; Maroni, P.; Borkovec, M. Direct Measurements Of Forces Between Different Charged Colloidal Particles And Their Prediction By The Theory Of Derjaguin, Landau, Verwey, And Overbeek (DLVO). Journal Of Chemical Physics, 138 (23), 2013.

165. Rutland, M. W.; Senden, T. J. Adsorption Of The Poly (Oxyethylene) Nonionic Surfactant C12E5 To Silica: A Study Using Atomic Force Microscopy. Langmuir, 9 (2), 412-418, 1993.

166. Ryan, J. N.; Elimelech, M.; Baeseman, J. L.; Magelky, R. D. Silica-Coated Titania And Zirconia Colloids For Subsurface Transport Field Experiments. Environmental Science & Technology, 34 (10), 2000-2005, 2000.

167. Sa, N. Y.; Lan, W. J.; Shi, W. Q.; Baker, L. A. Rectification Of Ion Current In Nanopipettes By External Substrates. ACS Nano, 7 (12), 11272-11282, 2013.

168. Sabuncu, A. C.; Grubbs, J.; Qian, S.; Abdel-Fattah, T. M.; Stacey, M. W.; Beskok,
A. Probing Nanoparticle Interactions In Cell Culture Media. Colloids And Surfaces B:
Biointerfaces, 95, 96-102, 2012.

Sang, J. M.; Du, H. T.; Wang, W.; Chu, M.; Wang, Y. D.; Li, H. C.; Zhang, H. A.;
Wu, W. G.; Li, Z. H. Protein Sensing By Nanofluidic Crystal And Its Signal Enhancement.
Biomicrofluidics, 7 (2), 2013.

170. Sanghavi, B. J.; Mobin, S. M.; Mathur, P.; Lahiri, G. K.; Srivastava, A. K. Biomimetic Sensor For Certain Catecholamines Employing Copper (II) Complex And Silver Nanoparticle Modified Glassy Carbon Paste Electrode. Biosensors And Bioelectronics, 39, 124-132, 2012.

171. Sanghavi, B. J.; Srivastava, A. K. Adsorptive Stripping Voltammetric Determination Of Imipramine, Trimipramine And Desipramine Employing Titanium Dioxide Nanoparticles And An Amberlite XAD-2 Modified Glassy Carbon Paste Electrode. Analyst, 138 (5), 1395-1404, 2013.

172. Schnitzer, O.; Yariv, E. Strong Electro-Osmotic Flows About Dielectric Surfaces Of Zero Surface Charge. Physical Review E, 89 (4), 2014.

173. Scott M. Davidson, M. B. A., Ali Mani. Chaotic Induced-Charge Electro-Osmosis.Physical Review E, (128302), 5, 2014.

174. Sengers, J. V.; Perkins, R. A.; Huber, M. L.; Friend, D. Viscosity Of H2O In The Critical Region. International Journal Of Thermophysics, 30 (2), 374-384, 2009.

175. Singh, K. P.; Kumar, M. Effect Of Gate Length And Dielectric Thickness On Ion And Fluid Transport In A Fluidic Nanochannel. Lab On A Chip, 12 (7), 1332-1339, 2012. Snyder, K. L.; Holmes, H. R.; Vanwagner, M. J.; Hartman, N. J.; Rajachar, R. M.
Development Of Vapor Deposited Silica Sol-Gel Particles For Use As A Bioactive
Materials System. Journal Of Biomedical Materials Research Part A, 101A (6), 1682-1693,
2013.

177. Sonnefeld, J.; Löbbus, M.; Vogelsberger, W. Determination Of Electric Double Layer Parameters For Spherical Silica Particles Under Application Of The Triple Layer Model Using Surface Charge Density Data And Results Of Electrokinetic Sonic Amplitude Measurements. Colloids And Surfaces A: Physicochemical And Engineering Aspects, 195 (1), 215-225, 2001.

178. Startsev, M. A.; Inglis, D. W.; Baker, M. S.; Goldys, E. M. Nanochannel Ph Gradient Electrofocusing Of Proteins. Analytical Chemistry, 85 (15), 7133-7138, 2013.

179. Stein, D.; Deurvorst, Z.; Van Der Heyden, F. H. J.; Koopmans, W. J. A.; Gabel, A.; Dekker, C. *Electrokinetic Concentration Of DNA Polymers In Nanofluidic Channels*. Nano Letters, *10* (3), 765-772, 2010.

