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Charged Semi-Permeable Shell with Encapsulated Polyions: Concentration Profile, Surface Potential, and Electrostatic Pressure

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Summary: We study theoretically the electrostatic equilibrium for a charged shell filled with a suspension of polyions (e.g., colloids, polyelectrolytes, etc.) and immersed in an infinite salt-free reservoir. The shell is impermeable for polyions, but allows free diffusion of counterions. From the solution of the linearized Poisson-Boltzmann equation we obtain the distribution of the potential and concentration profiles for polyions. We then derive explicit formulas for the electrostatic pressure exerted by the shell. If the overall charge of the filled shell has the same sign as the surface alone the pressure on the shell increases with increase of the surface charge density. Otherwise the surface charge density suppresses the electro-osmotic pressure due to the electrostatic attraction between the oppositely charged polyions and shell.

Keywords: charged shells; electro-osmotic equilibrium; electrostatic pressure; polyions

Introduction

In the present paper we study a charged shell encapsulating suspension of charged colloids or polyelectrolytes. The shell membrane is assumed to be semipermeable, allowing diffusion of the small counterions but not of the large polyions. The outer salt-free solution is at electro-osmotic equilibrium with the interior of this shell (Fig. 1). This situation is traditionally referred to as the Donnan equilibrium.[1] Examples of such systems abound in our everyday life. Such shells are liposomes with ion channels,[2] multilayer micro- and nano-vesicles,[3] bacterial and cell membranes,[4] viral capsids,[5] etc. Examples of such suspensions are dispersion paints, viscosity modifiers, charged dendrimers, micelles, and more. They play tremendous role in life science, since proteins and DNAs represent charged polyions. Similar system has been employed for a determination of elastic modulus of the shell.[6] Depending on the applications the swelling or rupture of the shells due to high internal pressure should be avoided or desired.[7,8]

It has been shown experimentally, that in contrast to encapsulated neutral species,[9] the inner spatial distribution of charged polyions is often non-uniform.[10] In our recent papers[11,12] we have made the first attempt to calculate an inner distribution of polyions, by using a model of a *neutral* semi-permeable shell. Our computer simulation study[11] has proven that characteristic density peaks of polyions at the shell are the consequence of counterion leakage. We have later predicted similar concentration profiles for polyions within a simple linear theory,[12] which also allowed us to evaluate a surface potential and an excess electro-osmotic pressure on the shell. Although theory and simulation have reproduced the main experimental trends, a non-zero charge density of the shell membrane was not taking into account. In reality, however, the majority of shells are charged. Thus, for example, the

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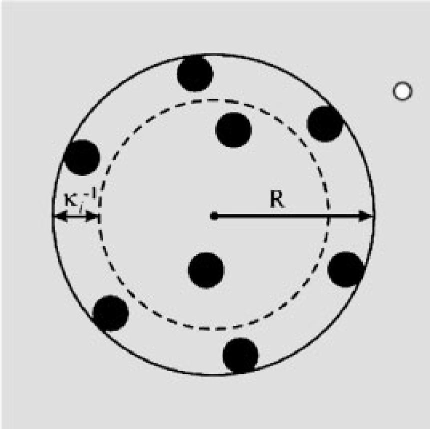

Figure 1.
Ion distribution inside and outside a semi-permeable shell. Polyions are depicted as spherical and remain encapsulated inside the shell. All free counter-ions are gone.

multilayer type of shells normally takes a charge of the last deposited polyelectrolyte layer and its value and sign can then often be adjusted by salt or pH-regulation.[10,13,14] It is the aim of the present paper to make a further step forward by considering the electro-osmotic equilibrium in the system of a *charged* shell. We show that in general the surface charges generate a constant additional electric potential in the shell, which does not affect the distribution of the ions. However, the surface charge density affects the electro-osmotic pressure on the shell via the Maxwell tensor components. If the overall charge of the filled shell has the same sign as the surface alone the pressure on the shell increases with increase of the surface charge density. If not, the surface charge density suppresses the electro-osmotic pressure due to the electrostatic attraction between polyions and the oppositely charged shell.

