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Abstract. With an overlapped electric double layer formed in a nanochannel, the electrolyte is subjected to two kind of interactions, the van der Waals interactions and the electric double layer (EDL) electrostatic interactions. The operating scale is different for these interactions. The electrostatic interaction formed near the interface is of significant interest in several applications from electrochemistry to nanofluidics. The classical Poisson-Boltzmann (PB) theory explains the EDL potential in detail, but this theory fails at smaller separation distances. Electric Double Layer (EDL) has great influence on fluid flows in nanochannels. Most of the nanochannels have circular or rectangular cross-section. Hence, there is a need to undertake thorough investigation of EDL effect in two dimensional nanochannels. In nanoconfinements electrolytes form an overlapped EDL. At this scale, the ion size and the nanochannel gap size becomes comparable. The steric effects become significant and thus, ion size cannot be neglected. In the present work, an analysis is performed to observe the steric effects on the electric potential distribution in a nanochannel. Then the analysis is moved on to the effects of the hydraulic diameter on electric potential distribution. The Modified Poisson-Boltzmann equation proposed originally by Bikerman (Philos. Mag. 1942, 33, 384) is solved numerically with the constant surface potential condition. This equation is highly nonlinear and thus numerical techniques have been used for its solution. In this paper, Bikerman's model equation is solved through numerical method to analyze the steric effects of ions on the electric potential distribution and ionic concentration in a nanochannel with variation in hydraulic diameter for a rectangular nanochannel. The electrokinetic phenomena is investigated in terms of the nanochannel electric potential, the steric factor and the nanochannel gap size. Investigations reveal the relation between EDL overlap phenomenon and finite size effects.

INTRODUCTION

With an overlapped electric double layer formed in a nanochannel, the electrolyte is subjected to two kinds of interactions, the van der Waals interactions and the electric double layer (EDL) electrostatic interactions. The operating scale is different for these interactions. The electrostatic interaction formed near the interface is of significant interest in several applications from electrochemistry to nanofluidics [1]. The classical Poisson-Boltzmann (PB) theory explains the EDL potential in detail, but this theory fails at smaller separation distances. Many efforts have been made in modifying the PB theory, to correct some inconsistencies. The EDL forces have been shown to affect many electrokinetic phenomena. When the lengthscale gets down to the nanoscale of O(10nm), the continuum approach holds valid, but the physics may not be the same as in the macroscale [2, 3]. In nanochannels, the coions are excluded at a level from the nanochannel due to the formation of overlapped EDL. In most of the theories, there is a basic assumption of treating the ions as point charges thereby neglecting the effect of ion sizes. But, the size of ions and the Debye length are comparable at nanoscale. Thus, their consideration in the theoretical formulation of the problem cannot be neglected.

Finite size of ions have significant influence on many different applications in nanoscale electrokinetic phenomena [4-13]. Corrections for Poisson-Boltzmann equations was introduced by Stern [14]. Bikerman was first to develop the complete ion-size-effect-induced modified Poisson-Boltzmann equation (MPB) model [15]. From then, Bikerman's (MPB) has been rewritten by many researchers such as Wicke and Eigen [16, 17], Wiegel et al.

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[18, 19], Borukhov et al. [20], Bohinc and co- researchers [21, 22], Kilic et al. [23], and Trizac et al. [24]. Kornyshev obtained an equation considering the steric effect using statistical mechanics approach based on the concept of Fermi distribution on the diffuse layer capacitances [25]. Bazant et al. [13] restated the MPB equations considering the steric and the electrostatic correlation effect. Das and Chakraborty [26] investigated the ion size effect leading to increase in the EDL overlap. Several studies have been conducted to understand EDL structure, but still there is a need to understand the effect on the electrokinetic phenomena of electrolyte in a nanochannel with considerations of finite ion size.

In this paper, Bikerman's model equation is solved through numerical method to analyze the steric effects of ions on the electric potential distribution and ionic concentration in a nanochannel with variation in hydraulic diameter for a rectangular nanochannel.

