

# Potential Distribution in a Nano Channel of an Electrolytic Solution by Finite Element Method

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## ABSTRACT

We introduced a numerical method to incorporate the variation of the dielectric constant of an electrolytic solution. We measured the transport of the ionic atmosphere of the system to be exists in Nano Channel whose dimensions are comparable to the Debye length of the ionic atmosphere. Rayleigh Ritz approximation was applied and the elemental equations were assembled and solved by Finite Element Method (FEM). Interestingly the assumptions involved were made on the basis of the Nobel Prize winning ion pair formation mechanism. The solutions give an extremely accurate prediction of the dielectric constant for a variety of salts and a wide range of concentrations.

**Keywords:** Nano Channel, FEM, Debye Length, Dielectric Constant, Potential Distribution

## 1. INTRODUCTION

Since the year 1961, K. S. Pitzer [1] has chosen the best available system proposed by Guggenheim [2], developed in a series of papers, detailed mathematical equations for activity coefficient, osmotic coefficient and other thermodynamic parameters of aqueous electrolyte solution. Still the permittivity parameter of the dielectric continuum, is being left un accounted in all the above attempts by several workers in the field. This parameter is essential to account for the short range as well as long range interactions, since it governs the electrostatic interactions. V.Brahmajirao et.al, [3] applied Glueckauff's model in his studies of acoustic parameters, thermodynamic characteristics, conductance, compressibility, & activity coefficient of electrolytic solutions and concluded that a systematic model incorporating lowering of dielectric property of electrolytic solutions is necessary for proper understanding of their behavior. We developed a mathematical model and reported series of papers in earlier [4, 5] communications. In this paper, we attempted to report the evaluations about dielectric decrement of ionic solution which accounts for the potential distribution in rectangular nanochannel by FEM.

## 2. MATHEMATICAL MODELING OF POTENTIAL DISTRIBUTION OF IONIC SOLUTION IN RECTANGULAR NANOCHANNEL

The space-charge model [6, 7] gives complete physical interpretations of ion transport through nanometer-sized channels. The space-charge model has been simplified by Pennathur and Santiago [8] to describe electro-kinetic transport in long nanochannels, confirmed by their experimental studies [9]. J.Barthel, R.Buchner, C. Akilan, C. Hefter, G. Rohman [10] contributed a lot of work to pinpoint that the Dielectric permittivity variation, consequent of increment in the concentration of an electrolyte leading to a decrement in the permittivity is essentially responsible for this. As the concentration increases the dielectric constant

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gradually decreases in three steps, and each reduction is reflected in the formation of a different species of Ion pairs. These reductions in the dielectric constant are depicted by the terms in  $\sqrt{c}$ ,  $c$  and  $c^{\frac{3}{2}}$  of the polynomial proposed by the author.

### 3. POTENTIAL DISTRIBUTION BY FINITE ELEMENT METHOD

The charge density  $\rho_j(r)$  in the volume element  $dv$  is given by

$$\rho_j(r) = n_1 z_1 e + n_2 z_2 e + \dots + n_i z_i e = \sum_i n_i z_i e \quad (1)$$

At electro-chemical equilibrium, the density of electrolyte 'i' follows a Boltzmann distribution and therefore

$$n_i = n_i^\infty e^{-\frac{z_i e \psi_j(r)}{kT}} \quad (2)$$

where  $n_i$ , the concentration (density) of ionic species 'i' in the volume element  $dv$  has been related to its bulk concentration  $n_i^\infty$ , the net charge density  $\rho_j(r)$  at any point 'r' becomes

$$\rho_j(r) = \sum_{i=1}^N z_i e n_i^\infty e^{-\frac{z_i e \psi_j}{kT}} \quad (3)$$

At this point of theory, Debye–Hückel made a move which was not only mathematically expedient but also turned out to be wise. They decided to carry out the analysis only for the systems in which the electrostatic potential  $\psi_j(r)$  would be small so that

$$z_i e \psi \ll k_B T$$

Or

$$\frac{Z_i e \psi}{k_B T} \ll 1$$

Based on this assumption, one can expand the exponential of equation (5.3) in a Taylor series,

$$\rho_j(r) = \sum_{i=1} z_i e n_i^\infty \left( 1 - \left( \frac{z_i e \psi(r)}{k_B T} \right) + \frac{1}{2!} \left( \frac{z_i e \psi(r)}{k_B T} \right)^2 - \dots \right) \quad (4)$$

and neglect all except first two terms, then

$$\rho_j(r) = \sum_{i=1} z_i e n_i^\infty - \sum_{i=1} \frac{z_i^2 e^2 n_i^\infty \psi}{k_B T} \quad (5)$$

