Research paper

Estimation of the electric double layer thickness in the presence of two types of ions in soil water

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ABSTRACT

The deficit of charges on the clay surface is balanced by the cations in soil water forming the electric double layer (EDL). In sodic soil monovalent Na^+ ions are dominant and hence, thickness of the EDL (β) is more than in the nonsodic soil where bivalent Ca^{2+} ions are dominant. For reclaiming the sodic soil, gypsum is added as a source of Ca^{2+} ions to replace the Na^+ ions from the EDL as well as for reducing β. In this paper, an analytical solution is derived to the nonlinear Poisson–Boltzman equation and the solution is used for computing β exactly. A comparison is made between β computed from the solutions of linearized and nonlinear Poisson–Boltzman equation. The solution to the linearized Poisson–Boltzman equation overestimates β. Therefore, it is appropriate to adopt the solution of the nonlinear Poisson–Boltzman equation for computing β.

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1. Introduction

The soil water is never chemically pure and contains various types of solutes (Hillel, 1998). Five cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, and NH_4^+) and four anions (NO_3^-, HCO_3^-, Cl^-, and SO_4^{2-}) are the dominant solutes in almost all soil solutions (Sumner, 2000). The types of ions and their proportions in soil water influence the soil physical and chemical properties (United States Salinity Laboratory Staff, 1954). Any accumulation of soluble salts that may be harmful to plants may be defined as soil salinity. In saline soil, the electrical conductivity of saturation extract (EC_e) is more than 4 dS m^{-1} at 25 °C and the exchangeable sodium percentage (ESP) is less than 15. Most of the salts in the soil solution have a positive effect on the soil structure. Therefore, water infiltration is not a major problem for the saline soil. But, in case of sodic soil, ESP is greater than 15 and EC_e is less than 4 dS m^{-1} at 25 °C. Also the soil structure is poor and the hydraulic conductivity ($\tilde{K}$) is low.

During the formation of the clay minerals, the lower valence cations isomorphically substitute the higher valence cations (Essington, 2004; Grim, 1953; Sparks, 1999). The deficit charges thus formed are customarily considered to be distributed uniformly over the clay surface. The overwhelming majority of surface area and electrostatic charge in a soil

residue in the less than 1 μm size fraction, with particles with radii between 20 and 1000 nm constitute the major part of the soil surface area (Borkovec et al., 1993). The negative charge on the clay surface is screened by an equivalent swarm of counter ions (e.g., Ca^{2+}, Mg^{2+}, K^+, Na^+, etc.) on the exterior surface (Bolt, 1978; Newman, 1987; Plaster, 2009). The negative charge on the clay surface and the swarm of positive counter ions is called electric double layer (Tan, 1982). The cations are heavily concentrated at the clay surface and their concentration reduces exponentially away from the surface. The case is opposite in the case of anions where the concentration of anions is lowest at the clay surface which increases away from the clay surface. There is still little consensus concerning the fraction of ions located within the double layer (Jougnot et al., 2009; Tournassat and Appelo, 2011; Tournassat et al., 2009). The triple layer model of Leroy and Revil (2004) includes a speciation model of the active crystallographic surface sites plus a classical description of the Stern and diffuse layers. The possibility of a truncature of the diffuse double layer has been studied by Goncalves et al. (2007). The EDL thickness (β) is the size of effective double layer where the cations are heavily concentrated and obstructs the flow of water through the pore of fixed size. When β is more, the effective pore space as well as permeability is less (Bagarello et al., 2005; Chiang et al., 1987; Yousaf et al., 1987). The Poisson–Boltzmann equation is the governing equation for the EDL theory. The solution of this equation is required to compute the EDL thickness. The EDL has been studied for one type of ions and its analytical solutions already exist (Appelo and Postma, 2005; Hunter, 1981; Mahanta et al., 2012). In sodic soils sodium ions are dominant and because of these monovalent ions electric double layer is larger than the EDL if multivalent ions would have

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Table 1

$\varphi(x)$ corresponding to the linearized and nonlinear Poisson–Boltzman equation for $\sigma = -0.058$ Cm^{-2}, $C_{Na^+}^b = 30$ mol m^{-3} and $C_{Ca^{2+}}^b = 10$ mol m^{-3}, corresponding $\kappa = 8.7 \times 10^8$ m^{-1}.

Assumed x (nm)	Potential, $\varphi(x)$(V) computed by approximate method for the assumed x	x (nm) corresponding to the potential given in column (2) computed by exact method {Eq.(A-9)}
0	−0.096	0
0.5	−0.062	0.185
1	−0.040	0.509
2	−0.017	1.387
3	−0.007	2.365
4	−0.003	3.361
5	−0.001	4.360
6	−0.0005	5.360

been there. Hence, it is more difficult to leach the salts for reclaiming the sodic soil than to reclaim the saline soil (Aringhieri and Giachetti, 2001; United States Salinity Laboratory Staff, 1954). The electric double layer thickness is governed by the concentrations of salts and types of cations in the soil water (Anandarajah, 2003; Park and O'Connor, 1980; Ranade and Gupta, 1987; Schofield, 1947; So and Aylmore, 1993).

