

Electric double layers interactions under condition of variable dielectric permittivity

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Abstract. In this paper, a theoretical method has been developed for the electric double layer interaction under condition of the variable dielectric permittivity of water. Using Poisson-Boltzmann equation (PBE), for one plate and two plates having similar or dissimilar constant charge or constant potential, we have investigated the electric double layer potential, its gradient and the disjoining pressure as well as the effect of variation of dielectric permittivity on these parameters. It has been assumed that plates are separated by a specific distance and contain a liquid solution in between. It is shown that reduction of the dielectric permittivity near the interfaces results in compression of electric double layers and affects the potential and its gradient which leads to a decreased electrostatic repulsion. In addition, it is shown that variation of dielectric permittivity in the case of higher electrolyte concentration, leads to a greater change in potential distribution between two plates.

Keywords: electric double layer; dielectric permittivity; poisson-boltzmann equation.

1. Introduction

Phenomena occurring in between the interface of solid and an electrolyte solution is of interest in nanotechnology, physics and chemistry. In particular the electric double layer (EDL) interaction between charged surfaces in liquids and electrolytes is of prime interest in intermolecular force studies. The theoretical basis describing such interactions is the well-known Poisson-Boltzmann equation (PBE) (Israelachvili 1991). In principle, the general PBE is a second-order non-linear differential equation and could not be solved analytically. However, several methods have been proposed for solving this problem (Hogg *et al.* 1966, Usui 1973, Chan *et al.* 1976, Chan *et al.* 1980, McCormack *et al.* 1995, Chan 2002, Zhang *et al.* 2004, Zhang *et al.* 2006). These methods are based on the linearized and nonlinear version of PBE and take into account constant potential and charge surfaces either for one plate or for two plates containing electric double layers. However, the methods presented in (Usui 1973, Chan *et al.* 1976, Chan *et al.* 1980, McCormack *et al.* 1995, Chan 2002) are only applicable to situation where surface charges are low, surfaces are identical and/or electrolytes are symmetric. To overcome the above mentioned limitations (Zhang *et al.* 2004, Zhang *et al.* 2006) calculated the EDL using one-dimensional PBE. Their solution is applicable to

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any electrolytes or mixture of electrolytes with similar/dissimilar surfaces. Although in general a three dimensional PBE is necessary to calculate the electric double layer force between parallel plates, however three-dimensional PBE can be transformed to one-dimensional PBE to speed up calculations (Stankovich and Carnie 1996). In general, when the local curvature of the plate is large in comparison with the Debye length, one-dimensional PBE gives adequate accuracy. In this case a potential distribution changes with distance between plates in one axis is more significant in comparison with its changes across the other axes. However, when the size of the plates is reduced and becomes comparable with the Debye length, one-dimensional PBE loses its accuracy and using three-dimensional PBE to model the EDL becomes necessary. In addition linearized version of PBE has acceptable accuracy only for small voltages (less than 40 (mV)) (Stankovich and Carnie 1996).

One of the most interesting phenomena in electric double layer interaction occurs when a significant reduction of water density exists near a hydrophobic surface. The density of water may change over a region with a width equal to several nanometers. The value of local density can be lower than its bulk value by tens of percents (Mezger *et al.* 2006). Under specific conditions the local value of the density may drop almost to zero (Doshi *et al.* 2005). The water viscosity reduces near hydrophobic surfaces. Furthermore temperature affects water viscosity (Voznyj and Churaev 1977). In addition, it has been found that structural changes of water in boundary layers and thin pores, affect its dielectric permittivity (Churaev 1990). Moreover, the reduction of dielectric permittivity of liquid leads to a decrease in liquid viscosity (Mishchuk 2008). In this paper we intend to study the effect of changes in permittivity on the electric double layer interaction. Due to insufficient knowledge of the way dielectric permittivity changes in a liquid near a hydrophobic surface we will simplify the problem by considering that changes only occur in the diffusion layer of the double layer and by assuming that liquid properties change stepwise (Mishchuk 2008).

In section II, based on the Poisson-Boltzmann equation, for a separate electric double layer with constant potential and constant charge surface, the effect of stepwise changes of the dielectric permittivity on the EDL potential, electric field and disjoining pressure is investigated. In section III, this effect is analyzed for the electric double layers with constant surface potential and surface charge, when there are two symmetric flat plates with similar charge or potential. The same study is carried for the case of asymmetric flat plates. In section VI, disjoining pressure of interaction is studied and finally, conclusions are given in section V.

2. Separate electric double layer under condition of variable dielectric permittivity

In this section, the analysis will be limited to the case of a univalent electrolyte, with constant surface potential and charge, and a stepwise change in dielectric permittivity. First, for the case of constant potential the one dimensional PBE (Lyklema 2005) which describes the electric potential is divided into two equations, one for the $0 \leq x \leq h_1$ interval and the other for $h_1 < x \leq \infty$

$$\frac{d^2 \psi_1(x)}{dx^2} - \frac{z^2 e^2 \rho_0}{\varepsilon_1 \varepsilon_0 k_B T} \psi_1(x) = 0 \quad (1)$$

$$\frac{d^2 \psi_2(x)}{dx^2} - \frac{z^2 e^2 \rho_0}{\varepsilon_2 \varepsilon_0 k_B T} \psi_2(x) = 0 \quad (2)$$

With the following conditions

$$\psi_1(0) = \psi_0 \quad (3)$$

$$\lim_{x \rightarrow \infty} \psi_2(x) = 0 \quad (4)$$

$$\psi_1(h_1) = \psi_2(h_1) \quad (5)$$

$$\varepsilon_1 \frac{d\psi_1(h_1)}{dx} = \varepsilon_2 \frac{d\psi_2(h_1)}{dx} \quad (6)$$

Where h_1 is the position at which the dielectric permittivity is changed. In this case, there are two inverse Debye lengths

$$k_1 = \sqrt{\frac{z^2 e^2 \rho_0}{\varepsilon_1 \varepsilon_0 k_B T}}, \quad k_2 = \sqrt{\frac{z^2 e^2 \rho_0}{\varepsilon_2 \varepsilon_0 k_B T}} \quad (7)$$

Where $e(C)$ is the elementary charge, k_B is the Boltzmann constant, $T(K)$ is the absolute temperature, z is the valence of ion, $\rho_0(mol/L)$ is the concentration of the electrolyte, ε_0 is the dielectric permittivity of the vacuum, ε_1 and ε_2 are the relative permittivity and $\psi_0(V)$ is the surface potential of the isolated double electrical layer.

