The Zeta Potential Calculation for Fluid Saturated Porous Media Using Linearized and Nonlinear Solutions of Poisson–Boltzmann Equation

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Abstract: Theoretical models have been developed to calculate the zeta potential based on the solution of the linearized approximation of the Poisson-Boltzmann equation (PB). The approximation is only valid for the small magnitude of the surface potential. However, the surface potential available in published experimental data normally does not satisfy that condition. Therefore, the complete analytical solution to the PB equation (nonlinear equation) needs to be considered. In this work, the comparison between the linearized and nonlinear solutions has been performed. The results show that the linearized solution always overestimates the absolute value of the electric potential in the electric double layer as well as the zeta potential. For a small magnitude of the surface potential ($|\varphi_d| \leq 25$ mV), the electric potential distribution predicted from the linearized solution is almost the same as that predicted from the nonlinear solution. It is also shown that the zeta potential computed from the linearized PB solution closely matches with that computed from the nonlinear solution for the fluid pH = 5 - 8 and the shear plane distance of 2.4×10^{-10} m. Therefore, the solution of the linearized PB equation can be used to calculate the zeta potential under that condition. This is validated by comparing the linearized and nonlinear solutions with experimental data in literature.

Keywords: Zeta potential, porous media, electric double layer, Poisson–Boltzmann equation.

1. Introduction

The electrokinetic phenomena are induced by the relative motion between the fluid and the solid surface. In a porous medium such as rocks or soils, the electric current density, linked to the ions within the fluid, is coupled to the fluid flow and that coupling is called electrokinetics e.g. [1]. Measurement of the electrokinetics in porous media is becoming increasingly more important in

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geophysical applications. For example, it could be used to map subsurface flow and detect subsurface flow patterns in oil reservoirs [e.g., 2- 6], geothermal areas and volcanoes [e.g.,7, 8, 9], detection of contaminant plumes [e.g., 10, 11]. It has also been proposed to use the monitoring of electrokinetics to detect at distance the propagation of a water front in a reservoir [e.g., 12] or to predict earthquakes [e.g., 13].

The zeta potential of a solid-liquid interface is one of the most important parameters in electrokinetics. Theoretical models have been developed to calculate the zeta potential based on the solution of the linearized approximation of the PB equation for the electric double layer [e.g., 14, 15]. The approximation is only valid for the small magnitude of the surface potential ($|\varphi_d| \leq 25\,\text{mV}$) [16, 17]. However, the surface potential available in published experimental data normally does not satisfy that condition. Therefore, a complete analytical solution to the nonlinear PB equation needs to be considered. Additionally, to the best of my knowledge the difference in the zeta potential calculation between the solutions of the linearized and nonlinear PB equation has not yet been evaluated. In this work, the comparison between the linearized and nonlinear solutions has been performed for silica surfaces because of the availability of input parameters for the model as well as experimental data in literature [e.g., 14, 15]. It is found that the linearized solution always overestimates the absolute value of the electric potential in the electric double layer (EDL) as well as the zeta potential. For a small magnitude of the surface potential ($|\varphi_d| \leq 25$ mV), the linearized PB solution could be used to predict the electric potential distribution in the EDL instead of the more complicated nonlinear PB solution. The results also show that at a given electrolyte concentration, the zeta potential computed from the linearized PB solution closely matches with that computed from the nonlinear solution for the fluid pH = 5 - 8 that are normally encountered in published experimental data and the shear plane distance of 2.4×10^{-10} m. Therefore, the solution of the nonlinear PB equation can be used to calculate the zeta potential under that condition. This is validated by comparing the linearized and nonlinear solutions with each other and with experimental data in literature. It should be noted that if the shear distance is taken as 2.4×10^{-9} m or larger value and the fluid pH is larger than 8, one needs to use the linearized PB solution to calculate the zeta potential.