The chemical amendments having calcium source are necessary to replace the existing sodium ions for augmenting the sodic soil reclamation (Borselli et al., 1996; FAO/UNESCO, 1973; Favaretto et al., 2006; Hillel, 1998; Sumner, 1993). When higher valence ions such as Ca^{2+} are applied through gypsum, less number of ions are required to compensate the same charge on the clay surface, which results in reduction of the EDL thickness and consequently increment in the hydraulic conductivity ($\tilde{K}$). Thus, EDL is the main factor which influences the sodic soil reclamation (FAO/UNESCO, 1973; Schmitz, 2006) and consideration of these two types of ions (both monovalent and divalent) is necessary for any sodification and desodification study. The Poisson–Boltzman equation is the governing equation of the EDL theory (Appelo and Postma, 2005; Van Olphen, 1977) and its solution is used to compute the thickness of EDL, β. The Poisson–Boltzmann (PB) theory has been a well-established model in a broad range of scientific research areas. In electrochemistry, it is known as the Gouy–Chapman (GC) theory (Chapman, 1913; Gouy, 1910); in solution chemistry, it is known as the Debye–Huckel theory (Debye and Huckel, 1923); in colloid chemistry, it is known as the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948); and in biophysics, it is known as the PB theory (Davis and McCammon, 1990; Honig and Nicholls, 1995). The Poisson–Boltzmann equation (PBE) represents a typical implicit solvent model, and provides a simplified continuum description of the discrete particle (e.g., water, ion, and protein molecule) distributions in solution. The numerical methods used to solve the
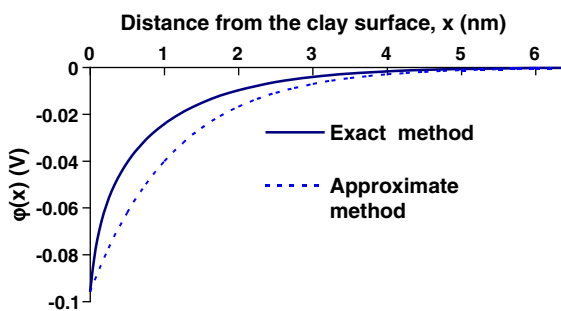

Fig. 1. The variation of $\varphi(x)$ obtained by the approximate method and by the analytical method when $\sigma = -0.058$ Cm^{-2}, $C_{Na^+}^b = 30$ mol m^{-3} and $C_{Ca^{2+}}^b = 10$ mol m^{-3}.
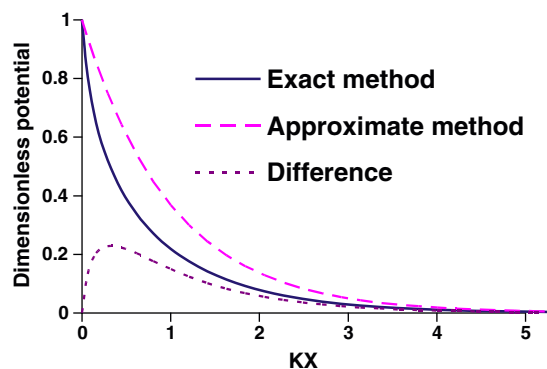

Fig. 2. The variation in dimensionless potential $\varphi(x) / \varphi(0)$ with respect to κx obtained by the approximate method and by the analytical method when $\sigma = -0.058$ Cm^{-2}, $C_{Na^+}^b = 30$ mol m^{-3} and $C_{Ca^{2+}}^b = 10$ mol m^{-3}.

Poisson–Boltzmann equation are: 1) finite element method (Chen et al., 2005; Xie and Zhou, 2007), 2) finite difference method (Wang, 2004; Zhou et al., 1996), 3) hybrid of finite element/boundary element method (Lu et al., 2007) and 4) hybrid of finite difference/boundary element method (Boschitsch and Fenley, 2004). For solving the Poisson–Boltzman equation, when the higher order terms of the expanded exponential function are neglected for simplification, does not give accurate result and the solution is an approximate one. Chapman (1913) and Gouy (1910) had given an approximate solution to the Poisson–Boltzman equation for single type of ions. Voyutsky had given an approximate solution to the linearized Poisson–Boltzman equation when more than one type of ions are present in soil water (Voyutsky, 1978). A more accurate β and potential distribution with distance from the pore wall is critical for the study of (among other subjects): transport properties in clay material (e.g. Tournassat and Appelo, 2011), clay–rock pore water composition (e.g. Appelo et al., 2008; Leroy et al., 2007), electrokinetic coupling (e.g. Pride, 1994), or surface tension prediction at air–water interface (e.g. Leroy et al., 2010). In this paper, a method is given to compute β exactly for two types of ions.

