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Research article

Electric energies of a charged sphere surrounded by electrolyte

István P. Sugár*

Neurology Department, Icahn School of Medicine at Mount Sinai, New York, NY 10029

*** Correspondence:** Email: istvansugar0@gmail.com.

Abstract: By using the recently generalized version of Newton's Shell Theorem [6] analytical equations are derived to calculate the electric potential energy needed to build up a charged sphere, and the field and polarization energy of the electrolyte inside and around the sphere. These electric energies are calculated as a function of the electrolyte's ion concentration and the radius of the charged sphere. The work needed to build up the charged sphere, E_{CC} (i.e. the total charge-charge interaction energy) decreases with increasing ion concentration of the electrolyte because of the electrolyte ions' increasing screening effect on the charge-charge interaction. The work needed to build up the charged sphere appears as a sum of the field and polarization energy of the electrolyte. At zero ion concentration the electrolyte's field energy is equal with E_{CC} while the polarization energy is zero. At high electrolyte ion concentrations ($C > 10 mol/m^3$) 50% of E_{CC} appears as the polarization energy of the electrolyte, 25% as the electrolyte's field energy inside the sphere and 25% as the electrolyte's field energy around the sphere.

Keywords: Debye length; screened potential; electrolyte's field energy; charge-charge interaction energy

1. Introduction

The head groups of membrane lipids have either single charge (e.g. tetraether lipids [1,2]) or electric dipole (e.g. phospholipids [3]). Theoretical models of lipid membranes usually focus on short range (Van der Waals) lateral interactions between nearest neighbor lipids and ignore the long range charge-charge interactions [3,4]. This is because in the case of long range interactions one has to consider the entire system rather than the interactions between the nearest neighbor lipids. In order to get closer to the solution of this problem recently we developed a generalized version of Newton's Shell Theorem [5,6]. According to the generalized Shell Theorem the potential around a charged sphere of radius R is (see Eq.9 in ref.6)

$$V(Z,Q)=\frac{k_eQ\lambda_D}{\varepsilon_r ZR}e^{-\frac{Z}{\lambda_D}}\sinh\left(\frac{R}{\lambda_D}\right)\qquad \text{at } Z>R \tag{1}$$

where Z is the distance from the center of the charged sphere (see Figure 1) and the potential at $Z\leq R$ is (see Eq.10 in ref.6)

$$V(Z,Q)=\frac{k_eQ\lambda_D}{\varepsilon_r ZR}e^{-\frac{R}{\lambda_D}}\sinh\left(\frac{Z}{\lambda_D}\right) \tag{2}$$

where $Q=4R^2\pi\rho_s$ is the total charge of the sphere and ρ_s is the surface charge density, λ_D is the Debye length in the electrolyte that is inside and around the charged sphere, k_e is the Coulomb's constant and ε_r is the relative static permittivity of the electrolyte. In ref.6 we also calculated the electric potential of two concentric charged spheres surrounded by electrolyte, and the membrane potential of a charged lipid vesicle surrounded by electrolyte with high ion concentration. At any electrolyte concentration one can calculate the electric potential of the charged lipid vesicle by numerical integration (see ref. 6).

In this paper we consider a single charged sphere (as in ref.6) and by using Eqs.1,2 analytical equations are derived to calculate the work needed to build up the charged sphere and the electrolyte's field energy inside and around the charged sphere. By means of these analytical equations one can also calculate the dependence of these energies from Q, R, C (electrolyte ion concentration) and T (absolute temperature).

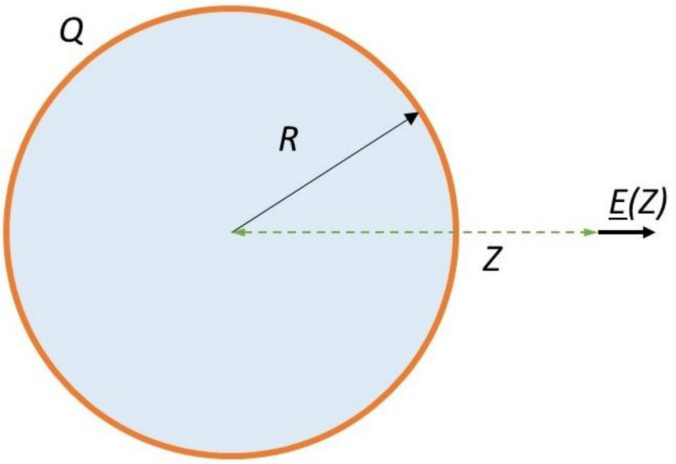

Figure 1. Charged sphere. Light blue area: intra-spherical region; orange circle: charged sphere of radius R with total charge Q; white area around the circle: extra-spherical region; black arrow: electric field strength, $\underline{E}(Z)$, at a distance Z from the center of the sphere.

