Donnan Equilibrium and Osmotic Pressure in Hollow Polyelectrolyte Microcapsules

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Abstract

A simple theoretical model of the Donnan equilibrium is applied to studies of distributions of ions between the external and internal volumes of hollow polyelectrolyte capsules as well as of concomitant osmotic pressure load on a capsule wall resulting from these distributions and the presence of polyanion. The model system consist of dispersed polyelectrolyte capsules in an electrolyte solution whereby two cases are considered with respect to the presence of the polyanion, either in the inner or external solution. It is assumed that the capsule wall is impermeable to polyanion, but water and all ions can freely penetrate. The model predictions are summarized by presenting the difference between the external pH, the pH of the inner solution and the osmotic pressure difference across the capsule wall, both in the dependence of sodium chloride concentration.

Keywords: Polyelectrolyte hollow capsule, Donnan equilibrium, osmotic pressure.

1. Introduction

The design of colloidal entities enabling a certain function is currently one of the topics of physical and colloid chemistry. Special interest is devoted to spatially organized reaction microenvironments, often named microreactors. Liposomes were first proposed as reactors for synthesizing particles and for modeling some cell functions.[1] The main problem of liposomes is their limited ability to vary the influx of reaction agents since the permeability of lipid bilayers can not be easily changed. Recently, a novel type of microcages based on Layer-by-Layer (LbL) adsorption of polyelectrolytes on colloidal particles with sequential removal of the core was introduced.[2,3] One of the important features of polyelectrolyte multilayers forming LbL polyelectrolyte capsules is their selective permeability. A variety of compounds can be entrapped in such polyelectrolyte capsules by different means, such as controllable changing of porosity of the polyelectrolyte multilayer polyelectrolyte capsule, polymerization or precipitation.[4] Actually, one can displace polyelectrolytes either exclusively in the interior of a polyelectrolyte capsule or in an external solution. Such displacement leads to entirely different chemical composition, including ion distribution, in the interior and exterior. The consideration of such phenomena is important to evaluate the physical and the chemical processes occurring in microreactors built of polyelectrolyte capsules. This makes the polyelectrolyte hollow capsules an important class of materials that may be employed in basic research as well as in diverse biomedical and technological applications.[5]

Up to now the mechanical properties of hollow polyelectrolyte capsules have been studied in few different ways. The micropipette aspiration technique which is widely used in the investigation of biological systems has been applied for studying mechanical properties of polyelectrolyte capsules.[6] The atomic force microscopy tech-

nique was also used for investigation of mechanical properties of polyelectrolyte capsules.[7, 8] Polyelectrolyte capsules under load and force were investigated with an AFM related force measuring device. The composition of capsules defines the elastic and plastic deformation modulus of capsules. Third, the osmotic technique using creation of an osmotic pressure difference between the external and the inner solution of capsules was used to investigate the deformation of polyelectrolyte capsules.[9] The mechanical behaviour of polyelectrolyte capsules has also been studied in microchannels with capsules flowing through constrictions.[10] The properties of the capsules were investigated before and after constrictions in microchannels.

A polyelectrolyte film is in most cases impermeable to polyanions of high molecular weight, whereas water and ions can freely penetrate the wall.[11] When at one side of the capsule wall, either in the inner or in the external solution, such polyanions are present, the ions H^+, OH^-, Na^+, Cl^- will be distributed between the two solutions according to a Donnan equilibrium. The existence of pH differences was observed and described in our earlier work.[12] Additionally, the distribution of water and ions may lead to differences in osmotic pressure between the external and the inner solution that can create tension in a capsule wall and is consequence, a concomitant increase in the capsule wall surface and change in capsule volume is observed.[13, 14]