2. Theoretical background of the zeta potential

2.1. Physical chemistry of the electric double layer

Solid grain surfaces of the rocks immersed in aqueous systems acquire a surface electric charge, mainly via the dissociation of silanol groups - $SiOH^0$ (where the superscript "0" means zero charge) and the adsorption of cations on solid surfaces. The reactions at a solid silica surface (silica is the main component of rocks) in contact with fluids have been well described in literature [e.g, 14, 15, 18]. The reactions at the silanol surfaces in contact with 1:1 electrolyte solutions are:

$$SiOH^0 \Leftrightarrow >SiO^- + H^+, \tag{1}$$

for deprotonation of silanol groups

and

$$SiOH^0 + Me^+ \Leftrightarrow SiOMe^0 + H^+, \tag{2}$$

for cation adsorption on silica surfaces (Me^+ refer to monovalent cations in the electrolytes such as K^+ or Na^+). It should be noted that further protonation of the silanol surfaces is expected only under extremely acidic conditions (pH < 2-3) and is not considered. Similarly, the protonation of doubly

coordinated groups (Si_2O^0) is not taken into account because these are normally considered inert [14, 15, 18].

According to [14, 15], the disassociation constant for deprotonation of the silica surfaces is determined as

$$K_{(-)} = \frac{\Gamma^0_{SiO^-}.\alpha^0_{H^+}}{\Gamma^0_{SiOH}}, \tag{3}$$

and the binding constant for cation adsorption on the silica surfaces is determined as

$$K_{Me} = \frac{\Gamma^0_{SiOMe}.\alpha^0_{H^+}}{\Gamma^0_{SiOH}.\alpha^0_{Me^+}}, \tag{4}$$

where Γ^0_i is the surface site density of surface species i (sites/m^2) and α^0_i is the activity of an ionic species i at the closest approach of the mineral surface (no units).

The total density of surface sites (Γ^0_S) is determined as follows

$$\Gamma^0_S = \Gamma^0_{SiOH} + \Gamma^0_{SiO^-} + \Gamma^0_{SiOMe} \tag{5}$$

The mineral surface charge density Q^0_S in C/m^2 can be found by

$$Q^0_S = -e.\Gamma^0_{SiO^-}, \tag{6}$$

where e is the elementary charge.

Due to a charged solid surface, an electric double layer (EDL) is developed at the liquid-solid interface when solid grains of rocks are in contact with the liquid. The EDL is made up of (1) the Stern layer where cations are adsorbed on the surface and are immobile due to the strong electrostatic attraction and (2) the diffuse layer where the number of cations exceeds the number of anions and the ions are mobile. The closest plane to the solid surface in the diffuse layer at which flow occurs is termed the shear plane and the electric potential at this plane is called the zeta potential (ζ).

2.2. Electric potential distribution in the EDL

Following assumptions are used in the EDL theory [e.g., 19, 20]: (1) ions in the double layer are considered as point charges and there are no chemical interactions between them; (2) charges on the solid grain surface are uniformly distributed; (3) the solid surface is a flat plate that is large relative to thickness of double layer and (4) the dielectric constant of the medium is the same everywhere in the liquid.

In the EDL theory, the local concentrations of cations, $C^+(x)$ and of anions, $C^-(x)$ (mol m^{-3}) in the liquid in the pore space at distance x from the solid surface are expressed as functions of the electric potential $\psi(x)$. According to Boltzmann theorem [e.g., 21, 22], one has

$$C^+(x) = C^+_b e^{\frac{-eZ\psi(x)}{k_bT}} \tag{7}$$

and

$$C^-(x) = C^-_b e^{\frac{eZ\psi(x)}{k_bT}} \tag{8}$$

where C_b^+ and C_b^- are concentration of the cations and concentration of the anions, respectively at large distance from the solid surface where the electric potential is zero ($\psi(\infty) = 0$), Z is the valence of the ions under consideration (dimensionless); k_b is the Boltzmann's constant (1.38×10^{-23} J/K), T is temperature (in K).

The Poisson equation relating the electric potential, $\psi(x)$ (in V) and volumetric charge density, $\rho(x)$ (in C m^{-3}) in the liquid is expressed as [e.g., 21, 22]

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_r \varepsilon_0} \tag{9}$$

where ε_r is the relative permittivity of the fluid (78.5 at 25°C for water), ε_o is the dielectric permittivity in vacuum (8.854×10^{-12} C^2 J^{-1} m^{-1}).

