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Micromechanical Theory for pH-Dependent Polyelectrolyte Multilayer Capsule Swelling

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ABSTRACT: Hollow polyelectrolyte multilayer capsules made of ionizable segments (e.g., carboxylic acid, amine, pyridine) have an equilibrium size that is independent of salt concentration and pH in a wide pH range but swell to a larger size at lower and higher pH. Besides, at the edges of the stability plateau their equilibrium size increases with increasing ionic strength. We set up a micromechanical theory in which we combine an expansive force due to ion entropy with an elastic contractive force and derive from balance of forces a simple expression for the equilibrium capsule size. The theory describes the influence of pH on size (including the wide plateau region as well as the steep increase in size at the edge of the pH plateau) almost quantitatively without fitting parameters as well as the increase in size with increasing ionic strength. This effect is contrary to what would be expected when the polymer charge would directly depend on *solution* pH instead of *local* pH within the shell and is a phenomenon comparable to the osmotic regime found for ionizable ("annealed") polyelectrolyte brushes at very low ionic strength, for which it is also observed that the brush expands when the salt concentration is increased.

Introduction

Polyelectrolyte multilayer microcapsules containing stimuli-responsive polymers have many potential applications as sensors, microcontainers, actuators, etc. Depending on the nature of the polymers introduced in the capsules, different stimuli such as pH, ionic strength, and temperature can result in distinct and often reversible modifications of the capsules. The observed effects vary from tunable permeability to morphological changes.[1−10] The polyelectrolyte multilayers are prepared via the layer-by-layer (LbL) technique introduced by Decher et al.[11] After the deposition of the polymers onto colloidal particles the templates can be dissolved, leading to stable microcapsules.[12]

Recent work[13−20] has focused on capsules formed of weakly charged polymers because of their potential use as pH-responsive systems, e.g., for drug delivery purposes. In recent experiments,[19,20] it has been observed that in an intermediate pH range the capsules keep their unperturbed size (equal to that of the colloidal template particles) but swell when the pH is decreased to below a critical value, $\mathrm{pH_{min}}$, or increased above $\mathrm{pH_{max}}$ (see Figure 1). With increasing ionic strength swelling increases (see Figure 2). Similar swelling effects were observed for microcapsules made from multilayers stabilized by hydrogen bonding when entering a pH range where they are charged.[21]

Our aim is to develop a theoretical framework to describe the size change as a function of material properties (shell wall thickness, Young's modulus, pK values) and external parameters (pH, ionic strength). Because the capsules swell to an equilibrium size (i.e., swelling stops after a certain thermodynamically most favorable size has been reached, at least on a time scale of several days), a theoretical approach in which capsule size is determined from a balance of forces seems suitable. Such an approach was used in ref 22 to describe capsule swelling due to an osmotic pressure difference across the shell due to polyelectrolytes enclosed in the hollow space within the capsule. An elastic force was introduced to describe the contractive force that counteracts the osmotic pressure.

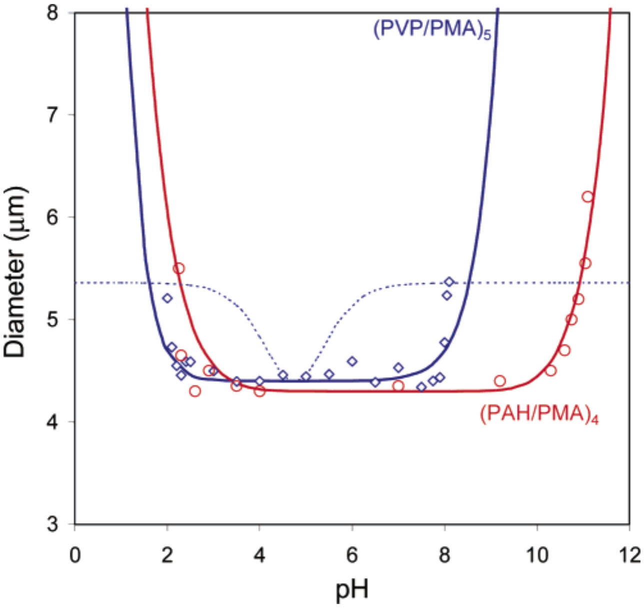

Figure 1. Capsule diameter as a function of pH (data points and error bars in refs 19 and 20) for the two experimental systems. Parameter settings for theory: $E = 30$ MPa, $\nu = 0.5$, $\beta = 0.5$, $\mathrm{p}K_\mathrm{A} = 4.5$. PAH/PMA: $h_0 = 13.5$ nm, $n = 3.2 \times 10^9$, $\mathrm{p}K_\mathrm{B} = 8.5$, $2R_0 = 4.3$ μm, 0 mM NaCl added; PVP/PMA: $h_0 = 19.5$ nm, $n = 4.0 \times 10^9$, $\mathrm{p}K_\mathrm{B} = 5$, $2R_0 = 4.4$ μm, 1 mM NaCl. Dashed line based on assuming that pH within the shell equals that in solution (0.5 mM NaCl, $E = 15$ GPa); see text for detailed discussion.

