



Research article

A generalization of the Shell Theorem.

Electric potential of charged spheres and charged vesicles surrounded by electrolyte

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Abstract: By using the screened Coulomb potential a generalized version of Newton's Shell Theorem is developed and analytical equations are derived to calculate i) the potential of a charged sphere surrounded by electrolyte, ii) the potential of two concentric charged spheres surrounded by electrolyte, and iii) the potential inside the membrane of a charged lipid vesicle surrounded by electrolyte with high ion concentration. By numerical integration the potential of a lipid vesicle is calculated at any electrolyte concentration.

Keywords: membrane potential; Debye-Hückel equation; screened potential; Debye length

1. Introduction

The headgroups of membrane lipids have either single charge (e.g. tetraether lipids [1,2]) or electric dipole (e.g. phospholipids [1,3]). 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 physics the Shell Theorem deals with a similar problem, determining the electric potential within and around a charged sphere (where there is vacuum inside and around the charged sphere of radius R). According to the Shell Theorem [5] the electric potential inside the charged sphere is constant, i.e.:

$$V(r) = \frac{k_e Q}{R} \quad (1)$$

where $r < R$ is the distance from the center of the charged sphere and Q is the sum of the charges spreaded homogeneously on the sphere surface and $k_e (= 9 \cdot 10^9 \text{ N m}^2 \text{ C}^{-2})$ is the Coulomb's constant. However if $r > R$ then the potential decreases with increasing distance, i.e.:

$$V(r) = \frac{k_e Q}{r} \quad (2)$$

In this paper, step by step, we generalize the Shell Theorem to get closer to the conditions of charged vesicles. First we consider a charged sphere which, like a charged vesicle, is filled and surrounded by electrolyte. Second, to imitate the inner and outer surface of the charged vesicle membrane, we consider two concentric charged spheres with electrolyte all around. Third, since the inside of the lipid membrane is hydrophobic (with dielectric constant $\varepsilon_m = 2$), we consider the two concentric charged spheres with electrolyte all around except between the region of the two spheres. Generalizing the Shell Theorem we found analytical solution for the potential in the first and second cases. In the third case, however, we got analytical solution only if the ion concentration of the electrolyte is so high that the Debye length is much shorter than the membrane thickness. In the cases of longer Debye lengths, i.e. at lower electrolyte concentrations, we provide numerical solutions for the potential. In order to get the electric potential in the above mentioned three cases the solution of the Debye-Hückel equation is utilized (or also called Screened Poisson Equation, [6]). The Debye-Hückel equation is a linearized version of the Poisson-Boltzmann equation and it can be used in the case of not particularly large external charges. However, in the case of large external charges, such as a charged macroscopic particle, the screening is substantially nonlinear and thus the Poisson-Boltzmann equation should be utilized. The Poisson-Boltzmann equation is solved either by numerical methods [7,8] or analytically by using a higher than first-order expansion of the exponential Boltzmann distribution [9]. Recently, D'yachkov provided an exact analytical solution of the Poisson-Boltzmann equation itself in the form of the logarithm of an infinite power series [10]. The deeper biophysical understanding of charged vesicles may help in the recent increase of their practical applications, such as application in: drug delivery [11], gene delivery by cationic liposomes [12–14], vaccine delivery [15,16], simulating cells for studying and predicting the interactions between biological active compounds and cell membranes [15], cosmetics [17,18] and food industry [19,20].

2. Model

2.1. Potential around a charged sphere surrounded by electrolyte

Charges that are embedded into electrolyte, but not part of the electrolyte itself, are called external charges. The potential, V , in this system can be calculated by solving the Debye-Hückel equation (or also called Screened Poisson Equation, [6]):

$$\nabla^2 V(\underline{r}) - \lambda_D^{-2} V(\underline{r}) = -\frac{\rho(\underline{r})}{\varepsilon_0 \varepsilon} \quad (3)$$

where $\rho(\underline{r})$ is the density of the external charge at position \underline{r} , ε_0 is the electric constant and ε is the relative static permittivity, λ_D is the Debye length. Note, that Eq.3 is valid if the electrolyte itself

is electrically neutral. The solution of this equation is:

$$V(\underline{r}) = \iiint d^3 \underline{r}' \frac{\rho(\underline{r}')}{4 \pi \epsilon_0 \epsilon} \frac{e^{-|\underline{r} - \underline{r}'| / \lambda_D}}{|\underline{r} - \underline{r}'|} \quad (4)$$

i.e. the potential is the superposition of the so called screened Coulomb potential of the external charges.

The screened Coulomb potential, produced at a distance r from an external point charge, q is [6,21,22]:

$$V(r) = \frac{k_e q}{\epsilon r} e^{-r/\lambda_D} \quad (5)$$

where $k_e = (4 \pi \epsilon_0)^{-1}$ is the Coulomb's constant. In our model (shown in Figure 1) a charged sphere of radius R_1 is surrounded by electrolyte.

