Decrease of permittivity of an electrolyte solution near a charged surface due to saturation and excluded volume effects

Ekaterina Gongadze, Aleš Iglič *

Laboratory of Biophysics, Faculty of Electrical Engineering, University of Ljubljana, Tržaška cesta 25, SI-1000 Ljubljana, Slovenia

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ABSTRACT

The dipole moment of a water molecule in liquid water differs from that of an isolated one because each molecule is further polarized by the electric field of its neighbours. In this work a formula for the spatial dependence of the relative permittivity of an electrolyte near a highly charged surface is obtained in which the mutual influence of the water molecules is taken into account by means of the cavity field. The orientational ordering of water dipoles is considered in the saturation regime. It is predicted that the relative permittivity of an electrolyte solution near the highly charged surface (i.e. in saturation regime) may be substantially decreased due to orientational ordering of water (saturation effect) and depletion of water molecules (excluded volume effect) due to accumulation of counterions.

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1. Introduction

The contact between a charged metallic or membrane surface and an electrolyte implies a particular spatial and orientational distributions of ion and water molecules near the charged surface [1–9] which is reflected in a decrease of permittivity for high enough surface charge densities of the charged surface [10–13].

In the absence of an explicit consideration of the orientational ordering of water molecules, the assumption of constant permittivity is largely a consequence of the constant number of water molecules in the Poisson–Boltzmann theory. Considering the orientational ordering of water, Outhwaite developed a modified PB theory of the electrical double layer composed of a mixture of hard spheres with point dipoles and finite sized ions [14,15]. The problem was also considered within lattice statistics [12,13,16] where the spatial dependence of the relative (effective) permittivity in the form

$$\varepsilon_r = 1 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \; \frac{\mathcal{F}(p_0 E\beta)}{E\,\mathcal{H}(\phi, E)}. \tag{1}$$

was derived, where

$$\mathcal{F}(u) = \mathcal{L}(u) \frac{\sinh u}{u}, \tag{2}$$

$$\mathcal{L}(u) = (\coth(u) - 1/u), \tag{3}$$

is the Langevin function and

$$\mathcal{H}(\phi, E) = 2n_0 \cosh(e_0 \phi\beta) + \frac{n_{0w}}{p_0 E\beta} \sinh(p_0 E\beta), \tag{4}$$

n_0 and n_{0w} are the bulk number densities of ions and water dipoles, respectively, $n_s = 1/a^3$ is the number density of lattice sites, a is the width of a single lattice site, p_0 the magnitude of a single water dipole moment in the electrolyte solution, E the magnitude of the electric field strength, ε_0 the permittivity of free space, $\beta = 1/kT$, kT the thermal energy and ϕ the electric potential.

In the approximation of a small electrostatic energy and small energy of dipoles compared to the thermal energy, i.e. small $e_0\phi\beta$ and small $p_0E\beta$, the relative permittivity within the Langevin–Bikerman model for finite sized ions (Eq. (1)) can be expanded into a Taylor series to get (assuming $n_s \approx n_{0w}$) [12]:

$$\varepsilon_r \cong 1 + \frac{n_{0w} p_0{}^2 \beta}{3\varepsilon_0} - \frac{n_{0w} p_0^2 \beta}{45\varepsilon_0}(p_0 E\beta)^2 - \frac{n_0 p_0^2 \beta}{3\varepsilon_0}(e_0 \phi\beta)^2. \tag{5}$$

Recently, Szalai et al. [17] published a mean spherical approximation (MSA) [18] based theory that is able to reproduce simulation results for the field dependence of the dielectric permittivity of a dipolar fluid in saturation regime [19]. The Langevin–Bikerman expression for ε_r (Eq. (1)) also takes into account the orientational ordering of water in the saturation regime (i.e. the saturation effect [19]) and the excluded volume effect. However the cavity and reaction fields were not taken into account [19–22]. As a consequence

* Corresponding author. Tel.: +386 1 4768 825; fax: +386 1 4768 850.
  E-mail address: ales.iglic@fe.uni-lj.si (A. Iglič).

the relative (effective) permittivity defined by Eq. (1) for zero electric field strength and zero potential, i.e. the bulk value of ε_r, [12]:

$$\varepsilon_r \cong 1 + \frac{n_{0w} p_0^2 \beta}{3\varepsilon_0}. \tag{6}$$

is equal to 78.5 for a magnitude of the effective dipole moment of water $p_0 = 4.79D$ [12] which is larger than the dipole moment of an isolated water molecule ($p_0 = 1.85D$) and also larger than the dipole moment of a water molecules in clusters ($p_0 = 2.7D$), and the dipole moment of an average water molecule in the bulk solution ($p_0 = 2.4 - 2.6D$) [23], since the cavity and reaction fields as well as correlations between water dipoles [22,24] are not explicitly taken into account.