2. Material and methods

The nonlinear Poisson–Boltzman equation has been solved here by an analytical method adopting Gaussian numerical integration for evaluating the EDL thickness (β) when both monovalent (Na$^+$, Cl$^-$) and divalent (Ca^{2+}, SO$_4^{2-}$) ions are present in the soil water. Voyutsky (1978) has solved the Poisson–Boltzmann equation for multiple ions neglecting the higher order terms and linearizing the equation. Therefore, his solution is the approximate one. The solution of the nonlinear Poisson–Boltzman equation and the computation of β using the solution are given in the Appendix. Solutions of the linearized and nonlinear Poisson–Boltzman equations have been compared.

2.1. Distributions of cations and anions and volumetric charge density, $\rho(x)$

When both monovalent (Na$^+$ and Cl$^-$) and divalent (Ca^{2+} and SO$_4^{2-}$) ions are present in the soil water, concentrations of ions at distance x from the clay surface are given by Boltzman theorem as:

$$C_{Na^+}(x) = C_{Na^+}^b e^{\frac{-FZ_1 \phi(x)}{RT}} \tag{1}$$

$$C_{Ca^{2+}}(x) = C_{Ca^{2+}}^b e^{\frac{-FZ_2 \phi(x)}{RT}} \tag{2}$$

$$C_{Cl^-}(x) = C_{Cl^-}^b e^{\frac{FZ_1 \phi(x)}{RT}} \tag{3}$$

Table 2
Obtaining the potential for single type of ions, $\psi(x)$ from the solution of the Poisson–Boltzman equation i.e. $\phi(x)$ for two type of ions by the exact method when $\sigma = -0.058$ Cm^{-2}.

$C_{Na^+}^b = 10, C_{Ca^{2+}}^b = 0.00001$		$C_{Na^+}^b = 10, C_{Ca^{2+}}^b = 0$
x (nm)	$\phi(x)$ (V) computed using Eq. (A-9)	$\psi(x)$ (V) computed using Eq. (14)
0	−0.2537	−0.2537
0.0206	−0.2337	−0.2338
0.0482	−0.2153	−0.2154
0.4272	−0.1315	−0.1315
1.0831	−0.0871	−0.0871
2.0044	−0.0578	−0.0578
3.0919	−0.0383	−0.0383
4.0272	−0.0275	−0.0275
5.2372	−0.0182	−0.0182

and

$$C_{SO_4^{2-}}(x) = C_{SO_4^{2-}}^b e^{\frac{FZ_2\phi(x)}{RT}} \tag{4}$$

where $\phi(x) =$ the potential at distance x from the surface of the clay when both monovalent and divalent ions are present in the soil water (V); F = Faraday's number i.e. 96,487 C/g-equivalent; R = gas constant (8.314 J mol^{-1} K^{-1}); T = absolute temperature (K); C is the concentration of ion indicated in the subscript while superscript 'b' stands for the bulk concentration of that ion (mol m^{-3}); Z_1 = valence of the Na$^+$ and Cl$^-$ ions; Z_2 = valence of the Ca^{2+} and SO$_4^{2-}$ ions; Eqs. (1) and (2) as well as Eqs. (3) and (4) are implicitly related as $\phi(x)$ is the function of both monovalent (Na$^+$, Cl$^-$) and divalent (Ca^{2+}, SO$_4^{2-}$) ions which are present in the soil water. When these two types of ions are present in the soil water, volumetric charge density, $\rho(x)$ is given by:

$$\rho(x) = FZ_1 C_{Na^+}^b \left(e^{\frac{-FZ_1\phi(x)}{RT}} - e^{\frac{FZ_1\phi(x)}{RT}} \right) + FZ_2 C_{Ca^{2+}}^b \left(e^{\frac{-FZ_2\phi(x)}{RT}} - e^{\frac{FZ_2\phi(x)}{RT}} \right) \tag{5}$$

which is similar to the expression given by Voyutsky for more than one type of ions (Voyutsky, 1978). In Eq. (5), $C_{Na^+}^b e^{\frac{-FZ_1\phi(x)}{RT}}$ represents the distribution of concentrations of Na$^+$ ions and $C_{Na^+}^b e^{\frac{FZ_1\phi(x)}{RT}}$ represents the distribution of concentrations of Cl$^-$ ions, as Na$^+$ and Cl$^-$ are symmetrical electrolytes and $C_{Cl^-}^b = C_{Na^+}^b$ (Newman, 1987). Similarly, $C_{Ca^{2+}}^b e^{\frac{-FZ_2\phi(x)}{RT}}$ represents the distribution of concentrations of Ca^{2+} ions and $C_{Ca^{2+}}^b e^{\frac{FZ_2\phi(x)}{RT}}$ represents the distribution of concentrations of SO$_4^{2-}$ ions, as Ca^{2+} and SO$_4^{2-}$ are symmetrical electrolytes and $C_{SO_4^{2-}}^b = C_{Ca^{2+}}^b$.