MATHEMATICAL FORMULATION

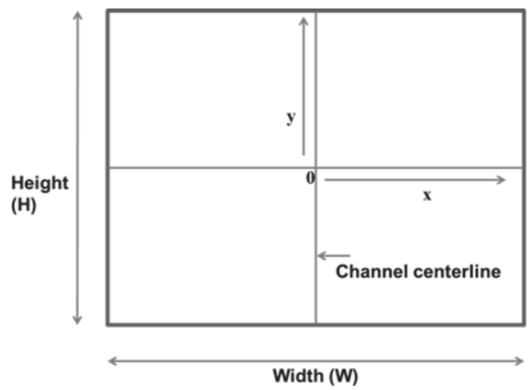

FIGURE 1. Geometry of the cross-section of a rectangular nanochannel.

We consider a symmetric electrolyte $z = z+ = |z-|$confined in a nanochannel cross- section. The electric potential at the nanochannel wall is V.

We adopt the Bikerman's model, in which the positive and negative ions have the distributions given by

$$n_{\pm} = \frac{n_b e^{\mp u}}{1+\gamma[\cosh u-1]} \tag{1}$$

where u is the dimensionless electric potential defined as $u = V/V_T$ with the thermal voltage $V_T = k_B T/(ze)$. γ is the steric effect parameter defined as $\gamma = 2a^3 n_b$, where a is the ionic radius and n_b is the number density of the ions in the bulk. Physically, γ can be interpreted as the volume fraction occupied by the ions in the bulk. Now the free charge densityρf is given in terms of the electric potential as

$$\rho_f = ze(n_+ - n_-) = \frac{-2n_b ze \sinh(u)}{1+\gamma[\cosh u-1]}. \tag{2}$$

Using hydraulic diameter d_h as the characteristic length scale $\left(\frac{4LW}{2(L+W)}\right)$ and nondimensionalizing the axis, we have the values x/d_h and y/d_h. Thus, we have the following dimensionless modified Poisson-Boltzmann equation given by

$$\nabla^2 u = K^2 \frac{\sinh u}{1+\gamma[\cosh u-1]} \tag{3}$$

where $K = (d_h \times \kappa)$ with the boundary conditions $u'(0) = 0, u(Wall) = \frac{V}{V_T}$. In (3), $\kappa^2 = \left(\frac{2n_b z^2 e^2}{\varepsilon\varepsilon_0 k_B T}\right)$ and κ^{-1} is the Debye screening length. In this work, we solve Eq. (3) for the 2-D problem to see the steric effects of ions on the electric potential distribution and ionic concentration in the nanochannel.

The simulation is carried out for two cases as shown below:

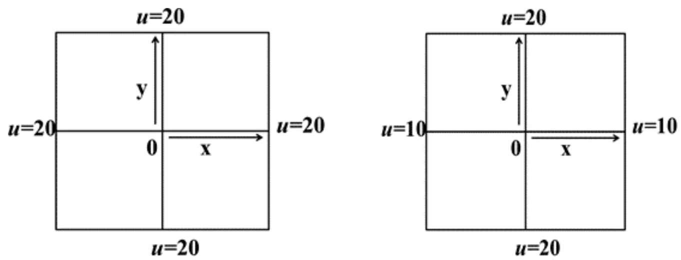

FIGURE 2. Two cases assumed for the simulation

Since, the governing equation is highly nonlinear and does not have an analytical solution, we use numerical study to obtain the solution. The numerical results are obtained by using COMSOL 4.3a.