In the past treatments of the cavity and reaction fields and the structural correlations between water dipoles in the Onsager [20], Kirkwood [21] and Fröhlich [22] models were limited to the case of small electric field strengths, i.e. they were far away from the saturation limit [17]. Later generalization of the Kirkwood–Onsager–Fröhlich theory in the saturation regime was performed by Booth [19]. However Booth's model does not consider the excluded volume effect in an electrolyte solution near the charged surface, as is taken into account in Eq.(1) within the Langevin–Bikerman model for the finite sized ions [12]. Booth's expression for the relative permittivity is therefore appropriate only for the Langevin Poisson–Boltzmann model for point-like ions [12].

Therefore in this work Eq.(1) is generalized by also taking into account the cavity field (but not also correlations between water dipoles) in the saturation regime at high electric field strengths important when considering an electrolyte solution in contact with highly charged implant and membrane surfaces [10,13].

2. Theory

In our model electronic polarization is taken into account considering a point-like and rigid (permanent) dipole located in the centre of a sphere with a volume equal to the average volume of a water molecule in the electrolyte solution. The permittivity of the sphere is n^2, where $n = 1.33$ is the optical refractive index of water. The relative (effective) permittivity of the electrolyte solution (ε_r) can then be expressed as:

$$\varepsilon_r = n^2 + \frac{|\mathbf{P}|}{\varepsilon_0 E}, \tag{7}$$

where $\mathbf{P}$ is the polarization vector due to orientation of permanent point-like water dipoles having dipole moment $\mathbf{p}$.

The external dipole moment ($\mathbf{p}_e$) of a point-like dipole at the centre of the sphere with permittivity n^2 can then be expressed in the form [22]: $\mathbf{p}_e = 3\mathbf{p}/(2+n^2)$, whence it follows $\mathbf{p} = (2+n^2)\mathbf{p}_e/3$. In our analysis short range interactions between the point-like rigid dipoles are neglected. The local electric field strength at the centre of the sphere with a permanent (rigid) point-like dipole is [22]:

$$\mathbf{E}_c = \frac{3\varepsilon_r}{2\varepsilon_r + n^2} \mathbf{E} + g\,\mathbf{p}, \tag{8}$$

where the first term represents the field inside a spherical cavity with dielectric permittivity n^2 embedded in a medium with permittivity ε_r, and the second term $g\,\mathbf{p}$ is the reaction-field acting on $\mathbf{p}$ (due to the dipole moment $\mathbf{p}$ of the point-like dipole itself). In the following, Eq.(8) is simplified (assuming $\varepsilon_r \gg n^2$):

$$\mathbf{E}_c = \frac{3}{2}\mathbf{E} + g\,\mathbf{p}. \tag{9}$$

The energy of the point like-dipole $\mathbf{p}$ in the local field $\mathbf{E}_c$ may be then written as:

$$W_i = -\mathbf{p}\cdot\mathbf{E}_c = -\mathbf{p}\cdot\left(\frac{3}{2}\mathbf{E} + g\,\mathbf{p}\right) = \gamma p_o\, E\cos(\omega) - g\,p_0^2, \tag{10}$$

where p_0 is the magnitude of the single water dipole moment $\mathbf{p}_e$, ω is the angle between the dipole moment vector $\mathbf{p}$ and the vector $-\mathbf{E}$, g $(2+n^2)^2/3^2 \to g$ and

$$\gamma = \frac{3}{2}\left(\frac{2+n^2}{3}\right). \tag{11}$$

In the case of an electrolyte solution in contact with a charged planar surface, the polarization $P(x)$ is then given by:

$$P(x) = n_w(x)\left(\frac{2+n^2}{3}\right)p_0\,\langle\cos(\omega)\rangle_B = -n_w(x)\left(\frac{2+n^2}{3}\right)p_0\mathcal{L}(\gamma p_0 E\beta), \tag{12}$$