2.2. Poisson–Boltzman equation when both monovalent (Na$^+$, Cl$^-$) and divalent (Ca^{2+}, SO$_4^{2-}$) ions are present in soil water

The Poisson equation relates the potential, $\phi(x)$ and the volumetric charge density, $\rho(x)$ (Bard and Faulkner, 2001; Butt and Graf, 2003; Yeung, 1992) as:

$$\frac{d^2\phi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon} \tag{6}$$

where $\varepsilon = \gamma\varepsilon_0 =$ permittivity of the medium (C^2 J^{-1} m^{-1}); $\gamma =$ dielectric constant of the medium (=78.5 at 25 °C for water, a dimensionless constant); and $\varepsilon_0 =$ permittivity of vacuum (= 8.854×10^{-12} C^2 J^{-1} m^{-1}).

2.3. Voyutsky's solution to linearized Poisson–Boltzman equation when two types of ions are present in soil water

The solution to linearized Poisson–Boltzman equation satisfying the boundary conditions as given by Voyutsky (1978) is:

$$\phi(x) = \phi(0)e^{-\kappa x} \tag{7}$$

where Debye–Huckel parameter, $k = \sqrt{\frac{2F^2}{\varepsilon RT} \left\{ Z_1^2 C_{Na^+}^b + Z_2^2 C_{Ca^{2+}}^b \right\}}$.

This linearization is possible for only small surface potentials ($\phi(0) \ll 25$ mV, Z = 1 at 25 °C) (Hunter, 1981; Van Olphen, 1977).

Eq. (7) gives the potential distribution when both monovalent and divalent ions are present in the soil water. This solution is an approximate one since the higher order terms appearing in the derivation are neglected for simplification. The thickness of the EDL (Mitchell, 1976; Newman, 1987; Van Olphen, 1977) is given by:

$$\beta = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon RT}{2F^2 \left\{ Z_1^2 C_{Na^+}^b + Z_2^2 C_{Ca^{2+}}^b \right\}}}. \tag{8}$$

Voyutsky has derived this equation for computation of β (Voyutsky, 1978). Thus, β can be determined if the bulk concentrations of Na$^+$ and Ca^{2+} ions in soil water are known. The center of gravity of space charge is located at a distance $1/\kappa$ from the surface, hence $1/\kappa$ is a measure for the thickness of the diffuse double layer ($1/\kappa$ is the Debye characteristic length introduced in the Debye–Huckel theory of strong electrolyte). Actually, the EDL extends beyond β (Hunter, 1981).

2.4. Determination of surface charge density (σ)

The surface charge density is estimated from the relation (Newman, 1987; Voyutsky, 1978; Yeung, 1992):

$$\sigma = -\int_0^\infty \rho(x)dx. \tag{9}$$

Incorporating $\rho(x)$ from the Poisson equation, Eq. (6) in Eq. (9),

$$\sigma = \int_0^\infty \varepsilon \frac{d^2\phi(x)}{dx^2} dx = -\varepsilon \left(\frac{d\phi(x)}{dx} \right)_{x=0}. \tag{10}$$

Applying the boundary condition that at $x = 0$, $\phi(0) = \phi_0$ Eq. (10) yields:

$$\left(\frac{d\phi(x)}{dx} \right)_{x=0} = \sqrt{\frac{2RT}{\varepsilon} \left\{ \left(\frac{FZ_1\phi(0)}{RT} \right)^2 C_{Na^+}^b + \left(\frac{FZ_2\phi(0)}{RT} \right)^2 C_{Ca^{2+}}^b \right\}}. \tag{11}$$

Substituting $\left(\frac{d\phi(x)}{dx} \right)_{x=0}$ in Eq. (10),

$$\sigma = -\varepsilon \sqrt{\frac{2RT}{\varepsilon} \left\{ \left(\frac{FZ_1\phi(0)}{RT} \right)^2 C_{Na^+}^b + \left(\frac{FZ_2\phi(0)}{RT} \right)^2 C_{Ca^{2+}}^b \right\}}. \tag{12}$$

Rearranging and substituting κ for $\sqrt{\frac{2F^2}{\varepsilon RT} \left\{ Z_1^2 C_{Na^+}^b + Z_2^2 C_{Ca^{2+}}^b \right\}}$,

$$\sigma = \varepsilon\kappa\phi(0) \tag{13}$$

From the (13), $\phi(0)$ can be determined when σ and $C_{Na^+}^b$, and $C_{Ca^{2+}}^b$ (hence, κ) are known.

