



## Pore-scale Distributions of Electric Potential, Ionic Concentrations and Volumetric Charge Density of Single-type Ions in Soil Water

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To understand the dynamism of soil reclamation, there is a need to study the distributions of electric potential, ionic concentrations, and charge density of ions in soil-water. The internal structure of the clay mineral has imbalance of charges. The counterions (cations) present in the soil water are attracted by the opposite charges on the clay surface. The charged surface and strongly held cations in soil water adjacent to the surface of the clay particle are generally considered to be comprised of two layers; hence, the whole system is referred to as the electric double layer (EDL) (Bolt and Bruggenwert, 1978; Mahanta *et al.*, 2015). The concentration of the counterions near the clay surface remains high and decreases with distance from the clay surface (Gouy, 1910; Chapman, 1913). A method to compute the inter-plate distance (pore size) has been given by Mahanta and Mishra (2014). Here, the distribution of ions and other parameters in a pore of clay soil is studied.

The Poisson-Boltzman (P-B) equation is the governing equation of EDL theory (Voyutsky, 1978; Yeung, 1992; Van Olphen, 1977). The solution to the P-B equation is required to illustrate the distribution of ions, potential etc. in a soil pore (Appelo and Postma, 2005; Mahanta, 2010; Mahanta *et al.*, 2014). In this study, numerical experiments of the EDL theory-based formulation advocated for simulating the pore-scale distributions of electric potential, ionic concentrations and volumetric ionic charge density in soil-water.

Computations of bulk concentration of ions  $C_b$ ,  $\lambda$ ,  $\sigma$  and  $\psi(0)$  can be made by the methods described by Mahanta *et al.* (2012). The distributions of potential, concentrations of anions and cations, volumetric charge density and gradient of potential with respect to distance from the clay surface have been computed using the solution of the linearized P-B equation and are compared with those obtained from the solution of nonlinear P-B equation for single-type of ions. Here, the results are presented for fine loamy soil for which surface charge density,  $\sigma = -0.058 \text{ Cm}^{-2}$ .

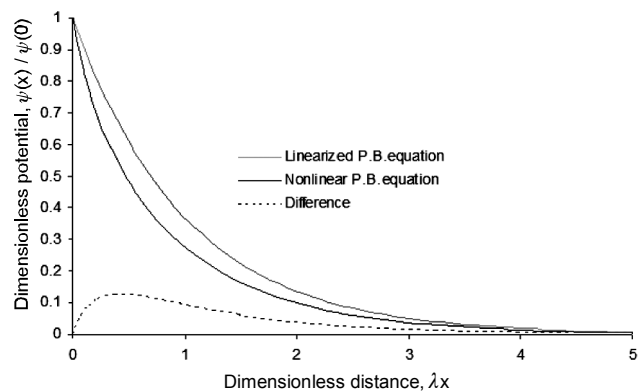
The dimensionless potential is given by  $\frac{\psi(x)}{\psi(0)} = e^{-\lambda x}$ .

This suggests that, at a particular value of  $\lambda x$  the dimensionless potential can be computed without any reference to the valency. Therefore, the variation of dimensionless potential with dimensionless distance is the same for both the monovalent and divalent ions. However, the dimensional potential  $\psi(x)$  at dimensional distance  $x$  differs for ions of different valencies.

Considering the solution of the nonlinear P-B equation (Mahanta, 2010; Mahanta *et al.*, 2012), the dimensionless potential can be written as:

$$\frac{\psi(x)}{\psi(0)} = \frac{2\sqrt{2\epsilon RTC_b}}{\sigma} \ln \left[ \frac{1 + A_1 e^{-Bx}}{1 - A_1 e^{-Bx}} - \sqrt{\left\{ \frac{1 + A_1 e^{-Bx}}{1 - A_1 e^{-Bx}} \right\}^2 - 1} \right]$$

The results are presented for monovalent ions using the solutions of linearized and nonlinear P-B equation for a lower bulk concentration,  $C_b = 50 \text{ mol m}^{-3}$ . Since for higher bulk concentration, there is no significant difference between the two solutions, a lower bulk concentration has been chosen for the purpose of comparison. The variations of dimensionless potential for monovalent ions is presented in Fig. 1.