For single type of ions in the liquid, $\rho(x)$ is given by [e.g., 20]

$$\rho(x) = NeZ[C^+(x) - C^-(x)] = NeZC_b(e^{-\frac{eZ\psi(x)}{k_bT}} - e^{\frac{eZ\psi(x)}{k_bT}}) \tag{10}$$

where $C_b = C_b^+ = C_b^-$ for symmetric electrolytes such as NaCl or CaSO$_4$ representing number of ions (anion or cation) expressed in mole per unit volume (mol m^{-3}), e is the elementary charge (e = 1.6×10^{-19} C) and N is the Avogadro's number (6.022×10^{23} /mol).

Putting Eq. (10) into Eq. (9), one obtains

$$\frac{d^2\psi(x)}{dx^2} = -\frac{NeZC_b}{\varepsilon_r \varepsilon_0}(e^{-\frac{eZ\psi(x)}{k_bT}} - e^{\frac{eZ\psi(x)}{k_bT}}) \tag{11}$$

or

$$\frac{d^2\psi(x)}{dx^2} = \frac{2NeZC_b}{\varepsilon_r \varepsilon_0}\sinh(\frac{eZ\psi(x)}{k_bT}) \tag{12}$$

Eq. (12) is known as the PB equation. The boundary conditions to be satisfied for flat solid surfaces are: (1) the potential at the surface $x = 0$, $\psi(0) = \varphi_d$ that is called the surface potential or Stern potential); (2) the potential in the bulk liquid at distance $x = \infty$, $\psi(\infty) = 0$ and $\left.\frac{d\psi(x)}{dx}\right|_{x=\infty} = 0$ [e.g., 20].

a) Linearized solution of Poisson–Boltzmann equation

It is seen that if $\left|\frac{eZ\varphi_d}{k_bT}\right| \ll 1$ ($|\varphi_d| \le 25$ mV for $Z = 1$ at 25° C), then $\sinh(\frac{eZ\psi(x)}{k_bT}) \approx \frac{eZ\psi(x)}{k_bT}$ [e.g., 16, 17, 23, 24]. Therefore, Eq. (12) linearizes as follows

$$\frac{d^2\psi(x)}{dx^2} = \frac{2Ne^2Z^2C_b}{\varepsilon_r \varepsilon_0 k_bT}\psi(x) \tag{13}$$

The solution to linearized PB equation satisfying the boundary conditions is given by [e.g., 25]

$$\psi(x) = \varphi_d \exp(-\frac{x}{\chi_d}) \tag{14}$$

where χ_d is called Debye length given by $\chi_d = \sqrt{\dfrac{\varepsilon_o \varepsilon_r k_b T}{2Ne^2 Z^2 C_b}}$ (C_b in mol m^{-3}). If C_b is in mol L^{-1},

then $\chi_d = \sqrt{\dfrac{\varepsilon_o \varepsilon_r k_b T}{2000 Ne^2 Z^2 C_b}}$.

b) Nonlinear solution of Poisson–Boltzmann equation

The exact solution to PB equation - Eq. (12) for single type of ions has been found in both [20] and [26]. However, the solution presented in [20] has a more simplified form as below:

$$\psi(x) = \frac{2k_b T}{eZ} \ln(\frac{1 - A\exp(-\dfrac{x}{\chi_d})}{1 + A\exp(-\dfrac{x}{\chi_d})}) \tag{15}$$

where $A = \dfrac{1 - \exp(\dfrac{eZ}{2k_b T}\varphi_d)}{1 + \exp(\dfrac{eZ}{2k_b T}\varphi_d)}$.

Therefore, Eq. (15) is used as the exact solution to nonlinear PB equation to calculate the zeta potential in this work.

2.3. The surface potential and zeta potential

In a theoretical model that has been well described in [e.g., 14, 15], the surface electric potential φ_d for a solid surface in contact with 1:1 electrolytes ($Z = 1$) is given by

$$\varphi_d = \frac{2k_b T}{3e} \ln\left\{ \frac{\sqrt{8.10^3 \varepsilon_o \varepsilon_r k_b T N}(10^{-pH} + K_{Me}C_b)}{2e\Gamma_S^0 K_{(-)}} \left[\frac{C_b + 10^{-pH} + 10^{pH-pK_w}}{\sqrt{C_b}} \right] \right\} \tag{16}$$

where pH is the fluid pH and K_w is the disassociation constant of water.