Theory and Discussion

We keep here our theoretical description at the simplest possible level by using the linearized Poisson-Boltzmann approach. This means that we treat polyions as point-like and neglect their correlations. Our strategy of a derivation follows the ideas and approach formulated in our previous work.[12] We consider the case when polyelectrolyte ions with an effective charge Z are trapped inside a shell with radius R. Since far away from the shell the concentration of the counterions tends to zero, the latter leak-out the shell completely. Hence, in a first-order approximation one can accept a zero concentration of counterions everywhere. The concentration of the polyelectrolyte ions can be expressed as

$$\begin{aligned} C_i &= \langle C\rangle[1 - Ze(\phi_i - \langle\phi_i\rangle)/k_BT] \\ C_o &= 0 \end{aligned} \tag{1}$$

where $\langle C\rangle$ and $\langle\phi_i\rangle$ are the average concentration and potential inside the shell, respectively. The solutions of the relevant Poisson-Boltzmann equation

$$\varepsilon_0\varepsilon\partial_r(r^2\partial_r\phi)/r^2 = -ZeC \tag{2}$$

are the following potentials

$$\begin{aligned} \phi_i &= \langle\phi_i\rangle + \frac{k_BT}{Ze} \\ &\quad + \left(\phi_s - \langle\phi_i\rangle - \frac{k_BT}{Ze}\right)\frac{R\sinh(\kappa_i r)}{r\sinh(\kappa_i R)} \\ \phi_o &= \phi_s\frac{R}{r} \end{aligned} \tag{3}$$

where $\kappa_i = \sqrt{Z^2e^2\langle C\rangle/\varepsilon_0\varepsilon k_BT}$ and ϕ_s is the surface potential. In the present case we consider a shell with constant surface charge density q_s. The latter is related to the electric field via the boundary condition

$$q_s = \varepsilon_0\varepsilon(\partial_r\phi_i)_R - \varepsilon_0\varepsilon(\partial_r\phi_o)_R \tag{4}$$

Substituting Eq. (3) in Eq. (4) yields the surface potential

$$\begin{aligned} \phi_s &= \langle\phi_i\rangle + \frac{k_BT}{Ze} \\ &\quad - \left(\langle\phi_i\rangle + \frac{k_BT}{Ze} - \frac{q_sR}{\varepsilon_0\varepsilon}\right)\frac{\tanh(\kappa_iR)}{\kappa_iR} \end{aligned} \tag{5}$$

Introducing this expression in Eq. (3) and integrating the result over the shell volume one yields the average potential in the form

$$\langle\phi_i\rangle = \frac{k_B T}{Ze}\left\{\frac{(\kappa_i R)^3}{3[\kappa_i R - \tanh(\kappa_i R)]} - 1\right\} + \frac{q_s R}{\varepsilon_0 \varepsilon} \qquad (6)$$

Hence, the final form of the surface potential from Eq. (5) reeds

$$\phi_s = \frac{k_B T}{Ze}\frac{(\kappa_i R)^2}{3} + \frac{q_s R}{\varepsilon_0\varepsilon} = \frac{Ze\langle C\rangle R^2/3 + q_s R}{\varepsilon_0\varepsilon} \qquad (7)$$

The surface potential ϕ_s as a function of $\kappa_i R$ is shown in Fig. 2. Note that the surface potential is proportional to the total charge of the shell including the polyions inside and in the case of electro-neutrality $\phi_s = 0$. Finally, after substituting Eqs. (6) and (7) in Eq. (3) the potential inside the shell acquires the form

$$\phi_i = \frac{k_B T}{Ze} \times \frac{(\kappa_i R)^3}{3[\kappa_i R - \tanh(\kappa_i R)]}\left[1 - \frac{\sinh(\kappa_i r)}{\kappa_i r\cosh(\kappa_i R)}\right] + \frac{q_s R}{\varepsilon_0\varepsilon} \qquad (8)$$

The radial distribution of inner and outer potentials calculated for different q_s is shown in Fig. 3. At zero surface charge density the potential is a continuous function. The ratio $\phi_o/\phi_s = R/r$ outside the shell does not depend on the bulk and surface charges at all. However, the surface charge density determines directly the slope of ϕ_i/ϕ_s according to Eq. (4) and depending on its sign q_s could also change the sign of this slope.