The solution is

$$\psi_1(x) = A e^{k_1 x} + B e^{-k_1 x} \quad (8)$$

$$\psi_2(x) = C e^{-k_2 x} \quad (9)$$

Where

$$A = \frac{\psi_0 (\varepsilon_1 k_1 - \varepsilon_2 k_2) e^{-k_1 h_1}}{(\varepsilon_1 k_1 + \varepsilon_2 k_2) e^{k_1 h_1} + (\varepsilon_1 k_1 - \varepsilon_2 k_2) e^{-k_1 h_1}} \quad (10)$$

$$B = \frac{\psi_0 (\varepsilon_1 k_1 + \varepsilon_2 k_2) e^{k_1 h_1}}{(\varepsilon_1 k_1 + \varepsilon_2 k_2) e^{k_1 h_1} + (\varepsilon_1 k_1 - \varepsilon_2 k_2) e^{-k_1 h_1}} \quad (11)$$

$$C = \frac{2 \psi_0 \varepsilon_1 k_1 e^{k_2 h_1}}{(\varepsilon_1 k_1 + \varepsilon_2 k_2) e^{k_1 h_1} + (\varepsilon_1 k_1 - \varepsilon_2 k_2) e^{-k_1 h_1}} \quad (12)$$

Second, consider the case of a univalent electrolyte with constant surface charge and a stepwise change in dielectric permittivity. Here again the one dimensional PBE which describes the electric potential is given by Eq. (1) for the $0 \leq x \leq h_1$ interval and Eq. (2) for the $h_1 < x \leq \infty$ interval. The relevant boundary conditions are now

$$\frac{d\psi_1(x)}{dx} = \frac{-\sigma_0}{\varepsilon_1 \varepsilon_0} \quad (13)$$

$$\psi_1(h_1) = \psi_2(h_1) \quad (14)$$

$$\varepsilon_1 \frac{d\psi_1(h_1)}{dx} = \varepsilon_2 \frac{d\psi_2(h_1)}{dx} \quad (15)$$

$$\lim_{x \rightarrow \infty} \frac{d\psi_2(x)}{dx} = 0 \quad (16)$$

Where σ_0 is the charge density.

The electric potential is obtained as

$$\psi_1(x) = A e^{k_1 x} + B e^{-k_1 x} \quad (17)$$

$$\psi_2(x) = C e^{-k_2 x} \quad (18)$$

Where inverse Debye lengths are given in Eq. (7) and

$$A = \frac{(\sigma_0 / \varepsilon_0) e^{-k_1 h_1} - (\varepsilon_2 k_2 \sigma_0 e^{-k_1 h_1}) / \varepsilon_0 \varepsilon_1 k_1}{\varepsilon_1 k_1 (e^{k_1 h_1} - e^{-k_1 h_1}) + \varepsilon_2 k_2 (e^{k_1 h_1} + e^{-k_1 h_1})} \quad (19)$$

$$B = A + \frac{\sigma_0}{\varepsilon_0 \varepsilon_1 k_1} \quad (20)$$

$$C = A (e^{(k_1 + k_2) h_1} + e^{(k_2 - k_1) h_1}) + \frac{\sigma_0 e^{(k_2 - k_1) h_1}}{\varepsilon_0 \varepsilon_1 k_1} \quad (21)$$

Figs. 1-3 represent the numerical results for $\psi(x)$ and $d\psi/dx$ when $\varepsilon_1 = \varepsilon_2$ and $\varepsilon_1 \neq \varepsilon_2$ with different values of electrolyte concentration ρ_0 for constant surface potential. In this numerical analysis, the dielectric permittivity was assumed $\varepsilon_2 = 80$, $\psi_0 = 10(mV)$, $h_1 = 2(nm)$, and the ratio of $\varepsilon_1 / \varepsilon_2$ was varied from 1 to .2. Also, the potential and its gradient are normalized by $\psi_0 = 10(mV)$. The obtained results show that when the dielectric permittivity changes stronger, the potential stronger reduces and at the same time the double electrical layer is compressed. Also,

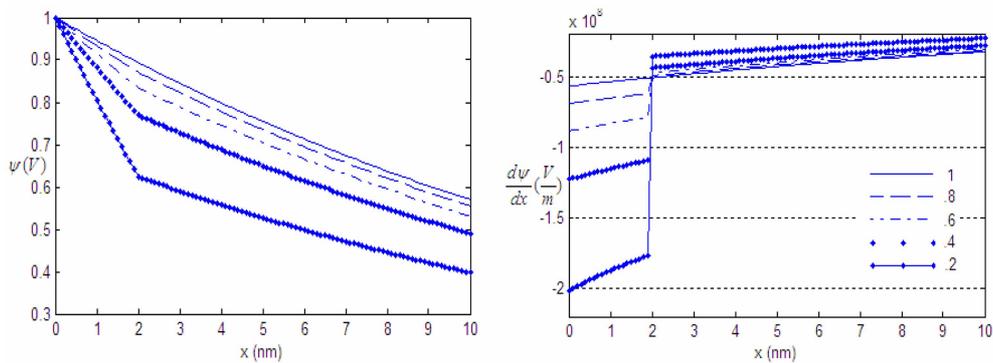


Fig. 1 Dependence of the potential and its gradient on the distance from surface and different values of $\varepsilon_1 / \varepsilon_2$ as depicted in the figure when $\rho_0 = 0.001$ in the case of constant surface potential