**Fig. 1.** Variations of dimensionless potential,  $\frac{\psi(x)}{\psi(0)}$  with respect to dimensionless distance,  $\lambda x$  from the clay surface, computed using the solutions of linearized and nonlinear P-B equation for  $C_b = 50 \text{ mol m}^{-3}$  of Na and Cl ions and  $\sigma = -0.058 \text{ Cm}^{-2}$

As seen in Fig. 1, the solution of the linearized P-B equation overestimates the dimensionless potential at intermediate distances from the clay surface. When monovalent ions are present in the soil water, the maximum difference in the dimensionless potentials, determined from the two solutions, is 0.127 which occurs at a dimensionless distance of 0.44 from the clay surface.

Using  $\psi(x)$  the distributions of the corresponding  $C^+(x)$  and  $C^-(x)$  are computed and are presented in Fig. 2. As seen in Fig. 2, the solution of the linearized P-B equation overestimates the distribution of concentrations of Na ions in soil water at intermediate distances from the clay surface. The maximum difference in the dimensionless concentrations of Na ions computed by these two methods, *i.e.*, the maximum value of

$$\frac{C^+(x) \text{ from solution of linearized P.B. eq.} - C^+(x) \text{ from solution of nonlinear P.B. eq.}}{C_b} = 15.1$$

and this occurs at a dimensionless distance of 0.147 from the clay surface. The Na ions, which have positive charges, are attracted towards the clay surface. Therefore, at  $x = 0$ ,  $\frac{C^+(x)}{C_b} = 83.1$  and as  $\lambda x \rightarrow \infty$ ,  $\frac{C^+(x)}{C_b} \rightarrow 1$ .

As seen in Fig. 2, the solution of the linearized P-B equation underestimates the distribution of Cl ion concentrations. The maximum difference in the dimensionless concentrations computed by these two methods is estimated as

$$\frac{C^-(x) \text{ using solution of linearized P.B. eq.} - C^-(x) \text{ using solution of nonlinear P.B. eq.}}{C_b} = 0.112$$

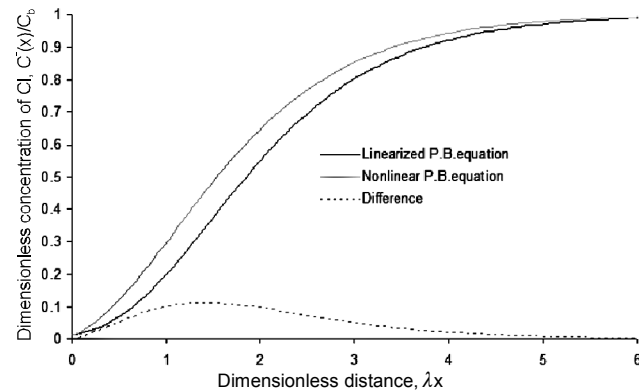
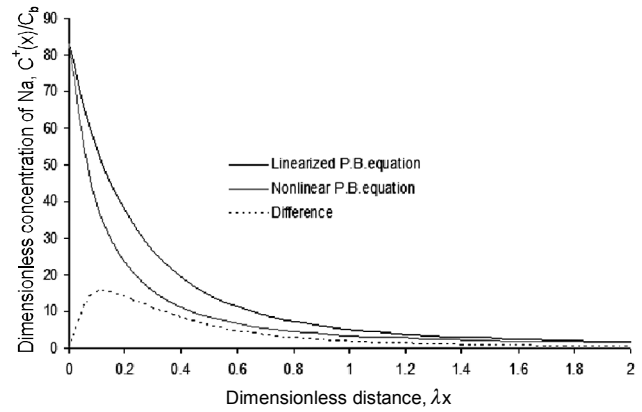
and this occurs at dimensionless distance of 1.397 from the clay surface.

$$\text{At } x = 0, \frac{C^-(x)}{C_b} = 0.012 \text{ and } x \rightarrow \infty, \frac{C^-(x)}{C_b} \rightarrow 1.$$

