

The Effects of the Electrical Double Layer on Giant Ionic Currents through Single Walled Carbon Nanotubes

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Abstract: A computational model of nanoelectrofluidic current through single wall carbon nanotubes was constructed using COMSOL. The Nernst-Planck, Navier-Stokes, and Poisson equations were solved over a 2-dimensional axisymmetric geometry. The key components of the model included an explicitly defined compact layer in agreement with Gouy-Chapman-Stern theory and a perfect slip condition at the outer Helmholtz plane. The simulation results agree well with experimental measurements. Analysis of the structure reveals that the thickness of the compact layer (which depends on the bulk solution concentration) is responsible for the characteristic device behavior. The compact layer thickness influences the proportions of charge carriers within the nanotube, which has a direct impact on electroosmotic flow.

Keywords: Electrical double layer, electroosmosis, and carbon nanotube.

1. Introduction

Electrokinetic flow through nanopores and nanochannels is a subject of active interest and research. The nanoscale dimensions of these devices enable analysis of small sample volumes and manipulation of samples on the level of a few molecules. Due to the small scale of these devices, surface properties, charge accumulations and screening effects become important. Nanopores have been designed with the function of detecting translocating macromolecules.^{6,7} Of particular interest to this study is the enhanced ionic conduction observed in nanochannels composed of single wall carbon nanotubes (SWCNTs).^{1,8}

Numerical models found in the literature typically fit the experimental data well. However, in all electrokinetic studies of nanochannels to date, the compact layer has been consistently neglected. The diffuse layer typically arises naturally out of the assumption of electrical charge at the channel wall and is thus included as a natural result of modeling the system. While neglecting the Stern layer is appropriate for channels much larger than the thickness of the electrical double layer, neglecting the compact layer in channels with radii at the scale of the Debye length fails to account for all relevant phenomena in electrolyte/surface interactions. The Gouy-Chapman-Stern theory of the electrical double layer is typically used to describe electric solution/surface interactions and should be considered. In nanochannels with a very small radius, one should expect a compact layer of finite thickness to have non-negligible influence. A numerical model of the complete Gouy-Chapman-Stern model based on Grahame interpretation³ presented by Yang and Zhang⁴⁻⁵ may serve as a basis for the electrical double layer in an improved model of electrokinetic flow through nanochannels.

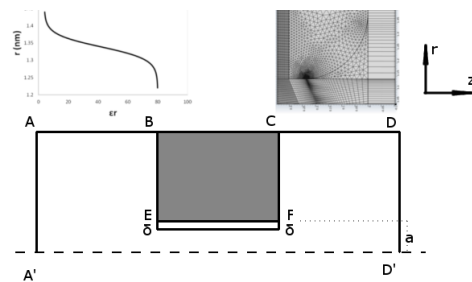


Fig.1 Axisymmetric geometry of the numerical model. TOP LEFT: Variation in the dielectric constant of the compact layer. TOP RIGHT: Meshing of the rounded corners at the mouth of the nanotube model.

2. Modeling Consideration

Governing equations:

Poisson, Nernst-Planck and Stokes equations were solved for this problem.

$$\nabla^2 V = -\frac{\rho(r, z)}{\epsilon_0 \epsilon_r}$$

$$\nabla \cdot (-D_j \nabla c_j - z_j \mu_{m,j} F c_j \nabla V) + u \cdot \nabla c_j = R_j$$

$$N_j = -D_j \nabla c_j - z_j \mu_{m,j} F c_j \nabla V + u c_j$$

$$\rho_V (u \cdot \nabla) u = \nabla \cdot \left[-PI + \gamma (\nabla u + (\nabla u)^T) - \frac{2}{3} \gamma (\nabla \cdot u) I \right] + \bar{F}_V$$

$$\nabla \cdot (\rho_V u) = 0$$

Geometry:

SWCNT nanochannel was modeled as a high-aspect ratio cylinder (Fig.1). A dielectric barrier material (in this case SiO₂, $\epsilon_r=3.9$) was included in the region between the channel and the reservoirs. The geometry was defined using a two dimensional axisymmetric model (about the longitudinal axis). The length of the channel was 50 nm and the model was evaluated with channel radii of $a=1$ nm or $a=1.44$ nm. A compact layer was defined at the interface of the channel and barrier material (δ , along boundary EF). The compact layer region was rectangular with length 50 nm and width between 0.15 and 0.66 nm. The fluid-side corners of this Stern layer were rounded in order to ease the computational difficulty of solving the model at the channel openings.

Modeling Aspects:

All modeling was performed in COMSOL 4.2a. Calculation of dimensionless quantities was based on a characteristic length equal to the nanochannel diameter and a mean free path of water equal to 0.3 nm. Numerically solving the fully coupled governing equations was computationally intensive and required a fine mesh. Rectangular mesh elements were used for the majority of the domain, with a fine triangular mesh defined near the openings of the nanochannel. Triangular elements were employed in the region near the rounded corners of the compact layer (upper right inset, Fig.1).

3. Results and Discussion

In evaluating the developed model, conductance and concentration relationships were used as the key metric. From a survey of the data presented in the literature, the device is expected to have a conductance between 0.7 nS and 3 nS at a solution concentration of 1M.⁸ The relationship between concentration and conductance may be characterized by a power fit ($G = A * c^b$), where the exponent (b) from the fit falls between 0.3 and 0.6.