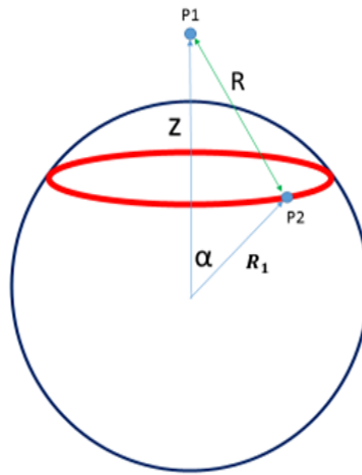


Figure 1. *Charged sphere.* Black circle represents the charged sphere of radius R_1 . The potential is calculated at point P1. Its distance from the center of the sphere is Z . The red ring represents charges on the charged sphere. Their distance from point P1 is R . α is the angle between vector Z and a vector pointing from the center of the sphere to any of the points (P2) on the red ring.

On the sphere point charges are homogeneously distributed with charge density ρ_1 . We would like to calculate the potential at point P1, located at a distance $Z > R_1$ from the center of the charged sphere (see Figure 1). First we calculate the potential induced by the charges located along the red ring shown in Figure 1:

$$V(\alpha, Z) \cdot d\alpha = \frac{k_e \rho_1 \cdot 2 \cdot R_1 \cdot \sin(\alpha) \cdot \pi \cdot R_1 \cdot d\alpha}{\epsilon R(\alpha, Z, R_1)} e^{-R(\alpha, Z, R_1) / \lambda_D} \quad (6)$$

where $2 \cdot R_1 \cdot \sin(\alpha) \cdot \pi \cdot R_1 \cdot d\alpha$ is the surface area of the red ring and $R(\alpha, Z, R_1)$ is the distance between point P1 and any of the point charges located on the red ring:

$$R(\alpha, Z, R_1) = \sqrt{(R_1 \cdot \sin(\alpha))^2 + (Z - R_1 \cdot \cos(\alpha))^2} = \sqrt{R_1^2 + Z^2 - 2 \cdot Z \cdot R_1 \cdot \cos(\alpha)} \quad (7)$$

The potential induced by the entire charged sphere at point P1 is:

$$V(Z) = \int_0^\pi V(\alpha, Z) d\alpha = \int_0^\pi \frac{k_e \cdot \rho_1 \cdot 2 \cdot R_1 \cdot \sin(\alpha) \cdot \pi \cdot R_1 \cdot d\alpha}{\varepsilon R(\alpha, Z, R_1)} e^{-R(\alpha, Z, R_1)/\lambda_D} \quad (8)$$

After the integration (see Appendix 1) the potential at $Z > R_1$ is

$$V(Z) = \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right) \quad (9)$$

where $Q_1 = 4R_1^2 \pi \cdot \rho_1$ is the total charge of the sphere, and the potential at $Z < R_1$ is

$$V(Z) = \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{R_1}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right) \quad (10)$$

2.2. Potential around two concentric charged spheres surrounded by electrolyte

Let us consider two concentric charged spheres, sphere 1 and 2, with radius R_1 and $R_2 (> R_1)$. The surface charge on sphere 1 and 2 is Q_1 and Q_2 , respectively and the spheres are surrounded everywhere by an electrolyte with Debye length λ_D .

The potential at $Z > R_2$ is the sum of the potential from sphere 1 and sphere 2. Based on Eq.9 the potential from sphere 1 is $V_1(Z) = \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right)$ and the potential from sphere 2 is $V_2(Z) = \frac{k_e \cdot Q_2 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_2} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_2}{\lambda_D}\right)$.

Thus in the case of $Z > R_2$ the total potential is

$$V(Z) = \frac{k_e \cdot \lambda_D}{\varepsilon \cdot Z} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \left\{ \frac{Q_1}{R_1} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right) + \frac{Q_2}{R_2} \cdot \sinh\left(\frac{R_2}{\lambda_D}\right) \right\} \quad (11)$$

If $Z > R_1$ but $Z < R_2$ the potential from sphere 1 can be obtained from Eq.9, $V_1(Z) = \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right)$, but the potential from sphere 2 can be obtained from an equation like Eq.10, $V_2(Z) = \frac{k_e \cdot Q_2 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_2} \cdot e^{-\frac{R_2}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right)$.

Thus in the case of $R_1 < Z < R_2$ the total potential is:

$$V(Z) = \frac{k_e \cdot \lambda_D}{\varepsilon \cdot Z} \cdot \left\{ \frac{Q_1}{R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right) + \frac{Q_2}{R_2} \cdot e^{-\frac{R_2}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right) \right\} \quad (12)$$

Finally, if $Z < R_1$ the potential from sphere 1 can be obtained from Eq.10, $V_1(Z) = \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{R_1}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right)$, while the potential from sphere 2 can be obtained from an equation similar to Eq.10, $V_2(Z) = \frac{k_e \cdot Q_2 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_2} \cdot e^{-\frac{R_2}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right)$.

Thus in the case of $R_1 > Z$ the total potential is:

$$V(Z) = \frac{k_e \cdot \lambda_D}{\varepsilon \cdot Z} \cdot \sinh\left(\frac{Z}{\lambda_D}\right) \left\{ \frac{Q_1}{R_1} \cdot e^{-\frac{R_1}{\lambda_D}} + \frac{Q_2}{R_2} \cdot e^{-\frac{R_2}{\lambda_D}} \right\} \quad (13)$$

2.3. Potential within the membrane of the charged vesicle – at high electrolyte concentration

Here we calculate the potential within the membrane of the charged vesicle when the electrolyte concentration is so high that the respective Debye length λ_D is much shorter than the membrane thickness, i.e. $R_2 - R_1$ (see Figure 2). For example, if the monovalent ion concentration of the electrolyte is $1000 \text{ mol} \cdot \text{m}^{-3}$, then the Debye length is about 0.304 nm while the membrane thickness is about 10 nm.