In the present work the Donnan distribution of ions, the pH difference and the osmotic pressure difference between the external and the inner solution are studied along with the dependence of conditions in the external solution with respect to the concentration of the added sodium chloride (NaCl) and different polyanion bearing negatively charged groups with different apparent pK (pKa). The physical sense of the different pKa is modeling of weak polyanions with different protonation groups, for instance carboxyl groups. We consider two different systems of hollow polyelectrolyte capsules, the first in which the polyanion is encapsulated, and the second with the polyanion in the external solution. The model consists of the traditional relations for the Donnan equilibrium that are applied together with the requirement of electroneutrality in the external and the inner solution. Considering a relation between the external pH and the inner solution pH gives us knowledge about monitoring conditions in the inner solution as well as controlling the tension in the capsule wall, both dependent on conditions in the external solution. The difference in osmotic pressure between the inner and the external solution is predicted and, depending on the mechanical properties of the capsule wall, is related to a value at which deformation of capsules could occur. Our predictions turn out to be useful in diverse experimental manipulations (preparation, fabrication and application) of polyelectrolyte hollow capsules.

2. The Model

The model system consists of a NaCl water solution separated by the semipermeable wall of the capsules, creating a confined microsized volume of the inner solution of the capsules and an infinitely large and unrestricted volume of the external solution. The capsule wall is permeable to water and ions and impermeable to polyions. The volume asymmetry of the two solutions is relevant in studying the two cases distinguished by polyanions positioned either in the inner solution or in the external solution.

A polyanion which has one charge per monomeric unit and undergoes the protonation reaction $c_P \rightleftharpoons c_{P^-} + c_{H^+}$ with the dissociation constant K_p is considered

$$K_p = \frac{c_{H^+} \cdot c_{P^-}}{c_P}, \tag{1}$$

where c_P and c_{P^-} indicate the monomeric concentration of protonated and deprotonated polyanions, respectively, and the total concentration of polyanion c_{P_t} is

$$c_{P_t} = c_P + c_{P^-}. \tag{2}$$

The electroneutrality condition for the inner solution and the external solution reads

$$c_{H_k^+} - c_{OH_k^-} + c_{Na_k^+} - c_{Cl_k^-} - c_{P_k^-} = 0, \quad k = i, o. \tag{3}$$

Indices *i* and *o* refer to the inner solution and the external solution, respectively. In the absence of the polyanions in the solution k one takes $c_{P_k^-}$. The symbols in the above expression denote concentrations of the respective ionic species. In the further treatment, one can easily apply the following well-known relations of the Donnan equilibrium of ions for the ideal case

$$\frac{c_{H_i^+}}{c_{H_o^+}} = \frac{c_{OH_o^-}}{c_{OH_i^-}} = \frac{c_{Na_i^+}}{c_{Na_o^+}} = \frac{c_{Cl_o^-}}{c_{Cl_i^-}}. \tag{4}$$

The osmotic pressure of each solution is calculated as

$$\Pi_k = RT\left(\sum_l c_{k,l} + \frac{1}{Z} c_{P_t,k}\right), \quad k = i, o. \tag{5}$$

T is the absolute temperature and *R* is the molar gas constant. *Z* is the degree of polymerization of the polyanion and the summation runs over concentration $c_{k,l}$ of all ion species *l* in the solution *k*. In the absence of the polyanion in the solution *k* one takes $c_{P_{tk}} = 0$.

2. 1. Case I: Encapsulated Polyanion

The concentration of the charged polyanion in the inner solution ($k = i$) can be expressed as

$$c_{P_i^-} = \frac{K_p \cdot c_{P_t}}{K_p + c_{H_i^+}}. \tag{6}$$

First, taking into account eq. (3) for $k = i$, we can substitute eqs. (4) and (6) in eq. (3) replacing all inner concentrations with external ones except for H_i^+. In the model calculations, the auto protolysis for water $K_w = c_{H^+} \cdot c_{HO^-} = 10^{-14}\, M^2$ is assumed. In this way the following expression can be obtained

$$c_{H_i^+} - \frac{K_w}{c_{H_i^+}} + c_{Na_o^+} \cdot \frac{c_{H_i^+}}{c_{H_o^+}} - c_{Cl_o^-} \cdot \frac{c_{H_o^+}}{c_{H_i^+}} - \frac{K_p \cdot c_{P_t}}{K_p + c_{H_i^+}} = 0. \tag{7}$$

Eq. (7) is solved iteratively for $c_{H_i^+}$ in dependence of the total concentration of polyanion C_{P_t} and for a concentration of NaCl in the external solution. Consequently, the pH of the inner solution is obtained. Then we can calculate all other inner concentrations of ions by the relations in eq. (4). The inner and the external osmotic pressure and its difference can easily be calculated by eq. (5).