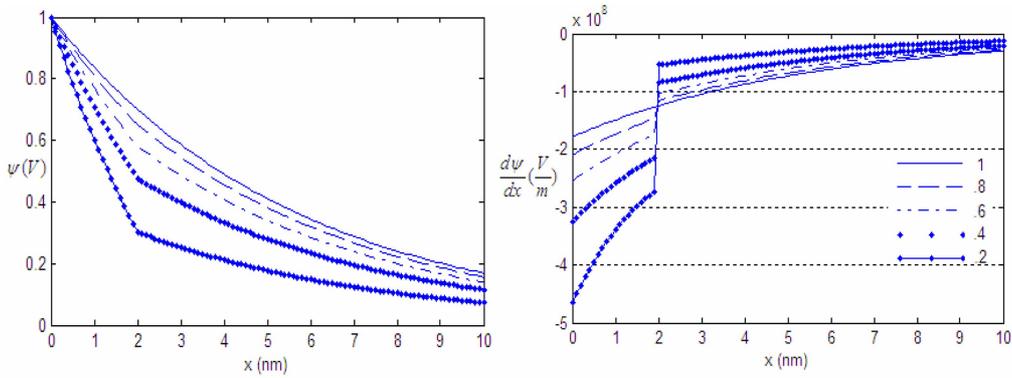


Fig. 2 Dependence of the potential and its gradient on the distance from surface and different values of ϵ_1 / ϵ_2 as depicted in the figure when $\rho_0 = 0.01$ in the case of constant surface potential

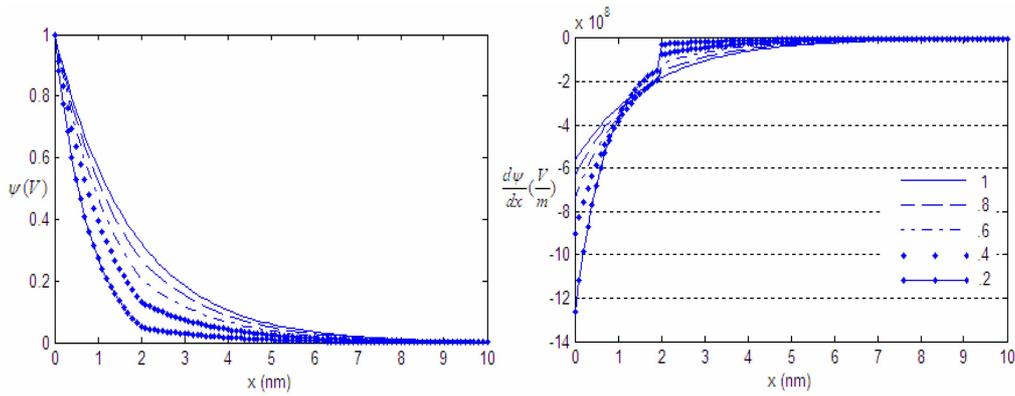


Fig. 3 Dependence of the potential and its gradient on the distance from surface and different values of ϵ_1 / ϵ_2 as depicted in the figure when $\rho_0 = 0.1$ in the case of constant surface potential

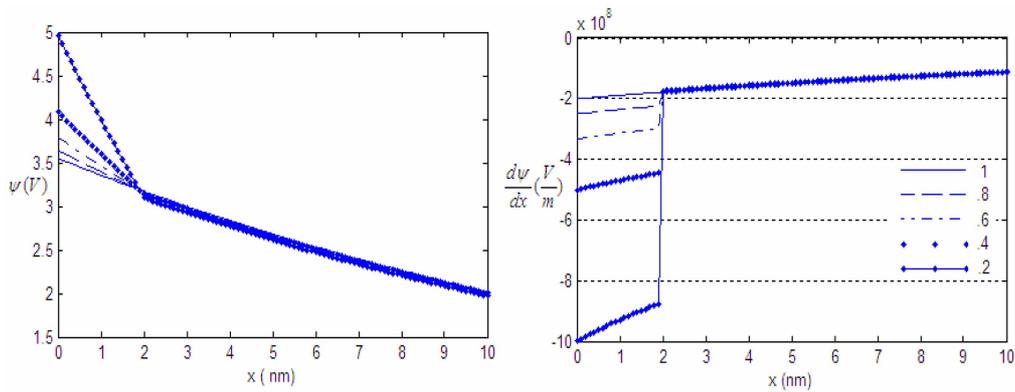


Fig. 4 Dependence of the potential and its gradient on the distance from surface and different values of ϵ_1 / ϵ_2 as depicted in the figure when $\rho_0 = 0.001$ in the case of constant surface charge

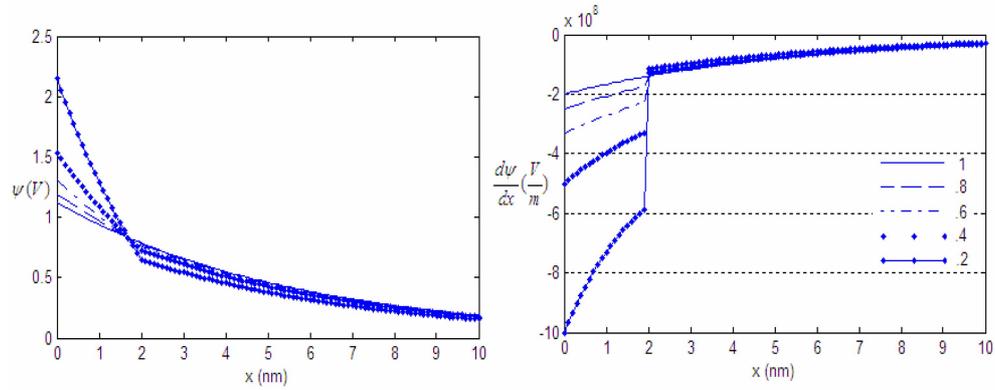


Fig. 5 Dependence of the potential and its gradient on the distance from surface and different values of $\varepsilon_1 / \varepsilon_2$ as depicted in the figure when $\rho_0 = 0.01$ in the case of constant surface charge