RESULTS AND DISCUSSION

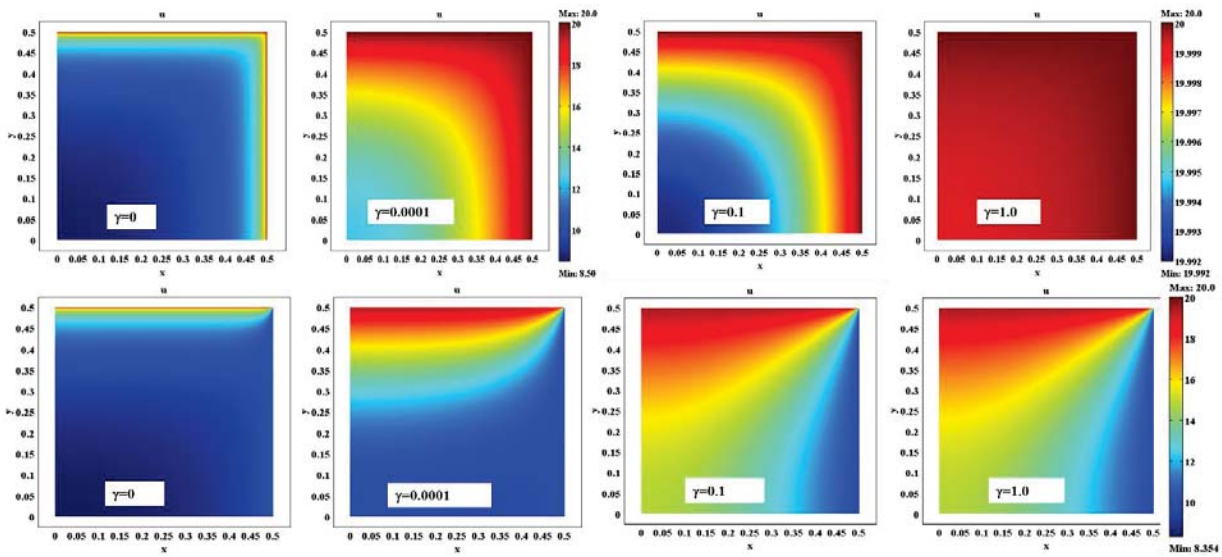

FIGURE 3. The electric potential distribution in one fourth of the cross-section for Case- I and II.

As observed from the figure-3, the upper row depicts electric potential distribution for Case-I and second row shows electric potential distribution for Case-II. As observed from the figure, the steric parameter γ effects the EDL overlapping phenomena. Also, increasing steric effect increases the extent of EDL overlap [26]. The ionic concentration of the counter-ions in the nanochannel decreases with increase in steric factor as observed in Figure 4 and 5. which leads to overlapping phenomena.

The effect of hydraulic diameter is shown in Figure 6 for case-I. It is observed that as hydraulic diameter increases, the extent of EDL overlap decreases due to increase in width of nanochannel. Also, steric effect induces increase in EDL overlap in nanochannels. To observe the effects on irregular geometries, one case of irregular cross-section was considered, and the electric potential distribution obtained is shown in Figure 7. It is observed from the figure that inclusion of steric effect increases the extent of EDL overlap, which is helpful in many applications.

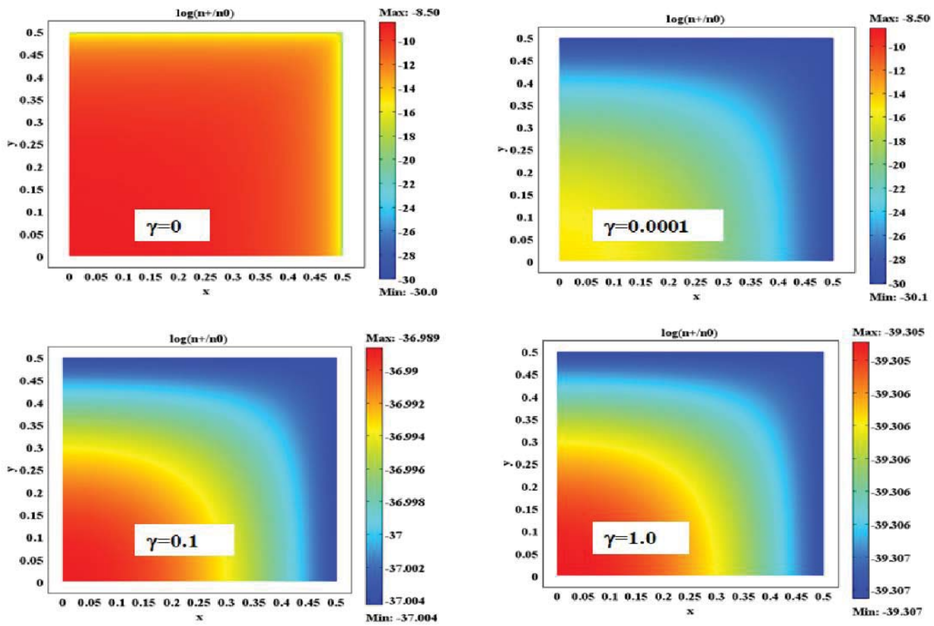

FIGURE 4. The ionic concentration **(n_+/n_0)** is shown for Case-I.

