

Excluded Volume Effect of Dipole Moment of Water Molecule on Electric Double Layer

Sin Jun Sik

In previous work [1–3] electrostatic properties of an electric double layer formed near a charged surface were studied by using a lattice statistical mechanical method. Within this approach, each particle in the solution occupies only one cell of a lattice with a proper lattice constant. For analytical simplicity, it is assumed that water molecules and ions are of the same size.

In this paper, we study properties of an electric double layer close to a plate charged surface by considering both water dipole moments and size effects of ions and water molecules.

The total free energy of the electrolyte solution can be written as follows. [1]

$$\begin{aligned} \frac{F}{kT} = & \frac{1}{8\pi l_B} \int (\Psi')^2 dV + \int \left[n_+(x) \ln \frac{n_+(x)}{n_0} + n_-(x) \ln \frac{n_-(x)}{n_0} \right] dV + \\ & + \int \left\langle n(x, \omega) \ln \frac{n(x, \omega)}{n_{0w}} \right\rangle_\omega dV + \lambda \int [n_s - \langle n(x, \omega) \rangle_\omega - n_+(x) - n_-(x)] dV \end{aligned} \quad (1)$$

where $\Psi' = e_0 \phi(x)/(kT)$ is the reduced electrostatic potential, $dV = Adx$ is the volume element with thickness dx and the area of the charged surface A . The first term in Eq. (1) is the energy of the electrostatic field and the second one is the free energy contribution of the positive and negative ions. The third one is the orientational contribution of water dipole moments to the free energy. n_+ and n_- are the number densities of counterions and coions, respectively. n_{0w} is the number density of water molecules in the bulk solution. The last term represents the constraint for orientation of the water dipoles.

In thermodynamic equilibrium, the number densities of ions and water molecules and the electrostatic potential near the charged surface are obtained by following expressions [1, 3].

$$n_s = n_+(x) + n_-(x) + n_w(x)$$

$$n_+(x) = \frac{n_0 e^{-e_0 \phi(x) \beta}}{n_0 e^{e_0 \phi(x) \beta} + n_0 e^{-e_0 \phi(x) \beta} + n_{0w} \left\langle e^{-\mathcal{P}_0 E \beta \cos \omega} \right\rangle_\omega} \quad (1)$$

$$n_-(x) = \frac{n_0 e^{e_0 \phi(x) \beta}}{n_0 e^{e_0 \phi(x) \beta} + n_0 e^{-e_0 \phi(x) \beta} + n_{0w} \left\langle e^{-\mathcal{P}_0 E \beta \cos \omega} \right\rangle_\omega} \quad (2)$$

$$n_w(x) = \frac{n_{0w} \left\langle e^{-\mathcal{P}_0 E \beta \cos \omega} \right\rangle_\omega}{n_0 e^{e_0 \phi(x) \beta} + n_0 e^{-e_0 \phi(x) \beta} + n_{0w} \left\langle e^{-\mathcal{P}_0 E \beta \cos \omega} \right\rangle_\omega} \quad (3)$$

The electrostatic potential can be determined by the modified Poisson-Boltzmann equation.

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = 2e_0 n_s n_0 \frac{\text{sh}[e_0 \phi(x) \beta]}{D[\phi(x), E(x)]} \quad (4)$$

$$\varepsilon_r = n^2 + n_s n_{0w} \frac{p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{F[\gamma p_0 E(x) \beta]}{D[\phi(x), E(x)] E(x)} \quad (5)$$

$$F(u) = [\text{ch}(u) - 1/u] \text{sh}(u)/u$$

$$D[\phi(x), E(x)] = 2n_0 \text{ch}[e_0 \phi(x) \beta] + \frac{n_{0w} \text{sh}[\gamma p_0 E(x) \beta]}{\gamma p_0 E(x) \beta}$$

The boundary condition at the charged surface is the below expression.

$$\phi'(x=0) = -\frac{1}{\varepsilon_0} \left(\sigma + n_s n_{0w} p_0 \frac{F(\gamma p_0 E(x) \beta)}{D[\phi(x), E(x)]} \Big|_{x=0} \right) \quad (6)$$

Since far away from the charged surface electric field strength vanishes, $\phi'(x \rightarrow \infty) = 0$. The dipole moment of a water molecule is $p_0 = 3.1\text{D}$ and the temperature of the solution is $T = 300\text{K}$. The size of a cell is $a = 0.3\text{nm}$. We solve the Poisson-Boltzmann equation by using the forth-order Runge-Kutta method.