The first term  $\sum_{i=1} Z_i e n_i^\infty$  gives the charge on the electrolyte solution as a whole. But this is zero because the solution as a whole must be electrically neutral. Therefore the charge density  $\rho_j(r)$  after 'linearized' Boltzmann distribution becomes

$$\rho_j(r) = - \sum_{i=1} \frac{z_i^2 e^2 n_i^\infty \psi}{k_B T} \quad (6)$$

Where  $\sum_{i=1}$  refer to the summation over all species of ions typified by 'i'.

Therefore, the electrical potential  $\psi$  and net charge density  $\rho$  at any point 'r' in the aqueous electrolyte solution is given by

$$\nabla^2 \psi(r) = -\frac{\rho(r)}{\epsilon_0 \epsilon_r} \quad (7)$$

This is known as Poisson equation. Where  $\nabla^2 \psi$  represents the divergence of the gradient in electrostatic potential,  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon_r$  is the dielectric constant which is varying smoothly and continuously with respect to concentration inside the compact layer of aqueous electrolyte solution [90, 93] and it is given by

$$\epsilon_r = \epsilon_w - \lambda_1 \sqrt{c} - \lambda_2 c - \lambda_3 c^{\frac{3}{2}} \quad (8)$$

Here  $\epsilon_r$  is the dielectric constant of the ionic solution and  $c$  is the total concentration of the aqueous electrolyte solution.  $\epsilon_w = 80$  is the dielectric constant of pure water.

From equations (5.1), (5.6) and (5.7)

$$\nabla^2 \psi(r) = -\frac{e}{\epsilon_0 \epsilon_r} \sum_{i=1} z_i n_i = \frac{1}{\epsilon_0 \epsilon_r} \sum_{i=1} \frac{z_i^2 e^2 n_i^\infty \psi}{k_B T} \quad (9)$$

This is the linearized Poisson-Boltzmann equation [92]. To increase accuracy in the numerical calculations and avoiding truncation errors, the author makes the equation dimensionless and thereby on the order of unity.

Define the electric potential scale  $\psi_0 = \frac{k_B T}{e} = \frac{RT}{F}$  and non-dimensionalizing the equation (5.9) with

$\psi(X, Y, Z) = \frac{\psi}{\psi_0}$ ,  $X = \frac{x}{L}$ ,  $Y = \frac{y}{w}$ ,  $Z = \frac{z}{h}$  we get

$$\epsilon_1^2 \frac{\partial^2 \psi}{\partial X^2} + \epsilon_2^2 \frac{\partial^2 \psi}{\partial Y^2} + \frac{\partial^2 \psi}{\partial Z^2} = h^2 k^2 \psi \quad (10)$$

Where

$$K = \sqrt{\frac{e^2 \sum_{i=1} z_i^2 n_i^\infty}{\epsilon_0 \epsilon_r k_B T}}, \epsilon_1 = \frac{h}{L}, \epsilon_2 = \frac{h}{w}$$

'k' called the Debye-Hückel parameter which is a function of concentration, ionic charge, temperature and dielectric constant of the solvent, having reciprocal length.

From 'k' we defined Electrical Double Layer (EDL) thickness, or Debye length,  $\lambda$ ' as

$$\lambda = \frac{1}{k} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_{i=1}^N z_i^2 n_i^\infty}} \quad (11)$$

$\varepsilon = \frac{\lambda}{h}$  is the ratio of the relative thickness of EDL to the height of channel. From equation (5.11), we get

$$h k = \frac{h}{\lambda} = \frac{1}{\varepsilon} \quad (12)$$

Consider the infinite parallel plate nano-channels ( $L \gg h$ ) so that terms with coefficients  $\varepsilon_1 = \frac{h}{L} \ll 0$  are supposed to be negligible in the governing equations. The equations (5.10) becomes

$$\frac{\partial^2 \psi}{\partial Y^2} + \frac{\partial^2 \psi}{\partial Z^2} = \frac{\psi}{\varepsilon^2} \quad (13)$$

subjected to the boundary conditions

$$Y = Z = 0, \psi = \psi_0, Y = Z = 1, \psi = \xi \quad (13a)$$

The electro-chemical properties of parallel surfaces will be the same if the nano-channel is symmetric. Therefore, for symmetric nano-channels we take the following boundary conditions.