By using the potential $V(Z,Q)$ of the charged sphere (Eqs.1,2) the electrolyte's field energy can be calculated in these two regions by the following equation [7]:

$$E_F=\frac{\varepsilon_r\varepsilon_0}{2}\int\underline{E}\cdot\underline{E}dv=\frac{\varepsilon_r\varepsilon_0}{2}\int\left(\frac{dV(Z,Q)}{dZ}\right)^2 4\pi Z^2 dZ \tag{3}$$

where $\varepsilon_0(=[4\pi k_e]^{-1})$ is the vacuum permittivity. Since our considered system is central symmetric the direction of the electric field vector, $\underline{E}$ is the radial direction (see Figure 1) and thus $|\underline{E}|=\frac{dV}{dZ}$ and at each region the integration is taken from the lower to the upper radius of the region (i.e. from 0 to R at the intra-spherical region and from R to ∞ at the extra-spherical region.

2. Model

To build a charged sphere it requires energy to overcome the repulsive forces between the charges already on the sphere and the charge approaching the surface of the sphere. Once the charge is on the surface of the sphere it is kept there by short range attractive forces. For example the charged lipids of a vesicle are kept in the membrane of the vesicle by the attractive, lateral, short-range interactions (Van der Waals interactions) with the surrounding lipid molecules [3,4]. According to the generalized Shell Theorem, Eqs.1,2, the potential on the surface of the partially charged sphere of radius R with charge q is:

$$V(R,q)=\frac{k_e q\lambda_D}{\varepsilon_r R^2}e^{-\frac{R}{\lambda_D}}\sinh\left(\frac{R}{\lambda_D}\right) \tag{4}$$

The electric potential energy needed to build a sphere of total charge Q is:

$$E_{CC}=\int_0^Q V(R,q)dq=\frac{k_e\lambda_D}{\varepsilon_r R^2}e^{-\frac{R}{\lambda_D}}\sinh\left(\frac{R}{\lambda_D}\right)\int_0^Q q dq=$$

$$\frac{k_e\lambda_D}{\varepsilon_r R^2}e^{-\frac{R}{\lambda_D}}\sinh\left(\frac{R}{\lambda_D}\right)\frac{Q^2}{2} \tag{5}$$

The electric field energy of the electrolyte inside the charged sphere, $Z\le R$, is calculated by using Eqs.2,3 (see Appendix 1):

$$E_{in}=\frac{\varepsilon_r\varepsilon_0}{2}\int_0^R\left(\frac{dV(Z,Q)}{dZ}\right)^2 4\pi Z^2 dZ=$$

$$\frac{k_e Q^2\lambda_D^2}{2\varepsilon_r R^2}e^{-\frac{2R}{\lambda_D}}\left\{\frac{1}{2\lambda_D}\sinh\left(\frac{R}{\lambda_D}\right)\cosh\left(\frac{R}{\lambda_D}\right)+\frac{R}{2\lambda_D^2}-\frac{1}{R}\sinh^2\left(\frac{R}{\lambda_D}\right)\right\} \tag{6}$$

The electric field energy of the electrolyte around the charged sphere, $Z>R$, is calculated by using Eqs.1,3 (see Appendix 2):

$$E_{out}=\frac{\varepsilon_r\varepsilon_0}{2}\int_R^\infty\left(\frac{dV(Z,Q)}{dZ}\right)^2 4\pi Z^2 dZ=$$

$$\frac{k_e Q^2\lambda_D}{\varepsilon_r R^2}e^{-2R/\lambda_D}\left(\frac{\lambda_D}{2R}+\frac{1}{4}\right)\sinh^2\left(\frac{R}{\lambda_D}\right) \tag{7}$$