The water dipole moments in the close vicinity of the charged surface are oriented towards the charged surface, whereas far away from the charged surface all orientations of water dipoles are equally probable.

As pointed out by Gongadze [3], due to the accumulation of counterions and the depletion of water molecules near the charged surface, the dielectric permittivity in the vicinity of the charged surface may be substantially changed. We consider how the decrease of the permittivity of electrolyte affects electric double layer capacitance.

For the surface charge density $\sigma = 0.2744\text{C/m}^2$ the relative number density of water molecules close to the charged surface is shown in Fig.1. The number density of water molecules first decreases with the increasing distance from the charged surface and reaches a minimum. It then increases and reaches a plateau value.

Fig. 2. shows the dependence of the surface charge density of the charged surface on the plate potential difference.

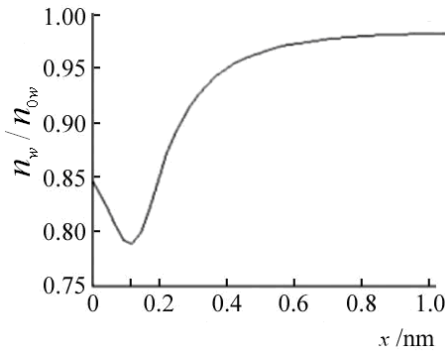


Fig. 1. The relative number density of water molecules versus the distance from the charged surface

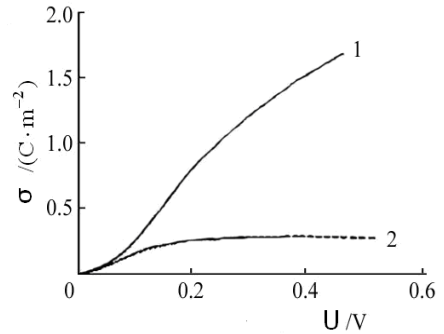


Fig. 2. The surface charge density of the charged surface versus the potential difference
1 and 2 stand for the case of the constant permittivity and the case of considering the excluded volume effect of water dipoles respectively

As shown in Fig. 2, in the case of water with constant permittivity the surface charge density of the charged surface first rapidly increases with increasing plate potential difference, whereas in the case when water dipole moments are considered the surface charge density is slowly increased.

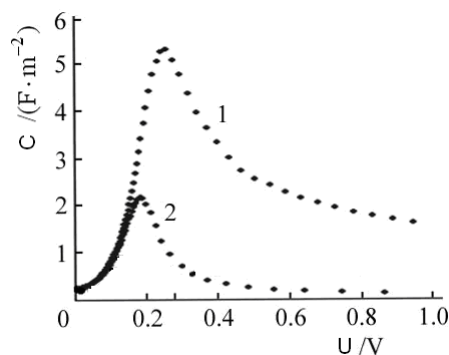


Fig. 3. The differential capacitance versus

the plate potential difference

1 and 2 stand for the case of the constant permittivity of water and the case of considering the excluded volume effect

The differential capacitance curve versus plate potential difference is depicted in Fig. 3.

As shown in Fig. 3, a characteristic humped shape of the double-layer capacitance curve exists for the two cases and in the case when water dipole moments are considered the magnitude and position of the maximum in the differential capacitance are smaller than the corresponding ones in the case of considering the orientational ordering of water dipole moments, respectively. Our results are in agreement with the experimental data on NaF electrolyte [4].

Conclusion

To conclude, we have found that in the case when the excluded volume effect of water dipole moments is considered, the double-layer capacitance and the surface charge density of charged surface become smaller than the corresponding ones in the case when dipole moments of water molecules aren't considered respectively.

References

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- [4] D. C. Grahame; *J. Am. Chem. Soc.*, **76**, 4819, 1954.