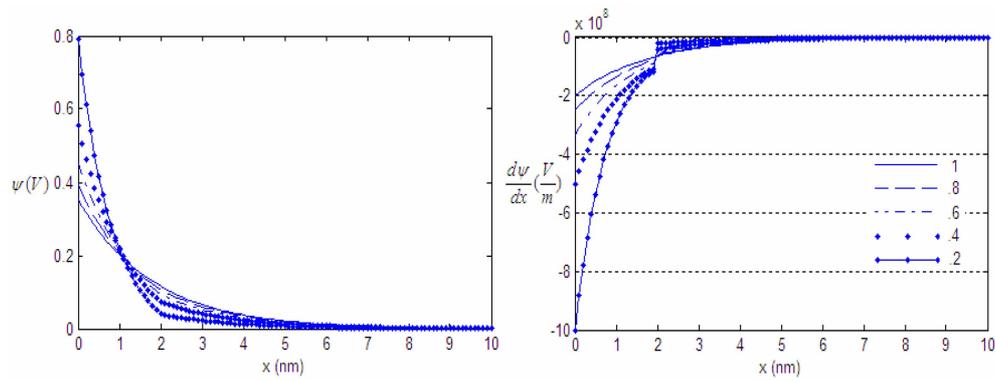


Fig. 6 Dependence of the potential and its gradient on the distance from surface and different values of $\varepsilon_1 / \varepsilon_2$ as depicted in the figure when $\rho_0 = 0.1$ in the case of constant surface charge

note that as electrolyte concentration is increased, the variation of dielectric permittivity effects the potential distribution more drastically.

In Figs. 4-6, the numerical results obtained for constant surface charge are shown. Similar to the previous test, In this case, potential and its gradient are normalized by $\psi_0 = 10(mV)$ and other parameters are equal to the first case. In this test, besides of the effect of dielectric variation on the potential distribution, we see that as the $\varepsilon_1 / \varepsilon_2$ ratio is reduced, the surface potential is enhanced. Also, as depicted in the potential distribution curves, when $x = 0$ lower concentration leads to a higher potential. On the other hand, in contrast, the variation of potential distribution is lower when the concentration is low. This trend is expected when considering Eqs. (7) and (17)-(21). Finally, as the distance from the surface is increased both potential and its gradient approach zero. For the case of potential gradient, we can see that for both constant surface potential and charge, reduction of $\varepsilon_1 / \varepsilon_2$ ratio leads to significant variation in the potential gradient distribution. Also, in the case of constant surface potential, higher electrolyte concentration, leads to the higher magnitude of potential gradient. This is also expected from Eqs. (8), (9) taking into account (7), (10)-(12). In the case of constant charge surface, as depicted in Figs. 4-6, variation of electrolyte concentration affect

the compression of potential gradient distribution, but it has no effect on the magnitude of the potential gradient at $x = 0$.

3. Interacting electrical double layers under condition of variable dielectric permittivity

In this section three cases are considered. First we investigate the flat symmetric electric double layers with constant surface potentials. Next the flat symmetric electric double layers with constant surface charges is considered and finally the asymmetric electric double layers with different constant surface potentials are studied.

First, the one dimensional PBE which describes the electric potential is divided into three equations, for $0 \leq x \leq h_1$, $h_1 < x \leq D - h_1$ and $D - h_1 \leq x \leq D$ interval

$$\frac{d^2 \psi_1(x)}{dx^2} - \frac{z^2 e^2 \rho_0}{\varepsilon_1 \varepsilon_0 k_B T} \psi_1(x) = 0 \quad (22)$$

$$\frac{d^2 \psi_2(x)}{dx^2} - \frac{z^2 e^2 \rho_0}{\varepsilon_2 \varepsilon_0 k_B T} \psi_2(x) = 0 \quad (23)$$

$$\frac{d^2 \psi_3(x)}{dx^2} - \frac{z^2 e^2 \rho_0}{\varepsilon_1 \varepsilon_0 k_B T} \psi_3(x) = 0 \quad (24)$$

The boundary conditions are

$$\psi_1(0) = \psi_0 \quad (25)$$

$$\psi_3(D) = \psi_0 \quad (26)$$

$$\psi_1(h_1) = \psi_2(h_1) \quad (27)$$

$$\varepsilon_1 \frac{d\psi_1(h_1)}{dx} = \varepsilon_2 \frac{d\psi_2(h_1)}{dx} \quad (28)$$

$$\psi_2(D - h_1) = \psi_3(D - h_1) \quad (29)$$

$$\varepsilon_2 \frac{d\psi_2(D - h_1)}{dx} = \varepsilon_1 \frac{d\psi_3(D - h_1)}{dx} \quad (30)$$

$$\frac{d\psi_2(D/2)}{dx} = 0 \quad (31)$$

The solution of Eqs. (22)-(24) with conditions given in Eqs. (25)-(31) is

$$\psi_1(x) = A e^{-k_1 x} + B e^{k_1 x} \quad (32)$$

$$\psi_2(x) = C e^{-k_2 x} + D e^{k_2 x} \quad (33)$$

$$\psi_3(x) = E e^{-k_1 x} + F e^{k_1 x} \quad (34)$$

Where inverse Debye lengths are determined by Eq. (7) and

$$A = \psi_0 \frac{\beta_1}{\beta_2} \quad (35)$$

$$B = \psi_0 - A \quad (36)$$

$$C = \frac{A[e^{k_1 h_1} - e^{-k_1 h_1}] + \psi_0 e^{k_1 h_1}}{[e^{k_2 h_1} + e^{k_2(D-h_1)}]} = \frac{E[e^{k_1(D-h_1)} - e^{k_1(D+h_1)}] + \psi_0 e^{k_1 h_1}}{[e^{k_2(D-h_1)} + e^{k_2 h_1}]} \quad (37)$$