The present work is based on that approach, but in our case the osmotic force is not due to enclosed polyelectrolyte but due to small ions. These ions are attracted to the capsule shell to compensate for the net charge excess of the polymers forming the capsule shell. At an intermediate pH the two polymers are

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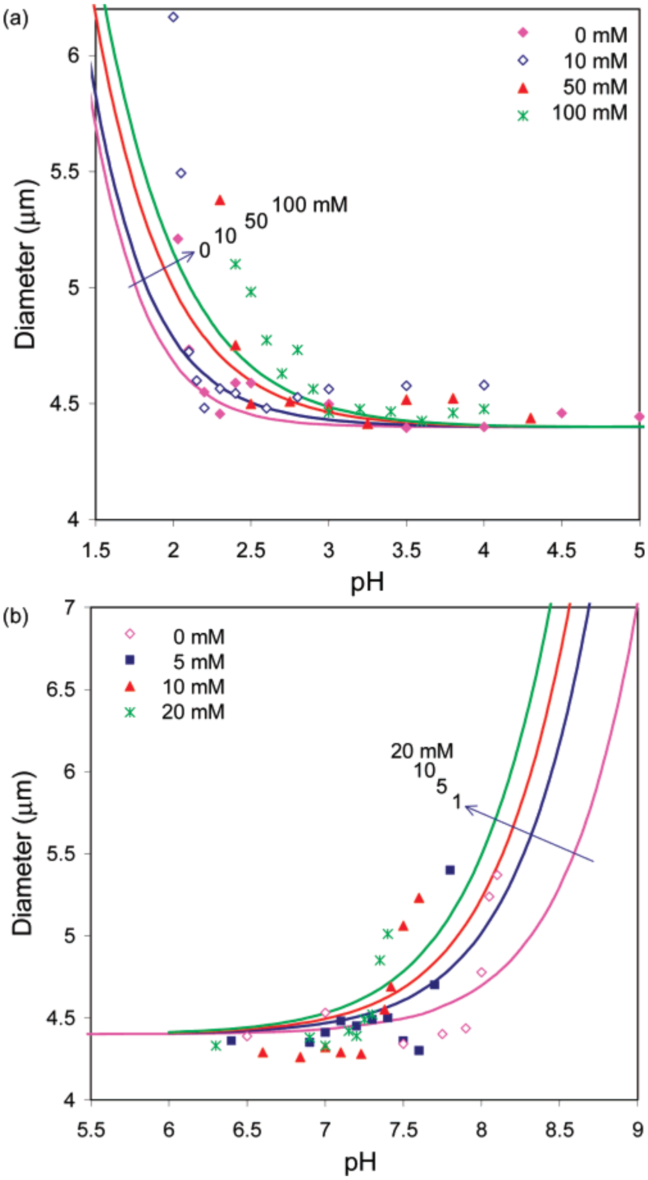

Figure 2. Influence of pH and ionic strength on capsule diameter for $(PVP/PMA)_5$. The caption gives the added amount of salt (additional to the ionic strength increase due to pH adjustment). Lines are based on theory; see Figure 1 for input parameters.

about equally charged, and ions are not required to close the charge balance; therefore, the expansive force is zero, and the capsule has its unperturbed size. Moving away from the pH where the two polymers exactly compensate one another's charge, pH_{ideal}, one would expect that a charge excess develops and the capsule starts to increase in size. However, in the experiments a wide pH plateau is observed for which the size does not increase notably (see Figure 1). The present theory accounts for this effect by taking into consideration that the charge of a polyelectrolyte is not dependent on the *solution* pH, but on the *local* pH within the multilayer (pH used here as a measure of local proton concentration): for a relatively small change of solution pH from pH_{ideal} it turns out to be energetically more favorable for the system to change the electrostatic potential within the multilayer such as to keep the pH in the multilayer close to pH_{ideal} and the entire shell (almost) uncharged than to accept a net charge excess and have the shell expand (which would result in an increase of elastic energy). Moving with pH further away from pH_{ideal}, at some point the energetic penalty associated with the increase of electrostatic potential becomes too high, and it becomes more favorable for the system that a net polymer charge develops; consequently, the capsule starts to expand.

The increased ion concentration next to and within the shell—when a net polymer charge develops—results in an osmotic, expansive pressure. The reason for the expansive force is that when more space becomes available for the ions within and next to the shell, the ion concentration can decrease, and this leads to a favorable decrease of free energy (one can also say that the electrostatic potential and surface charge density of the shell will be reduced with increasing size). The creation of space for the ions can occur in two manners: first of all because the chains within the shell move further apart from one another (lower shell polymer density, like in a charged polymer gel, or brush, that expands) and, second, by increasing the shell outer surface area creating more area for the diffuse layer of small ions on each side of the shell wall.