According to the definition, the zeta potential is the electric potential at the shear plane. Therefore, one has

$$\zeta = \psi(x)\big|_{x=\chi_\varsigma} \tag{17}$$

where $\psi(x)$ is the electric potential distribution in the EDL given by Eq (14) or Eq. (15), χ_ς is the shear plane distance (the distance from the solid surface to the shear plane). There is currently no method to evaluate the shear plane distance. There are few independent reports of the shear plane distance. For example, the shear plane distance χ_ς is found to be 2.4×10^{-10} m in [15] but 2.0×10^{-9} m in [27].

3. Results and discussion

A system of 1:1 symmetric electrolytes (e.g., NaCl, KNO$_3$) and silica solid surfaces are considered for the modeling in this work because of the availability of input parameters for the model as well as experimental data in literature [e.g., 14, 15]. Therefore, the valence $Z = 1$ is used from Eq. (7) to Eq. (15).
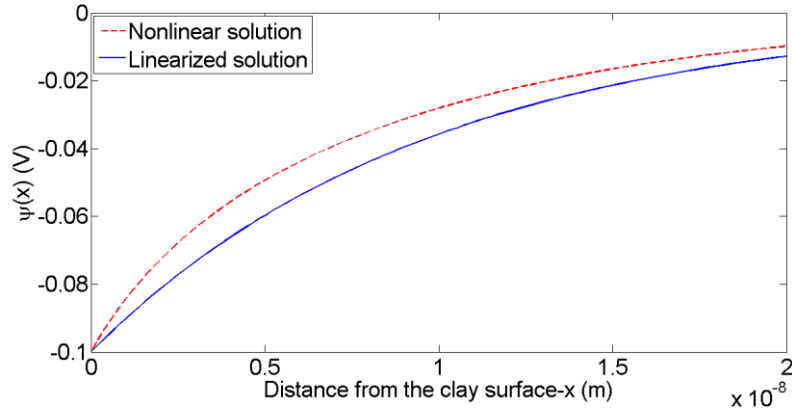
(a) $\varphi_d = -0.1$ V; C$_b$ =10^{-3} mol/L
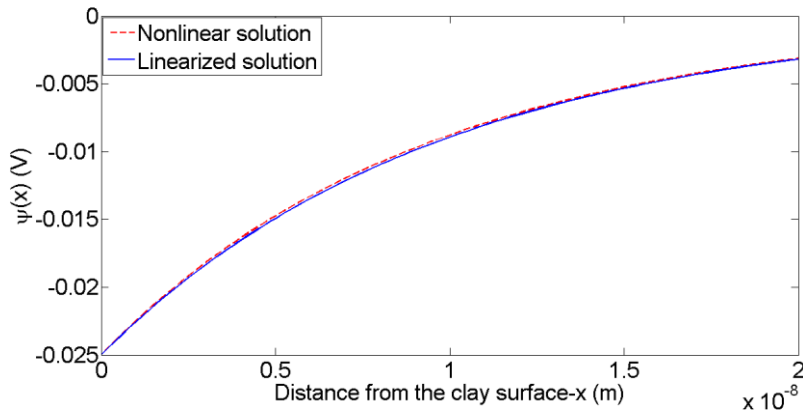
(b) $\varphi_d = -0.025$ V; C$_b$ =10^{-3} mol/L

Figure 1. The variations of the electric potential with respect to distance x from the solid surface computed using the solutions of the linearized and nonlinear PB equation.

3.1. The distribution of $\psi(x)$

The variation of the electric potential $\psi(x)$ with respect to distance x from the solid surface predicted from the linearized and nonlinear solutions (Eq. (14) and Eq. (15), respectively) for two different values of the surface potential ($\varphi_d = -0.1$ V and $\varphi_d = -0.025$ V) is shown in Fig. 1 (electrolyte concentration C_b is taken to be 10^{-3} M). It is seen that the solution of linearized PB