2. 2. Case II: Polyanion in the External Solution

In the case when the polyanion is in the external solution, the polyanion determines the external pH. Substituting eq. (2) and (3), the latter with respect to $k = o$, in eq. (1) and taking into account that $c_{Na_o^+} = c_{Cl_o^-}$ we obtained the relation

$$K_P \left(c_{P_t} - c_{H_o^+} - \frac{K_w}{c_{H_o^+}} \right) - c_{H_o^+} \left(c_{H_o^+} - \frac{K_w}{c_{H_o^+}} \right) = 0 \tag{8}$$

which can be solved iteratively for pH_o as a function of the total concentration of polyanion c_{P_t} and the pKa value of the polyanion. Combining eq. (3) and (4) we obtain the following relation

$$H_i^+ = \sqrt{\frac{c_{H_o^+} c_{Cl_o^-} + K_w}{1 + \dfrac{c_{Na_o^+}}{c_{H_o^+}}}}. \tag{9}$$

First pH_o is calculated from eq. (8), then the inner concentration $c_{H_i^+}$ and thus pH_i can be calculated by eq. (9). The osmotic pressure difference is calculated in the same way as for case I.

3. Results and Discussion

In the calculations we assume idealized conditions, which means that in the absence of polyanion (polymer and monomer weights Mw = 70000 and Mn = 205 corre-

spond to weak polyelectrolytes with molecular weight similar to PSS (poly(sodium styrenesulfonate)) which is widely used polymer in this field of research),[9, 13] the external solution as well as the inner solution is a pure NaCl solution at neutral pH. The idealized case may serve for inspection of the effect of added NaCl on the conditions inside the capsules such as the inner pH, concentrations of ions, and the osmotic pressure difference across the capsule wall. It is observed that the polyanion with its counterions and pKa value strongly determines these relations. The macrocontinuum Donnan model is a special case of the more general microcontinuum Poisson-Boltzmann (PB) theory and not just an approximation.[15] The Donnan model considers homogenous charge distribution, while PB accounts for inhomogeneous charge distribution around polyelectrolytes. A transition from the PB to the classic Donnan model can be established by decreasing the charge density, and the distance between polymers is decreased if osmotic pressure is kept constant. At a low ionic strength that corresponds to the Debye screening length being larger than separation between polyelectrolytes, it was observed that the potential between the polyelectrolytes predicted by the PB cell model is nearly uniform and the Donnan model can be applied.[16] At a high ionic strength when the Debye screening length (κ^{-1}) is smaller than the separation between polyelectrolytes and bigger than the diameter-thickness of polyelectrolytes, the potential varies between polyelectrolytes and the Donnan model overestimates the mean potential.[17] Aubouy et al. studied electrostatic interactions between spherical and cylindrical charged particles analytically.[18] At the limit of high salt concentration when κ^{-1} is less than or equal to the size of charged particles, there is good agreement between the solution of the nonlinear Poisson-Boltzmann equation and linear analytical Debye-Hückel approximation. When $Z_{eff} \lambda_B/a \sim Z_{bar_e} \lambda_B/a \geq 3.1$, and taking into account a deviation of 5% from linearity relation between Z_{eff} and Z_{bar_e}, there is no accumulation of micro ions around charged particles with a radius of 5 nm, if the bare charge is less than 22 in a 3.7 mM 1:1 electrolyte solution. In the case of particles with a radius of 10 nm, there is no condensation if Z_{bar_e} is less than 43 in a 0.9 mM 1 : 1 electrolyte solution. The Bjerrum length λ_B is defined as $\lambda_B = e^2/(4\pi\varepsilon k_B T)$ where e is an elementary charge, ε represents a permittivity of the solvent considered as dielectric continuum; $\lambda_B = 0.72$ nm for water at room temperature, Z_{bar_e} is a bare structural charge of macro-ion in units of elementary charge. The high charged macro-ion accumulates in its immediate vicinity counter-ions, and this system may be considered as a single entity carrying an effective charge Z_{eff} which and is much lower than Z_{bar_e}. Within a linearization approximation, the effective pair interactions between two spherical macro-ions takes Debye-Hückel form with the effective charge Z_{eff}.