To describe the electrostatic problem accurately, including both above elements, we would have to consider the polymer density profiles within the multilayers in detail, calculate the electrostatic potential profile inside and outside the shell,[23] and determine for each shell layer thickness and polymer density the associated free energy (which has contributions from ion entropy, electrostatic field energy and, for ionizable polymers, chemical contributions related to proton adsorption/desorption[24−26]). After combining with the elastic energy, we can then minimize the total free energy to find the equilibrium shell thickness and capsule size. In this approach, one could use a one-dimensional version of the Poisson equation and use for the ions a modified Boltzmann expression that includes their volumetric interaction with each other and with the polymer chains.[26] More accurate would be to include as well a more detailed description of the correlation of ions around the polymer chains, for instance by using a (cylindrical) heterogeneous cell model.[24] Additionally, we would need to include how the elasticity modulus depends on shell polymer density, pH, etc., and finally we would need to assume that when the shell reduces its polymer density (chains move further apart), the resulting expansion is isotropic; that is, a certain relative expansion in its thickness is equal to a relative expansion in its perimeter, thus its diameter.

To circumvent many of these unknown aspects and to come to a relatively simple model for capsule swelling instead, we will follow a direction given in Figure 2 of ref 23, namely that within the multilayer structure the electrostatic potential is rather constant and close to zero (no ion excess) with only a sharp peak in potential (and a concomitant ion concentration increase) near the edges. This approach is supported by experimental work in ref 27, which showed that when moving from the solution−film interface into the polyelectrolyte multilayer film the electrostatic potential rapidly decays to zero. Also, Schlenoff et al.[28] measured that in a multilayer the cationic and anionic polymers compensate each other's charge without requiring additional salt ions to close the charge balance. Thus, we will assume in the present work that the electrostatic potential within the shell wall is constant (independent of location), right up to the edges of the shell, while we neglect a charge excess due to ions within the shell and thus only consider the ions in the two diffuse layers on each side of the shell wall. Because of the assumed constant potential over the shell wall, we do not have to consider the exact positions of the polymers within the shell—all polymer charges "feel" the same electrostatic potential.

In the next section we derive the micromechanical model for the size of capsules as a function of elasticity modulus, shell thickness, pH, and ionic strength; subsequently, we compare the model with experimental data for the swelling of capsules with a diameter of ~4.5 μm consisting of the following two polycation/polyanion pairs, namely, poly(allylamine hydrochloride) (PAH)/poly(methacrylic acid) (PMA) and poly(4-vinylpyridine) (PVP)/PMA. With respect to the elasticity modulus we will initially assume that it does not depend on pH or ionic strength. This is justified by the fact that E modulus experiments for other systems did not show a notable dependence for ionic strength below 1 M,[7,30] while in ref 31 the measured E modulus decreased by only ~10% when 100 mM salt was added. Later we will use an empirical E ionic strength dependence to improve the fit of the model to the experiments.

Theory

In our theoretical model we neglect ions within the shell and therefore do not need further information on the polymer density within the shell. We assume a constant electrostatic potential within the shell and therefore can neglect the exact position of polymers within the shell.The two main forces we consider are electrostatics (or ion entropy), which is an expanding force, because a larger particle has more space for the ions in the diffuse double layers around it. Elasticity is a contractive force which tries to keep the particle diameter close to the unperturbed diameter D_0.

The elastic energy per capsule is for ideal, Hookean, behavior given by[22]

$$U^{\mathrm{elas}} = \frac{\pi E h_0}{1-\nu}\Delta D^2 \tag{1}$$

where E is the elasticity, or Young's, modulus, h_0 the (unperturbed) wall thickness, ν Poisson's ratio ($\nu = 0.5$ for most rubbers), and ΔD the difference between D, the capsule diameter, and D_0, the unperturbed diameter. (Note that energy has dimension kT and length nm, and thus the E modulus must be expressed in kT/nm^3.)

Electrostatically, we describe the multilayer shell as a charged, infinitely thin plane with the diffuse layers of small ions on both sides.[29] In a planar geometry (we assume both the thickness, h_0, and the Debye length, κ^{-1}, to be small compared to the capsule diameter, D) electroneutrality is given by[32]

$$y = 2\ \mathrm{arcsinh}\left(\frac{Z^{\dagger}\pi\lambda_{\mathrm{B}}}{\kappa}\right) \tag{2}$$

where $Z^{\dagger}$ is the net polymer charge per unit surface area ($A = \pi D^2$), λ_{B} the Bjerrum length, c_{∞} the ionic strength (in numbers per volume), and y the dimensionless electrostatic potential at/in the capsule shell wall. The Bjerrum length is given by

$$\lambda_{\mathrm{B}} = \frac{e^2}{4\pi\epsilon kT} \qquad \kappa^2 = 8\pi\lambda_{\mathrm{B}}c_{\infty} \tag{3}$$

where e, ϵ, k, and T have their usual meaning (in aqueous solution, $\lambda_{\mathrm{B}} = 0.72$ nm).