3. Results and discussion

3.1. Comparison between solutions to the linearized and nonlinear Poisson–Boltzman equation

A comparison is made between the solutions to the linearized and nonlinear Poisson–Boltzman equation. The surface charge densities for fine loamy type of soil and sandy loam soil were computed (Mahanta, 2010) to be $\sigma = -0.058 \text{ Cm}^{-2}$ and $\sigma = -0.168 \text{ Cm}^{-2}$ respectively using data of Manchanda and Khanna (1981) and Sumner (2000). For a given value of x, $\phi(x)$ is computed using Eq. (7) which is the solution to the linearized Poisson–Boltzman equation. For this computed value of $\phi(x)$, the corresponding x is obtained using Eq. (A-9). The results are presented in Table 1. It is observed in the table that the x computed by the solution of nonlinear equation for same $\phi(x)$ was always less than the x value used in the Voyutsky's solution. When the given x value increased, the difference with the x values computed by nonlinear method increased up to a certain distance. The variations of $\phi(x)$ with x as obtained by the analytical (exact) method and by the Voyutsky's solution (approximate) are presented in Fig. 1. As seen from the figure, the approximate method overestimates the absolute value of the potential. The variations of dimensionless potentials, $\frac{\phi(x)}{\phi(0)}$ with dimensionless distance, κx corresponding to the solutions of the linearized and nonlinear Poisson–Boltzman equation are presented in Fig. 2. Also the variation of the difference between the dimensionless potentials with κx computed by these two is shown in the figure. There is no difference between dimensionless potentials computed by the exact and the approximate method at the two extreme dimensionless distances.

The maximum difference in dimensionless potential is 0.23 which occurs at $\kappa x = 0.29$ from the clay surface. Thus, the solution to the nonlinear Poisson–Boltzman equation is preferable to the approximate solution.
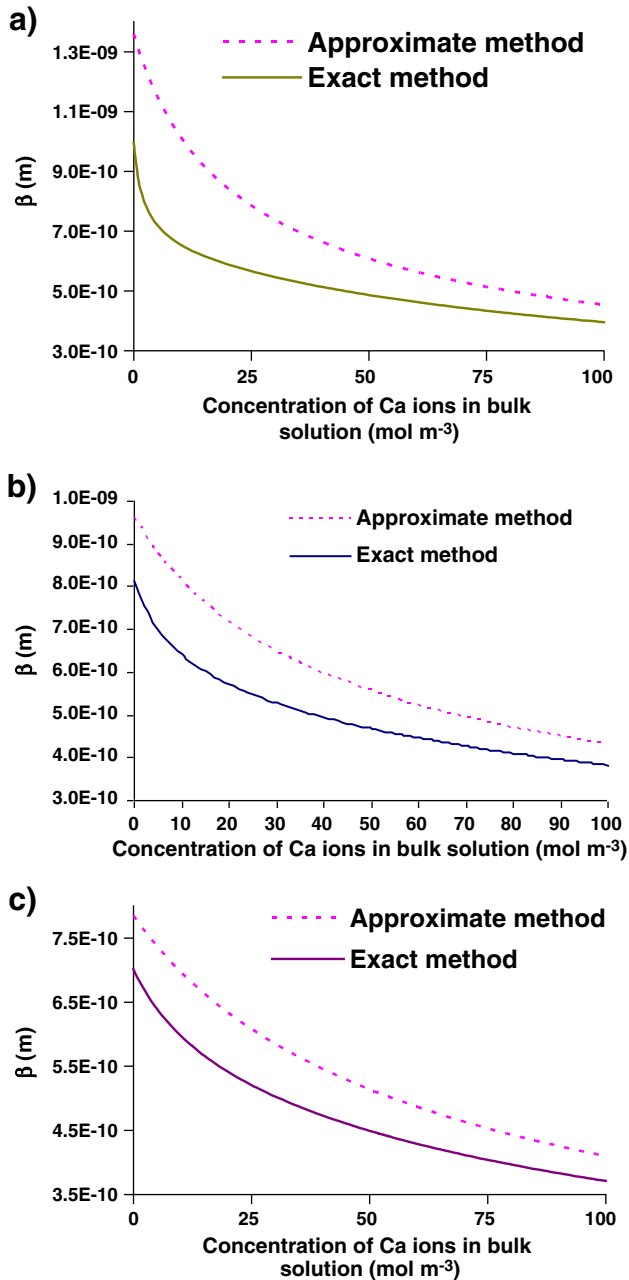
Fig. 3. The variation of β due to increase in the bulk concentration of Ca ions in soil water when (a) $C^b_{Na^+} = 50 \text{ mol m}^{-3}$ (b) $C^b_{Na^+} = 100 \text{ mol m}^{-3}$ (c) $C^b_{Na^+} = 150 \text{ mol m}^{-3}$, for $\sigma = -0.058 \text{ Cm}^{-2}$.