$$D = C e^{k_2 D} \quad (38)$$

$$E = \psi_0 \frac{\beta_3}{\beta_4} \quad (39)$$

$$F = \psi_0 e^{k_1 D} - E e^{2k_1 D} \quad (40)$$

$$\beta_1 = \varepsilon_1 k_1 e^{-k_1 h_1} + \varepsilon_2 k_2 e^{-k_1 h_1} \frac{(e^{k_2 h_1} - e^{k_2(D-h_1)})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (41)$$

$$\beta_2 = \varepsilon_1 k_1 (e^{k_1 h_1} + e^{-k_1 h_1}) + \varepsilon_2 k_2 \frac{(e^{k_2(D-h_1)} - e^{k_2 h_1})(e^{k_1 h_1} - e^{k_2 h_1})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (42)$$

$$\beta_3 = \varepsilon_1 k_1 e^{k_1 h_1} + \varepsilon_2 k_2 e^{k_1 h_1} \frac{(e^{k_2(D-h_1)} - e^{k_2 h_1})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (43)$$

$$\beta_4 = \varepsilon_1 k_1 (e^{k_1(D-h_1)} + e^{k_1(D+h_1)}) + \varepsilon_2 k_2 \frac{(e^{k_2 h_1} - e^{k_2(D-h_1)})(e^{k_1(D-h_1)} - e^{k_2(D+h_1)})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (44)$$

Eqs. (32)-(44) are used to obtain the results of numerical analysis for the potential distribution between two flat plates and its gradient those are illustrated in Figs. 7-9. It may be concluded that as $\varepsilon_1 / \varepsilon_2$ is decreased from 1 to 0.2, the electric double layer is further compressed and the

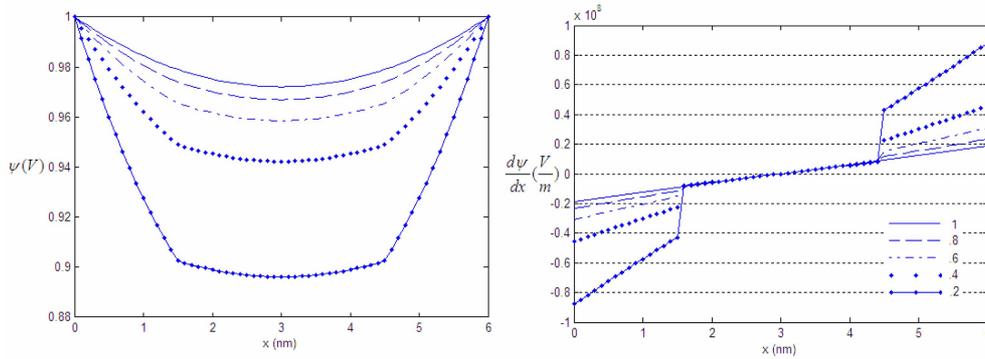


Fig. 7 Potential distribution and its gradient in the gap between the two charged plates at different $\varepsilon_1 / \varepsilon_2$ and $\rho_0 = 0.001$

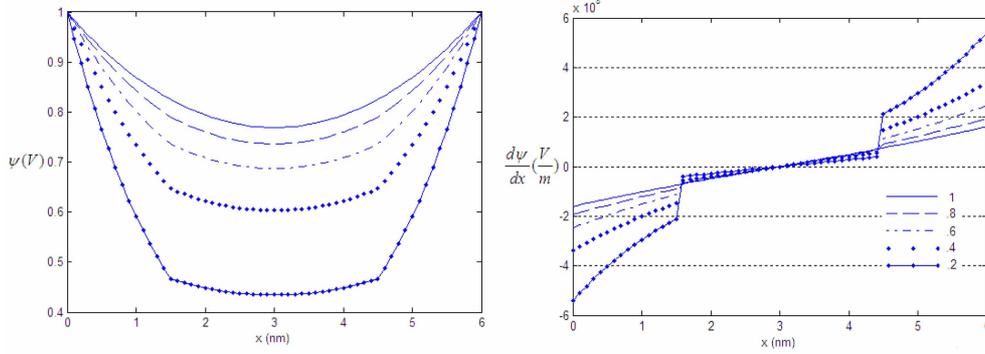


Fig. 8 Potential distribution and its gradient in the gap between the two charged plates at different $\varepsilon_1 / \varepsilon_2$ and $\rho_0 = 0.01$

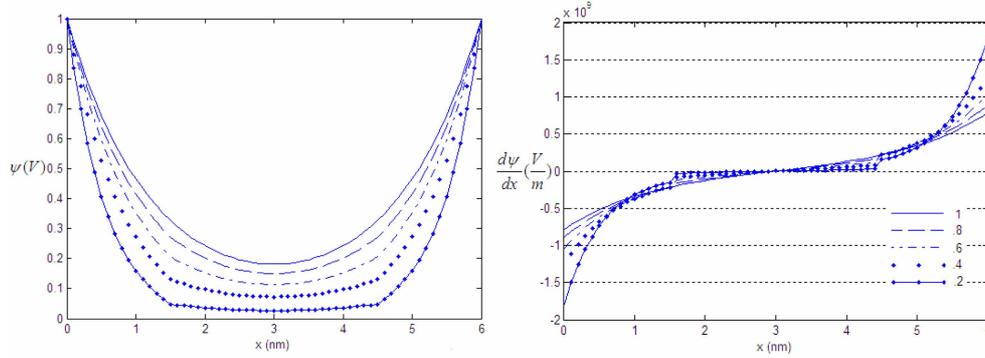


Fig. 9 Potential distribution and its gradient in the gap between the two charged plates at different $\varepsilon_1 / \varepsilon_2$ and $\rho_0 = 0.1$

potential at the middle of the two plates is reduced. Also, an increase in electrolyte concentration results in increase in the variation of potential distribution between two plates. Furthermore, as $\varepsilon_1 / \varepsilon_2$ is reduced the potential gradient is increased at each plate. In this numerical analysis, the dielectric permittivity is $\varepsilon_2 = 80$, $h_1 = 1.5(\text{nm})$, $\psi_0 = 10(\text{mV})$ and the potential and its gradient are normalized by $\psi_0 = 10(\text{mV})$.