In this case the screening effect of the electrolyte is so strong that if only a part of the straight line between a membrane charge and the P1 point (see Figure 2) crosses the intra-vesicular electrolyte the potential from that charge reduces to close to zero. Thus at the intra-vesicular surface of the membrane only those charges contribute to the potential at point P1 where $\alpha < \alpha_1$ (see Figure 2A). These charges are not screened at all because there is no electrolyte in the membrane. However, at the extra-vesicular surface of the membrane only those charges contribute to the potential at point P1 where $\alpha < \alpha_1 + \alpha_2$ (α_1 and α_2 are defined in Figure 2B).

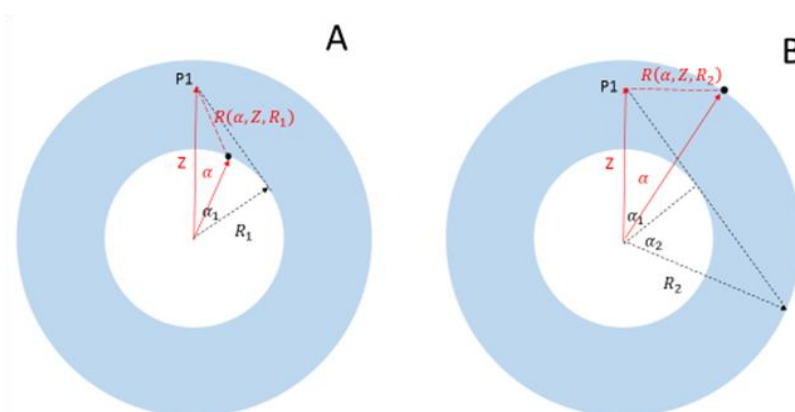


Figure 2. Model of charged vesicle. Light blue ring represents the membrane of the vesicle. R_1 and R_2 is the inner and outer radius of the vesicle membrane, respectively. P1: an intra-membrane point, at distance Z from the center of the vesicle, where we calculate the potential. A) In this figure we consider a charge (black dot) on the intra-vesicular surface of the membrane. α is the angle between the vectors pointing from the center of the vesicle to P1 and to the black dot. The line between P1 and the black dot is within the membrane (see red dashed line. Its length is marked by $R(\alpha, Z, R_1)$). When α is larger than α_1 the line between P1 and the black dot is partly within the membrane and partly within the intra-vesicular electrolyte. B) In this figure we consider a charge (black dot) on the extra-vesicular surface of the membrane. α is the angle between the vectors pointing from the center of the vesicle to P1 and to the black dot. The line between P1 and the black dot is within the membrane. Its length is marked by $R(\alpha, Z, R_2)$. When α is larger than $\alpha_1 + \alpha_2$ the line between P1 and the black dot is partly within the membrane and partly within the intra-vesicular electrolyte.

At a point within the vesicle membrane, i.e. when $R_1 < Z < R_2$, the potential produced by the charges located at the intra-vesicular surface of the membrane is $V_1(Z)$ and by the charges located at the extra-vesicular surface of the membrane is $V_2(Z)$. Where (from Appendix 2)

$$V_1(Z) = \int_0^{\alpha_1} V_1(\alpha, Z) d\alpha = \frac{k_e \cdot Q_1}{2 \cdot \varepsilon_m} \int_0^{\alpha_1} \frac{\sin(\alpha) \cdot d\alpha}{R(\alpha, Z, R_1)} =$$

$$\frac{k_e \cdot Q_1}{2 \cdot \varepsilon_m R_1 \cdot Z} [\sqrt{(Z - R_1)(Z + R_1)} - (Z - R_1)] \quad (14)$$

and

$$V_2(Z) = \int_0^{\alpha_1 + \alpha_2} V_2(\alpha, Z) d\alpha = \frac{k_e \cdot Q_2}{2 \cdot \varepsilon_m} \int_0^{\alpha_1 + \alpha_2} \frac{\sin(\alpha) \cdot d\alpha}{R(\alpha, Z, R_2)} =$$

$$\frac{k_e \cdot Q_2}{2 \cdot \varepsilon_m \cdot R_2 \cdot Z} \left[\sqrt{Z^2 + R_2^2 - 2R_1^2 + 2\sqrt{(Z^2 - R_1^2)(R_2^2 - R_1^2)}} - (R_2 - Z) \right] \quad (15)$$

where Q_1 and Q_2 is the total charge of the intra-vesicular and extra-vesicular surface of the membrane, respectively, $\varepsilon_m = 2$ is the dielectric constant of the membrane. $R(\alpha, Z, R_1)$ and $R(\alpha, Z, R_2)$ are defined in the legends to Figure 2 (and can be calculated by Eq.7)