To derive an expression for the electrostatic free energy, we use the low-potential Debye–Hückel (DH) limit, after which eq 2 simplifies to

$$y = 2\,\frac{Z^{\dagger}\pi\lambda_{\mathrm{B}}}{\kappa} \tag{4}$$

In the DH limit, the electrostatic free energy (of a capsule of a fixed charge Z) is given by

$$F^{\mathrm{elec}} = {}^{1}/{}_{2}Zy \tag{5}$$

where $Z = Z^{\dagger}A$, the total polymer charge per capsule (the capsule surface area $A = 4\pi R^2$). On capsule swelling, Z is constant but $Z^{\dagger}$ is not constant; thus, the relevant combination of eqs 1, 3, 4, and 5 is

$$F^{\mathrm{tot}} = \frac{\kappa Z^2}{8c_{\infty}A} + \frac{\pi E h_0}{1-\nu}\Delta D^2 \tag{6}$$

which we can differentiate with respect to D to obtain at equilibrium the force balance

$$-\frac{1}{2\pi}\frac{\mathrm{d}F^{\mathrm{tot}}}{\mathrm{d}D} = 0 = \frac{\kappa Z^2}{8c_{\infty}A^2}D - \frac{E h_0}{1-\nu}\Delta D \tag{7}$$

which gives us a fourth-order polynomial in D. To simplify, we assume that $D \sim D_0$ (thus $A \sim A_0$, where 0 refers to the unperturbed state) and obtain

$$\frac{\Delta D}{D_0} = \pi\lambda_{\mathrm{B}}(1-\nu)\frac{Z^2}{E h_0 {A_0}^2\kappa} \tag{8}$$

which shows that the relative change in diameter $\Delta D/D_0$ scales with the polymer charge excess, Z, squared, the ionic strength to the power $-1/2$, and elasticity E and initial thickness h_0 to the power -1.

Now, in the case that the polymers are ionizable instead of having a fixed charge, as was assumed up to now, free energy expressions may change, but the final expression for the force, eq 7, and the resulting diameter, given by eq 8, should not change. This is because the electrostatic expansive force on the capsule depends on the capsule polymer charge, Z, and not on the mechanism by which the charge is established. (It does not depend on whether the polymers are ionizable or have a fixed charge.) Therefore, also in the case of ionizable polymer we can use eq 8, but with the charge Z now self-consistently related to y via

$$Z = n\sum_{\mathrm{A,B}} z_i\beta_i\alpha_i \tag{9}$$

where the total number of monomers per capsule that carry an ionizable group is n, the β's are the fraction of monomers that are either cationic or anionic, A stands for the polyanions, B for the polycations, z_i is the charge sign (+1 for the polycation segments B; −1 for the polyanions A), and α_i is the ionization degree, which is obtained from[24,26,33]

$$\alpha_i = (1 + 10^{z_i(\mathrm{pH}-\mathrm{p}K_i)}\mathrm{e}^{z_i y})^{-1} \tag{10}$$

where pH is the solution pH and pK_i is the intrinsic pK value, a thermodynamic number related to the proton adsorption energy.[26,33] Intrinsic pK values are independent of (local) pH, ionic strength, etc., are tabulated, e.g., ~4.5 for a carboxylic group and ~6−9 for most amine groups, and should not be confused with apparent pK values. Apparent pK values are a direct measure of the ionization degree, namely according to $\mathrm{p}K_{\mathrm{app}} = \mathrm{pH} - z\ {}^{10}\log((1-\alpha)/\alpha)$, and are related to intrinsic pK values according to $\mathrm{p}K_{\mathrm{app}} = \mathrm{p}K_{\mathrm{intr}} - y/\ln(10)$. The objective of the current theory is to calculate electrostatic potentials, y, within the shell and to obtain values for the ionization degrees, α_i, of the two types of polymer within the shell (which typically tend to be higher than in solution). To obtain the (two) ionization degrees, α_A and α_B, we solve eqs 9 and 10 together with eq 2 and use $Z^{\dagger} = Z/A_0$, after which the diameter increase is given by eq 8.

At a certain intermediate pH, pH*, the capsule is exactly uncharged with both Z and y zero (for equal numbers of anion and cation segments, i.e., $\beta_A = \beta_B = 0.5$, pH* is exactly between pK_A and pK_B). At higher values of pH the capsule is negatively charged; below pH* it is positively charged (predicted values for the capsule surface charge can be up to ±150 mC/m^2). For both of our experimental systems charge reversal at an intermediate pH has been experimentally observed.[5,17,20]