$$Y = Z = 0 \text{ and } Y = Z = 1, \psi = 0 \quad (13b)$$

In order to find the electric potential distribution for the system of equations (13), (13a) and (13b) by Finite Element Method, the variation formation is constructed over a typical element. First, we multiply the equation (13) with the test function  $V(Y, Z)$  and integrate the result over a typical element  $R_e$  gives

$$\iint_{R_e} \left[ \left( \frac{\partial \psi}{\partial Y} \frac{\partial V}{\partial Y} + \frac{\partial \psi}{\partial Z} \frac{\partial V}{\partial Z} \right) - V \frac{\psi}{\varepsilon^2} \right] dYdZ - \int_{c_e} V q_n ds = 0 \quad (14)$$

Where

$$q_n = \eta_y \frac{\partial \psi}{\partial Y} + \eta_z \frac{\partial \psi}{\partial Z}$$

$\eta_y$  and  $\eta_z$  directional cosines of a unit vector  $\hat{n}$  on the boundary  $c_e$  and  $ds$  is an arc length of infinitesimal element along the boundary.

The next step in the finite element solution of this problem is to set up a finite element model of the given equation. To do this, we approximate  $\psi$  by the expression

$$\psi = \sum_{j=1}^n \psi_j \phi_j \quad (15)$$

Where  $\Psi_j = \Psi(Y_j, Z_j)$  and  $\Phi_i$  have the symmetry property

$$\phi_i(Y_j, Z_j) = \delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases} \quad (16)$$

Substituting equation (15) in equation (14), and putting  $V = \phi_i$ , we obtain

$$\sum_{j=1}^n \iint_{R_e} \left( \frac{\partial \phi_i}{\partial Y} \frac{\partial \phi_j}{\partial Y} + \frac{\partial \phi_i}{\partial Z} \frac{\partial \phi_j}{\partial Z} \right) \psi_j dYdZ - \frac{1}{\varepsilon^2} \iint_{R_e} \psi \phi_i dYdZ - \int_{c_e} \phi_i q_n ds = 0 \quad (17)$$

The equation (17) can be written in the form

$$\sum_{j=1}^n K_{ij}^{(e)} \psi_j^{(e)} = F_i^{(e)} \quad (18)$$

Where  $K_{ij}^{(e)}$  is the weighted stiffness matrix given by

$$K_{ij}^{(e)} = \iint_{R_e} \left( \frac{\partial \phi_i}{\partial Y} \frac{\partial \phi_j}{\partial Y} + \frac{\partial \phi_i}{\partial Z} \frac{\partial \phi_j}{\partial Z} \right) dY dZ \quad (19)$$

and

$$F_i^{(e)} = \frac{1}{\epsilon^2} \iint_{R_e} \psi \phi_i dY dZ + \int_{c_e} \phi_i q_n ds \quad (20)$$

#### 4. RESULTS OF ELECTRICAL POTENTIAL BY FEM

The plots in Figure 1 and 2 represents Electric potential distribution profile of the two dimensional nanochannel. The software used in drawing the plot recognizes the central region to correspond to a larger potential. This is displayed by the bluish green color. The edge of the plot colored rose red corresponds to the lower potential region of the plot. We find that these plots are in the form of a cup (shown in three dimensions). In the plots, the profile formed the cup with the bottom in the negative segment indicating that the profile gradually becomes positive as we approach the origin along the X-axis. The profile is not

