



The effect of surface charge regulation on conductivity in fluidic nanochannels



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ABSTRACT

The precise electrostatic potential distribution is very important for the electrokinetic transport in fluidic channels. This is especially valid for small nanochannels where the electric double layers formed at the walls are comparable to the channel width. It can be expected that due to the large surface to volume ratio in such systems, they will exhibit properties that are not detectable in larger channels, capillaries and pores. We present a detailed numerical analysis of the current transport in fluidic nanochannels. It is based on solving the Poisson–Boltzmann equation with charge regulation boundary conditions that account for the surface–aqueous solution chemical equilibria. The focus is on studying the effect of the pH on the current transport. The pH is varied by adding either HCl or KOH. The analysis predicts non-monotonous and sometimes counterintuitive dependence of the conductivity on the pH. The channel conductivity exhibits practically no change over a range of pH values due to a buffering exerted by the chemical groups at the walls. An unexpected drop of the conductivity is observed around the wall isoelectric point and also in the vicinity of pH = 7 even though the concentration of ions in the channel increases. These observations are explained in the framework of charge regulation theory.

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1. Introduction

Electrostatic fields often occur and determine the physical and chemical behavior of solutions at the nanometer length scale in the vicinity of interfaces. The origin of the electrostatic potentials lies in the interaction of an interface with an adjacent polar liquid (usually water). The interaction may include dissociation of surface ionic groups or adsorption of ions from the bulk or both.

The presence of electrostatic fields results in the formation of an electric double-layer [1], and results in ionic conductivities that can deviate significantly from bulk values [2,3]. Experimental results on the conductivity of nanochannels have demonstrated interesting new phenomena including ion-current rectification [4,5], saturation of conductivity at low concentrations [3], and related the pH value to ionic conductance [6].

The mathematical formulation of this problem in continuum approximation based on the Poisson–Boltzmann (PB) equation is straightforward when using Dirichlet or Neumann boundary conditions, corresponding to constant surface potential, and constant surface-charge density respectively [1]. However, the most physically relevant boundary condition is given by the thermodynamic equilibrium between free and bound ions at the surface. This is particularly important if one needs a better quantitative descrip-

tion of the potential as a function of various parameters. Such situations occur in phenomena involving colloid stability, nanofabrication and assembly, and transport phenomena in nanochannels.

Charge regulation boundary conditions were first formulated by Ninham and Parsegian [7]. Later Chan, et al. generalized the approach to include dissimilar surfaces [8]. A closed-form solution to the PB equation using charge regulating boundary conditions was derived by Behrens and Borkovec [9]. A variety of other charge regulation models have been developed that account for the Stern layer, ion adsorption [10], and they make use of various approximations to the chemical equilibria [11,12]. Additionally, triple-layer and four-layer models have been used to explicitly account for the difference between the Stern layer, and diffuse Gouy–Chapman layer in regimes of relatively high ion concentration [13,14]. However, it should be noted that for the analysis solutions with high ionic density it is much better to use rigorous and self-consistent statistical mechanical approaches such as density functional theory [15–17].

The surface charge or potential of a nanochannel has a strong influence on ionic conductivity. This is due to redistributing the counter ions and coions in the electric double-layer which for very small channels occupies most of the volume. We address the effect of the isoelectric point, pH, and surface-bulk chemical equilibria using a 2-pK charge regulation model [8]. This model has been demonstrated to provide an excellent description of the ionization

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process of water–solid interfaces [18]. Using this model we calculate the conductivity of ions in a nanochannel. We find that the conductivity can increase, or decrease compared to bulk conductivity depending on the chemical equilibria, and double-layer overlap. Our analysis considers the case of infinite parallel flat plate geometries. Other geometries such as cylindrical are not considered, since the results will be qualitatively similar.

2. Theory

The ionic conductivity γ_b of a bulk electrolyte at low concentrations (<1 mM) is determined by [2],

$$\gamma_b = \frac{e^2}{k_B T} \sum_i z_i^2 n_i^0 D_i, \quad (1)$$

where e is the fundamental unit of charge, n_i^0 is the bulk number concentration of ion i , $k_B T$ is the thermal energy, D_i are the ionic diffusion coefficients, and z_i are the charge numbers. For low concentrations the diffusion coefficients of the ions are considered to be constant.

In a nanochannel Eq. (1) needs to be modified to reflect the effect of the electric double layer near the surfaces of the nanochannel which results from spatially varying ion distributions. The conductivity of the nanochannel of width L is given by γ_c , which includes both surface and electro-osmotic effects becomes [2],

$$\gamma_c = \frac{1}{L} \int_{-L/2}^{L/2} \frac{e^2}{k_B T} \left\{ \sum_i z_i^2 n_i^0 D_i \exp \left[\frac{-z_i e \Psi(x)}{k_B T} \right] - \frac{\rho(x) \varepsilon_r \varepsilon_0 e [\zeta - \Psi(x)]}{\eta k_B T} \right\} dx, \quad (2)$$

where x is the spatial coordinate, ε_r is the relative permittivity of the solution, ε_0 is the permittivity of free space, η is the viscosity of the solvent, and $\Psi(x)$ is the potential distribution due to the electric double layer, ρ is the free charge density, and ζ is the so-called zeta potential. For this study we consider ζ to be equal to the surface potential. Here and below we consider the origin to be located at the center of the channel. The second term in the integrand takes into account the convective current due to electroosmotic flow.