Now, consider the case where a symmetric structure is employed with the constant charge at both surfaces. Hence, the one dimensional PBE which describes the electric potential is divided into three Eqs. (22)-(24). In this case the boundary conditions are

$$\frac{d\psi_1(0)}{dx} = \frac{-\sigma_0}{\varepsilon_0 \varepsilon_1} \quad (45)$$

$$\frac{d\psi_3(D)}{dx} = \frac{\sigma_0}{\varepsilon_0 \varepsilon_1} \quad (46)$$

$$\psi_1(h_1) = \psi_2(h_1) \quad (47)$$

$$\varepsilon_1 \frac{d\psi_1(h_1)}{dx} = \varepsilon_2 \frac{d\psi_2(h_1)}{dx} \quad (48)$$

$$\psi_2(D - h_1) = \psi_3(D - h_1) \quad (49)$$

$$\varepsilon_2 \frac{d\psi_2(D - h_1)}{dx} = \varepsilon_1 \frac{d\psi_3(D - h_1)}{dx} \quad (50)$$

$$\frac{d\psi_2(D/2)}{dx} = 0 \quad (51)$$

The solutions of Eq. (22) with condition given in Eqs. (45)-(51) are given by Eqs. (32)-(34) with

$$A = \sigma_0 \frac{\beta_1}{\beta_2} \quad (52)$$

$$B = \frac{\sigma_0}{k_1 \varepsilon_0 \varepsilon_1} + A \quad (53)$$

$$C = \frac{A[e^{k_1 h_1} - e^{-k_1 h_1}] + \frac{\sigma_0 e^{-k_1 h_1}}{k_1 \varepsilon_0 \varepsilon_1}}{[e^{k_2 h_1} + e^{k_2(D-h_1)}]} = \frac{E[e^{k_1(D-h_1)} - e^{k_1(D+h_1)}] + \frac{\sigma_0 e^{-k_1 h_1}}{k_1 \varepsilon_0 \varepsilon_1}}{[e^{k_2(D-h_1)} + e^{k_2 h_1}]} \quad (54)$$

$$D = C e^{k_2 D} \quad (55)$$

$$E = \sigma_0 \frac{\beta_3}{\beta_4} \quad (56)$$

$$F = \psi_0 e^{k_1 D} - E e^{2k_1 D} \quad (57)$$

$$\beta_1 = \frac{\sigma_0}{\varepsilon_0} e^{-k_1 h_1} + \frac{\sigma_0 \varepsilon_2 k_2 e^{-k_1 h_1} (e^{k_2 h_1} - e^{k_2(D-h_1)})}{k_1 \varepsilon_0 \varepsilon_1 (e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (58)$$

$$\beta_2 = \varepsilon_1 k_1 (e^{k_1 h_1} - e^{-k_1 h_1}) + \varepsilon_2 k_2 \frac{(e^{k_2(D-h_1)} - e^{k_2 h_1})(e^{k_1 h_1} + e^{-k_1 h_1})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (59)$$

$$\beta_3 = \frac{\sigma_0}{\varepsilon_0} e^{k_1 h_1} - \frac{\sigma_0 \varepsilon_2 k_2 e^{k_1 h_1} (e^{k_2 h_1} - e^{k_2(D-h_1)})}{k_1 \varepsilon_0 \varepsilon_1 (e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (60)$$

$$\beta_4 = \varepsilon_1 k_1 (e^{k_1(D-h_1)} + e^{k_1(D+h_1)}) - \varepsilon_2 k_2 \frac{(e^{k_2(D-h_1)} - e^{k_2 h_1})(e^{k_1(D-h_1)} - e^{k_1(D+h_1)})}{(e^{k_2 h_1} + e^{k_2(D-h_1)})} \quad (61)$$

Numerical result obtained for this case is given in Fig. 10. From this Fig. one can conclude that as the $\varepsilon_1 / \varepsilon_2$ is decreased the potential is reduced at the middle however it is increased at each of plates surfaces. Note that in this test similar to previous tests, the potential and its gradient are normalized by $\psi_0 = 10(mV)$

Finally, we consider the asymmetric case for different constant surface potentials on two plates. Therefore, the one dimensional PBE which describes the electric potential is divided into two equations, namely (1) and (2) with the following conditions

$$\psi_1(0) = \psi_{10} \quad (62)$$

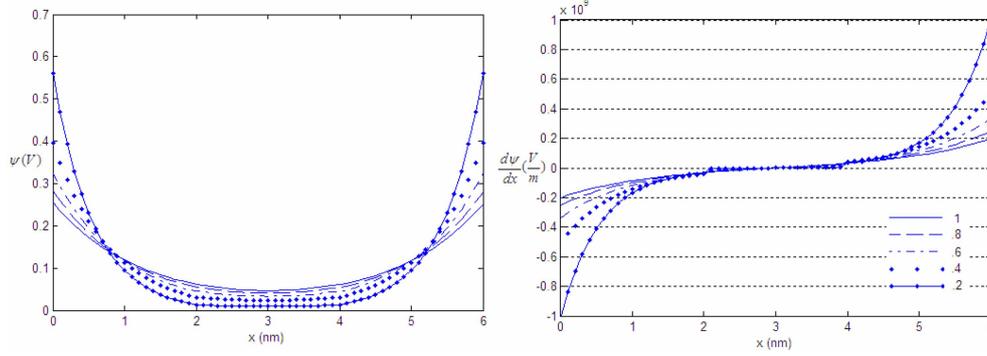


Fig. 10 Potential and electric field distribution in the gap between the two charged plates at $h_1 = 2$ nm when $\rho_0 = 0.1$ with different ratio of $\varepsilon_1 / \varepsilon_2$ as depicted