where

$$\langle\cos\omega\rangle_B = \frac{\int\limits_0^{\pi} \cos\omega\,\exp\left(-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2\right)d\Omega}{\int\limits_0^{\pi} \exp\left(-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2\right)d\Omega} = -\mathcal{L}(\gamma p_0 E\beta), \tag{13}$$

and $d\Omega = 2\pi\sin\omega\,d\omega$ is an element of solid angle and x is the distance from the charged surface in the perpendicular direction. Since $\sigma < 0$, the projection of the polarization vector $\mathbf{P}$ on the x-axis points in the direction from the bulk to the charged surface and $P(x)$ is considered negative. Ion and water distribution functions can be written in the form:

$$n_+(x) = n_s\,\frac{n_0 e^{-e_0\phi\beta}}{n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w}\left\langle e^{-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2}\right\rangle_\omega}, \tag{14}$$

$$n_-(x) = n_s\,\frac{n_0 e^{e_0\phi\beta}}{n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w}\left\langle e^{-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2}\right\rangle_\omega}, \tag{15}$$

$$n_w(x) = n_s\,\frac{n_{0w}\left\langle e^{-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2}\right\rangle_\omega}{n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w}\left\langle e^{-\gamma p_o E\beta\cos(\omega) + \beta g\,p_0^2}\right\rangle_\omega}. \tag{16}$$

For simplicity we neglect $\beta\,g\,p_0^2$:

$$\left\langle e^{-\gamma p_o E\beta\cos(\omega) + \beta g p_0^2}\right\rangle_\omega = \frac{2\pi\int\limits_\pi^0 d(\cos\omega)e^{-\gamma p_o E\beta\cos(\omega)}}{4\pi} = \frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta}. \tag{17}$$

is the dipole Boltzmann factor after rotational averaging over all possible angles ω. Eqs. (14)–(17) can be rewritten as:

$$n_+(x) = n_0 e^{-e_0\phi\beta}\,\frac{n_s}{\mathcal{D}(\phi, E)}, \tag{18}$$

$$n_-(x) = n_0 e^{e_0\phi\beta}\,\frac{n_s}{\mathcal{D}(\phi, E)}, \tag{19}$$

$$n_w(x) = \frac{n_{0w}\,n_s}{\mathcal{D}(\phi, E)}\,\frac{1}{\gamma p_0 E\beta}\,\sinh(\gamma p_0 E\beta). \tag{20}$$

where:

$$\mathcal{D}(\phi, E) = 2n_0 \cosh(e_0\phi\beta) + \frac{n_{0w}}{\gamma p_0 E\beta} \sinh(\gamma p_0 E\beta). \tag{21}$$

Combining Eqs. (12) and (20) gives the polarization in the form:

$$P(x) = -\left(\frac{2+n^2}{3}\right) \frac{p_0 n_{0w}}{\mathcal{D}(\phi, E)} \frac{n_s}{\gamma p_0 E\beta} \sinh(\gamma p_0 E\beta)\mathcal{L}(\gamma p_0 E\beta). \tag{22}$$

Using the definition of $\mathcal{F}(u)$ (Eq.(2)), Eq.(22) reads:

$$P = -p_0 n_{0w} n_s \left(\frac{2+n^2}{3}\right) \frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)}. \tag{23}$$

Combining Eqs. (7) and (23) finally yields the relative (effective) permittivity of the electrolyte solution in contact with a charged surface:

$$\varepsilon_r = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \left(\frac{2+n^2}{3}\right) \frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)E}. \tag{24}$$

The average microscopic volume charge density $\rho(x)$ is the sum of the contributions of the local net ion charges and the dipole moments, represented by the polarization P (see for example [30,31]):

$$\rho(x) = e_0(n_+(x) - n_-(x)) - \frac{dP}{dx}. \tag{25}$$

Using Eq. (22) and distribution functions (18)–(19), the expression for the average microscopic volume charge density of the electrolyte solution (Eq. (25)) reads:

$$\rho(x) = -2e_0 n_0 n_s \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi, E)} + n_{0w} p_0 \, n_s \left(\frac{2+n^2}{3}\right) \frac{d}{dx}\left[\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)}\right]. \tag{26}$$

Inserting the volume charge density (26) into the Poisson Eq. (31)

$$\phi'' = -\frac{\rho(x)}{\varepsilon_0 n^2}, \tag{27}$$

where ϕ'' is the second derivative of the electric potential ϕ with respect to x, we get:

$$\phi'' = \frac{2e_0 n_0 n_s}{\varepsilon_0 n^2} \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi, E)} - \frac{n_{0w} n_s p_0}{\varepsilon_0 n^2}\left(\frac{2+n^2}{3}\right)\frac{d}{dx}\left[\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)}\right]. \tag{28}$$