In order to calculate the spatially varying potential $\Psi(x)$ we use the PB equation which reads [19],

$$\frac{d^2 \Psi}{dx^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{e}{\varepsilon_0 \varepsilon_r} \sum_i z_i n_i^0 \exp \left(\frac{-z_i e \Psi}{k_B T} \right). \quad (3)$$

The PB approach assumes ions are point charges in a structureless solvent, and does not account for coulombic interactions within the solvent, or ion–solvent correlations. These assumptions are appropriate when length-scales are large enough that the solvent can be treated as a continuum and ion concentrations are low enough that ion–ion correlations are small. These assumptions, however can be problematic at the nanoscale at high potentials and where the continuum approximation breaks down [20–22]. The PB equation is only accurate when ions do not crowd the interface. For this reason we only consider solutions where the bulk ionic concentration is less than 1 mM and where the counter-ion concentration is less than 0.1 M at the interface.

We are interested in the conductivity dependence on bulk pH. The charge regulation model is the most appropriate for studying this case. Charge regulation takes place when the surface charge at an interface is controlled by chemical equilibria for adsorption and desorption of potential determining ions.

The charge regulation model we use assumes that the interface can be described as an amphoteric surface “A” that participates in two chemical equilibria,



where K_+ and K_- are the dissociation constants. According to these two chemical equilibria, the amphoteric surface can acquire a negative, positive or neutral charge. The boundary conditions are then expressed in terms of the surface charge density as a function of surface potential $\sigma(\Psi_s)$ [8],

$$\begin{aligned} \sigma(\Psi_s) &= e N_s \frac{[\text{AH}_2^+] - [\text{A}^-]}{[\text{AH}] + [\text{AH}_2^+] + [\text{A}^-]} \\ &= e N_s \frac{\delta \sinh[e(\Psi_N - \Psi_s)/k_B T]}{1 + \delta \cosh[e(\Psi_N - \Psi_s)/k_B T]}, \end{aligned} \quad (6)$$

where $\delta \equiv 2\sqrt{K_-/K_+}$, N_s is the surface concentration of ionizable groups at the surface, and Ψ_s is the potential at the surface of the nanochannel. The Nernst potential [8] is,

$$\Psi_N = \ln(10) \frac{k_B T}{e} (\text{pI} - \text{pH}_b), \quad (7)$$

the isoelectric point of the surface is expressed by,

$$\text{pI} = \frac{\text{pK}_+ + \text{pK}_-}{2}, \quad (8)$$

and for mathematical convenience we use a quantity ΔpK which is defined as,

$$\Delta \text{pK} = \text{pK}_- - \text{pK}_+, \quad (9)$$

where $\text{pK}_\pm = -\log_{10}(K_\pm)$.

Since the PB Eq. (3), is a 2nd order differential equation two boundary conditions are required to determine a particular solution. The first boundary condition comes from the symmetry of the system. The modeled symmetric channel consists of two parallel flat surfaces of identical composition. This is equivalent to setting $d\Psi/dx = 0$ at the center of the channel where $x = 0$.

For the second boundary condition we use $\Psi(L/2) = \Psi_s$, where L is the width of the channel. The value of Ψ_s is not known a priori for a given set of charge regulating boundary conditions, but its value is to be found self-consistently. Hence a guess for Ψ_s is made and used to solve the PB equation to recover $\sigma(\Psi_s)$ and iterated on Eq. (6) using a root finding algorithm. Solutions of the PB equation yield complete information of the ion distributions that we use to compute ionic conductivities for these systems using Eq. (2).

3. Results and discussion

In this study we calculate conductivities of electrolytes in nanochannels with surface charge regulating parameters pI , ΔpK , and N_s . Varying these parameters allows us to illustrate their effect on surface phenomena within the range of experimentally determined values for a number of materials used to construct nanochannels. Example materials include, SiO_2 ($\text{pI} \approx 2$, $\Delta \text{pK} \approx 8$, $N_s \approx 5$ sites/ nm^2), Al_2O_3 ($\text{pI} \approx 8$, $\Delta \text{pK} \approx 4$, $N_s \approx 8$ sites/ nm^2) and Ta_2O_5 ($\text{pI} \approx 3$, $\Delta \text{pK} \approx 2$, $N_s \approx 10$ sites/ nm^2) [23]. For this paper, all results are generated with $N_s \approx 8$ sites/ nm^2 . We choose this value because it is physically sensible and representative, it reduces our parameter space, and because we do not expect our results to differ qualitatively for different values of N_s .

Bulk pH is controlled by adding either HCl or KOH, and we do not add any background electrolyte, therefore the total ionic strength and hence the Debye length κ^{-1} is dependent on pH. The Debye screening parameter κ is defined as [24],

$$\kappa^2 = \frac{e^2}{\varepsilon_r \varepsilon_0 k_B T} \sum_i z_i^2 n_i^0. \quad (10)$$

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