2.5. Analytical solution of nonlinear Poisson–Boltzman equation for single type of ions

The analytical solution of nonlinear Poisson–Boltzman equation for single type of ions (Mahanta, 2010; Mahanta et al., 2012) is:

$$\psi(x) = \frac{1}{p} \ln \left[\frac{1 + A_1 e^{-Bx}}{1 - A_1 e^{-Bx}} - \sqrt{ \left\{ \frac{1 + A_1 e^{-Bx}}{1 - A_1 e^{-Bx}} \right\}^2 - 1 } \right] \tag{14}$$

where $\psi(x) =$ potential at distance x from the surface of the clay for single type of ions (V); $p = \frac{FZ}{2RT}$, $A_1 = \frac{\cosh(p\psi(0)) - 1}{\cosh(p\psi(0)) + 1}$ and $B = 4p\sqrt{\frac{2RTC_b}{\varepsilon}}$. The results of this solution are compared with the results obtained through the analytical solution for two types of ions by limiting one type of ions.
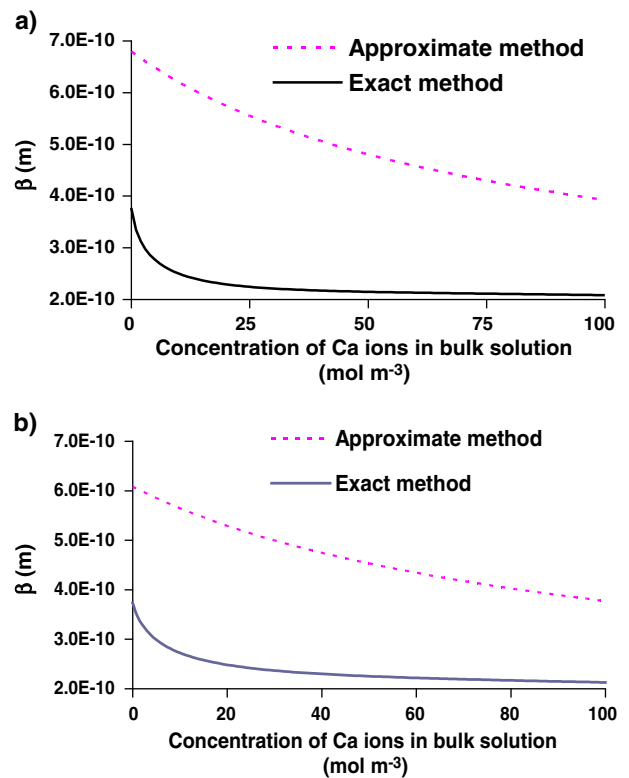
Fig. 4. The variation of β due to increase in bulk concentration of Ca ions in soil water when (a) $C^b_{Na^+} = 200 \text{ mol m}^{-3}$ (b) $C^b_{Na^+} = 250 \text{ mol m}^{-3}$, for $\sigma = -0.168 \text{ Cm}^{-2}$.

The results for single type of ions present in soil water can be obtained from the solution derived for two types of ions by limiting the bulk concentration of one. Potential, $\phi(x)$ for two types of ions for $C_{Na^+}^b = 10$ mol m^{-3}, and $C_{Ca^{2+}}^b = 10^{-05}$ mol m^{-3} computed using Eq. (A-9) is compared with the potential, $\psi(x)$ for single type of ions obtained from Eq. (14) for $C_{Na^+}^b = 10$ mol m^{-3}. A comparison between the two sets of results is made in Table 2 and it is seen that there is little difference between the computed values of $\phi(x)$ and $\psi(x)$. Therefore, the Gaussian numerical integration adopted for solving the nonlinear Poisson–Boltzman equation when both monovalent and divalent ions are present in the soil water is adequate.

3.2. β computed by the exact method and by the approximate method

Gypsum is added for reclaiming the sodic soil. When gypsum is added, the bulk concentration of Ca ions is increased in the soil water. With increase in bulk concentration of Ca ions, the thickness of electric double layer is decreased. In Fig. 3, the reduction in thickness of double layer with increase in bulk concentration of Ca for initial bulk concentration of Na ions equal to (a) 50, (b) 100 and (c) 150 mol m^{-3} respectively is presented. The electric double layer thickness has been computed by the exact method as well as by the approximate method. The results are applicable for fine loamy type of soil for which $\sigma = -0.058$ Cm^{-2} (Manchanda and Khanna, 1981). The results for sandy loam soil having $\sigma = -0.168$ Cm^{-2} are presented in Fig. 4a,b. With higher σ, a higher value of $C_{Na^+}^b$ will provide electrical neutrality. For a given σ, there is

minimum bulk concentration for which electrical neutrality is possible. Therefore, results are presented for higher value of $C_{Na^+}^b$.

From Figs. 3 and 4, it can be inferred that when gypsum is added to the sodic soil, with increase in bulk concentration of Ca ions, the electric double layer decreases exponentially. The thickness of the double layer is the maximum when the bulk concentration of Ca ions is equal to zero. There is about 40 to 50% reduction in thickness when the bulk concentration of Ca ions increases from 0 to 100 mol m^{-3}.