In the most common cases of fabrication of polyelectrolyte microcapsules, the polyelectrolytes used are

PAH and PSS.[3–9, 12, 13, 19–21] We are considering the constant volume of the capsules, but their assembly properties can influence the response to pH and salt stimuli. It has been shown that polyelectrolyte multilayers assembled at pH lower than 8.5 don't respond to pH.[22] Multilayers assembled at various system parameters can be pH dependent.[23] Also, capsules prepared with cross-linked melamine formaldehyde (MF) cores are pH responsive, as assembled PAH (poly(allylamine hydrochloride)) is not completely protonated. Those capsules treated with acetone and immersed in different NaCl solutions show changes of volume.[24] In the case of polystyrene cores, PAH\PSS capsules are not sensitive to pH lower then 10 and salt concentrations lower than 3 M.[19, 25] Volume dependence of microcapsules is blocked after crosslinking of the polyelectrolyte layers.[26] Capsules prepared with MF particles have pH tuneable permeability for dextran at lower pH values.[27] Capsules fabricated with PS particles also show pH tuneable permeation properties for polyanion at high pH values.[20, 21] The respective predictions are given in Figures 1–4 and their importance for handling the system experimentally is discussed in the following section.

Nonuniform pK is the most common in the biological and chemical system,[28] however, weak polyelectrolytes can have single pKa like PAH.[29] The complicated titration behaviour of interacting monomer sites can be described as weighted sum of Hendersen-Hasselbalch (HH) curves, and the total average protonation of polyelectrolyte molecules equals the sum of HH curves.[30] Our predictions show a tendency of small ion distribution between inner and outer capsules solutions also in dependence of different values of pKa. Taking into account sum of different titration curves with different values of pKa the predicted results would be in the region between the two given curves for our chosen values of pKa 2 and 4.

3. 1. Case I: Encapsulated Polyanion

The system consists of hollow polyelectrolyte capsules filled with the polyanion at various monomer concentrations and immersed in pure water or an NaCl aqueous solution. Figure 1 shows dependencies of the inner pH as a function of the external NaCl solution for different inner concentrations of total polyanion and different pKa values. A higher concentration of deprotonated polyanion attracts more positively charged ions into the polyelectrolyte capsules, which means a lower pH and higher difference in pH between the external and the inner solutions. At very low NaCl concentrations ($c_{NaCl} < 10^{-7}$ M), the inner pH assumes values of pure water-charged polyanion solution whereby the pH difference attains the largest possible values. Under these conditions, the polyanion is highly protonated, and the degree of protonation depends on the pKa values. A higher pKa value results in a less protonated polyanion and a higher inner pH value. At these extremely low values of NaCl concentration,