2.4. Potential within and around the charged vesicle membrane – at any electrolyte concentration

When the electrolyte concentration is not high enough then every charge of the vesicle membrane contributes to the potential. In this case the potential at a distance Z from the center of the vesicle can be calculated by the following integrals:

$$V(Z) = \frac{k_e Q_1}{2} \int_0^\pi \frac{\sin(\alpha) d\alpha}{\varepsilon(Z) R(\alpha, Z, R_1)} e^{-\frac{R_{(e1)}(\alpha, Z)}{\lambda_D}} + \frac{k_e Q_2}{2} \int_0^\pi \frac{\sin(\alpha) d\alpha}{\varepsilon(Z) R(\alpha, Z, R_2)} e^{-\frac{R_{(e2)}(\alpha, Z)}{\lambda_D}} \quad (16)$$

where λ_D is the Debye length in the electrolyte and $R(\alpha, Z, R_1)$ is the distance between point P1 (located at a distance Z from the center of the vesicle) and the charge located at the intra-vesicular surface of the membrane. The part of the distance that goes through electrolyte is marked by $R_{(e1)}(\alpha, Z)$. While $R(\alpha, Z, R_2)$ is the distance between point P1 and the charge located at the extra-vesicular surface of the membrane. The part of the distance that goes through electrolyte is marked by $R_{(e2)}(\alpha, Z)$. The dielectric constant is $\varepsilon(Z) = \varepsilon_m = 2$ at $R_1 < Z < R_2$ and $\varepsilon(Z) = \varepsilon_e = 80$ at $0 < Z < R_1$ and at $R_2 < Z$.

The integrals in Eq.16 can be calculated only numerically. Depending on the value of Z , the location of the charge and the value of angle α there are eleven cases for calculating $R_{(e1)}(\alpha, Z)$ and $R_{(e2)}(\alpha, Z)$ listed in Table A1 (see Appendix 4).

In Eq.16 the first integral refers to those cases in Table A1 (see Appendix 4) where the charges belong to the intra-vesicular surface. i.e.: case IV, V, VIII, IX, XI and thus

$$\frac{k_e Q_1}{2} \int_0^\pi \frac{\sin(\alpha)}{\varepsilon(Z) R(\alpha, Z, R_1)} e^{-R_{(e1)}(\alpha, Z)/\lambda_D} d\alpha$$

$$= \frac{k_e Q_1}{2} \sum_{i=\{IV, V, VIII, IX, XI\}} \int_{\alpha_{min}^i}^{\alpha_{max}^i} \frac{\sin(\alpha)}{\varepsilon(Z) R(\alpha, Z, R_1)} e^{-R_{(e1)}^i(\alpha, Z)/\lambda_D} d\alpha \quad (17)$$

In Eq.16 the second integral refers to those cases in Table A1 (see Appendix 4) where the charges belong to the extra-vesicular surface. i.e.: case I, II, III, VI, VII, X and thus

$$\begin{aligned} & \frac{k_e Q_2}{2} \int_0^\pi \frac{\sin(\alpha)}{\varepsilon(Z) R(\alpha, Z, R_2)} e^{-R_{(e2)}(\alpha, Z)/\lambda_D} d\alpha \\ &= \frac{k_e Q_2}{2} \sum_{i=\{I, II, III, VI, VII, X\}} \int_{\alpha_{min}^i}^{\alpha_{max}^i} \frac{\sin(\alpha)}{\varepsilon(Z) R(\alpha, Z, R_2)} e^{-R_{(e2)}^i(\alpha, Z)/\lambda_D} d\alpha \end{aligned} \quad (18)$$

Note, that based on Eq.A2 one can get the analytical form of the above integrals only in the following four cases: I, VI, VIII, XI.

3. Results

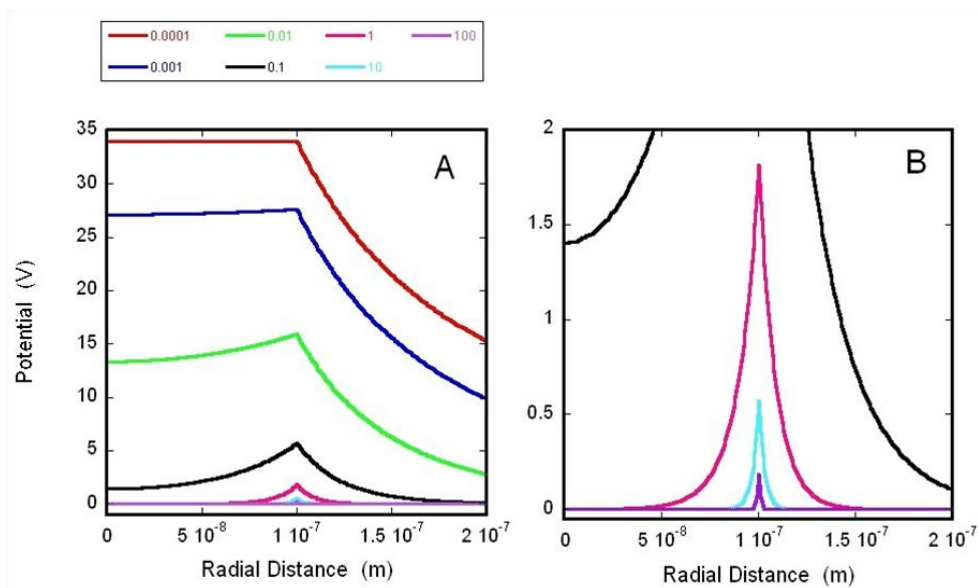


Figure 3. Calculated potential inside and around a charged sphere. A) The potential, $-V$, as a function of the radial distance from the center of the charged sphere is calculated by Eqs.9,10. The radius of the charged sphere is: $R_1 = 10^{-7}m = 100nm$. The total charge of the sphere is: $Q_1 = -3.35 \cdot 10^{-14}C$. Each curve was calculated at a certain monovalent ion concentration of the electrolyte. The concentrations belonging to a certain color are shown in mol/m^3 above Figure 3A. The Debye lengths (in m) belonging to each concentration are listed in Table 1. B) Calculated potentials within the region: $0V < -V(Z) < 2V$.