Results and Discussion

In this section we compare theoretical and experimental results on two systems, namely poly(allylamine hydrochloride)/poly(methacrylic acid) (PAH/PMA) (four bilayers) and poly(4-vinylpyridine)/PMA (PVP/PMA, five bilayers). For experimental details on capsule preparation, protocols for the swelling experiments, and the measurement of capsule diameter, see refs 19 and 20. For the polyanion/cation ratio, β_i, we use $\beta_i = 0.5$; thus, we assume to have in the shell as many ionizable anionic as cationic polymer segments. Interestingly, small variations of β between $0.4 < \beta_i < 0.5$ do not make a notable difference in the predicted size. For the Young's modulus we use $E = 30$ MPa ($= 7.3\ kT/\text{nm}^3$), which is in the range of values for E for multilayer capsules from literature.[31,34] We use the experimental values for the wall thickness h_0, namely $h_0 = 13.5$ nm for the (PAH/PMA)$_4$ system and $h_0 = 19.5$ nm for the (PVP/PMA)$_5$ system for dried capsule shells. In solution the thickness can be increased due to water present within the shells. For the intrinsic pK values we use $pK_A = pK_{PMA} = 4.5$ (the polyanion in both cases) and $pK_B = 5$ when PVP is the polycation or $pK_B = 8.5$ in the case of PAH, which are values in line with literature.[5,6,35−37] On the basis of data in refs 13 and 38, we derive that there are $\sim 4 \times 10^8$ segments of each polymer per bilayer in a 4.5 μm diameter shell. Thus, for the (PAH/PMA)$_4$ capsules containing four bilayers we have a total number of polyelectrolyte segments of $n \sim 3.2 \times 10^9$, and for (PVP/PMA)$_5$ $n \sim 4 \times 10^9$, which are the numbers that will be used in the calculation. The electrostatic force in the theory depends on the ionic strength c_∞ (resulting in κ) which is induced by the *added* salt as well as by the salt due to the addition of acid/base to adjust pH; this we describe by $10^{-\text{pH}} + 10^{\text{pH}-14}$ (M). All experiments were done at room temperature.

Attempts were made to fit the model to the data using a polymer charge Z that was independent of the local electrostatic potential, namely by setting $y = 0$ in eq 10; this makes the ionization degrees, and thus charge, independent of the presence of other polymer and independent of salt (but still a function of *solution* pH). [Actually, this is equivalent to setting (erroneously) the intrinsic and apparent pK values equal to one another.] However, in this case we could not fit to the data of Figure 1 at all. A best attempt is the dashed line in Figure 1 for the (PVP/PMA)$_5$ system where we had to use a 500 times increased value for the E modulus (a quite unrealistic 15 GPa instead of the typical experimental value of 30 MPa) and still do not get a satisfactorily fit ($c_{\text{salt}} = 0.5$ mM at all pH values; salt addition due to pH addition must be neglected for a best fit). Clearly, the charge of the polymer is not dependent directly on the solution pH, but on the pH within the shell. Furthermore, now with Z independent of ionic strength, eq 8 predicts that with increasing ionic strength, and thus increasing κ, the capsule diameter should swell less. Experimental data, however (see for instance Figure 2), show the opposite trend, which can be explained, as we will discuss, when we describe the ionizable character of the polymer accurately when y is self-consistently obtained from the charge neutrality balance (after which the polymer charge excess Z becomes positively dependent on c_{salt}).

Figure 1 gives the diameter, D, as a function of pH for the two systems in case no salt is added. The data are quite well described by the model, though for the (PVP/PMA)$_5$ system we have to include 1 mM of additional salt (which could readily have remained in the system after capsule preparation despite several washing−centrifugation cycles).

Figure 2 describes the salt influence on capsule swelling for the (PVP/PMA)$_5$ system concentrating on an expanded view, including theoretical curves [data with error bars are given in ref 20; typically, in the nonswollen state the error (derived as the standard deviation from fitting the 30−50 data points for diameter by a normal distribution) is 0.2 μm and in the swollen state 0.3−0.6 μm]. In Figure 2a, the data sets for 0 and 10 mM added salt cannot be distinguished, probably because the ionic strength of a pH 2 solutions is 10 mM already; however, together with the two other data sets (50 and 100 mM) we see that the pH value at which the capsules start to swell increases. Vice versa, for a given pH value we see that the capsules swell with increasing ionic strength (see also Figure 5 to be discussed further on). In agreement with the experiments, the theoretical prediction is also that around pH 2 the capsule diameter should not be very different between 0 and 10 mM added salt. Furthermore, though the theoretical curves do not give a very exact match to the data, the experimental observation of an increasing capsule diameter with increasing ionic strength is reproduced quite well.