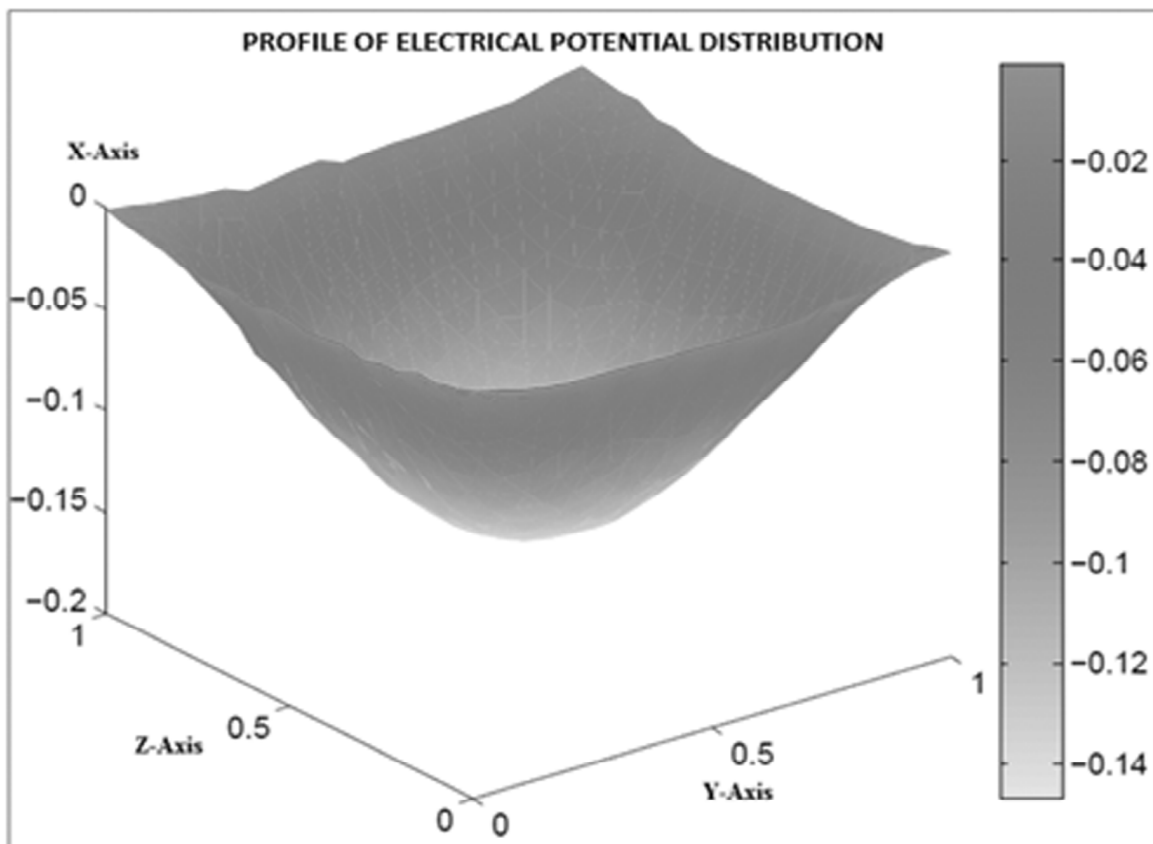


Figure 1: Potential Distribution of an electrolyte solution in 3D nanochannel with height 1 nm and width 1 nm