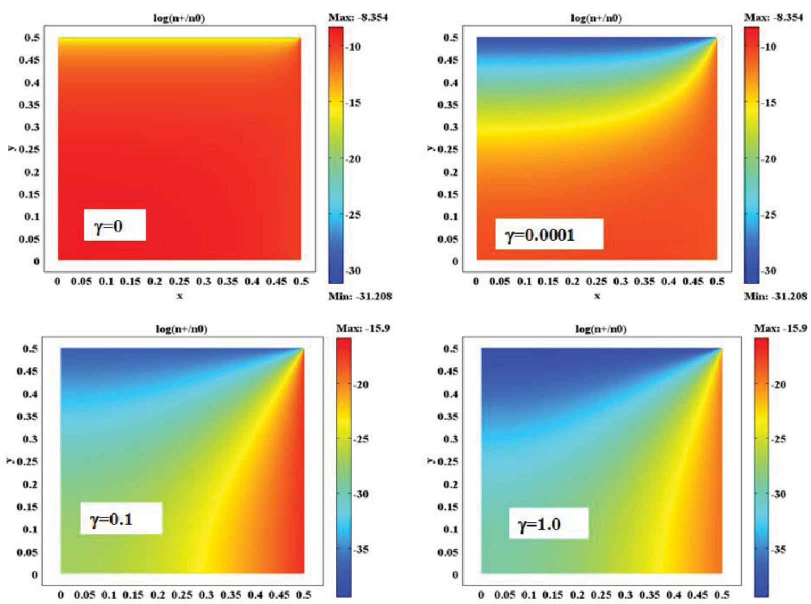

FIGURE 5. The ionic concentration **(n_+/n_0)** is shown for Case-II.

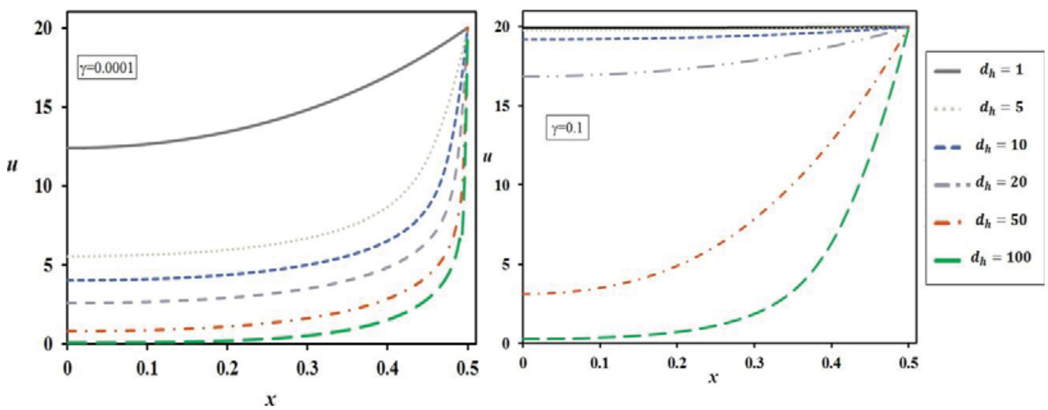

FIGURE 6. Effect of hydraulic diameter on electric potential distribution for (a) γ = 0.0001 and (b) γ = 0.1.

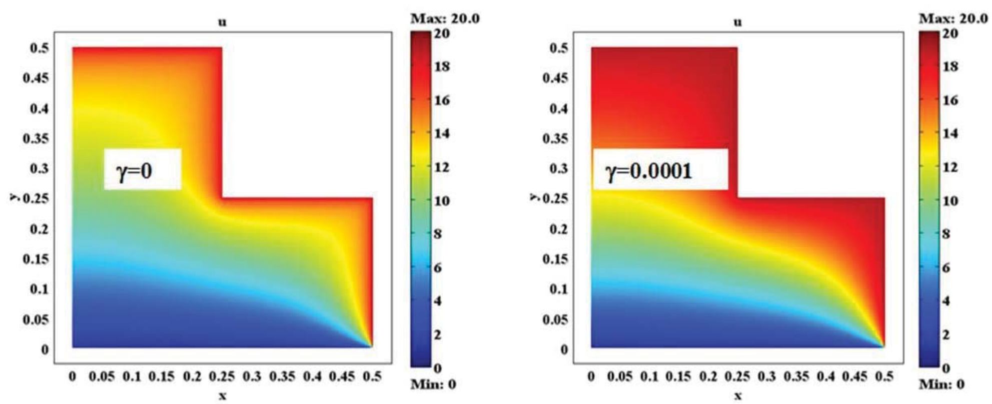

FIGURE 7. Electric potential distribution for (a) γ = 0.0 and (b) γ = 0.0001 for irregular geometry.