4. Conclusions

Based on the study the following conclusions are drawn:

1) The solution derived for the nonlinear Poisson–Boltzman equation when both monovalent and divalent ions are present in soil water is amenable to computation of electric double layer through Gaussian numerical integration.
2) The solution to the linearized Poisson–Boltzman equation overestimates the thickness of the electric double layer. Therefore, it is appropriate to adopt the solution of the nonlinear Poisson–Boltzman equation for computing β.
3) With increase in bulk concentration of Ca, the electric double layer decreases exponentially. There is about 40 to 50% reduction in thickness when the bulk concentration of Ca ions increases from 0 to 100 mol m^{-3}.

Appendix A

A.1. Analytical solution of nonlinear Poisson–Boltzman equation when both monovalent (Na$^+$, Cl$^-$) and divalent (Ca^{2+}, SO$_4^{2-}$) ions are present in soil water

Incorporating $\rho(x)$ from Eq. (5) in Eq. (6), the Poisson–Boltzman equation is:

$$\frac{d^2\phi(x)}{dx^2} = -\frac{F}{\varepsilon}\left[Z_1 C_{Na^+}^b\left(e^{\frac{-FZ_1\phi(x)}{RT}}-e^{\frac{FZ_1\phi(x)}{RT}}\right)+Z_2 C_{Ca^{2+}}^b\left(e^{\frac{-FZ_2\phi(x)}{RT}}-e^{\frac{FZ_2\phi(x)}{RT}}\right)\right]. \tag{A-1}$$

Arranging and making the same transformations as Voyutsky did for solving the Poisson–Boltzman equation (Voyutsky, 1978),

$$\frac{d}{dx}\left(\frac{d\phi(x)}{dx}\right) = -\frac{F}{\varepsilon}\left[Z_1 C_{Na^+}^b\left(e^{\frac{-FZ_1\phi(x)}{RT}}-e^{\frac{FZ_1\phi(x)}{RT}}\right)+Z_2 C_{Ca^{2+}}^b\left(e^{\frac{-FZ_2\phi(x)}{RT}}-e^{\frac{FZ_2\phi(x)}{RT}}\right)\right]. \tag{A-2}$$

Simplifying,

$$2\frac{d\phi(x)}{dx}d\left(\frac{d\phi(x)}{dx}\right) = -\frac{2F}{\varepsilon}\left[Z_1 C_{Na^+}^b\left(e^{\frac{-FZ_1\phi(x)}{RT}}-e^{\frac{FZ_1\phi(x)}{RT}}\right)+Z_2 C_{Ca^{2+}}^b\left(e^{\frac{-FZ_2\phi(x)}{RT}}-e^{\frac{FZ_2\phi(x)}{RT}}\right)\right]d\phi(x). \tag{A-3}$$

Integrating both sides and taking into account that, as $x \to \infty$, $\phi(x) \to 0$, and $\frac{d\phi(x)}{dx} \to 0$,

$$\left(\frac{d\phi(x)}{dx}\right)^2 = \frac{2}{\varepsilon}\left[C_{Na^+}^b RT\int_0^{\phi(x)}\left(e^{\frac{FZ_1\phi(x)}{RT}}-e^{\frac{-FZ_1\phi(x)}{RT}}\right)d\left(\frac{FZ_1\phi(x)}{RT}\right)+C_{Ca^{2+}}^b RT\int_0^{\phi(x)}\left(e^{\frac{FZ_2\phi(x)}{RT}}-e^{\frac{-FZ_2\phi(x)}{RT}}\right)d\left(\frac{FZ_2\phi(x)}{RT}\right)\right]. \tag{A-4}$$

Performing the integration appearing in the right hand side,

$$\frac{d\phi(x)}{dx} = = \pm\sqrt{\frac{4RT}{\varepsilon}\left[C_{Na^+}^b\left(\cosh\left(\frac{FZ_1\phi(x)}{RT}\right)-1\right)+C_{Ca^{2+}}^b\left(\cosh\left(\frac{FZ_2\phi(x)}{RT}\right)-1\right)\right]}. \tag{A-5}$$

As $\frac{d\phi(x)}{dx}$ is positive, the positive root is considered.
Let, $B_1 = \frac{4RT}{\varepsilon}C_{Na^+}^b$ and $B_2 = \frac{4RT}{\varepsilon}C_{Ca^{2+}}^b$, where the unit of B_1 and B_2 is V^{2}m^{-2}.