180. Stein, D.; Kruithof, M.; Dekker, C. Surface-Charge-Governed Ion Transport In Nanofluidic Channels. Physical Review Letters, 93 (3), 035901, 2004.

181. Stigter, D. On The Viscoelectric Effect In Colloidal Solutions1. The Journal Of Physical Chemistry, 68 (12), 3600-3602, 1964.

182. Tagliazucchi, M.; Szleifer, I. Stimuli-Responsive Polymers Grafted To Nanopores And Other Nano-Curved Surfaces: Structure, Chemical Equilibrium And Transport. Soft Matter, 8 (28), 7292-7305, 2012.

183. Taskiran, A.; Schirmeisen, A.; Fuchs, H.; Bracht, H.; Roling, B. Time-Domain Electrostatic Force Spectroscopy On Nanostructured Lithium-Ion Conducting Glass Ceramics: Analysis And Interpretation Of Relaxation Times. Physical Chemistry Chemical Physics, 11 (26), 5499-5505, 2009.

184. Taton, T. A.; Mirkin, C. A.; Letsinger, R. L. Scanometric DNA Array Detection With Nanoparticle Probes. Science, 289 (5485), 1757-1760, 2000.

185. Thomassen, L. C.; Rabolli, V.; Masschaele, K.; Alberto, G.; Tomatis, M.; Ghiazza, M.; Turci, F.; Breynaert, E.; Martra, G.; Kirschhock, C. E. Model System To Study The Influence Of Aggregation On The Hemolytic Potential Of Silica Nanoparticles. Chemical Research In Toxicology, 24 (11), 1869-1875, 2011.

186. Toikka, G.; Hayes, R. A.; Ralston, J. Adhesion Of Iron Oxide To Silica Studied By Atomic Force Microscopy. Journal of Colloid and Interface Science, 180 (2), 329-338, 1996.

187. Tsukahara, T.; Mawatari, K.; Hibara, A.; Kitamori, T. Development Of A Pressure-Driven Nanofluidic Control System And Its Application To An Enzymatic Reaction. Analytical And Bioanalytical Chemistry, 391 (8), 2745-2752, 2008.

188. Ullien, D.; Cohen, H.; Porath, D. The Effect Of The Number Of Parallel DNA Molecules On Electric Charge Transport Through 'Standing DNA'. Nanotechnology, 18 (42), 2007.

189. Valkovska, D. S.; Danov, K. D. Influence Of Ionic Surfactants On The Drainage Velocity Of Thin Liquid Films. Journal Of Colloid And Interface Science, 241 (2), 400-412, 2001.

190. Van Der Heyden, F. H.; Stein, D.; Dekker, C. Streaming Currents In A Single Nanofluidic Channel. Physical Review Letters, 95 (11), 116104, 2005.

191. Van Der Heyden, F. H. J.; Bonthuis, D. J.; Stein, D.; Meyer, C.; Dekker, C. Electrokinetic Energy Conversion Efficiency In Nanofluidic Channels. Nano Letters, 6 (10), 2232-2237, 2006.

192. Van Der Heyden, F. H. J.; Bonthuis, D. J.; Stein, D.; Meyer, C.; Dekker, C. Power Generation By Pressure-Driven Transport Of Ions In Nanofluidic Channels. Nano Letters, 7 (4), 1022-1025, 2007.

193. Van Der Heyden, F. H. J.; Stein, D.; Dekker, C. Streaming Currents In A Single Nanofluidic Channel. Physical Review Letters, 95 (11), 116104, 2005.

194. Van Honschoten, J. W.; Brunets, N.; Tas, N. R. Capillarity At The Nanoscale. Chemical Society Reviews, 39 (3), 1096-1114, 2010.

195. Varela, J. A.; Bexiga, M. G.; Åberg, C.; Simpson, J. C.; Dawson, K. A. Quantifying Size-Dependent Interactions Between Fluorescently Labeled Polystyrene Nanoparticles And Mammalian Cells. Journal Of Nanobiotechnology, 10 (1), 1-6, 2012.

196. Velegol, D.; Thwar, P. K. Analytical Model For The Effect Of Surface Charge Nonuniformity On Colloidal Interactions. Langmuir, 17 (24), 7687-7693, 2001.