Eq.(28)) can be rewritten in a more general form as (Appendix A):

$$\nabla\cdot[\varepsilon_0 \varepsilon_r(\mathbf{r})\nabla\phi(\mathbf{r})] = -\rho_{free}(\mathbf{r}), \tag{29}$$

where $\rho_{free}(\mathbf{r})$ is the macroscopic (net) volume charge density of coions and counterions (see also Eqs. (18) and (19)):

$$\rho_{free}(\mathbf{r}) = e_0 n_+(\mathbf{r}) - e_0 n_-(\mathbf{r}) = -2e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi, E)}, \tag{30}$$

while $\varepsilon_r(\mathbf{r})$ is defined by Eq. (24). The boundary conditions are:

$$\nabla\phi(\mathbf{r} = \mathbf{r}_\sigma) = -\frac{\sigma\mathbf{n}}{\varepsilon_0 \varepsilon_r(\mathbf{r} = \mathbf{r}_\sigma)}, \tag{31}$$

$$\phi(\mathbf{r} \to \infty) = 0. \tag{32}$$

For $\gamma \to 1$ and $n \to 1$ the equations of the above described model transform into equations of Langevin–Bikerman model [12,13].

3. Results and discussion

Eq. (29) was solved numerically for planar geometry using the Finite Element Method (FEM) within the Comsol Multiphysics 3.5a Software program package (COMSOL AB, Stockholm). The space dependence of ε_r (Eq. (24)) in Eq. (29) was taken into account in an iterative procedure, where the initial value of ε_r was a constant equal to the permittivity of the bulk solution. The boundary conditions (31) and (32) were taken into account.

Figs. 1 and 2 show the spatial dependence of n_+/n_s, n_w/n_s and ε_r in planar geometry for three values of the surface charge density σ calculated within the presented model. The decrease of ε_r towards the charged surface is a consequence of the increased depletion of water molecules near the charged surface (excluded volume effect) and increased orientational ordering of water dipoles (saturation effect). The depletion of water molecules near the charged surface is due to excluded volume effect as a consequence of accumulation of counterions near the charged surface. Comparison between the predictions of our model for different values of σ shows that the decrease of relative permittivity of the electrolyte solution near the highly charged surface is pronounced with increasing σ.
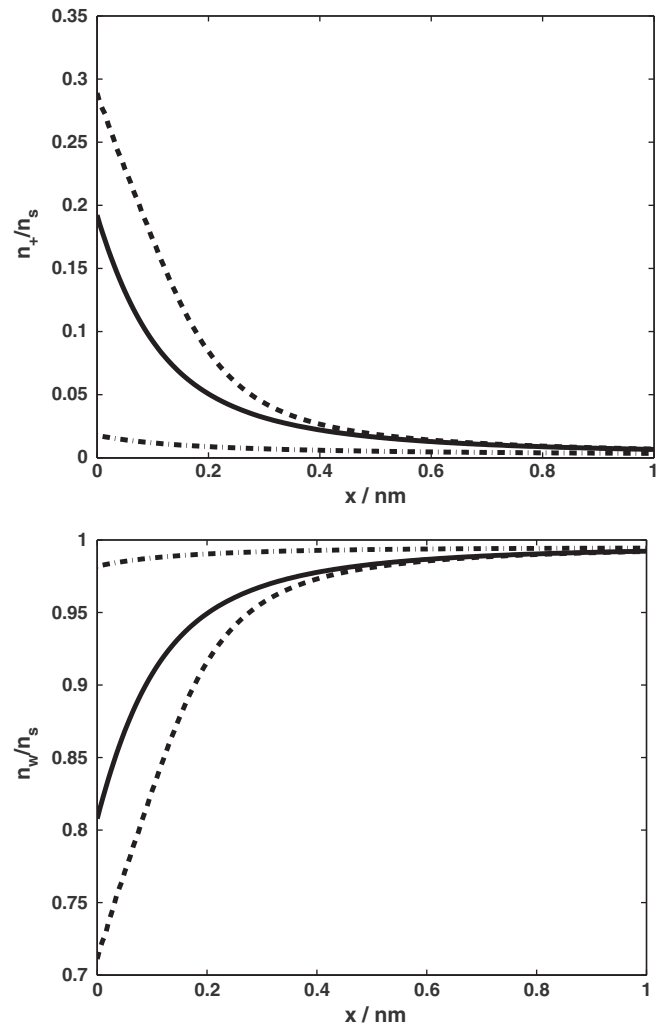