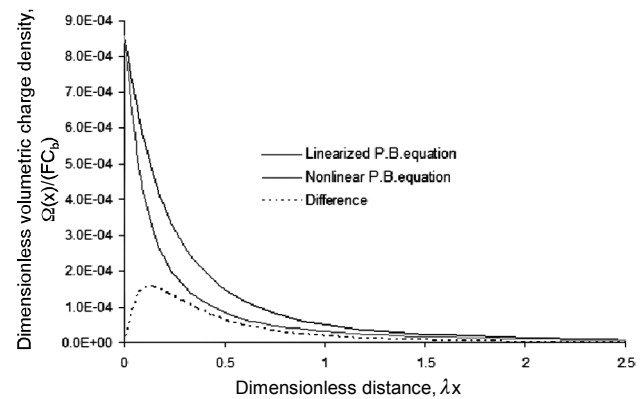
It is found that at  $x = 0$ , for divalent cations ( $Ca^{2+}$ ),  $\frac{C^+(x)}{C_b} = 83.1$  and for divalent anions ( $SO_4^{2-}$ ),  $\frac{C^-(x)}{C_b} = 0.012$ . Thus, as stated earlier, whether the ions are monovalent or divalent, the distribution of dimensionless concentrations for single type of ions in the soil water remains the same.

The distribution of volumetric charge density,  $\Omega(x)$  is computed and variation of dimensionless charge density are presented in Fig. 3. As seen from Fig. 3, the dimensionless volumetric charge density,  $\frac{\Omega(x)}{FC_{bNa^+}}$  computed from the solution of the linearized

P-B equation for monovalent ions is overestimated at intermediate distances from the clay surface. The maximum difference in the dimensionless volumetric charge densities computed by these methods is  $1.56 \times 10^{-4}$  which occurs at the dimensionless distance of 0.147 from the clay surface.

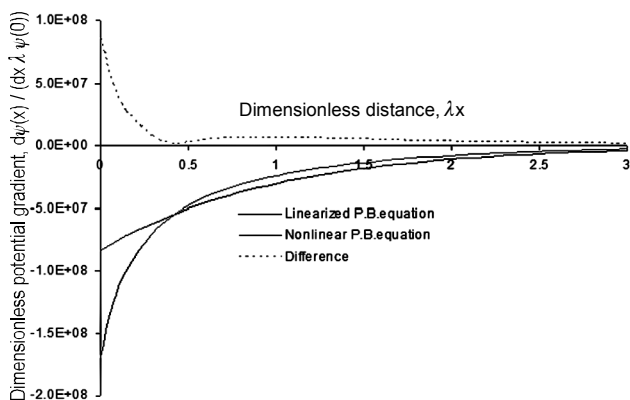


**Fig. 2.** Distribution of dimensionless concentration of (a) Na ions, *i.e.*  $\frac{C^+(x)}{C_b}$  and (b) Cl ions *i.e.*  $\frac{C^-(x)}{C_b}$  in soil water with respect to distance from the clay surface computed from the solutions of nonlinear and the linearized P-B equation for  $C_b = 50 \text{ mol m}^{-3}$  and  $\sigma = -0.058 \text{ Cm}^{-2}$



**Fig. 3.** Distribution of dimensionless volumetric charge density, *i.e.*  $\frac{\Omega(x)}{FC_{bNa^+}}$  with respect to distance from the clay surface, computed from the solutions of nonlinear and linearized P-B equation for  $C_b = 50 \text{ mol m}^{-3}$  for Na and Cl ions and  $\sigma = -0.058 \text{ Cm}^{-2}$

For divalent ions, the maximum difference in the dimensionless volumetric charge density computed by the two solutions is  $3.13 \times 10^{-4}$  which is twice of that for the monovalent ions.



**Fig. 4.** Distribution of  $\frac{1}{\psi(0)\lambda} \frac{d\psi(x)}{dx}$  ions compound from the solutions of nonlinear and the linearized P-B equation with respect to distance from the clay surface for  $C_0 = 50 \text{ mol m}^{-3}$  of (a) Na and Cl ions and  $\sigma = -0.058 \text{ Cm}^{-2}$

The dimensionless potential gradients,  $\frac{1}{\psi(0)\lambda} \frac{d\psi(x)}{dx}$  computed from the two solutions are shown in

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