The potential, V , inside and around a charged sphere of radius R_1 is calculated by Eqs.9,10. The radius of the charged sphere, $R_1 = 10^{-7}m = 100nm$, is a typical size of a large unilamellar vesicle (LUV) [23]. The total charge of the sphere is: $Q_1 = -3.35 \cdot 10^{-14}C$. This is the total charge of a PLFE (bipolar tetraether lipid with the polar lipid fraction E) vesicle of radius R_1 if the cross sectional area of a PLFE is $0.6nm^2$ and the charge of a PLFE molecule is $1.6 \cdot 10^{-19}C$ [1,2]. In Figure 3 the potential multiplied by -1 is plotted as a function of the radial distance, Z , from the center of the sphere in the case of different monovalent ion concentrations of the electrolyte.

Table 1. Monovalent ion concentrations of electrolytes and the respective Debye lengths.

Electrolyte concentration ($\text{mol} \cdot \text{m}^{-3}$)	Debye length, λ_D (m)
0.0001	$9.62 \cdot 10^{-7}$
0.001	$3.04 \cdot 10^{-7}$
0.01	$9.62 \cdot 10^{-8}$
0.1	$3.04 \cdot 10^{-8}$
1.0	$9.62 \cdot 10^{-9}$
10.0	$3.04 \cdot 10^{-9}$
100.0	$9.62 \cdot 10^{-10}$

*Note, that the dielectric constant of the electrolyte decreases with increasing ion concentration. However in the above concentration region the decrease is within one percent [24,25]. Thus in our calculations the dielectric constant is taken $\epsilon_e = 80$ at the above electrolyte concentrations.

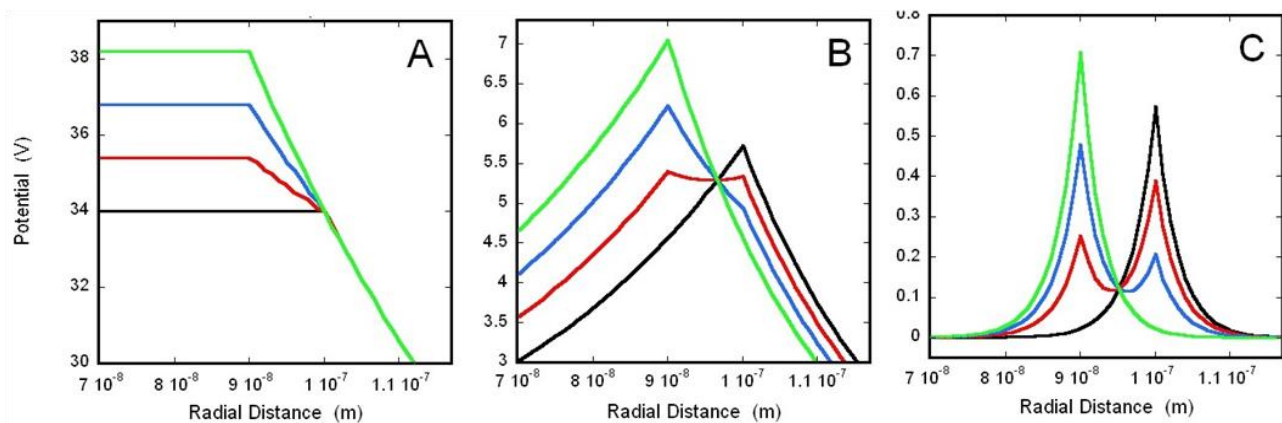


Figure 4. Potential within and around two concentric charged sphere surrounded by electrolyte. The potential, $-V$, as a function of the radial distance from the center of the charged spheres is calculated by Eqs.11-13. The radius of the smaller and larger sphere is $R_1 = 0.9 \cdot 10^{-7} \text{m}$ and $R_2 = 10^{-7} \text{m}$, respectively, while the total charge of the smaller and larger sphere is Q_1 and Q_2 . In our calculations always $Q_1 + Q_2 = Q = -3.35 \cdot 10^{-14} \text{C}$. In the case of black line: $Q_2 = Q$, red line: $Q_2 = 2Q/3$, blue line: $Q_2 = Q/3$, green line: $Q_2 = 0 \text{C}$. A) Concentration of electrolyte (of monovalent ions) is 0.0001mol/m^3 and the respective Debye length is $\lambda_D = 9.62 \cdot 10^{-7} \text{m}$. B) Concentration of electrolyte (of monovalent ions) is 0.1mol/m^3 and the respective Debye length is $\lambda_D = 3.04 \cdot 10^{-8} \text{m}$. C) Concentration of electrolyte (of monovalent ions) is 10mol/m^3 and the respective Debye length is $\lambda_D = 3.04 \cdot 10^{-9} \text{m}$.