increasing NaCl concentration strongly affects the Donnan distribution of the permeable ions. Increasing NaCl concentration lowers the pH difference, which is clearly seen in the pH_i curves approaching the external pH values. At NaCl concentration of the same magnitude as the monomer concentration of polyanion, the Donnan ratio of permeate ions almost reaches the value one, which means that the differences in concentrations of ions between the two solutions and hence the pH difference are diminished. In practice, 1 M of NaCl is a large enough amount of NaCl for such predictions. The degree of polyanion protonization is changed concomitantly with pH changes. For different pKa values, the pH curves merge, indicating that the polyanion becomes highly deprotonated irrespective of its pKa. Here, for the conditions chosen this occurs at a NaCl concentration two magnitudes lower than the polyanion concentration.
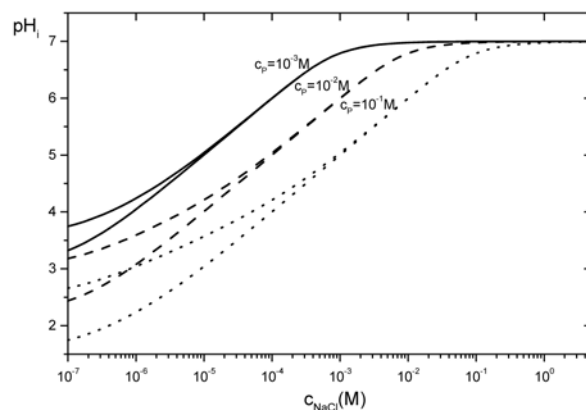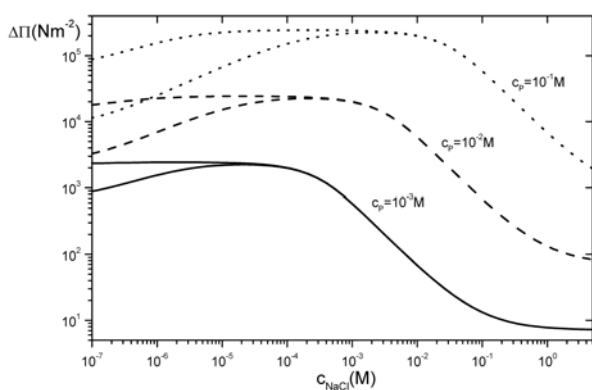

Figure 1. Theoretical prediction of the pH of the inner solution dependent on added NaCl in the external solution, for encapsulated polyanion. Parameters for the theoretical curves were an external solution pH of 7; the total monomeric polyanion concentration was 10^{-3} M (full lines), 10^{-2} M (dashed lines) and 10^{-1} M (dotted lines), for curves from top to bottom, respectively, and the pKa of the polyanion 2 (lower lines) and 4 (higher lines).

Changing the external concentration of added NaCl and consequent redistribution of water and permeate ions across the capsule wall leads to different osmotic pressures in the external and the inner solution. Figure 2 shows predictions of the difference in osmotic pressure between the inner and the external solutions ($\Delta\Pi = \Pi_i - \Pi_o$). The following discussion is organized with respect to the NaCl concentration added at which the osmotic pressure difference assumes a maximal value, and correspondingly, low and high NaCl concentration regions are obtained. In the NaCl free medium, the inner osmotic pressure results from contributions of ions as counterions to the polyanion. Two cases with respect to two different pKa values of the polyanion considered are distinguished under these idealized conditions as well as in the region of low NaCl concentrations. This is in accordance with the

predictions shown in Figure 1. A higher pKa of the polyanion means a lower concentration of deprotonated groups of the polyanion, and consequently, a higher inner pH, a lower inner osmotic pressure and a lower osmotic pressure difference. The situation of merging curves with increasing NaCl concentration is discussed above.

The increasing external NaCl concentration is followed by sodium entry into the capsule interior. However, because of the electroneutrality condition in the inner solution, hydrogen ions are expelled, the inner pH is increased, and the highly deprotonated polyanion prevents chlorine ions from entering the capsules. Sodium ions counterbalance the negative charge of the polyanion, which means that, according to the Donnan equilibrium, the inner concentration of sodium ions is much higher than the external one. The contribution of hydrogen ions to the inner osmotic pressure diminishes and the other components are of negligible importance due to their concentrations. Under these conditions, the osmotic pressure difference increases and attains a maximal value. It can be seen that the NaCl concentration at the $\Delta\Pi$ maximum is one or two orders of magnitude lower than the monomeric concentration of the polyanion.