3. Results

Here we calculate two types of electric energies: 1) E_{CC}, the electric potential energy needed to build up the charged sphere and 2) E_{in} and E_{out}, the electrolyte's field energy inside and around the charged sphere, respectively. We assume that the overall neutral electrolyte contains only monovalent positive and negative ions and calculate the electric energies in the following range of monovalent ion concentrations: $0.0001 - 100.0 \mathrm{mol/m^3}$. Note, that the relative static permittivity of the electrolyte decreases with increasing ion concentration. However in the above concentration region the decrease is within one percent [8,9]. Thus in our calculations the relative static permittivity is taken as constant ($\varepsilon_r = 78$). In this case, i.e. in the case of monovalent ions, the Debye length (in m) is [10]:

$$\lambda_D = \left(\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 N_a 2C}\right)^{\frac{1}{2}} \tag{8}$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12} C^2 J^{-1} m^{-1}$ is the vacuum permittivity, ε_r is the relative static permittivity of the electrolyte, $k_B = 1.38 \cdot 10^{-23} JK^{-1}$ is the Boltzmann constant , T is the absolute temperature, $e = 1.6 \cdot 10^{-19} C$ is the charge of a positive monovalent ion, $N_a = 6 \cdot 10^{23} \mathrm{mol}^{-1}$ is the Avogadro's number, C is the monovalent (positive or negative) ion concentration (in $\mathrm{mol/m^3}$) of the electrolyte inside and around the charged sphere. In our calculation we take always $T = 300K$.

Based on Eq.5 in Figure 2 E_{CC} is calculated as a function of the electrolyte ion concentration at three different radii of the charged sphere. In the case of our calculations the surface charge density of the charged sphere at every radius is $\rho_s = -0.266 \mathrm{C/m^2}$. This is the charge density of PLFE (bipolar tetraether lipid with the polar lipid fraction E) vesicles if the cross sectional area of a PLFE is $0.6 \mathrm{nm}^2$ and the charge of a PLFE molecule is $-1.6 \cdot 10^{-19} C$ (see refs.1,2,6).

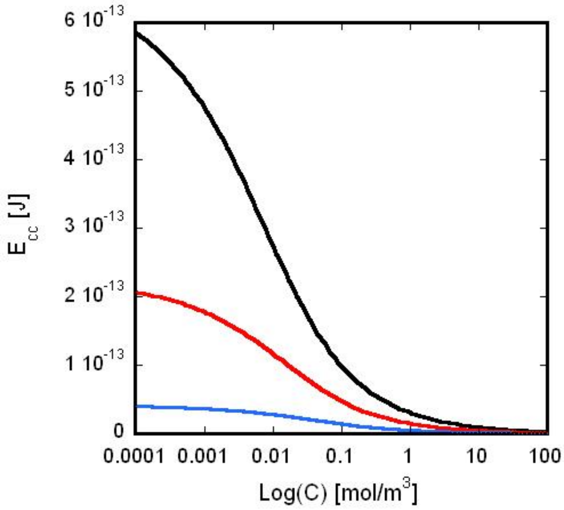

Figure 2. Calculated electric potential energy (E_{CC}) of a charged sphere surrounded by electrolyte. The energy is plotted against the ion concentration (C) of the electrolyte. The radius of the charged sphere is: $R = 100$ nm (black curve), $R = 70$ nm (red curve), $R = 40$ nm (blue curve). In the case of every charged sphere the charge density, ρ_s is the same: $-0.266 \mathrm{C/m^2}$.

The field energy of the electrolyte inside (E_{in}) and around (E_{out}) the charged sphere is calculated by Eq.6 and Eq.7, respectively. These calculated energies are plotted against the ion concentration of the electrolyte (see Figures 3B and 3A).