197. Verma, A.; Stellacci, F. Effect Of Surface Properties On Nanoparticle-Cell Interactions. Small, 6 (1), 12-21, 2010.

198. Verwey, E. J. W. Theory Of The Stability Of Lyophobic Colloids. Journal Of Physical And Colloid Chemistry, 51 (3), 631-636, 1947.

199. Verwey, E. J. W.; Overbeek, J. T. G.; Van Nes, K. Theory Of The Stability Of Lyophobic Colloids: The Interaction Of Sol Particles Having An Electric Double Layer. Elsevier New York, 1948.

200. Wang, Y. H.; Wang, L. G.; Hampton, M. A.; Nguyen, A. V. Atomic Force Microscopy Study Of Forces Between A Silica Sphere And An Oxidized Silicon Wafer In Aqueous Solutions Of Nacl, Kcl, And Cscl At Concentrations Up To Saturation. Journal Of Physical Chemistry C, 117 (5), 2113-2120, 2013.

201. Wang, Z.-W.; Li, G.-Z.; Guan, D.-R.; Yi, X.-Z.; Lou, A.-J. *The Surface Potential Of A Spherical Colloid Particle: Functional Theoretical Approach*. Journal Of Colloid And Interface Science, *246* (2), 302-308, 2002.

202. Weisenhorn, A.; Maivald, P.; Butt, H.-J.; Hansma, P. Measuring Adhesion, Attraction, And Repulsion Between Surfaces In Liquids With An Atomic-Force Microscope. Physical Review B, 45 (19), 11226, 1992.

203. Wesley T.E. Van Den Beld, W. S., Albert Van Den Berg, Jan C.T. Eijkel. Frequency Dependent AC Electroosmotic Flow In Nanochannels. In *MEMS 2014*, San Francisco, CA, USA, 2014.

204. Xu, Z. H.; Chi, R.; Difeo, T.; Finch, J. A. Surface Forces Between Sphalerite And Silica Particles In Aqueous Solutions. Journal Of Adhesion Science And Technology, 14 (14), 1813-1827, 2000.

205. Xue, S.; Hu, N.; Qian, S. Z. Tuning Surface Charge Property By Floating Gate Field Effect Transistor. J. Colloid Interface Sci., 365 (1), 326-328, 2012.

206. Xue, S.; Yeh, L. H.; Ma, Y.; Qian, S. Z. Tunable Streaming Current In A Ph-Regulated Nanochannel By A Field Effect Transistor. Journal Of Physical Chemistry C, 118 (12), 6090-6099, 2014. 207. Yan, L. M.; Ji, X. B.; Lu, W. C. Molecular Dynamics Simulations Of Electroosmosis In Perfluorosulfonic Acid Polymer. Journal Of Physical Chemistry B, 112 (18), 5602-5610, 2008.

Yang, M.; Yang, X. H.; Wang, Q.; Wang, K. M.; Fan, X.; Liu, W.; Liu, X. Z.; Liu,
J. B.; Huang, J. Anomalous Effects Of Water Flow Through Charged Nanochannel Membranes. RSC Advances, 4 (51), 26729-26737, 2014.

209. Yeh, L.-H.; Xue, S.; Joo, S. W.; Qian, S.; Hsu, J.-P. Field Effect Control Of Surface Charge Property And Electroosmotic Flow In Nanofluidics. The Journal Of Physical Chemistry C, 116 (6), 4209-4216, 2012.

210. Yeh, L.-H.; Zhang, M.; Hu, N.; Joo, S. W.; Qian, S.; Hsu, J.-P. Electrokinetic Ion And Fluid Transport In Nanopores Functionalized By Polyelectrolyte Brushes. Nanoscale, 4 (16), 5169-5177, 2012.

211. Yeh, L.-H.; Zhang, M.; Qian, S. Ion Transport In A Ph-Regulated Nanopore. Analytical Chemistry, 85 (15), 7527-7534, 2013.

212. Yeh, L. H.; Hsu, J. P.; Qian, S.; Tseng, S. J. Counterion Condensation In Ph-Regulated Polyelectrolytes. Electrochemistry Communications, 19, 97-100, 2012.