Interestingly, this observation of a polyelectrolyte structure swelling with increased ionic strength is in general quite uncommon and is only observed for weakly charged systems at very low ionic strength, such as for ionizable polyelectrolyte brushes, where it is called the osmotic brush regime.[39−43] Also for the electrostatic contribution to the surface pressure of phospholipid membranes this nonmonotonic behavior has been described.[44] To explain this phenomenon, let us first consider a brush with a fixed charge. In this case, upon addition of salt, the electrostatic potential will decrease and the brush will consequently shrink because the ion osmotic pressure decreases and the elastic forces in the chains make the brush contract. However, for ionizable segments, the situation is different at very low ionic strength when the ionization degree of the polymer segments is very low due to the very high electrostatic potentials. Now, upon addition of salt, electrostatic potentials are reduced (just as for the situation of a fixed polymer charge) while simultaneously the ionization degree (thus, charge per chain) increases, an effect that overrules the decreasing potential. That the ion osmotic pressure, Π, increases can be quantified as follows: $\Pi = 2c_\infty(\cosh y - 1) = 2c_\infty[(1 + (\alpha c_b/2c_\infty)^2)^{1/2} - 1]$ with c_b the brush segment density. For low α (osmotic brush limit) this simplifies to $\Pi = (\alpha c_b)^2/4c_\infty$, which shows that with increasing ionic strength the direct $1/c_\infty$ influence on Π can be overruled if α increases fast enough with c_∞. Indeed, inserting eq 10 for α (in the low α and high y limit) the osmotic pressure becomes $\Pi \propto \sqrt{c_b c_\infty}$, which is an increasing function with c_∞, resulting in a brush expansion with increasing ionic strength. At higher ionic strength a maximum in brush thickness is reached, and with further addition of salt the brush collapses again.

For multilayer capsules the expansive surface pressure Π—obtained from taking minus dF/dA of the electrostatic term in eq 6—is given by $\Pi \propto Z^{\dagger 2} c_\infty^{-1/2}$. Now with α small and y high

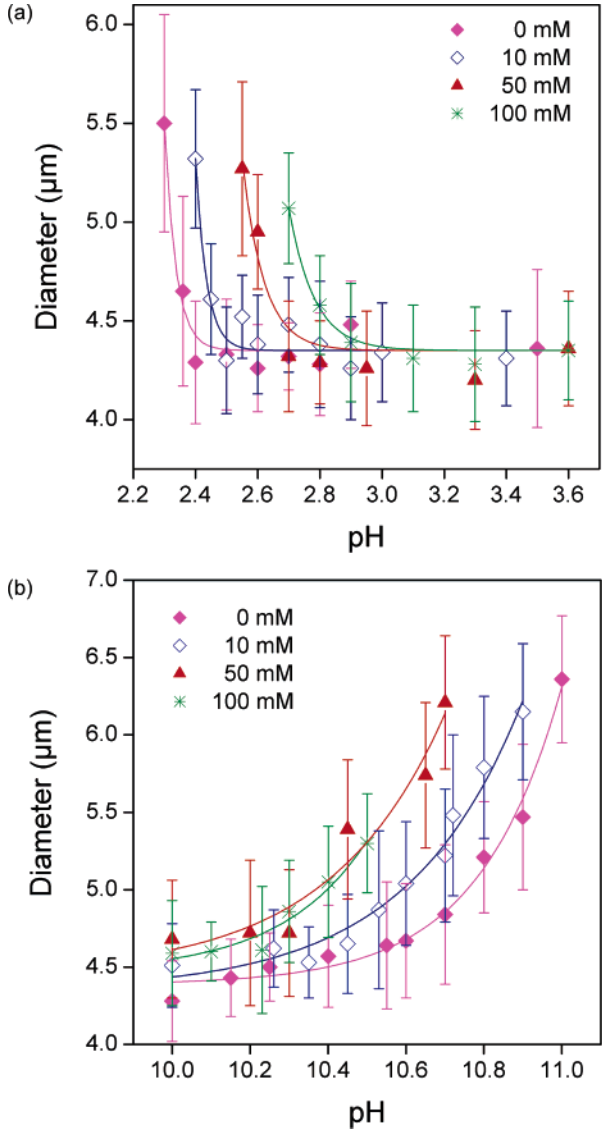

Figure 3. Experimental data plus error bars for the influence of pH and ionic strength on capsule diameter for (PAH/PMA)$_4$. Lines are guide to the eye.

at very low ionic strength, we obtain from eqs 2 and 10 that $Z^\dagger \propto c_\infty^{1/3}$ and thus as final result $\Pi \propto c_\infty^{1/6}$, which shows that Π (and thus capsule size) positively depends on ionic strength in the low-c_∞ limit. Because of this positive dependence of capsule size on ionic strength, we suggest that our system is a new example of the osmotic regime for ionizable polyelectrolyte structures.

Figure 3 presents the experimental data with error bars for the system (PAH/PMA)$_4$, which are reproduced in Figure 4 with theoretical curves included. At basic conditions the theory describes the data best, but both at basic and acidic conditions the increase of diameter with pH, and the influence of ionic strength, is rather well reproduced.

Figure 5 shows data for the influence of ionic strength on capsule diameter for the (PVP/PMA)$_5$ system, for one pH value, namely pH 2.3, together with a theoretical prediction. The solid line is based on a constant value for E, independent of ionic strength. Whereas the experimental observation is that the diameter steadily increases with ionic strength, this theoretical prediction is that the diameter increase levels off. A first explanation for the difference could be that with increasing ionic strength the elasticity modulus gradually decreases.[31] To test this hypothesis, we plot in Figure 5a results of a calculation in which the elasticity modulus decreases as a function of ionic strength (namely, following $E = 30/(A + B^* c_{\text{salt}}^3)$ MPa with the empirical parameters $A = 0.9$ and $B = 1.4 \times 10^{-5}$ with c_{salt} in mM; dashed line). Using this expression, E remains independent of ionic strength up to ∼15 mM, in agreement with the observation that the swelling is about the same for 0 and 10 mM added salt (see Figure 2, ∼5 and ∼15 mM total salt concentration at pH 2.3), and only starts to increase further at higher ionic strength. Figure 5a shows that using this simple empirical function it is possible to obtain a good fit of the model to the data for diameter vs ionic strength at pH 2.3. Obviously, we are aware that this expression for the decrease of E with ionic strength is empirical and without a physical basis.