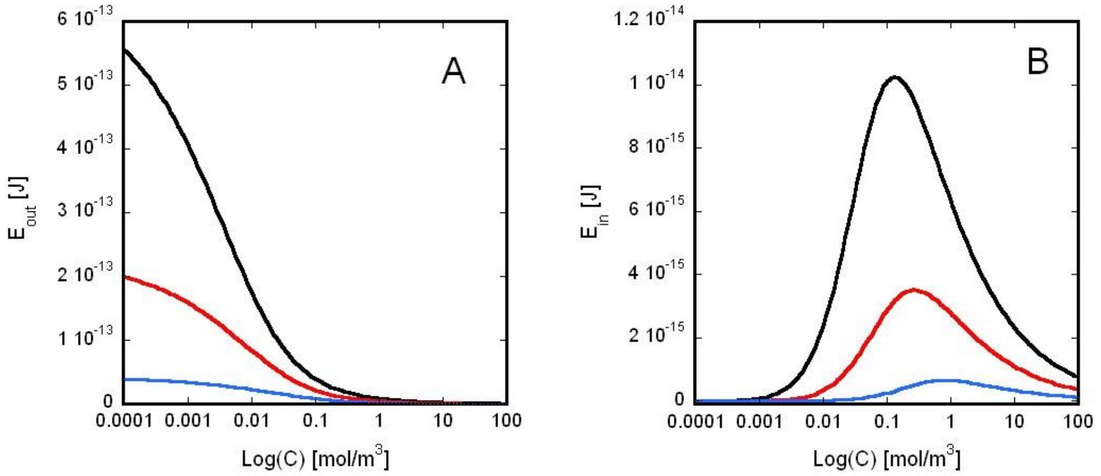

Figure 3. Calculated field energy of the electrolyte around and inside the charged sphere. The field energies of the electrolyte A) around $(\mathrm{E_{out}})$ and B) inside $(\mathrm{E_{in}})$ the charged sphere are plotted against the ion concentration (C) of the electrolyte. The radius of the charged sphere is: $\mathrm{R} = 100\,\mathrm{nm}$ (black curve), $\mathrm{R} = 70\,\mathrm{nm}$ (red curve), $\mathrm{R} = 40\,\mathrm{nm}$ (blue curve). In the case of every charged sphere the charge density, ρ_s is the same: $-0.266^{\cdot}\mathrm{C/m^2}$.

4. Discussion

By using Eqs.5,6 and 7 one can calculate the energy needed to build a charged sphere and the field energy of the electrolyte surrounding the sphere inside and around. In the case of zero ion concentration these energies can be obtained from the above mentioned equations by taking infinite long Debye length (see Appendix 3):

$$\mathrm{E_{CC}} = \frac{\mathrm{k_e Q^2}}{2\varepsilon_r \mathrm{R}} \tag{9}$$

$$\mathrm{E_{in}} = 0 \tag{10}$$

$$\mathrm{E_{out}} = \frac{\mathrm{k_e Q^2}}{2\varepsilon_r \mathrm{R}} \tag{11}$$

The results in Eqs.10,11 are in accordance with the Shell Theorem [5]. According to the Shell Theorem at zero electrolyte ion concentration the electric potential inside the charged sphere is constant (see Eq.1 at ref.6). Thus the electric field strength is zero and according to Eq.3 the electric field energy $(\mathrm{E_F})$ is zero too. Also, according to the Shell Theorem at zero electrolyte ion concentration the electric potential around the charged sphere is $\mathrm{V}(\mathrm{Z} > R) = \mathrm{k_e Q}/(\varepsilon_r \mathrm{Z})$ (see Eq.2 in ref.6). After substituting this into Eq.3 we get a result similar to Eq.11.

With increasing electrolyte ion concentration the electrical screening increases while the Debye length is approaching zero. As a consequence the energies, $\mathrm{E_{CC}}, \mathrm{E_{in}}$ and $\mathrm{E_{out}}$, approach zero too (see Appendix 4).

In Figure 4 we compare the electric potential energy, $\mathrm{E_{CC}}$ with the electrolyte's field energy within and around the sphere (i.e.: $\mathrm{E_{in}/E_{CC}}$ (dashed lines) and $\mathrm{E_{out}/E_{CC}}$ (solid lines)) and with the polarization energy $\mathrm{E_{pol}/E_{CC}}$ (dotted lines, see explanation below) .

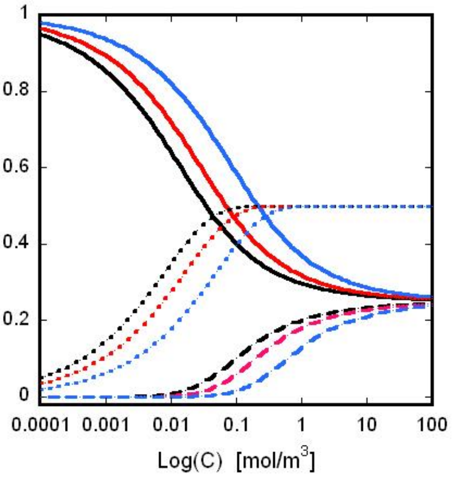

Figure 4. Electrolyte's field energies and polarization energy ($\mathrm{E_{in}}$, $\mathrm{E_{out}}$ and $\mathrm{E_{pol}}$) relative to the electric potential energy ($\mathrm{E_{CC}}$) are plotted against the ion concentration of the electrolyte (C). Radius of the charged sphere: $100\ \mathrm{nm}$ (black lines), $70\ \mathrm{nm}$ (red lines), $40\ \mathrm{nm}$ (blue lines). Solid lines: $\mathrm{E_{out}/E_{CC}}$ vs. C. Dashed lines: $\mathrm{E_{in}/E_{CC}}$ vs. C. Dotted lines: $\mathrm{E_{pol}/E_{CC}}$ vs. C (calculated by Eq.12).