$$\psi_2(D) = \psi_{20} \quad (63)$$

$$\psi_1(h_1) = \psi_2(h_1) \quad (64)$$

$$\varepsilon_1 \frac{d\psi_1(h_1)}{dx} = \varepsilon_2 \frac{d\psi_2(h_1)}{dx} \quad (65)$$

h_1 is the position at which the dielectric permittivity is changed. In this case, there are two Debye inverse lengths given by Eq. (7). The solution of Eqs. (1)-(2) with conditions given in Eqs. (62)-(65) is

$$\psi_1(x) = Ae^{-k_1x} + Be^{k_1x} \quad (66)$$

$$\psi_2(x) = Ce^{-k_2x} + De^{k_2x} \quad (67)$$

Where

$$A = \frac{\beta_1 \alpha_4 - \beta_2 \alpha_2}{\alpha_1 \alpha_4 - \alpha_2 \alpha_3} \quad (68)$$

$$B = \psi_{10} - A \quad (69)$$

$$C = \frac{\beta_2 \alpha_1 - \beta_1 \alpha_3}{\alpha_1 \alpha_4 - \alpha_2 \alpha_3} \quad (70)$$

$$D = \psi_{20} e^{-k_2 D} - C e^{-2k_2 D} \quad (71)$$

$$\alpha_1 = e^{-k_1 h_1} - e^{k_1 h_1} \quad (72)$$

$$\alpha_2 = e^{k_2(h_1 - 2D)} - e^{-k_2 h_1} \quad (73)$$

$$\alpha_3 = -\varepsilon_1 k_1 (e^{-k_1 h_1} + e^{k_1 h_1}) \quad (74)$$

$$\alpha_4 = \varepsilon_2 k_2 (e^{-k_2 h_1} + e^{k_2(h_1 - 2D)}) \quad (75)$$

$$\beta_1 = \psi_{20} e^{-k_2(D-h_1)} - \psi_{10} e^{k_1 h_1} \tag{76}$$

$$\beta_2 = \varepsilon_2 k_2 \psi_{20} e^{-k_2(D-h_1)} - \psi_{10} \varepsilon_1 k_1 e^{k_1 h_1} \tag{77}$$

Using Eqs. (66)-(77), the results obtained for numerical calculation of the potential distribution in between two plates are depicted in Figs. 11-14. Note that such as previous cases, the potential and its gradient are normalized by $\psi_0 = 10(mV)$.

Figs. 11-12 show the effect of electrolyte concentration and the role of dielectric permittivity on potential distribution when the charges on both plates are of the same polarity but different in magnitude.

As depicted, upon the reduction of $\varepsilon_1 / \varepsilon_2$ value, the variations of potential distribution and potential gradient distribution, between two plates are increased.

On the other hand from Figs. 13-14, where the two plates poses charges with different polarity and magnitude a decrease in the ratio of $\varepsilon_1 / \varepsilon_2$ leads to a decrease in the potential between two plates.

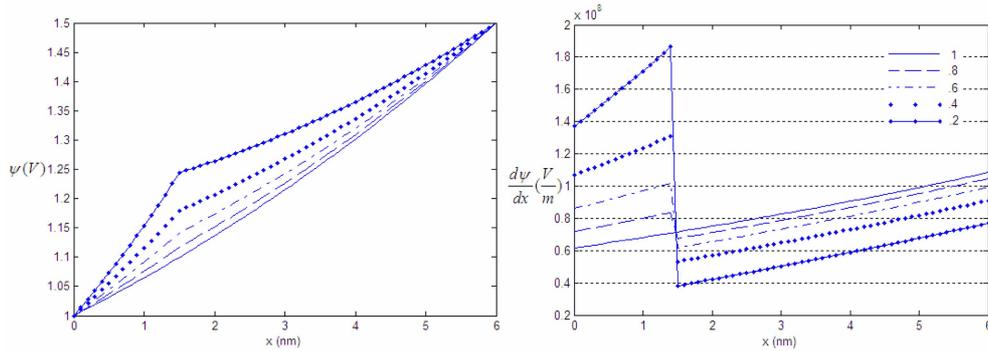


Fig. 11 Potential and electric field distribution in the gap between the two charged plates at $h_1 = 1.5$ nm and different values of $\varepsilon_1 / \varepsilon_2$ when $\rho_0 = 0.001$

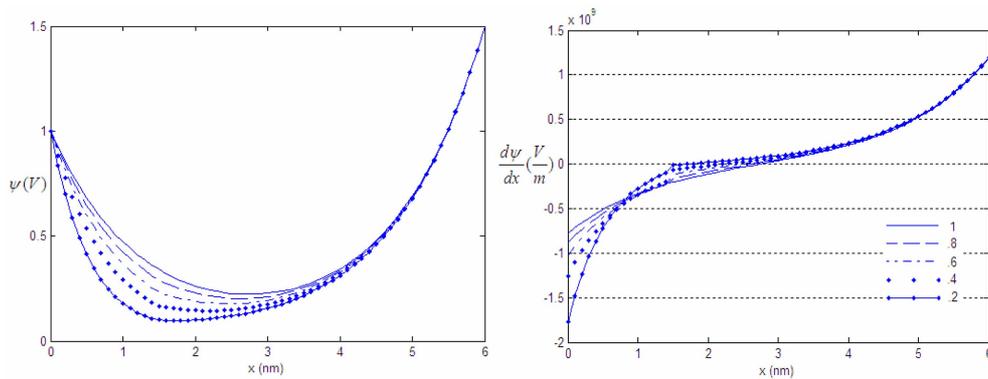


Fig. 12 Potential and electric field distribution in the gap between the two charged plates at $h_1 = 1.5$ nm and different values of $\varepsilon_1 / \varepsilon_2$ when $\rho_0 = 0.1$