With a further increase of the NaCl in the external solution, the inner concentration of sodium ions steeply increases. Since the polyanion is deprotonated, the electroneutrality condition can now be fulfilled only by an appropriate entry of chlorine ions. The contribution of sodium and chlorine ions to the inner osmotic pressure becomes overwhelming, and consequently, $\Delta\Pi$ lowers. At the limit of high NaCl concentration it becomes of the same value, as it is a sole contribution of the polyanion, and all ion species involved are almost equally distributed across the capsule wall.
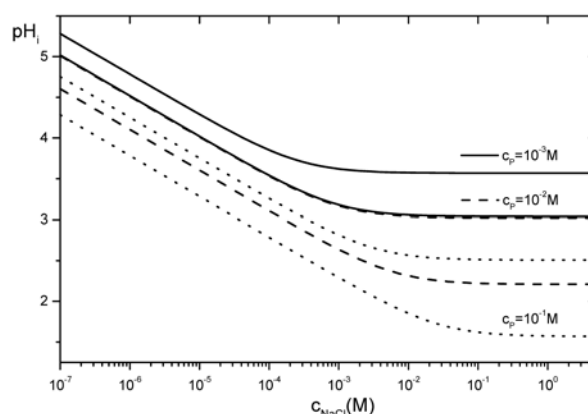
The maximal osmotic pressure difference predicted in the present model is of such a magnitude that the capsules can be deformed. There is experimental evidence for such observations.[13] The experiments were performed in a NaCl free medium at 0.1 M monomeric concentration of encapsulated polymer, and a value of the inner osmotic pressure of $1.9 \cdot 10^5$ Pa can be measured from that reference. This is in accord with the predicted maximal osmotic pressure difference predicted by the model at conditions of micromolar NaCl concentration, and the same concentration of encapsulated polyanion.

3. 2. Case II: Polyanion in the External Solution

The model system consists of hollow polyelectrolyte capsules immersed in a water solution with various concentrations of polyanion and NaCl. Because of the protonation reaction of the polyanion, the external solution acidity is determined by the polyanion concentration and pKa. In the model, the pH of the external solution is independent of NaCl added to the external solution. The properties of the inner solution, such as the pH, can be changed by addition of NaCl to the external solution (Fig. 3). The condition of electroneutrality defines the properties of the inner solution. When no NaCl is present in the external solution, in this idealized case the inner solution has a neutral pH of 7. Small concentrations of added NaCl can significantly decrease the inner pH. The decrease depends on the concentration of polyanion and pKa. For parameter values used in this calculation, a decrease of about two to three pH units is predicted for NaCl added in micromolar concentrations. The decrease in inner pH which follows increasing NaCl concentration can be

Figure 2. Theoretical prediction of the osmotic pressure difference ($\Delta\Pi$; $\Delta\Pi = \Pi_{IN} - \Pi_{OUT}$) dependent on added NaCl in the external solution for encapsulated polyanion with a total monomeric concentration of 10^{-3} M (full lines), 10^{-2} M (dashed lines) and 10^{-1} M (doted lines), for curves from bottom to top, respectively. Other model parameters were the external solution pH of 7, degree of polymerization Z = 341 and the pKa of the polyanion 2 (higher lines) and 4 (lower lines).

Figure 3. Theoretical prediction of the pH of the inner solution independent on added NaCl in the external solution, for polyanion in the external solution. Parameters for the theoretical curves were a total polyanion monomeric concentration of 10^{-3} M (full lines), 10^{-2} M (dashed lines) and 10^{-1} M (doted lines), for curves from top to bottom, respectively and pKa of the polyanion 2 (lower lines) and 4 (higher lines).

understood in terms of the electroneutrality condition which is achieved mostly by a counterbalance between H^+ and Cl^- ions where the contribution of sodium ions is of minor importance. The limit value of the inner pH equals the external solution pH (see eq. 9), and therefore it is determined by the polyanion, its concentration and pKa. The inner pH reaches an approximate limit value when the concentration of added NaCl is roughly equal to the concentration of polyanion in the external solution. With a further increase of NaCl concentration, the sodium ions counterbalance the chlorine ions in the capsule interior.

The dependence of osmotic pressure difference between external solution and inner solution ($\Delta\Pi = \Pi_o - \Pi_i$) on NaCl concentration is presented in Fig. 4. The osmotic pressure difference is induced by the presence of polyanion in the external solution. In the NaCl free and low NaCl concentration region, the osmotic pressure in the external solution is determined mostly by the protonation of polyanion and the concentration of counterions. On the other hand, the inner osmotic pressure is negligible. With increasing external NaCl concentration, it starts to increase because of the increasing contributions of H^+ and Cl^- ions, and consequently, $\Delta\Pi$ is lowered. For the values of our system parameters, this occurs when the external solution concentration of NaCl is about three orders of magnitude lower than the monomeric concentration of polyanion. As in the case of the pH curves (Fig. 3), when the concentration of NaCl in the external solution approaches equality to the concentration of polyanion, the osmotic pressure difference approaches a limit value that corresponds to a sole polyanion contribution to the osmotic pressure. The osmotic pressure difference is also dependent on the dissociation constant pKa of the polyanion. It is obvious that a lower pKa value affects a higher concentration of H^+ ions, and therefore, a higher value of