As is seen ϕ_i is a superposition of the potentials generated by the polyions and

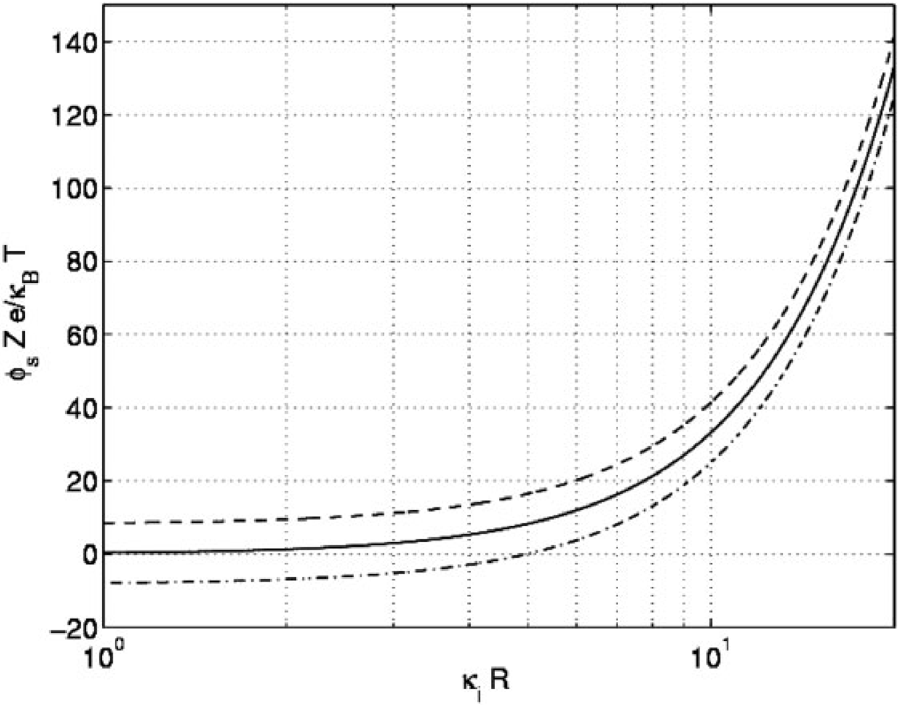

Figure 2.
Surface potential of a nanoshell as a function of $\kappa_i R$. Parameters are $R = 50$ nm, $Z = -15$, for dashed, solid, and dash-dotted curves the surface charge density takes values $q_s = -0.2$, 0, and 0.2 mC/m^2, respectively.

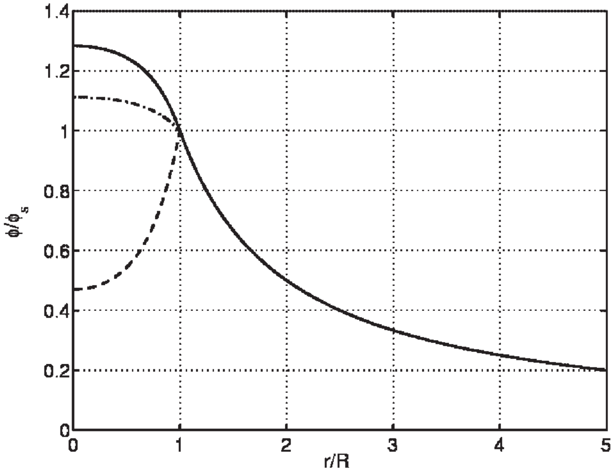

Figure 3.
A radial distribution of a potential at $\kappa_i R = 4$, $Z = -15$ and different q_s normalized by a surface potential, ϕ_s. Dashed, solid, and dash-dotted curves correspond to $q_s = -0.2$, 0, and 0.2 mC/m^2.

the surface charges. Since the latter is, however, a constant it does not affect the distribution of the polyions inside the shell. This is evident from the concentration profile

$$C_i = \langle C \rangle \frac{(\kappa_i R)^2}{3[\kappa_i R \coth(\kappa_i R) - 1]} \times \frac{R \sinh(\kappa_i r)}{r \sinh(\kappa_i R)} \quad (9)$$

calculated from Eq. (1) by using Eqs. (6) and (8), which is exactly as calculated before for a neutral shell.[12] The physical reason is that forces acting on ions from different parts of the shell cancel each other, so that the total force vanishes. Note, however, that in case of added salt the more complicated scenario would be expected since the distribution of inner potential becomes, in general case, non-uniform.[15]