Incorporating B_1 and B_2 and rearranging,

$$\frac{d\varphi(x)}{\sqrt{B_1 \cosh\left(\frac{FZ_1\varphi(x)}{RT}\right) + B_2 \cosh\left(\frac{FZ_2\varphi(x)}{RT}\right) - (B_1 + B_2)}} = dx. \tag{A-6}$$

Integrating Eq. (A-6) between lower limit $x = x_{j-1}$, $\phi(x) = \phi(x_{j-1})$ and upper limit $x = x_j$, $\phi(x) = \phi(x_j)$,

$$\int_{\varphi(x_{j-1})}^{\varphi(x_j)} \frac{d\varphi(x)}{\sqrt{B_1 \cosh\left(\frac{FZ_1\varphi(x)}{RT}\right) + B_2 \cosh\left(\frac{FZ_2\varphi(x)}{RT}\right) - (B_1 + B_2)}} = \int_{x_{j-1}}^{x_j} dx \tag{A-7}$$

or

$$x_j - x_{j-1} = \frac{1}{\sqrt{B_1}} \int_{\phi(x_{j-1})}^{\phi(x_j)} \frac{d\phi(x)}{\sqrt{\cosh\left(\frac{FZ_1\phi(x)}{RT}\right) + \frac{B_2}{B_1}\cosh\left(\frac{FZ_2\phi(x)}{RT}\right) - \left(1 + \frac{B_2}{B_1}\right)}}. \tag{A-8}$$

For $j = 1$, $x_{j-1} = 0$ and $\phi(x_{j-1}) = \phi(0)$. Gauss quadrature is adopted to carry out the integration numerically. Substituting, $\phi(x) = \frac{\phi(x_{j-1}) + \phi(x_j)}{2} - \frac{\phi(x_{j-1}) - \phi(x_j)}{2}\xi$ and $d\phi(x) = -\frac{\phi(x_{j-1}) - \phi(x_j)}{2}d\xi$ where ξ is a dummy variable with lower limit -1 and upper limit 1.

$$x_j - x_{j-1} = -\frac{1}{\sqrt{B_1}} \times$$

$$\int_{-1}^{1} \frac{\frac{\phi(x_{j-1}) - \phi(x_j)}{2}d\xi}{\sqrt{\cosh\left[\frac{FZ_1}{RT}\left\{\frac{\phi(x_{j-1}) + \phi(x_j)}{2} - \frac{\phi(x_{j-1}) - \phi(x_j)}{2}\xi\right\}\right] + \frac{B_2}{B_1}\cosh\left[\frac{FZ_2}{RT}\left\{\frac{\phi(x_{j-1}) + \phi(x_j)}{2} - \frac{\phi(x_{j-1}) - \phi(x_j)}{2}\xi\right\}\right] - \left(1 + \frac{B_2}{B_1}\right)}} \tag{A-9}$$

$\phi(x_j)$ is obtained starting from the origin i.e. $\varphi(0) = \varphi_0$ at $x = 0$ in succession. For an assumed $\phi(x_j)$, corresponding x_j is obtained from Eq. (A-9), for known $\phi(x_{j-1})$ and x_{j-1}. Ninety six Gaussian abscissa and weights are used for evaluating the integral.

A.2. Estimation of the thickness of EDL

The thickness of EDL can be computed using the analytical solution as follows:
a) Consider the lower limit of potential $\phi(x_{j-1}) = \phi(0)$, and the upper limit $\phi(x_j) = \frac{\phi(0)}{e}$. Hence,

$$\beta = -\frac{1}{\sqrt{B_1}} \times \int_{-1}^{1} \frac{\frac{\phi(0) - \frac{\phi(0)}{e}}{2}d\xi}{\sqrt{\cosh\left[\frac{FZ_1}{RT}\left\{\frac{\phi(0) + \frac{\phi(0)}{e}}{2} - \frac{\phi(0) - \frac{\phi(0)}{e}}{2}\xi\right\}\right] + \frac{B_2}{B_1}\cosh\left[\frac{FZ_2}{RT}\left\{\frac{\phi(0) + \frac{\phi(0)}{e}}{2} - \frac{\phi(0) - \frac{\phi(0)}{e}}{2}\xi\right\}\right] - \left(1 + \frac{B_2}{B_1}\right)}}. \tag{A-10}$$

b) The center of gravity of the space charge ($\bar{x}$) in the EDL is also called the thickness of the double layer (Van Olphen, 1977). The distance of the center of gravity from the clay surface ($\bar{x}$) is obtained taking moment of $\phi(x)$ about the origin. $\bar{x}$ is given by:

$$\bar{x} = \frac{\int_0^\infty \varphi(x)x \, dx}{\int_0^\infty \varphi(x)dx} = \frac{\sum_{j=0}^{\infty} \frac{\{\varphi(x_{j+1}) + \varphi(x_j)\}}{2}(x_j - x_{j-1})\left(x_j + \frac{(x_{j+1} - x_j)}{2}\right)}{\sum_{j=0}^{\infty} \frac{\{\varphi(x_{j+1}) + \varphi(x_j)\}}{2}(x_j - x_{j-1})}. \tag{A-11}$$

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