$\Delta\Pi$. In the case of encapsulated polyanions, the pressure gradient cause an increase in size resulting in a rupture which has been experimentally observed.[13]
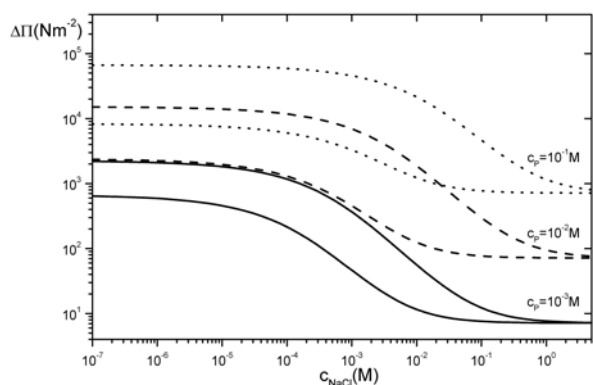
In the case of polyanion in the external solution, the osmotic pressure difference considered could be of such a magnitude that capsules undergo deformation. Gao et al. performed buckling experiments in which a deformation of capsules was induced by the osmotic pressure of polymer counter ions in the external solution.[9] The critical pressure derived was 3.5×10^5 Pa, which is the order of magnitude of the osmotic pressure difference of 10^5 Pa calculated by our model for a polyanion monomeric concentration of 0.2 M. The deviation may be caused by different amount of salt.

4. Conclusions

In this study we modeled the behavior of a reservoir of confined dimensions, which either contains or excludes polyanions while ions are freely distributed between an external compartment of infinite dimensions and an inner one. The distribution of electrolyte ions influences the pH and the osmotic pressure applied to the "walls" of the reservoir. The type of employed polyanions, i.e. the pKa of the groups the polyanions bears, has an influence only at low NaCl concentration and at low pH. The osmotic pressure, produced mainly by associated ions, is dependent non-monotonically on NaCl concentration and reaches a maximum at a certain point related to the polyion concentration. In particular, taking into consideration the polyanion, it governs the Donnan distribution of ions with respect to its negative charge. When it is encapsulated it attracts sodium ions into capsules which expel hydrogen ions from the inner solution. When in the external solution it drives hydrogen and chlorine ions into the inner solution of the capsules. In this way it affects the inner pH as well as the osmotic pressure difference across the capsule wall.

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Figure 4. Theoretical prediction of the osmotic pressure difference ($\Delta\Pi$; $\Delta\Pi = \Pi_{OUT} - \Pi_{IN}$) dependent on added NaCl in the external solution for polyanion in the external solution with total monomeric concentration of 10^{-3} M (full lines), 10^{-2} M (dashed lines) and 10^{-1} M (doted lines) for curves from bottom to top, respectively. Other model parameters were degree of polymerization Z = 341 and pKa of the polyanion 2 (higher lines) and 4 (lower lines).

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Povzetek

Teoretičen model Donnanovega ravnovesja smo uporabili v študiji porazdelitve malih ionov med zunanjim in notranjim volumnom votlih polielektrolitskih kapsul, zaradi česar se spreminja tudi osmozna obremenitev stene kapsul ob prisotnosti poliiona. Model opisuje disperzijo polielektrolitskih kapsul v elektrolitski raztopini, kjer je poliion prisoten v zunanji ali notranji raztopini kapsule. Predpostavili smo, da je stena kapsule neprepustna za poliion in prepustna za vodo in majhne ione. Modelne napovedi so podane kot vrednosti pH notranje raztopine v odvisnosti od natrijevega klorida in razlike osmoznih tlakov na steno kapsule v odvisnosti od natrijevega klorida.