According to Figure 4 close to zero ion concentration in the electrolyte $\mathrm{E_{CC}} \cong \mathrm{E_{out}}$ while $\mathrm{E_{in}} \cong 0$, i.e. the energy needed to build up the charged sphere is close to the electrolyte's field energy around the sphere. In this case building up the charged sphere one works only against the repulsion of the charges already present in the sphere and the respective electrolyte's field energy appears only around the sphere.

However when the ion concentration of the electrolyte is higher than zero the work is expended also on the polarization of the electrolyte, $\mathrm{E_{pol}}$. Namely, when the surface charge of the sphere is zero the average charge density in the electrolyte is zero everywhere. At negative surface charge of the sphere the average charge density close to the surface of the sphere is positive and it is decreasing with increasing distance from the surface. In this case the energy available to build up the electrolyte's field energy inside and around the charged sphere is: $\mathrm{E_{CC}} - \mathrm{E_{pol}} (= \mathrm{E_{in}} + \mathrm{E_{out}})$. Thus:

$$\frac{\mathrm{E_{pol}}}{\mathrm{E_{CC}}} = 1 - \left(\frac{\mathrm{E_{in}}}{\mathrm{E_{CC}}} + \frac{\mathrm{E_{out}}}{\mathrm{E_{CC}}}\right) \tag{12}$$

With increasing electrolyte ion concentration the Debye length decreases (see Eq.8) while the screening effect of the electrolyte increases and thus the work to build up the charged sphere, $\mathrm{E_{CC}}$ decreases considerably (see Figure 2). From about $10\ \mathrm{mol/m^3}$ electrolyte ion concentration close to one quarter of the energy for building up the charged sphere appears as the electrolyte's field energy inside the sphere, while another quarter appears as the electrolyte's field energy around the sphere, and half of it appears as the polarization energy (see Figure 4).

The electrolyte's field energy around the charged sphere $\mathrm{E_{out}}$ also decreases with increasing electrolyte ion concentration (see Figure 3A) because the screening increases. But as it was mentioned above E_{out} decreases more than E_{CC} with increasing electrolyte ion concentration (see Figure 4, solid lines).

Figure 3B shows the electrolyte's field energy inside the charged sphere as a function of the ion concentration of the electrolyte. Here the electrolyte's field energy is zero at zero ion concentration, $E_{in} = 0$ (Eq.10), because in this case the electric potential is constant inside the charged sphere (Eq.1 in ref.6) and thus the respective field strength is zero. At higher than zero ion concentration of the electrolyte $E_{in} > 0$ because the absolute value of the electric potential decreases toward the center of the sphere (Figure 3A in ref.6) and thus the respective field strength is not zero. However, at very high electrolyte ion concentration E_{in} reduces to close to zero. This is the case because of the increased screening the electric potential, V inside the sphere becomes close to zero, i.e. close to constant and thus $dV/dZ \cong 0$.

Finally, Figures 2,3 show that the energies (E_{CC}, E_{in}, E_{out}) are decreasing with decreasing radius of the charged sphere while the charge density of the sphere, ρ_s remains the same. This is the case because according to Eqs.5–7 these energies are proportional to the square of the total charge of the sphere. In the case of zero electrolyte ion concentration after substituting $Q = \rho_s 4\pi R^2$ into Eqs.9, 11 we get $E_{CC} = E_{out} {\sim} R^3$.

5. Conclusions

In this paper we considered a charged sphere surrounded by electrolyte. By using the generalized Shell Theorem [6] analytical equations have been derived to calculate the electric energies of this system (Eqs.5–7). The work needed to build up the charged sphere, E_{CC} decreases with increasing ion concentration of the electrolyte because the increasing screening effect on the charge-charge interaction. The energy needed to build up the charged sphere appears as sum of the electrolyte's field energy and the polarization energy of the electrolyte. At zero ion concentration the electrolyte's field energy around the charged sphere (E_{out}) is equal with E_{CC}, while the electrolyte's polarization energy $\left(E_{pol}\right)$ and the electrolyte's field energy inside the sphere (E_{in}) are both equal with zero. At high electrolyte ion concentrations ($C > 10\, mol/\mathrm{m}^3$) half of E_{CC} is for the polarization of the electrolyte and the other half is for the field energy of the electrolyte (i.e. $E_{out} \cong E_{in} \cong 0.25 \cdot E_{CC}$).

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Conflict of interest

The author declares no conflict of interest.

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