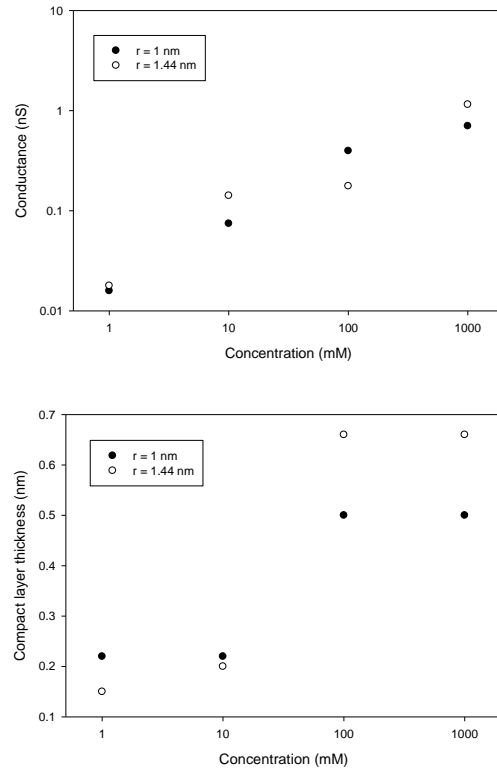


Fig.2 Conductance/concentration relationship was found to be in good agreement with experimental observations. The compact layer thickness was found to be dependent on bulk solution concentration as expected.

The enhanced ionic current was due to electroosmosis as has been noted in previous studies. However, it was observed that the electroosmotic fluid velocity was dependent on the compact layer thickness and bulk solution concentration (Fig.2). The fluid velocity was proportional to the concentration of the bulk fluid (Fig.3). A statistically significant trend was

observed with the fluid velocity reducing in magnitude as the compact layer thickness increased. The decrease in fluid velocity corresponds to an effective narrowing of the channel. Therefore, the restriction of fluid flow via thick compact layers at high solution concentrations is responsible for the characteristic relationship between device conductance and solution concentration. By impeding the electroosmotic velocity of the fluid at high bulk concentrations, the conductance at high concentration is made to be lower than if the compact layer were of constant thickness relative to concentration. In this case, the ionic conductance of carbon nanotubes is enhanced by electroosmosis at all concentrations within the range of 1mM to 1M, but the conductance is more enhanced at lower concentrations due to a thinner compact layer. By regulating the fluid flow through this naturally occurring mechanism, conductance at low solution concentrations is more enhanced proportionally than the conductance at higher concentrations, leading to the characteristic power relationship between concentration and conductance with an exponent between 0.3 and 0.6.

As the internal volume of the nanotube is restricted, the steady state, volume averaged number of ions in the channel is reduced. The majority carrier (in this case K^+) is more sensitive to volume restriction due to representing a higher proportion of available charge carriers. The result is that the carrier differential (K-Cl) is reduced as the compact layer thickness increases. A reduced charge differential reduces the electroosmotic volume force, resulting in a reduced fluid velocity. Since the compact layer thickness (which is inversely related to the effective channel thickness) is dependent on bulk solution concentration, the electroosmotic velocity is therefore mediated by the bulk concentration through the electrical double layer.

4. Conclusions

A computational model of the nanoelectrofluidic behavior of single walled carbon nanotubes was constructed. All parameters and boundary conditions were within known ranges and no artificial conditions were imposed on the model. The complete Gouy-Chapman-Stern electrical

double layer was included and found to be critical to the observed behavior of carbon nanotube devices. The small diameter of nanotubes is similar to the scale of the compact layer of the electrical double layer, resulting in a non-negligible reduction of the internal volume. A straightforward relationship emerges between the relative number of charge carriers within the nanotube, the compact layer thickness, and bulk solution concentration. The relationship between the model conductance and bulk concentration is in good agreement with experimentally observed behavior.

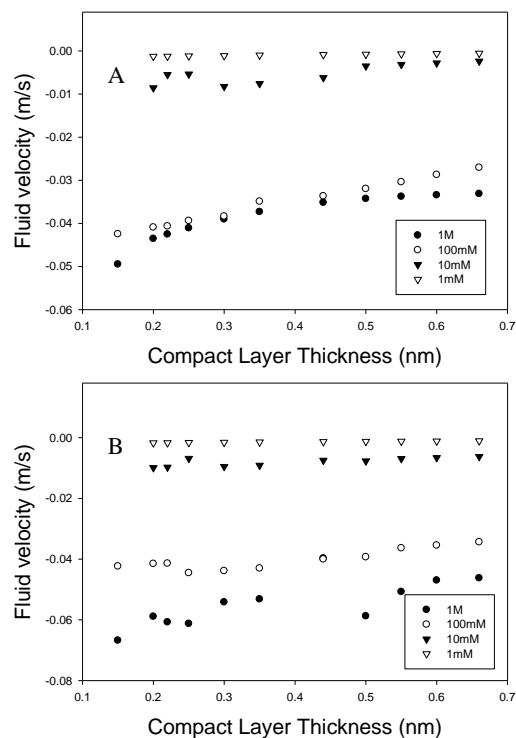


Fig.3 Fluid velocity versus compact layer thickness for nanochannels with radius 1nm (A) and 1.44 nm (B).

5. References

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7. Appendix

k_B	Boltzmann's constant	1.38065e-23 (J/K)
T	Temperature	296.65 (K)
z_j	Valence of solvated electrolytes	-1 for Cl^- +1 for K^+
F	Faraday's constant	96485.34 (C/mole)
ϵ_0	Permittivity of free space	8.8542e-12 (F/m)
V_0	Potential applied across the length of the channel	0.0125 (V)
D_j	Diffusion coefficient for solvated electrolytes	Cl^- : 2.03e-5(cm ² /s) K^+ : 1.96e-5(cm ² /s)
$u_{m,j}$	Mobility of solvated electrolytes	Cl^- : 8.23e-13 (s mol/kg) K^+ : 7.95e-13 (s mol/kg)
ϵ_b	Relative permittivity of the SiO ₂ device barrier	3.9
ϵ_s	Relative permittivity of the electrolyte solution	80