Fig. 1. The relative number density of counter ions (n_+/n_s) and water dipoles (n_w/n_s) (calculated using Eq. (18) and Eq. (20) as a function of distance from a planar charged surface x calculated for three values of surface charge density: $\sigma = -0.1\,\text{As/m}^2$ (dashed-dotted line), $\sigma = -0.2\,\text{As/m}^2$ (full line) and $\sigma = -0.3\,\text{As/m}^2$ (dashed line). Values of parameters assumed: bulk concentration of salt $n_0/N_A = 0.15\,\text{mol/l}$, dipole moment of water $p_0 = 3.1 D$, optical refractive index $n = 1.33$, bulk concentration of water $n_{ow}/N_A = 55\,\text{mol/l}$, where N_A is Avogadro number.
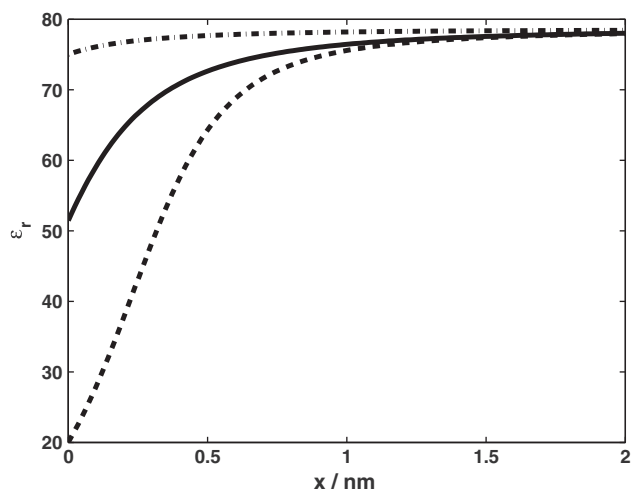
Fig. 2. The relative permittivity ε_r (Eq. (24)) as a function of distance from a planar charged surface x calculated for three values of surface charge density: $\sigma = -0.1$ As/m^2 (dashed-dotted line), $\sigma = -0.2$ As/m^2 (full line) and $\sigma = -0.3$ As/m^2 (dashed line). Values of parameters are the same as in Fig. 1.

In the approximation of a small electrostatic energy and small energy of the dipoles compared to the thermal energy, i.e. small $e_0\phi\beta$ and small $\gamma p_0 E\beta$, the relative permittivity within our model for finite sized ions (Eq. (24)) can be expanded into a Taylor series (assuming $n_s \approx n_{0w}$) to get:

$$\varepsilon_r \cong n^2 + \frac{3}{2}\left(\frac{2+n^2}{3}\right)^2 \frac{n_{0w}p_0{}^2\beta}{3\varepsilon_0} - \frac{27}{8}\left(\frac{2+n^2}{3}\right)^4 \frac{n_{0w}p_0^2\beta}{45\varepsilon_0}(p_0E\beta)^2 -$$
$$- \frac{3}{2}\left(\frac{2+n^2}{3}\right)^2 \frac{n_0 p_0^2\beta}{3\varepsilon_0}(e_0\phi\beta)^2. \tag{33}$$

In the limit of vanishing electric field strength ($E \to 0$) and zero potential ($\phi \to 0$) the above equation gives the Onsager expression for bulk permittivity:

$$\varepsilon_r \cong n^2 + \left(\frac{2+n^2}{3}\right)^2 \frac{n_{0w}p_0{}^2\beta}{2\varepsilon_0}. \tag{34}$$

In the above expression for the relative (effective) permitivitty (Eq. (24)) the value of the dipole moment $p_0 = 3.1D$ corresponds to the bulk permittivity $\varepsilon_r = 78.5$ (Eq. (34)). This value is considerably smaller than the corresponding value in the Langevin–Bikerman model (where $p_0 = 4.79D$) (see Eq. (6)) [12,13] which does not take into account the cavity field [22], and is also close to the experimental values of the effective dipole moment of water molecules in clusters ($p_0 = 2.7D$) and in bulk solution ($p_0 = 2.4 - 2.6D$) [23]. The permittivity derived within the model presented (Eq. (24)) does not negate the previous predictions of the Langevin–Bikerman model [12,13] where all the equations (including the expression for the relative permittivity) have a similar structure as in the presented model, only the effective value of the water dipole moment (p_0) in the old Langevin–Bikerman model [12,13] is larger.