CONCLUSIONS

We have modeled the electrokinetic phenomena in a nanochannel considering the size effects of ions in the electrolyte. It is observed that steric effect increases the extent of EDL overlap in nanochannel. Also, hydraulic diameter has an opposite effect on electric potential in the nanochannel. With increase in hydraulic diameter, the EDL overlap decreases in the nanochannels. Garcia et al. [27] investigated the transport properties in nanochannels with respect to ionic size, permittivity, and viscosity related effects. The analysis shows the influence of the said parameters in the ion-transport and fluid-flow in nanochannels. Nazari et al. [28] reviewed the transport phenomena in nano and molecular confinements. Understanding the fluid transport properties at this scale is very essential for future technologies.

REFERENCES

1. M. Tagliazucchi, and I. Szleifer, Materials Today, 2015. **18**(3): p. 131-142.
2. F. Baldessari, Journal of Colloid and Interface Science, 2008. **325**(2): p. 526-538.
3. S. Chakraborty, *Encyclopedia of Microfluidics and Nanofluidics*. 2008, Springer US. p. 460-469.
4. A. Garai, and S. Chakraborty, Electrophoresis, 2010. **31**(5): p. 843- 849.
5. H. Zhao, The Journal of Physical Chemistry C, 2010. **114**(18): p. 8389-8397.
6. A. S. Khair, and T.M. Squires, Journal of Fluid Mechanics, 2009. **640**: p. 343-356.
7. B. D. Storey, et al., Physical Review E, 2008. **77**(3): p. 036317.
8. S. Chanda, and S. Das, Physical Review E, 2014. **89**(1): p. 012307.
9. S. Das, Physical Review E, 2012. **85**(1): p. 012502.
10. Y. Liu, et al., Langmuir, 2008. **24**(6): p. 2884-2891.
11. M. Z. Bazant, et al., Advances in Colloid and Interface Science, 2009. **152**(1–2): p. 48-88.
12. M. Z. Bazant, et al., *Nonlinear electrokinetics at large voltages.* New Journal of Physics, 2009. **11**(7): p. 075016.
13. M. Z. Bazant, B.D. Storey, and A.A. Kornyshev, Physical Review Letters, 2011. **106**(4): p. 046102.
14. O. Stern, Z. Elektrochem, 1924. **30**.
15. J. J. Bikerman, Philosophical Magazine 1942. **33**(220): p. 384-397.
16. M. Eigen, and E. Wicke, Naturwissenschaften, 1951. **38**(19): p. 453-454.
17. M. Eigen, and E. Wicke, The Journal of Physical Chemistry, 1954. **58**(9): p. 702-714.
18. P. Strating, F.W. Wiegel, Journal of Physics A: Mathematical and General, 1993. **26**(14): p. 3383.
19. P. Strating, and F.W. Wiegel, Physica A: Statistical Mechanics and its Applications, 1993. **193**(3–4): p. 413-420.
20. I. Borukhov, D. Andelman, and H. Orland, Physical Review Letters, 1997. **79**(3): p. 435-438.
21. K. Bohinc, et al., Bioelectrochemistry, 2002. **57**(1): p. 73-81.
22. K. Bohinc, V. Kralj-Iglič, and A. Iglič, Electrochimica Acta, 2001. **46**(19): p. 3033-3040.
23. M. S. Kilic, M.Z. Bazant, and A. Ajdari, Physical Review E, 2007. **75**(2): p. 021502.
24. E. Trizac, E. and J.-L. Raimbault, Physical Review E, 1999. **60**(6): p. 6530-6533.
25. A. A. Kornyshev, The Journal of Physical Chemistry B, 2007. **111**(20): p. 5545-5557.
26. S. Das, and S. Chakraborty, Physical Review E, 2011. **84**(1): p. 012501.
27. J.J. López-García, J. Horno, and C. Grosse, The Journal of Physical Chemistry C, 2020. 124 (19), 10764-10775.
28. M. Nazari, A. Davoodabadi, D. Huang, T. Luo, and H. Ghasemi. ACS Nano, 2020. 14 (12), 16348-16391.