213. Yeh, L. H.; Zhang, M.; Qian, S. Ion Transport In A Ph-Regulated Nanopore. Analytical Chemistry, 85, 7527-7534, 2013.

214. Yeh, L. H.; Zhang, M.; Qian, S.; Hsu, J. P. Regulating DNA Translocation Through Functionalized Soft Nanopores. Nanoscale, 4 (8), 2685-2693, 2012.

215. Yeh, L. H.; Zhang, M. K.; Joo, S. W.; Qian, S.; Hsu, J. P. Controlling Ph-Regulated Bionanoparticles Translocation Through Nanopores With Polyelectrolyte Brushes. Analytical Chemistry, 84 (21), 9615-9622, 2012. Yusko, E. C.; Johnson, J. M.; Majd, S.; Prangkio, P.; Rollings, R. C.; Li, J.; Yang,
J.; Mayer, M. Controlling Protein Translocation Through Nanopores With Bio-Inspired
Fluid Walls. Nature Nanotechnology, 6 (4), 253-260, 2011.

Zhang, H. C.; Hou, X.; Zeng, L.; Yang, F.; Li, L.; Yan, D. D.; Tian, Y.; Jiang, L. *Bioinspired Artificial Single Ion Pump.* Journal Of The American Chemical Society, 135
(43), 16102-16110, 2013.

218. Zhang, M.; Ai, Y.; Sharma, A.; Joo, S. W.; Kim, D. S.; Qian, S. Electrokinetic Particle Translocation Through A Nanopore Containing A Floating Electrode. Electrophoresis, 32 (14), 1864-1874, 2011.

219. Zhang, M.; Yeh, L.-H.; Qian, S.; Hsu, J.-P.; Joo, S. W. DNA Electrokinetic Translocation Through A Nanopore: Local Permittivity Environment Effect. The Journal Of Physical Chemistry C, 116 (7), 4793-4801, 2012.

Zheng, Z.; Hansford, D. J.; Conlisk, A. T. Effect Of Multivalent Ions On Electroosmotic Flow In Micro- And Nanochannels. Electrophoresis, 24 (17), 3006-3017, 2003.

221. Zhmud, B.; Meurk, A.; Bergström, L. Evaluation Of Surface Ionization Parameters From AFM Data. Journal of Colloid and Interface Science, 207 (2), 332-343, 1998.

222. Zhong, S.; Li, H.; Chen, X. Y.; Cao, E. H.; Jin, G.; Hu, K. S. Different Interactions Between The Two Sides Of Purple Membrane With Atomic Force Microscope Tip. Langmuir, 23 (8), 4486-4493, 2007.

223. Zhou, K.; Perry, J. M.; Jacobson, S. C. Transport And Sensing In Nanofluidic Devices. Annual Review of Analytical Chemistry, 4, 321-341, 2011.

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Presidential Fellowship of Turkey	2004-2008

PUBLICATIONS:

- 1- Yu M, Atalay S, Qian S (2014) Electroosmotic Flow In Charge Regulated Nanoslit, (In Preparation). (Yu And Atalay Contributed Equally).
- 2- Atalay S, Yeh LH, Qian S (2014) Proton Enhancement in an Extended Nanochannel, Langmuir, 30 (43), pp 13116-13120.
- 3- Atalay S, Barisik M, Beskok A, Qian S (2014) Surface Charge Of A Nanoparticle Interacting With A Flat Substrate, Journal of Physical Chemistry C, 118 (20), Pp 10927-10935.

- 4- Atalay S, Yu Ma, Qian S (2014) Analytical Model for Charge Properties of Silica Particles, Journal Colloid Interface Science, 425(2014), 128-130. (Selected as cover article in Journal Colloid Interface Science).
- 5- Barisik M, Atalay S, Beskok A, Qian S (2014) Size Dependent Surface Charge Properties of Charge Regulated Nanoparticles, Journal of Physical Chemistry C, 118 (4), pp 1836-1842. (Barisik and Atalay contributed equally).

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- Atalay S, Beskok A, Qian S (2014) Surface Charge Properties of Nanoparticle: Size Dependency and Boundary Effect. ECS 226th Meeting, Cancun-Mexico, October/2014.
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- 4- Atalay S, Benard E (2011) *Transient Cavity Flow*, 23rd Scottish Fluid Mechanics Meeting, 19th May 2010, Dundee, Scotland, UK.