By using Eqs.11-13 the potential was calculated within and around two concentric charged spheres (see Figure 4).

The sum of Eq.14 and Eq.15 gives the potential within the membrane of the vesicle filled and surrounded by electrolyte with high ion concentration.

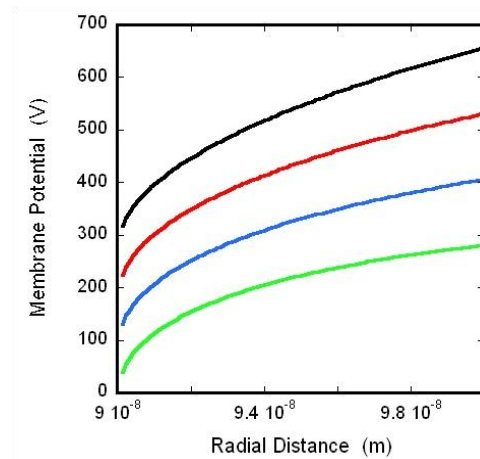


Figure 5. Potential within the vesicle membrane at high electrolyte concentration.

The vesicle membrane potential, $-V$, as a function of the radial distance from the center of the vesicle is calculated by the sum of Eq.14 and Eq.15. These equations are valid only at high ion concentrations at the intra- and extra-vesicular electrolyte, i.e.: when $\lambda_D \ll (R_2 - R_1)$. The radius of the inner- and outer surface of the vesicle membrane is $R_1 = 0.9 \cdot 10^{-7}m$ and $R_2 = 10^{-7}m$, respectively, while the total charge of the inner and outer surface of the vesicle membrane is Q_1 and Q_2 . In our calculations always $Q_1 + Q_2 = Q = -3.35 \cdot 10^{-14}C$. In the case of the black curve: $Q_2 = Q$, red curve: $Q_2 = 2Q/3$, blue curve: $Q_2 = Q/3$, green curve: $Q_2 = 0C$. The dielectric constant of the membrane is $\epsilon_m = 2$.

In Eq.16 after performing the numerically integrations we get the radial dependence of the potential of charged vesicle (see Figure 6).

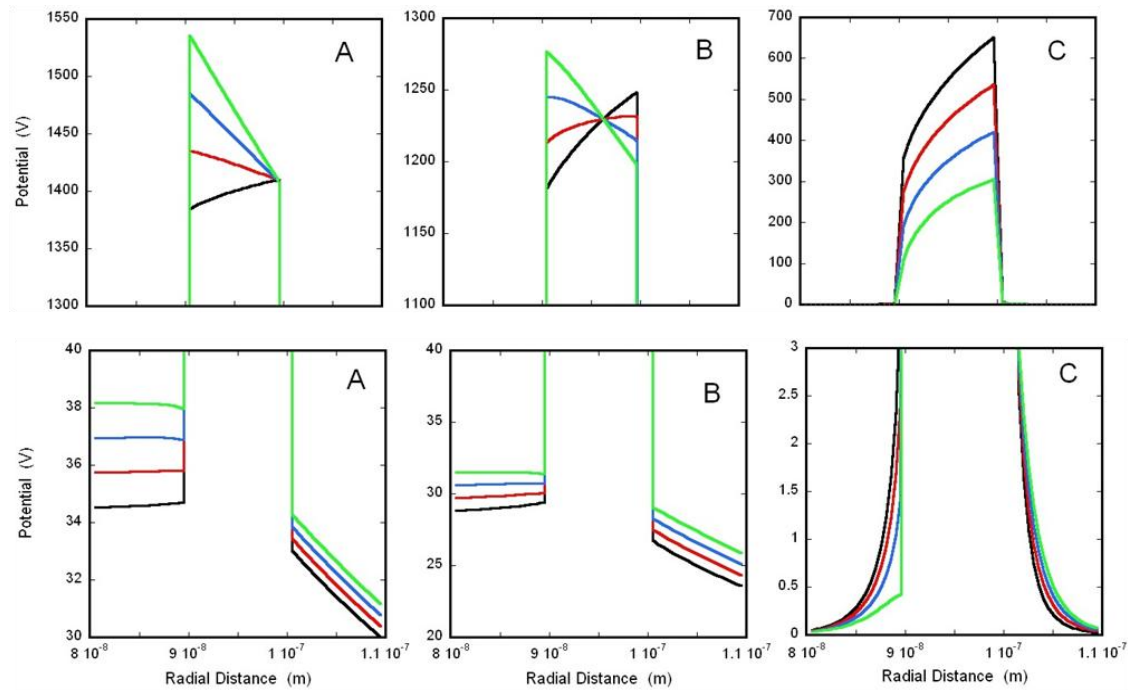


Figure 6. Potential within and around the charged vesicle membrane at different electrolyte concentrations. The potential, $-V$, within and around the charged vesicle membrane is calculated by Eq.16. The radius of the inner- and outer surface of the vesicle membrane is $R_1 = 0.9 \cdot 10^{-7} \text{ m}$ and $R_2 = 10^{-7} \text{ m}$, respectively, while the total charge of the inner and outer surface of the vesicle membrane is Q_1 and Q_2 . In our calculations always $Q_1 + Q_2 = Q = -3.35 \cdot 10^{-14} \text{ C}$. In the case of the black curve: $Q_2 = Q$, red curve: $Q_2 = 2Q/3$, blue curve: $Q_2 = Q/3$, green curve: $Q_2 = 0 \text{ C}$. A) Concentration of electrolyte (of monovalent ions) is 0.0001 mol/m^3 and the respective Debye length is $\lambda_D = 9.62 \cdot 10^{-7} \text{ m}$. B) Concentration of electrolyte (of monovalent ions) is 0.001 mol/m^3 and the respective Debye length is $\lambda_D = 3.04 \cdot 10^{-7} \text{ m}$. C) Concentration of electrolyte (of monovalent ions) is 10 mol/m^3 and the respective Debye length is $\lambda_D = 3.04 \cdot 10^{-9} \text{ m}$. Note, each subfigure is divided into a high- and low-potential part.