On comparison of the relative permittivity ε_r in the Langevin–Bikerman model (Eqs. (1) and (5)) [12,13] with ε_r derived in this work (Eqs. (24) and (33)) it can be seen that in both models ε_r decreases with increasing E and $|\phi|$. It can be further seen that considering the cavity field in the presented model leads to a stronger decrease of relative permittivity than by considering only the orientational ordering of water molecules and the excluded volume effect in the Langevin–Bikerman model (compare Eqs. (5) and (33)).

4. Conclusions

The orientation of water near a charged membrane surface and a charged implant surface is important in many biological processes such as binding of ligands to the active sites of enzymes, transport of ions through channel proteins or interactions of cells with implant surfaces [3,4,8,10,13,25–27]. As shown in the past, the properties of the electric double layer may be influenced by the ordering of water molecules [4,10,12,13,25,26,28] and the depletion of water molecules [12,13] in the region of the electric double layer. Close to the charged surface the saturation and excluded volume effects may result in a decrease of permittivity [10–14].

The effective dipole moment of the water molecule must be known before a satisfactory statistical mechanical description of water and aqueous solutions is possible [29]. The dipole moment of a water molecule in liquid water differs from that of an isolated water molecule because each water molecule is further polarized by the electric field of the neighbouring water molecules [29]. In order to capture this effect in the theoretical description of permittivity of water, the concept of cavity and reaction fields and the correlations between water dipoles [20–22] were introduced for small magnitudes of the electric field, i.e. far away from the saturation limit [17] of the water orientational ordering. Later generalization of the Kirkwood–Onsager–Fröhlich theory in the saturation regime was performed for constant electric field strength as well [17,19]. However, it was shown recently within the Langevin–Bikerman model that in an electrolyte solution in contact with a highly charged implant (electrode) or membrane surface the influence of the excluded volume effect (not taken into account in Booth's model of permittivity) should also be allowed for while considering the spatial variation of relative permittivity of an electrolyte solution near the highly charged surface [12,13].

The Langevin–Bikerman model [12,13] on the other hand does not take into account the cavity field, therefore it was generalized in this work by simultaneously considering the influence of water ordering (saturation effect), the cavity field as well as the excluded volume effect. The corresponding analytical expression for the spatial dependence of the relative (effective) permittivity (Eq.(24)) was derived. Based on this formula it can be seen that the relative permittivity of the electrolyte solution near the highly charged surface (i.e. in the saturation regime) may be substantially decreased due to orientational ordering of water (saturation effect) and depletion of water molecules due to accumulation of counterions (volume excluded effect) (see also [12]). Comparison between the predictions of the Langevin–Bikerman model [12,13] and the model presented in this work shows that consideration of the cavity field makes the reduction of permittivity of an electrolyte solution near the highly charged surface even stronger.

Appendix A

Eq. (28) can be rewritten in more general form as:

$$\nabla \cdot \left[\varepsilon_0 n^2 \nabla\phi(\mathbf{r})\right] + n_{0w}n_s p_0 \left(\frac{2+n^2}{3}\right)\nabla \cdot \left[\mathbf{n}\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)}\right] =$$
$$= 2e_0 n_0 n_s \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi, E)}, \tag{A.1}$$

where $\mathbf{n} = \nabla\phi/|\nabla\phi| = \nabla\phi/E$. It follows from Eq. (A.1) that

$$\nabla\cdot\left[\varepsilon_0\left(n^2 + \frac{n_{0w}n_s p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right)\frac{1}{E}\frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi,E)}\right)\nabla\phi(\mathbf{r})\right] = \qquad (A.2)$$
$$= 2e_0 n_0 n_s \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi,E)}.$$

The above Eq. (A.2) can finally be rewritten in the form:

$$\nabla\cdot[\varepsilon_0\varepsilon_r(\mathbf{r})\nabla\phi(\mathbf{r})] = -\rho_{free}(\mathbf{r}), \qquad (A.3)$$

where $\rho_{free}(\mathbf{r})$ is the macroscopic (net) volume charge density of coions and counterions (Eq. (30)), while $\varepsilon_r(\mathbf{r})$ is defined by Eq. (24).

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