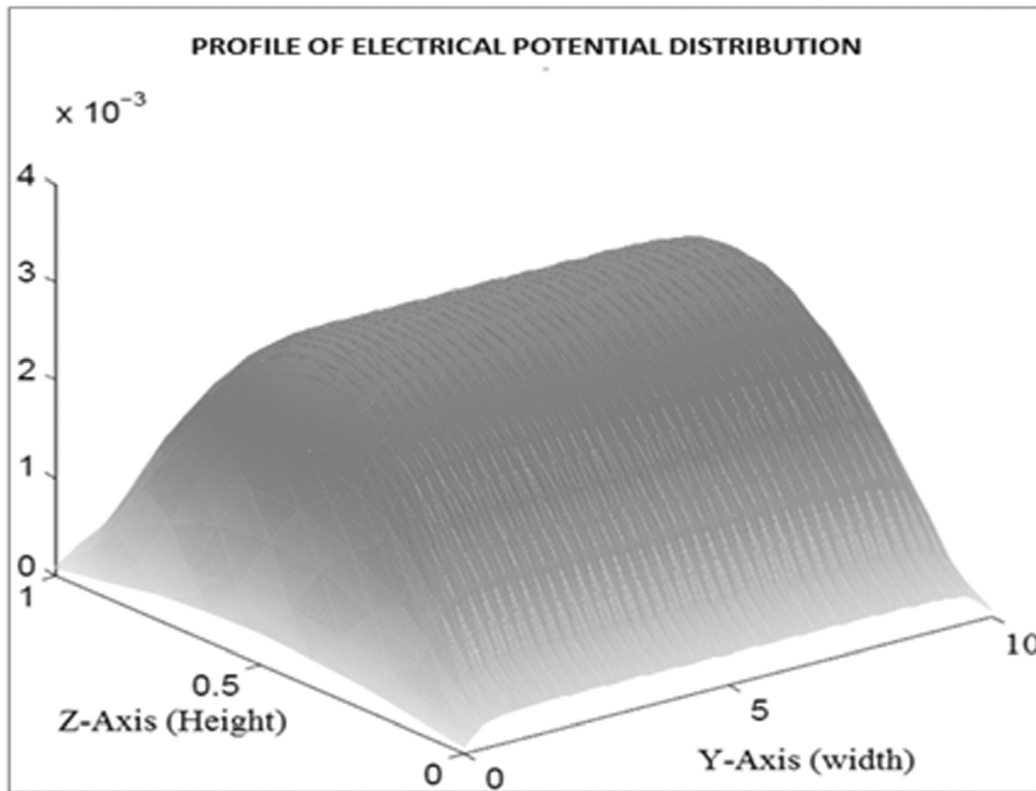


Figure 2: Potential Distribution of an electrolyte solution in 3D nanochannel with height 1 nm and width 10 nm

traced in the positive segment. This is to be attributed to the value of 1 nm for the width and height of nanochannel assigned in our evaluation in finite element technique. It must be recalled that similar plots for the profile of potential in the finite difference method were plotted for width of 4 nm and above. Consequently, in those plots the positive segments were traced. When the width for the nanochannel exceeded 4 nm, we find that the profiles corresponding to positive potential segment were recorded both in finite difference method as well as finite element technique. More experimental data is necessary to probe into the reasons for this. The edge of this cup corresponds to the potential for the lesser value of width and height. The bottom of the cup corresponds to the higher potential region. We find that for lesser values of width this profile is almost symmetric about the X-axis. Also we observe the typical elements clearly corresponding to the lesser number.

## 5. CONCLUSION

We applied the Finite Element Method to solve one and two dimensional coupled system of Poisson – Boltzmann equations, and the solutions give an extremely accurate prediction of the dielectric constant for a variety of salts and a wide range of concentrations. By incorporating the variation of dielectric constant of aqueous electrolyte solution into basic equations, improvement in the predictable nature of electrical potential in the electro-osmotic flow of a nano channel could be achieved.

## REFERENCES

- [1] K. S. Pitzer and L. Brewer, in revised edition of ‘Thermodynamics’ by G. N. Lewis and M. Randall, McGraw-Hill, New York, N.Y., (1961)
- [2] E. A. Guggenheim (1935), *Phil. Mag*, 19,588; *Ibid* (1955) *Trans. Faraday. Soc* , 51, 747.
- [3] PadidhajuRajendra, Shahnaz Bathul, and V. Brahmajirao. “A New Model For Incorporating the Variations of the Dielectric Permittivity of the Medium: Part (1) Potential Distribution of an Electrical Double Layer in Rectangular Nano channel by Applying Finite Element Method Technique.” *arXiv preprint arXiv:1602.06324* (2016).

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- [4] Padidhapu Rajendra, Shahnaz Bathul, and V. Brahmajirao. "Electrical Potential, Mass Transport and Velocity Distribution of Electro-osmotic Flow in a Nanochannel by Incorporating the Variation of Dielectric Constant of Aqueous Electrolyte Solution." *arXiv preprint arXiv:1602.06971* (2016).
- [5] Padidhapu Rajendra, Shahnaz Bathul, and V. Brahmajirao. "Least Square and Gauss Jordan Methods applied to fit the Dielectric data Vs. Concentration of Ionic Liquids." *International Journal of Science and Technology* 2.1 (2013).
- [6] Gross, R., and J. Osterle, 1968, *J. Chem. Phys.* 49, 228.
- [7] Wang, X.-L., T. Tsuru, S.-I. Nakao, and S. Kimura, 1995, *J. Membr. Sci.* 103, 117.
- [8] Pennathur, S., and J. G. Santiago, 2005a, *Anal. Chem.* 77, 6772.
- [9] Pennathur, S., and J. G. Santiago, 2005b, *Anal. Chem.* 77, 6782.
- [10] Barthel et.al (1995), Dielectric relaxation of electrolyte solutions in acetonitrile, *Journal of solution chemistry*, Vol. 24 (1), pp. 1-17.