equation overestimates the absolute value of the electric potential for $\varphi_d = -0.1$ V as shown in Fig. 1(a). For the smaller absolute value of the surface potential $\varphi_d = -0.025$ V, the prediction from the nonlinear and linearized solutions is almost the same as shown in Fig. 1(b). It is inferred that the difference in the electric potential distribution predicted by the two solutions increases with increasing absolute value of the surface potential. For a small magnitude of the surface potential ($|\varphi_d| \leq 25$ mV), the linearized PB solution could be used to predict the electric potential distribution in the EDL as expected in literature [e.g., 16, 17]. The variation of $\psi(x)$ with distance x for two different electrolyte concentrations ($C_b = 10^{-2}$ M and $C_b = 10^{-3}$ M) is also shown in Fig. 2. It is seen that the deviation of the electric potential obtained by the nonlinear and linearized solutions is more for lower the electrolyte concentration.
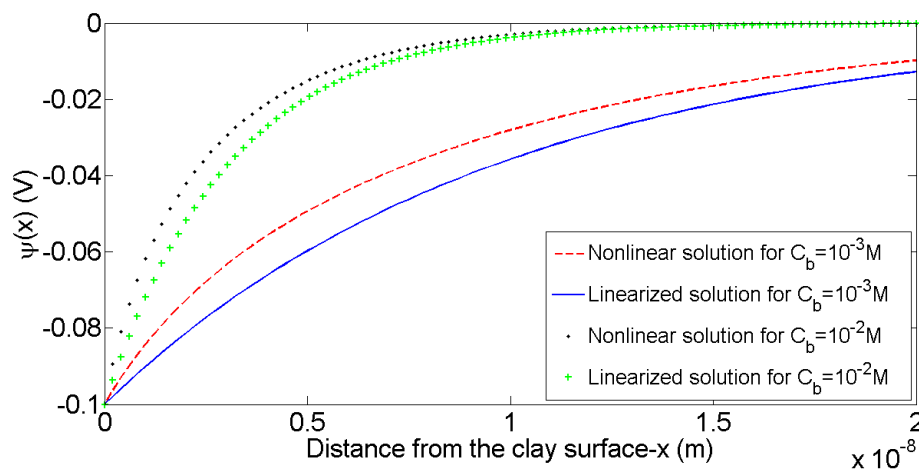

Figure 2. The variations of the electric potential with respect to distance x using the solutions of the linearized and nonlinear PB equation for two different electrolyte concentrations.

3.2. The zeta potential comparison

To evaluate the variation of the zeta potential with respect the electrolyte concentration from both the linearized and nonlinear solutions of the PB equation, one need to calculate the surface potential from Eq. (16). Input parameters that are available in [14, 15] for silica are used for Eq. (16). Namely, the value of the disassociation constant $K_{(-)}$ is taken as $10^{-7.1}$. The surface site density Γ_S^0 is taken as 10×10^{18} site/m². The disassociation constant of water K_w is taken as 9.214×10^{-15} at 25°C ($pK_w = -\log_{10}(K_w)$). The fluid pH is taken as 7. The binding constant for cation adsorption of Na⁺ on silica surface K_{Me}(Na⁺) is taken as $10^{-7.5}$. The shear plane distance χ_ζ is taken as 2.4×10^{-10} m and 2.4×10^{-9} m for comparison.