The jump of the normal component of the pressure tensor across the shell surface can be then calculated via the expression

$$\Delta P_N = k_B T \langle C \rangle - Ze \langle C \rangle (\phi_s - \langle \phi_i \rangle) + \frac{\varepsilon_0 \varepsilon}{2} \left[\kappa_i^2 (\phi_s - \langle \phi_i \rangle)^2 - (\partial_r \phi_i)_R^2 + (\partial_r \phi_o)_R^2 \right]$$

which accounts both for the osmotic pressure and the Maxwell tensor contributions. Using our results above this expression can be rewritten as

$$\Delta P_N = k_B T \langle C \rangle \times \left\{ \frac{1}{2} + \frac{(\kappa_i R)^4}{18[\kappa_i R \coth(\kappa_i R) - 1]^2} \right\} + \frac{q_s^2}{2\varepsilon_0 \varepsilon} + \frac{Ze \langle C \rangle q_s R}{3 \varepsilon_0 \varepsilon} \quad (10)$$

This first term in Eq. (10) represents purely the excess osmotic pressure on the shell due to the inner polyion solution.[12] It is enhanced by the self-repulsion effect of the surface charges given by the second term in Eq. (10). An interesting effect is the interaction between the surface charge and polyions leading to the last term in Eq. (10). As seen if the surface charge has the same sign as the polyion's charge this effect increases the pressure acting on the shell. In contrast, if polyions and shell are oppositely charged, the attraction between the shell and the polyions effectively decreases the pressure supported by the shell. Note that in the case of electro-neutrality the sum of the last two terms is not equal to zero even if $\phi_s = 0$.

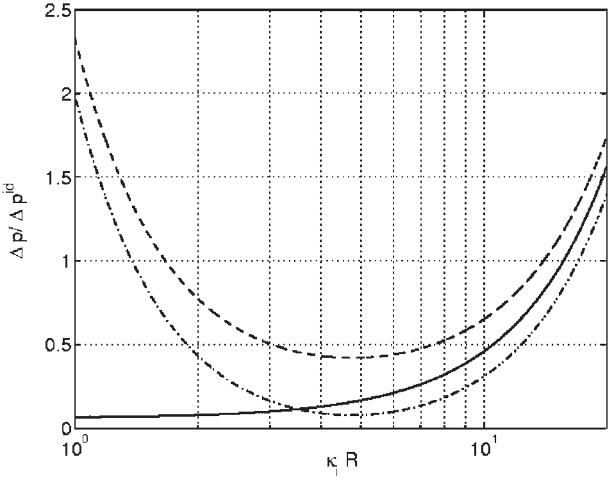

Figure 4.
A ratio of an excess pressure exerted by the shell filled by polyions of $Z=-15$ to the osmotic pressure of the corresponding bulk solution, $p^{id}=k_BT\langle C\rangle(1-Z/z)$. Dashed, solid, and dash-dotted curves correspond to $q_s=-0.2$, 0, and 0.2 mC/m^2.

Pressure trends are illustrated in Fig. 4. In the case of zero surface charge density the pressure increases with $\kappa_i R$ due to the osmotic component. At lower values of $\kappa_i R$, this component is negligible and the main effect on the pressure increase is due to the surface charge density. Of course, in any case the pressure of a shell with similar bulk and surface charges is larger than that in the opposite case, where the electrostatic attraction between the shell surface charges and the polyions decreases the overall pressure on the shell. As seen the latter effect could even suppress the pressure bellow that for $q_s=0$ at large $\kappa_i R$.

Conclusion

We have calculated the potential of the charged semi-permeable shell filled with polyions and the pressure acting on the shell membrane. It is shown that the charge of the shell does not affect the inner distribution of polyions, but significantly changes the inner potential and pressure on the shell. If the overall charge of the filled shell has the same sign as the surface alone the pressure on the shell increases with increase of the surface charge density. Otherwise the surface charge density suppresses the electro-osmotic pressure due to the electrostatic attraction between the oppositely charged polyions and shell.

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