4. Discussion

By using Eqs.9, 10 one can calculate the potential of a charged sphere filled and surrounded by electrolyte. These equations are generalization of the Shell Theorem (given by Eqs.1, 2) where the charged sphere is in vacuum. One can get from Eqs.9, 10 the equations of the Shell Theorem by taking infinite long Debye length (that is characteristic for vacuum):

at $Z > R_1$

$$V(Z) = \lim_{\lambda_D \rightarrow \infty} \left\{ \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \sinh\left(\frac{R_1}{\lambda_D}\right) \right\} =$$

$$\lim_{\lambda_D \rightarrow \infty} \left\{ \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{Z}{\lambda_D}} \cdot \left[\frac{R_1}{\lambda_D} + \frac{1}{3!} \left(\frac{R_1}{\lambda_D} \right)^3 + \frac{1}{5!} \left(\frac{R_1}{\lambda_D} \right)^5 + \dots \right] \right\} = \frac{k_e \cdot Q_1}{\varepsilon \cdot Z} \quad (19)$$

and at $Z < R_1$

$$V(Z) = \lim_{\lambda_D \rightarrow \infty} \left\{ \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{R_1}{\lambda_D}} \cdot \sinh\left(\frac{Z}{\lambda_D}\right) \right\} =$$

$$\lim_{\lambda_D \rightarrow \infty} \left\{ \frac{k_e \cdot Q_1 \cdot \lambda_D}{\varepsilon \cdot Z \cdot R_1} \cdot e^{-\frac{R_2}{\lambda_D}} \cdot \left[\frac{Z}{\lambda_D} + \frac{1}{3!} \left(\frac{Z}{\lambda_D} \right)^3 + \frac{1}{5!} \left(\frac{Z}{\lambda_D} \right)^5 + \dots \right] \right\} = \frac{k_e \cdot Q_1}{\varepsilon \cdot R_1} \quad (20)$$

According to the Shell Theorem the potential inside the charged sphere is constant. Similarly, at low ion concentrations (between $0 - 0.001 \text{ mol/m}^3$), the potential close to constant inside the charged sphere (see Figure 3A). At higher ion concentrations however as a consequence of the increased screening the potential drops both outward and inward from the surface of the charged sphere (see Figure 3B).

Similar to the result of the Shell Theorem in the case of two concentric charged spheres, surrounded by electrolyte of low ion concentration, the potential is constant within the smaller sphere (see Figure 4A). If there is any amount of charge on the inner sphere the potential linearly decreases from the inner to the outer sphere. While the potential is constant from the center to the outer sphere if only the outer sphere is charged. At high ion concentrations, because of the high screening, however, the potential has two maxima at the radii of the charged spheres (see Figure 4C).

In the case of charged vesicles the charges are located at the inner and outer surface of the vesicle membrane. Like in the case of the above mentioned charged double spheres the intra- and extra-vesicular space is filled by electrolyte, but there is no electrolyte between the two charged spheres. The inner part of the lipid membrane is hydrophobic. If the electrolyte concentration is high the membrane potential can be calculated analytically by Eqs.14, 15. Figure 5 shows the calculated membrane potential if the total membrane charge is divided between the outer and inner membrane surface on four different ways. Interestingly, in each case the membrane potential increases with increasing radial distance even if the charge is zero at the outer membrane surface (see green line in Figure 5). As we mentioned before in this case the screening effect of the electrolyte is so strong that if only a part of the straight line between a membrane charge and the P1 point (see Figure 2) crosses the intra-vesicular electrolyte the potential from that charge reduces to zero. Thus at the intra-vesicular surface of the membrane only those charges contribute to the potential at point P1 where $\alpha < \alpha_1$. However, at the extra-vesicular surface of the membrane only those charges contribute to the potential at point P1 where $\alpha < \alpha_1 + \alpha_2$ (α_1 and α_2 are defined in Figure 2). The charges contributing to the potential at point P1 are situated on two spherical caps. The surface area of the spherical cap on the intra-vesicular surface of the membrane is:

$$S_1 = 2 \cdot R_1^2 \cdot \pi \cdot [1 - \cos(\alpha_1)] = 2 \cdot R_1^2 \cdot \pi \cdot \left[1 - \frac{R_1}{Z} \right] \quad (21)$$

while based on Eq.A8 on the extra-vesicular surface of the membrane the surface area of the spherical cap is:

$$S_2 = 2 \cdot R_2^2 \cdot \pi \cdot [1 - \cos(\alpha_1 + \alpha_2)] = 2 \cdot R_2^2 \cdot \pi \cdot \left[1 - \frac{R_1^2 - \sqrt{(Z^2 - R_1^2)(R_2^2 - R_1^2)}}{Z \cdot R_2} \right] \quad (22)$$