Fig. 3 shows the variations of the zeta potential with electrolyte concentration using the solutions of the linearized and nonlinear PB equation. It is found that the zeta potential in magnitude predicted from the linearized solution is significantly larger (up to 15%) than that predicted from the nonlinear solution in the studied range of electrolyte concentration for the shear plane distance of 2.4×10^{-9} m. However, a slight difference in the zeta potential is observed for the shear plane distance of 2.4×10^{-10} m.
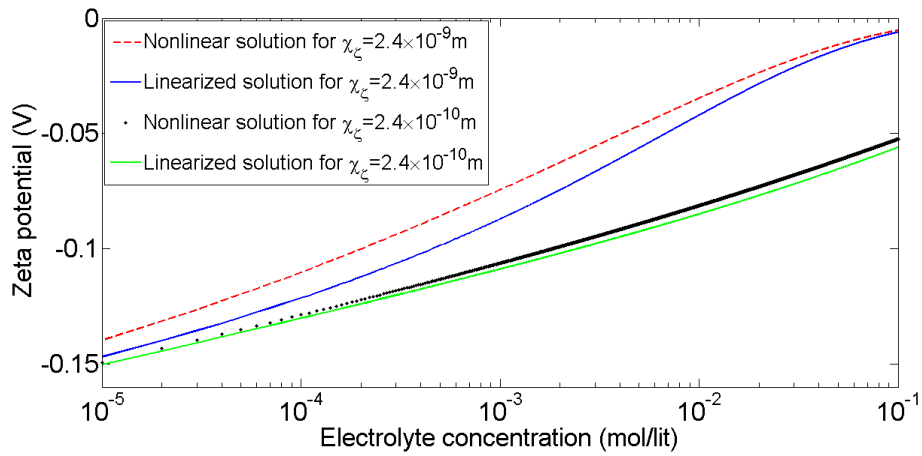
Figure 3. The variations of the zeta potential with electrolyte concentration using the solutions of the linearized and nonlinear PB equation for $\chi_\zeta = 2.4\times10^{-9}$ m and $\chi_\zeta = 2.4\times10^{-10}$ m.
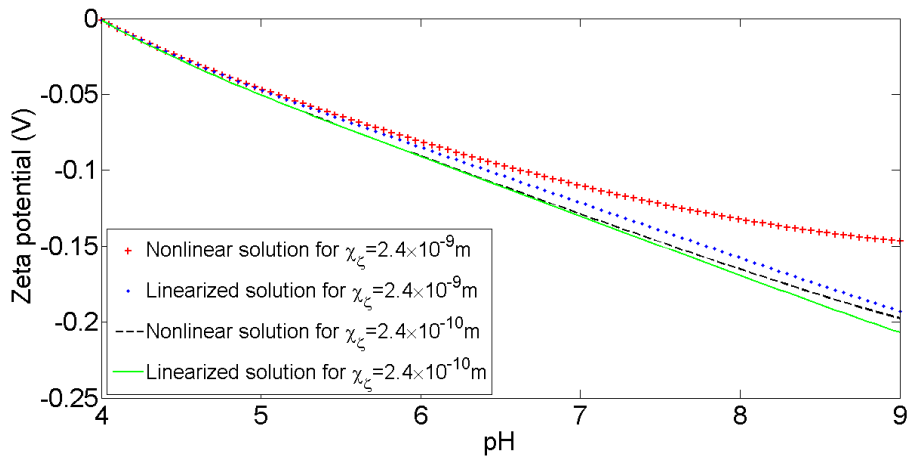

Figure 4. The variations of the zeta potential with fluid pH using the solutions of the linearized and nonlinear PB equation for $\chi_\zeta = 2.4\times10^{-9}$ m and $\chi_\zeta = 2.4\times10^{-10}$ m ($C_b = 10^{-4}$ M).

The variations of the zeta potential with fluid pH are also predicted using the linearized and nonlinear solutions at $C_b = 10^{-4}$ M as shown in Fig. 4. The results show that the zeta potential in magnitude increases with increasing fluid pH as reported in 28. Besides that, the difference of the zeta potential between the linearized and nonlinear PB solutions increases with increasing fluid pH. For fluid pH=5 - 8 that is normally encountered in published data and $\chi_\zeta = 2.4\times10^{-10}$ m, the values of the zeta potential predicted from the linearized and nonlinear solutions are almost the same.
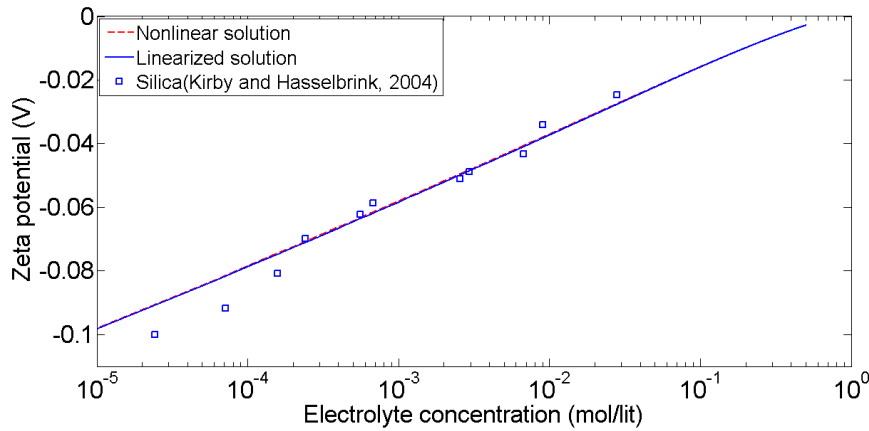
(a) T = 22.6°C, pH = 7, K_{Me} = $10^{-7.5}$, $K_{(-)}$ = $10^{-8.4}$, Γ_S^0 = 10×10^{18} site/m^2 and χ_ζ = 2.4×10^{-10} m
(Experimental data obtained from Kirby and Hasselbrink, 2004 [28])
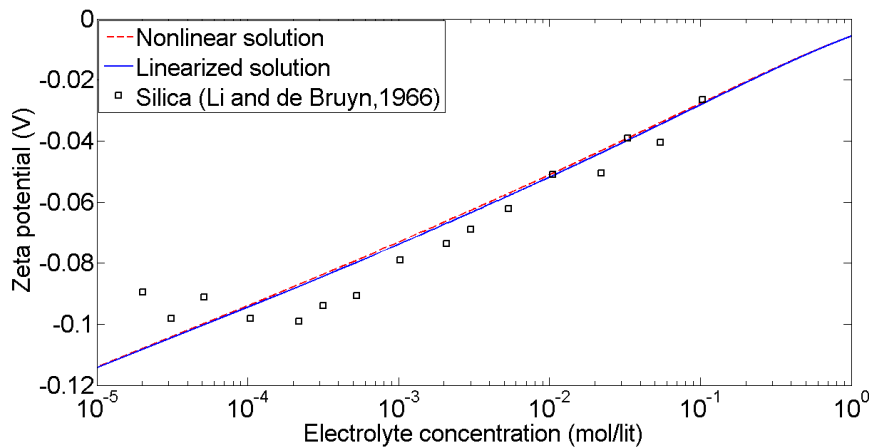
(b) T = 23°C, pH = 7, K_{Me} = $10^{-7.5}$, $K_{(-)}$ = $10^{-8.0}$, Γ_S^0 = 10×10^{18} site/m^2 and χ_ζ = 2.4×10^{-10} m
(Experimental data obtained from Li and de Bruyn, 1966 [29]).