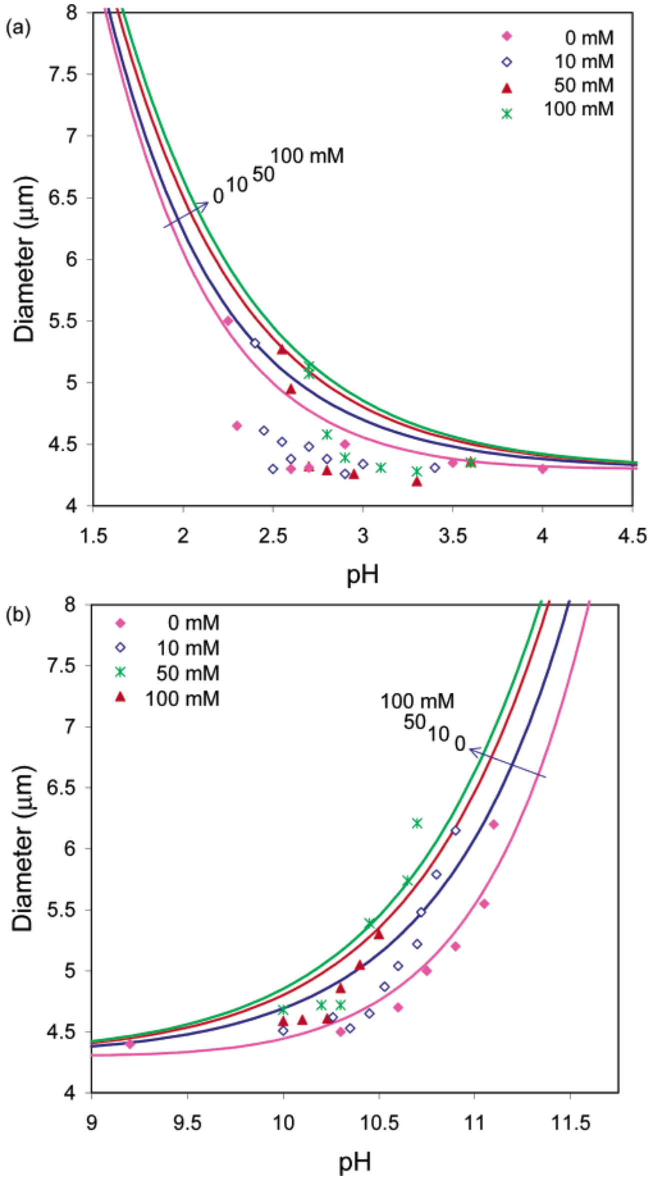

Figure 4. Influence of pH and ionic strength on capsule diameter for (PAH/PMA)$_4$. The caption gives the added amount of salt (additional to the ionic strength increase due to pH adjustment). Lines are based on the theory; see Figure 1 for input parameters.

A final calculation is to use the derived $E(c_{\text{salt}})$ expression and repeat the calculation associated with Figure 2 (that was for a fixed E) (see Figure 5b). As in Figure 2 the predictions for 0 and 10 mM added salt remain close to one another, in agreement with the data. However, whereas in Figure 2 the increase of diameter with ionic strength beyond 10 mM was