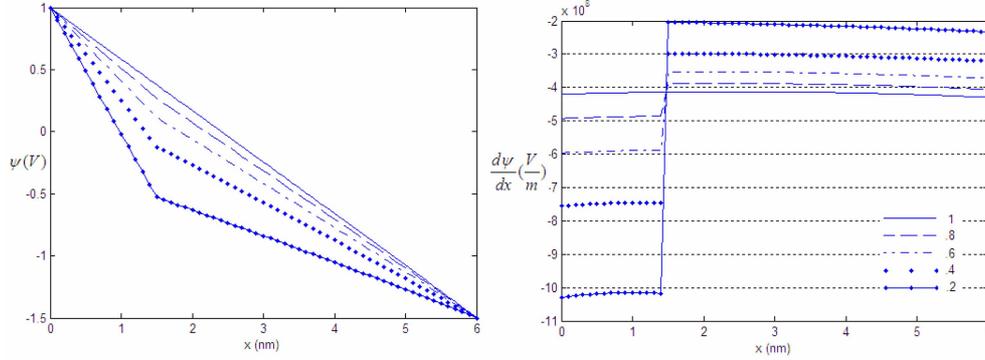


Fig. 13 Potential and electric field distribution in the gap between the two charged plates at $h_1 = 1.5$ nm and different values of $\varepsilon_1 / \varepsilon_2$ when $\rho_0 = 0.001$

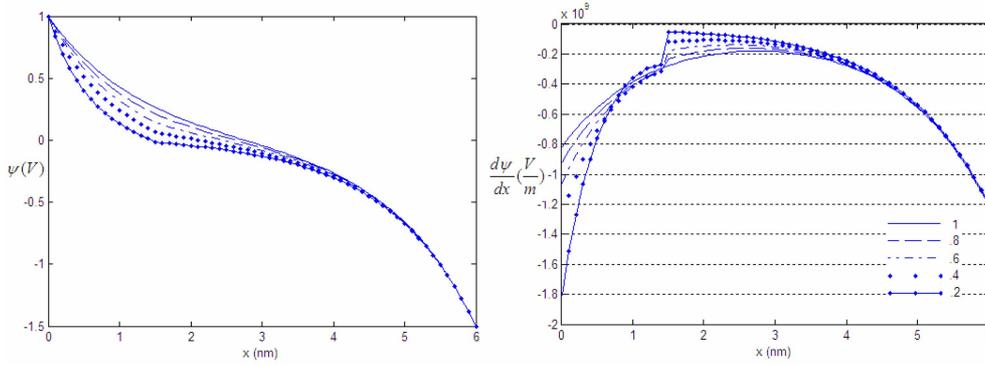


Fig. 14 Potential and electric field distribution in the gap between the two charged plates at $h_1 = 1.5$ nm and different values of $\varepsilon_1 / \varepsilon_2$ when $\rho_0 = 0.1$

4. Disjoining pressure of interaction under condition of variable dielectric permittivity

The pressure between two surfaces using Eq. (1) is given by

$$P(x) = - \int_0^{\psi(x)} \rho(\psi) d\psi - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\partial \psi(x)}{\partial x} \right)^2 \quad (78)$$

Substituting Eq. (2) in Eq. (46) we get

$$P(x) = \frac{\rho_0 k_B T}{\varepsilon \varepsilon_0} \left[\exp\left(\frac{-ze\psi(x)}{k_B T}\right) - 1 \right] - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\partial \psi(x)}{\partial x} \right)^2 \quad (79)$$

Positive P implies repulsion while a negative P represents attraction. The pressure acting on the electrolyte and the plate surfaces is uniform in between the two plates (independent of position x).

The results of numerical analysis for the disjoining pressure P as a function of $\varepsilon_1 / \varepsilon_2$ is given in Fig. 15. For simplicity all pressures are normalized by the value of the disjoining pressure P_0 at the constant dielectric permittivity of water $\varepsilon_1 = \varepsilon = 80$. These results are related to three different plates distances, 2 (nm), 6 (nm) and 16 (nm), respectively. As expected as the dielectric permittivity is reduced near the surface, disjoining pressure is also reduced.

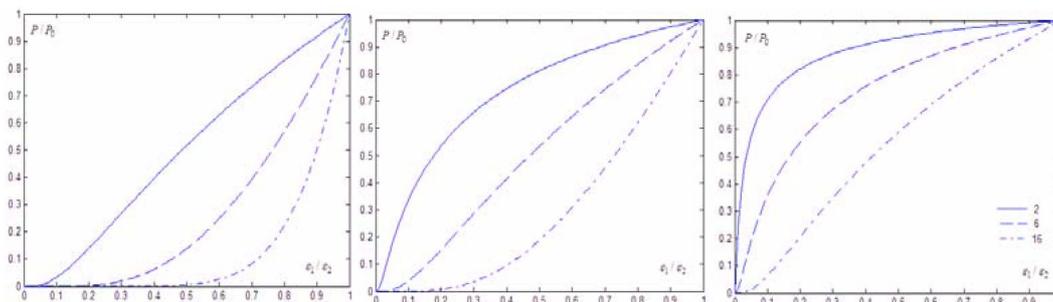


Fig. 15. Change of the disjoining pressure P/P_0 at variation of the ratio $\varepsilon_1/\varepsilon$ in the near-surface layers having different length as depicted in figure, $\varepsilon=80$ and different concentrations: 0.1 (mol/L) (left), 0.01 (mol/L) (middle) and 0.001 (mol/L) (right)

5. Conclusions

In this paper, we obtained general relationships which depict the impact of local values of dielectric permittivity on the structure of the separate electric double layer with constant surface potential and charge, also for similar constant surface potential and charge electric double layers and dissimilar constant surface potential of EDL and for two double electrical layers. It was shown that taking into account changes of the dielectric permittivity results in a very strong reduction of the electrostatic repulsion between the plates. In addition, electrolyte concentration has significant effect on the distribution of potential and its gradient between two plates in the case of varying dielectric permittivity. In other words, higher concentration of electrolyte and higher changes of dielectric permittivity, pronounces the variation of potential in between two surfaces.

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