Figure 5. The zeta potential as a function of electrolyte concentration compared with experimental data from [28, 29] for silica.

Glover et al. [15] have compared the zeta potential as a function of electrolyte concentration predicted from the linearized solution to published experimental data for silica. They used the input parameters for modeling as: (1) T = 22.6°C, pH = 7, K_{Me} = $10^{-7.5}$, $K_{(-)}$ = $10^{-8.4}$, Γ_S^0 = 10×10^{18} site/m^2 and χ_ζ = 2.4×10^{-10} m for the experimental data obtained from [28] (see Fig. 5a); (2) T = 23°C, pH = 7, K_{Me} = $10^{-7.5}$, $K_{(-)}$ = $10^{-8.0}$, Γ_S^0 = 10×10^{18} site/m^2 and χ_ζ = 2.4×10^{-10} m for the experimental data obtained from [29] (see Fig. 5b). The same input parameters are used in this work to compare the

experimental data to those predicted from the nonlinear solution (see the dashed lines in Fig. 5). It is seen that the theoretical results obtained from the linearized and nonlinear solutions are in very good agreement with each other for pH = 7 and $\chi_\zeta = 2.4 \times 10^{-10}$ m as stated above. Additionally, they are also in agreement with the general trend in the experimentally derived zeta-potential values from [28, 29] (see symbols).

4. Conclusions

The comparison between the linearized and nonlinear PB solutions has been performed for silica surfaces. It is found that the linearized solution always overestimates the absolute value of the electric potential in the EDL as well as the zeta potential. For a small magnitude of the surface potential ($|\varphi_d| \leq 25$ mV), the linearized PB solution could be used to predict the electric potential distribution in the EDL instead of the more complicated nonlinear PB solution. It is also shown that the degree of deviation between the linearized and nonlinear solution in determining the zeta potential strongly depends on electrolyte concentration, fluid pH and shear plane distance. At a given electrolyte concentration, the zeta potential computed from the linearized PB solution closely matches with that computed from the nonlinear solution for the fluid pH = 5 - 8 that is normally encountered in published experimental data and the shear plane distance of 2.4×10^{-10} m. Therefore, the solution of linearized PB equation can be used to calculate the zeta potential under that condition. This is validated by comparing the linearized and nonlinear solutions with experimental data in literature. In particularly, if the shear distance is taken as 2.4×10^{-9} m and the fluid pH is larger than 8, the nonlinear PB solution needs to be taken into account to calculate the zeta potential.

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