Thus the total charge contributing to the potential at point P1 is:

$$\rho_1 \cdot S_1 + \rho_2 \cdot S_2 = \frac{Q_1}{2} \left[1 - \frac{R_1}{Z} \right] + \frac{Q_2}{2} \left[1 - \frac{R_1^2 - \sqrt{(Z^2 - R_1^2)(R_2^2 - R_1^2)}}{Z \cdot R_2} \right] \quad (23)$$

In Figure 7 $(\rho_1 \cdot S_1 + \rho_2 \cdot S_2)/Q$ is plotted against the radial distance of point P1.

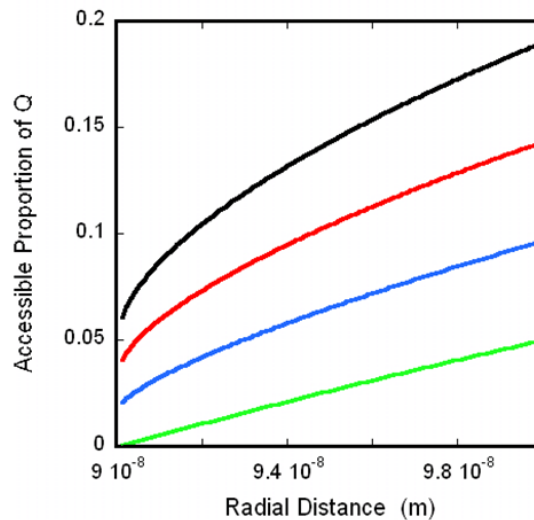


Figure 7. Proportion of total charge contributing to the potential within the vesicle membrane. To calculate the accessible proportion of the total charge of the vesicle membrane we used Eq.23. The radius of the inner- and outer surface of the vesicle membrane is $R_1 = 0.9 \cdot 10^{-7}m$ and $R_2 = 10^{-7}m$, respectively, while the total charge of the inner and outer surface of the vesicle membrane is Q_1 and Q_2 . In our calculations always $Q_1 + Q_2 = Q = -3.35 \cdot 10^{-14}C$. In the case of the black curve: $Q_2 = Q$, red curve: $Q_2 = 2Q/3$, blue curve: $Q_2 = Q/3$, green curve: $Q_2 = 0 C$.

The similar characteristics of the curves in Figure 5 and Figure 7 shows that the potential in the vesicle membrane close to proportional to the amount of charges that are not screened out by the highly concentrated electrolyte surrounding the vesicle membrane. Note also that the membrane potential calculated from the sum of Eq.14 and Eq.15 is similar to the result of the numerical integration of Eq.16 (compare Figure 5 with Figure 6C where the electrolyte concentration is $10 \text{ mol}/m^3$).

In the case of low electrolyte concentration, when every charge of the vesicle membrane contributes to the potential, the potential close to linearly decreases within the membrane with increasing radial distance (see Figure 6A). This is similar to the change of the potential between two charged spheres immersed into electrolyte with low ion concentration (see Figure 4A).

This can be explained by the Shell Theorem that works well at low electrolyte concentration. According to Eq.2 the membrane potential, caused by the charges on the intra-vesicular surface, is

close to linearly decreasing within the interval (R_1, R_2) because $\frac{[R_2 - R_1]}{R_2} \ll 1$. On the other hand, according to Eq.1, the membrane potential, created by the charges on the extra-vesicular surface of the membrane, is constant. Thus the total membrane potential decreases also close to linearly. When there is no charge on the intra-vesicular surface, i.e. $Q_2 = Q$, based on Eq.1 one may expect constant membrane potential. However, the membrane potential is not constant but slightly increasing (see black curve in Figure 6A). This maybe the case because the ion concentration of the electrolyte is slightly higher than zero. With further increasing electrolyte concentration the membrane potential belonging to $Q_2 = 2 \cdot Q/3$ increases too (see red curve in Figure 6B). Finally we should mention the fundamental differences between Figure 4 and Figure 6. Since the dielectric constant in the membrane is 40 times smaller than in the intra- and extra-vesicular space there is a sudden 40 times jump and 40 times drop of the potential at R_1 and R_2 , respectively.

Conclusions

By using the screened Coulomb potential a generalized version of the Shell Theorem is developed and analytical equations are derived to calculate i) the potential of a charged sphere surrounded by electrolyte, ii) the potential of two concentric charged spheres surrounded by electrolyte, iii) the membrane potential of a charged lipid vesicle surrounded by electrolyte with high ion concentration. By numerical integration the potential of a lipid vesicle is calculated at any electrolyte concentration. In general with increasing ion concentration the screening effect of the electrolyte increases and the overall potential of the above mentioned spheres, vesicles is decreasing. With increasing distance from the outer surface of the charged sphere or vesicle the potential decrease is steeper in the case of higher electrolyte concentration. Inside the charged sphere or vesicle at low electrolyte concentration the potential is close to constant. However with increasing electrolyte concentration the decrease of the potential towards the center of the sphere (or vesicle) becomes steeper.

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Conflict of interest

The author declares no conflict of interest.

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