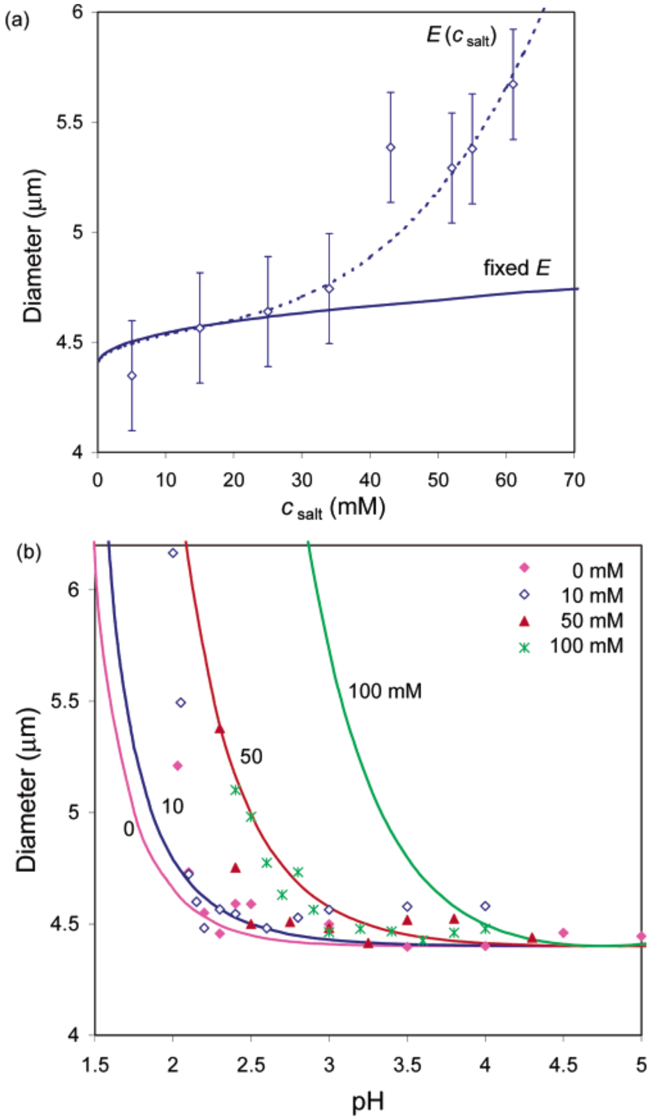

Figure 5. (a) Diameter of (PVP/PMA)$_5$ capsules at pH 2.3. The ionic strength, c_{salt}, is the total salt concentration. The solid line is based on a fixed value for the elasticity modulus, E, whereas the dashed curve is based on E decreasing with c_{salt} to the power 3 (see text). (b) Data and theory of Figure 2a including the empirical $E-c_{salt}$ relation from (a).

somewhat underestimated, the ionic strength effect is now too pronounced and overestimating the actual dependence. An advantage, however, of using the empirical $E(c_{salt})$ function is that the strong increase of diameter with decreasing pH, as is experimentally observed, is better reproduced.

To summarize, in the current work we have derived a simple expression for the influence of ionic strength, pH, elasticity modulus, and wall thickness on the equilibrium diameter of polyelectrolyte multilayer capsules. In the derivation we have made several assumptions such as ideal elastic behavior, a simple double-layer model for the electroneutrality balance, and the Debye−Hückel (DH) approximation that assumes low electrostatic potentials, and finally we have made a simplification that assumed that the capsule diameter remains close to the unperturbed diameter. We have taken data from the literature for E, ν, n, h_0, pK_A, and pK_B after which the model fits the data to a quite satisfactory degree, correctly predicting (1) the existence of a wide pH plateau in which the size does not deviate from its unperturbed values and (2) that the capsule size increases with increasing ionic strength. It must be remarked, however, that the DH assumption that requires electrostatic potentials, y, to be below unity is actually not completely valid for our system: in many cases (especially without addition of salt) we find that predicted y values are much larger than unity. Also, we find that making a more complicated calculation in which R is not assumed close to R_0 gives different results as well. These two elements can be included in a more accurate model. However, the model becomes immediately much more complicated and loses its relative simplicity. In that case other improvements should also be considered such as replacing the double-layer model by the full one-dimensional Poisson model within the shell. In the present work, however, the aim has been to develop a first, simple, model that includes what we believe are the essential forces operating during elastic swelling of multilayer capsules composed of weakly charged polyelectrolytes.

Conclusions

A micromechanical scaling theory has been developed to describe the equilibrium swelling of polyelectrolyte multilayer capsules made of ionizable polymer segments. The model includes an elastic force as well as the osmotic pressure of the counterions associated with the shell (attracted from the bulk toward the shell to compensate for the charge excess of the polymers) that tends to expand the shell. In the model ions within the shell structure are neglected, and only those in the two diffuse layers on each side of the shell are considered, while the electrostatic potential across the shell is assumed to be constant. This simplifies the equations significantly, not requiring further information on shell thickness and shell internal structure. The model captures the essential experimental features such as a wide pH plateau in which the size remains close to the unperturbed (initial) value, the sharp increase in size at the edges of the plateau, and the fact that at the edges of the pH plateau the size increases with increasing ionic strength.

The model includes the fact that the polymer charge depends on local electrostatic potential, which turns out to be essential because if we assume that the polymer charge only depends on *solution* pH the data such as in Figure 1 cannot be described to any degree of accuracy, and neither is it possible to describe the influence of ionic strength, which is to increase the size of the capsules. Instead, a decrease in size would be predicted.

The increase in capsule size with ionic strength (in both theory and experiment) is a quite interesting phenomenon, not typically observed in experiments and theory for polyelectrolyte structures. However, swelling with increasing ionic strength is observed and predicted when the polyelectrolyte molecules are ionizable and the ionic strength is low; this is the “osmotic” regime where the ionization degree (charge) of the polymers is low, and with increasing ionic strength the polymer charge increases. We suggest that at the edges of the stability plateau multilayer capsules consisting of two types of oppositely charged, ionizable, polyelectrolyte molecules are another example of the osmotic regime in polyelectrolyte systems.

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